



## Water for a Healthy Country

Hypersalinity and phosphorus availability:  
the role of mineral precipitation in the Coorong  
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Milena Fernandes and Jason Tanner

May 2009



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## Hypersalinity and phosphorus availability: the role of mineral precipitation in the Coorong lagoons of South Australia

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## Foreword

The environmental assets of the Coorong, Lower Lakes and Murray Mouth (CLLAMM) region in South Australia are currently under threat as a result of ongoing changes in the hydrological regime of the River Murray, at the end of the Murray-Darling Basin. While a number of initiatives are underway to halt or reverse this environmental decline, rehabilitation efforts are hampered by the lack of knowledge about the links between flows and ecological responses in the system.

The CLLAMM program is a collaborative research effort that aims to produce a decision-support framework for environmental flow management for the CLLAMM region. This involves research to understand the links between the key ecosystem drivers for the region (such as water level and salinity) and key ecological processes (generation of bird habitat, fish recruitment, etc). A second step involves the development of tools to predict how ecological communities will respond to manipulations of the “management levers” for environmental flows in the region. These levers include flow releases from upstream reservoirs, the Lower Lakes barrages, and the Upper South-East Drainage scheme, and dredging of the Murray Mouth. The framework aims to evaluate the environmental trade-offs for different scenarios of manipulation of management levers, as well as different future climate scenarios for the Murray-Darling Basin.

One of the most challenging tasks in the development of the framework is predicting the response of ecological communities to future changes in environmental conditions in the CLLAMM region. The CLLAMMecology Research Cluster is a partnership between CSIRO, the University of Adelaide, Flinders University and SARDI Aquatic Sciences that is supported through CSIRO’s Flagship Collaboration Fund. CLLAMMecology brings together a range in skills in theoretical and applied ecology with the aim to produce a new generation of ecological response models for the CLLAMM region.

This report is part of a series summarising the output from the CLLAMMecology Research Cluster. Previous reports and additional information about the program can be found at <http://www.csiro.au/partnerships/CLLAMMecologyCluster.html>

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## Executive Summary

The Coorong is a long and shallow lagoonal system running southeast from the mouth of the River Murray in South Australia. Prolonged drought conditions have resulted in the progressive expansion of hypersaline waters from the South to the North Lagoon. Despite very high phytoplankton biomass, with concentrations of chlorophyll *a* > 100  $\mu\text{g L}^{-1}$ , the system has very low concentrations of inorganic nutrients. Phosphorus-limitation might occur intermittently as a result of nitrogen inputs from groundwater, or when salinities drop below 70  $\text{g L}^{-1}$ , promoting the growth of  $\text{N}_2$ -fixing cyanobacteria.

The availability of phosphorus in a semi-enclosed aquatic system like this typically relies on mineralization of organic matter in the sediments and release to the overlying water. In this work, we evaluated the likely mechanisms controlling this coupling between the sediments and the water column according to salinity and season. The study was done in the summer and winter of 2007 over 3 sites along the north-south gradient spanning salinities from 37 to 163  $\text{g L}^{-1}$ . In order to provide some insight into the processes actively sequestering phosphorus in the sediments, we investigated phosphorus speciation between organic and inorganic phases. The latter include phosphorus weakly trapped by metals (mostly oxide-bound), more strongly retained phases formed *in situ* (authigenic phases such as carbonate fluorapatite, biogenic apatite, other forms associated to carbonate) or through rock weathering and erosion (detrital phases such as apatite of igneous or metamorphic origin). The distribution of phosphorus between phases was compared to the concentration of phosphate in porewaters, the content of carbonate and gypsum in the sediments, and the interactions between the Fe(III)/Fe(II) redox couple and sulfide.

At salinities <70  $\text{g L}^{-1}$ , sedimentary phosphorus concentrations are regulated by association to oxides or organic phases. Adsorption to Fe(III) in amorphous oxyhydroxides accounts for less than 50% of phosphorus bound to oxides, suggesting that crystalline iron phases (e.g. goethite and hematite) might also play an important role in regulating phosphorus concentrations. At these comparatively low salinities, cyanobacteria might play an important role by fixing nitrogen from the atmosphere and pushing the system to phosphorus-limitation. In this case, management scenarios should consider the potential for phosphorus locked into oxide or organic phases to be released to the water column through changes in redox conditions.

At salinities >95  $\text{g L}^{-1}$ , phosphorus co-precipitation with carbonates is observed, but only during winter. In summer, co-precipitation is potentially inhibited by competing dissolved organic matter exudates from algal and microbial mats, and concurrent mineralisation of this organic matter acting to lower pH values and partially dissolve amorphous Ca-Mg-P precipitates formed in winter. These processes lead to higher availability of phosphorus in porewaters to fuel primary productivity during the warmer months of the year. The decision-making process to reduce eutrophication in this part of the Coorong through management actions thus needs to take into consideration the interplay between salinity levels (influencing the abundance of  $\text{N}_2$ -fixing organisms), groundwater inputs (increasing nitrogen availability) and seasonality (regulating phosphorus availability).

# 1. Introduction

The Coorong is a 115 km long, <4 km wide, shallow lagoonal system running southeast from the mouth of the River Murray in South Australia. Connectivity to the sea is limited by sand accumulation at the Murray mouth, and freshwater inflows reduced by a series of barrages damming water into the Lower Lakes (Webster 2005). The lagoons constitute a wetland of international importance for migratory birds, but a prolonged drought affecting southern Australia has resulted in hypersaline conditions and a reduction in habitat types suitable for both fish stocks and bird life (Lamontagne *et al.* 2004). A constriction between the North and South lagoons further promotes evaporation and hypersalinity by limiting water exchange (Webster 2006). Currently salinities range between 35 g L<sup>-1</sup> in the north and 200 g L<sup>-1</sup> in the south (DEH, unpublished data).

Despite these extreme conditions, the Coorong is characterized by high phytoplankton biomass in the water column, particularly in the South Lagoon where chlorophyll *a* concentrations exceed 100 µg L<sup>-1</sup> (Thomas and Lang 2003). The levels of particulate nitrogen and phosphorus, and dissolved organic compounds, are also high and increase southwards faster than the salinity, suggesting internal sources of organic matter (Ford 2007). In contrast, the concentrations of bioavailable dissolved inorganic nitrogen (DIN = ammonium + nitrate, <4 µM) and dissolved inorganic phosphorus (DIP = phosphate, <1 µM) are low and apparently insufficient to support phytoplankton biomass. This paradox suggests a tight coupling between nutrient mineralization and biomass uptake, or nutrient limitation leading to very low rates of primary productivity despite high phytoplankton standing stocks.

Throughout the lagoons, total nitrogen (TN) appears in excess of total phosphorus (TP), with TN:TP molar ratios always exceeding the Redfield value of 16 for phytoplankton (Ford 2007). Ratios are approximately 25 in the north, but reach as much as 55 in the south. However, more than 60% of total nitrogen, and 30% of total phosphorus, is locked into dissolved organic fractions of low bioavailability (Haese *et al.* submitted). This results in DIN:DIP molar ratios typically below 5. Considering these numbers, the system might be phosphorus-limited if there is a tight coupling between the mineralization of dissolved organic forms and uptake by primary producers, or nitrogen-limited if the breakdown of dissolved organic forms is too slow to sustain primary productivity. High ammonium concentrations, potentially derived from groundwater discharges, are observed intermittently in the South Lagoon (Ford 2007; Haese *et al.* submitted), confirming that phosphorus-limitation might occur under current conditions in some areas. Phosphorus-limitation is also likely to take place when salinities fall below 70 g L<sup>-1</sup>, as N<sub>2</sub>-fixing cyanobacteria can thrive at lower salinities, shifting the phytoplankton community from nitrogen to phosphorus limitation (Marcarelli *et al.* 2006).

The availability of phosphorus in many semi-enclosed aquatic systems relies on mineralization of organic matter in the sediments and release to the overlying water. The biogeochemical pathways involved in this benthic-pelagic coupling are unknown for the Coorong, and are the focus of this work. Two processes are likely to influence phosphorus availability in the system: (1) the formation of Fe(III)oxyhydroxides under oxidizing conditions, and (2) the precipitation of calcite in supersaturated hypersaline waters. Both of these minerals show strong affinity for phosphorus and could act to sequester this nutrient in the sediments (Golterman 1995; Stal *et al.* 1996). The balance between adsorption to iron and mineral precipitation with calcite is influenced by redox and pH (Gomez *et al.* 1999). Under anaerobic conditions Fe(III) in oxyhydroxides is reduced to Fe(II), the latter reacting with sulfide to produce highly insoluble FeS, which acts as a sink for Fe in the sediments (de Wit *et al.* 2001; Viaroli *et al.* 2004). On the other hand, pH fluctuations are particularly significant for the stability of Ca-P precipitates, leading to the release of phosphorus into the water column or a shift in sedimentary partition to Fe(III)oxyhydroxides (de Jonge and Villerius 1989; Lopez and Morgui 1992).

In order to provide some insight into the processes actively sequestering phosphorus in the sediments, we investigated phosphorus speciation between organic and inorganic phases. The latter include phosphorus weakly trapped by metals (mostly oxide-bound), more strongly

retained phases formed *in situ* (authigenic phases such as carbonate fluorapatite, biogenic apatite, other forms associated to carbonate) or through rock weathering and erosion (detrital phases such as apatite of igneous or metamorphic origin). The study was done in the summer and winter of 2007 over 3 sites along the north-south gradient spanning salinities from 37 to 163. The distribution of phosphorus between phases was compared to the concentration of phosphate in porewaters, the content of carbonate and gypsum in the sediments, and the interactions between the Fe(III)/Fe(II) redox couple and sulfide, to provide clues of the mechanisms regulating the availability of phosphorus with salinity and season.

## 2. Methods

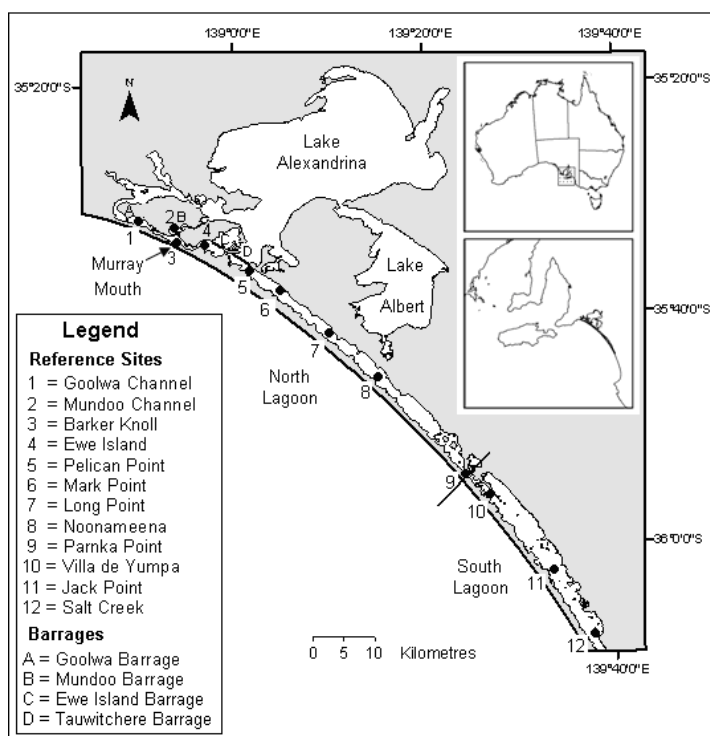
### 2.1. Sampling

Sediment cores were collected between 19-21 of February and 28-31 of August 2007 from both shallow (~0.5 m) and deep (1-2 m) stations at Pelican Point and Long Point in the North Lagoon, and Jack Point in the South Lagoon (Figure 1). These sites were chosen as representative of the salinity gradient along the lagoons (Table 1).

Sediment cores were collected using 71 mm (i.d.) PVC tubes capped with rubber bungs, and the overlying water in the tube carefully discarded to minimise surface disturbance.

Samples for determination of iron pools and acid volatile sulfide (AVS) were sub-cored immediately after collection. Iron samples were sub-cored with a 10 mL plastic centrifuge tube pushed into the sediment to a depth of 1 cm. AVS samples were sub-cored with a 50 mL plastic centrifuge tube pushed into the sediment to a depth of 1 cm, and fixed with 5 mL of 20% (w/v) zinc acetate solution. These samples were immediately frozen in dry ice and stored at  $-80^{\circ}\text{C}$ .

For the other analyses, the top 1 cm of the cores was sliced and samples transferred into pre-combusted glass jars, transported on ice and stored frozen at  $-20^{\circ}\text{C}$ . Samples for porewater analysis were transferred into 50 mL centrifuge tubes and transported on ice. Within a couple of hours, these samples were centrifuged at 1,400 g for 10 min, the supernatant filtered ( $0.45\ \mu\text{m}$ ) and stored frozen.



**Figure 1. Pelican Point (site 5), Long Point (site 7) and Jack Point (site 11) in relation to other CLLAMMecology reference sites in the Coorong Lagoons.**

**Table 1. Water temperature and salinity at the three collection sites during summer and winter.**

		T (°C)	Salinity (g L <sup>-1</sup> ) <sup>1</sup>
Summer	Pelican Point	25.7	37
	Long Point	23.2	42
	Jack Point	26.3	163
Winter	Pelican Point	16.5	50
	Long Point	15.1	66
	Jack Point	14.8	97

<sup>1</sup>Department for Environment and Heritage quarterly sampling data, measured as conductivity and transformed to salinity based on the equation proposed by Ian Webster for the Coorong (personal communication):

Chlorinity (g L<sup>-1</sup>)= (0.295\*conductivity(μS cm<sup>-1</sup>)\*(1+0.000238\*conductivity (μS cm<sup>-1</sup>)<sup>0.67</sup>))/1000, and multiplying chlorinity by the factor 1.8055 to obtain salinity.

## 2.2. Iron and acid volatile sulfide

Total reactive iron and ferrous iron were determined using a method modified from Lovley and Phillips (1986; 1987), with ferrous ethylene diammonium sulfate tetrahydrate as the calibration standard. Total reactive iron comprises both Fe(III) available for microbial reduction and Fe(II) which readily reacts with dissolved sulfides to form iron sulfides. For determination of total reactive iron, approximately 1 g of wet sediment was extracted for 1 h with 20 mL of 0.25 M hydroxylamine hydrochloride in 0.25 M HCl at room temperature. Acidified hydroxylamine reduces Fe(III) to Fe(II). The initial step in the extraction of total reactive iron was performed with lids loosely placed on the tubes as it served to dissolve carbonates. It was followed by a 2 h extraction in an end-to-end shaker with lids tightly closed. An aliquot of the extract (0.2 mL) was reacted with 20 mL of ferrozine (1 g L<sup>-1</sup>) in HEPES buffer (50 mM), filtered through a 0.2 μm polycarbonate filter, and the absorbance measured at 562 nm. For determination of ferrous iron, 1 g of wet sediment was extracted and analysed using the same procedure as that described for total reactive iron with the exception that the extractant was 0.5 M HCl. The concentration of the ferric iron pool was calculated as the difference between the total and ferrous iron pools. Acid volatile sulfide (AVS) was determined on wet samples using the cold diffusion method (Ahern *et al.* 2004; Hsieh *et al.* 2002).

## 2.3. Carbonate

Samples were freeze-dried, sieved to 500 μm to remove large shell fragments, and homogenized with a mortar and pestle. Carbonate content was determined with a pressure transducer (RS Components, part 348-8065, Iso-Tech voltameter IDM 91) by measuring the increase in pressure generated by the CO<sub>2</sub> released after acidification of aliquots with 5.5 N HCl at room temperature.

## 2.4. Gypsum

Samples were freeze-dried, sieved to 500 μm to remove large shell fragments, and homogenized with a mortar and pestle. Gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O) was determined using the thermogravimetric method of Artieda *et al.* (2006). Approximately 10 g was sequentially dried at 70°C and 90°C, and gypsum determined as the loss in weight between these temperatures, assuming a water loss of 14.95% for pure gypsum. Results below 2% are interpreted with caution as the method gives a much lower precision at these concentrations.

## 2.5. Phosphorus fractionation

In order to separate the phases in which phosphorus appears in the sediments, we used the method developed by Anderson and Delaney (2000). This method is a modified version of the SEDEX procedure (Ruttenberg 1992) and neglects phosphorus weakly adsorbed to clay surfaces. We assumed that in the hypersaline waters of the Coorong, high ionic strength would substantially limit the availability of clay sorption sites, resulting in negligible amounts of surface-adsorbed phosphorus.

Samples were freeze-dried, sieved to 500  $\mu\text{m}$  to remove large shell fragments, and ground in a ball mill grinder to <125  $\mu\text{m}$ . Approximately 0.1 g was weighed into a plastic centrifuge tube, with extraction following the steps detailed in Table 2. Extractions were performed at room temperature using an end-to-end shaker. Samples were centrifuged at 2,500 rpm ( $\sim 1,000$  g) for 5 min, and the extractant filtered through a polypropylene membrane (0.45  $\mu\text{m}$ ) after discarding the first 2 mL.

Flow injection analysis (FIA) was performed on diluted extracts (water:extract 6:1 v/v) using a Lachat QuickChem QC8500 Automated Ion Analyser. Standards and blanks were matrix-matched to the same dilution as the samples. Phosphate was analysed with the molybdate method, with the heater set at 37°C and absorbance measured at 880 nm (Lachat 2003). The oxide phase required a longer heater coil (650 cm) than the other phases (175 cm). To evaluate extraction efficiency, the total phosphorus content of each sample was also analysed by ICP-AES after digestion with nitric acid, hydrogen peroxide, and hydrochloric acid (US Environmental Protection Agency 1991).

**Table 2. Extraction procedure employed to determine phosphorus fractionation in the sediments (from Anderson and Delaney, 2000).**

Phase	Chemical Treatment	Volume (mL)	Extraction Time (h)
Oxide	0.22 M sodium citrate +	10	6
	0.033 M sodium dithionite +		
	1.0 M sodium bicarbonate		
	1 M $\text{MgCl}_2$		
Authigenic	MilliQ water	10	2
	1 M sodium acetate buffered	10	6
	1 M $\text{MgCl}_2$	10	2
	1 M $\text{MgCl}_2$	10	1
	MilliQ water	10	1
Detrital	1 N HCl	13	16
Organic	50% (w/v) $\text{MgNO}_3$	1	24
	1 N HCl	13	

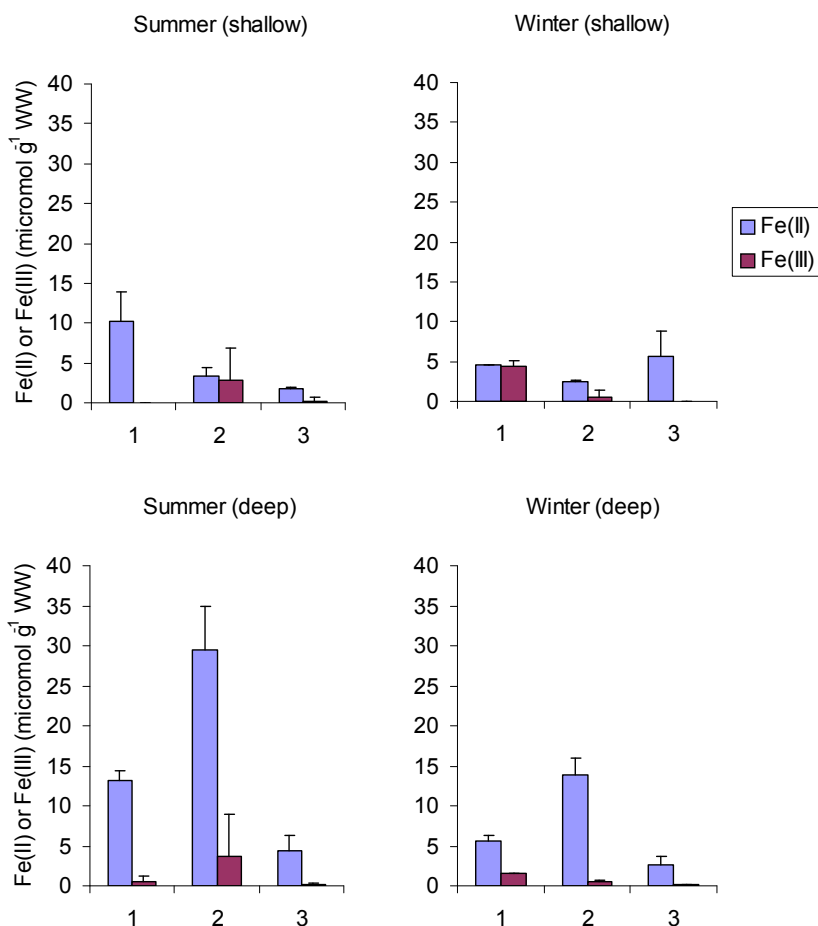
## 2.6. Porewater phosphate

Phosphate was determined by FIA in a Lachat QuickChem QC8500 Automated Ion Analyser using dilution factors >2 for samples from the North Lagoon, and >5 for samples from the South Lagoon (Lachat 2003). Water content, determined by weight difference before and after freeze-drying sediments (see above), was used to calculate the relative contribution of P in porewaters to total P in the sediments.

### 3. Results

#### 3.1. Iron

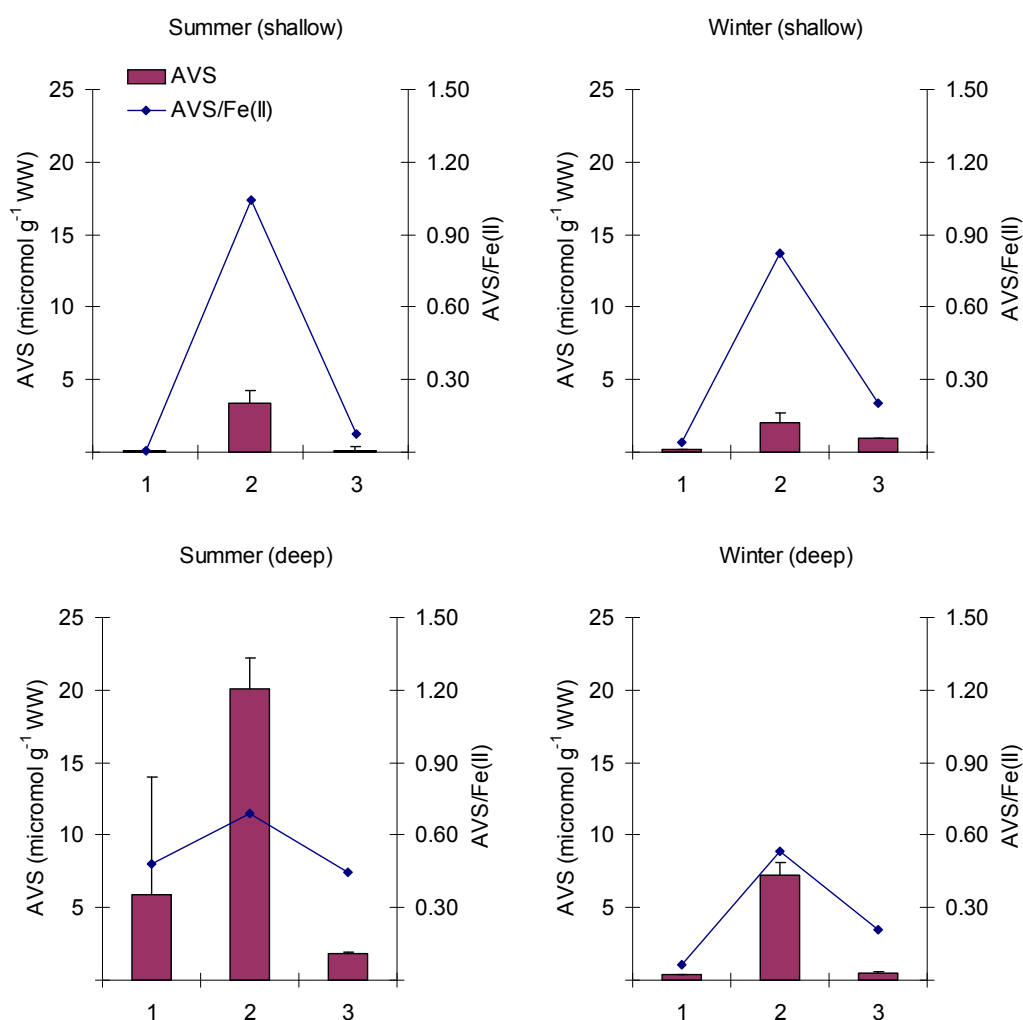
For a few samples, the concentration of ferrous iron extracted with HCl was higher than the concentration of total reactive iron extracted with acidified hydroxylamine. These results suggest the inefficient extraction of Fe(II) with hydroxylamine, perhaps as a consequence of the presence of Fe(II)-containing carbonate phases (e.g. siderite and ankerite), which have a lower extraction efficiency in acidified hydroxylamine when compared to HCl (Poulton and Canfield 2005; Raiswell *et al.* 1994). Thus, for those samples where the concentration of ferrous iron was higher than the concentration of total reactive iron, we assumed there was no microbially available Fe(III) and all iron was in ferrous forms. Indeed, iron was mostly found as reduced Fe(II), which comprised more than 90% of the total in deeper sites (Figure 2). Ferrous iron concentrations were generally higher during summer. Ferric iron was virtually absent in the South Lagoon, but appeared in comparatively high levels in some shallow sites of the North Lagoon.



**Figure 2. Fe(III) and Fe(II) contents (per gram wet weight) during summer and winter in shallow and deep sediments collected from sites 1 (Pelican Point), 2 (Long Point) and 3 (Jack Point).**

### 3.2. Acid-volatile sulfide

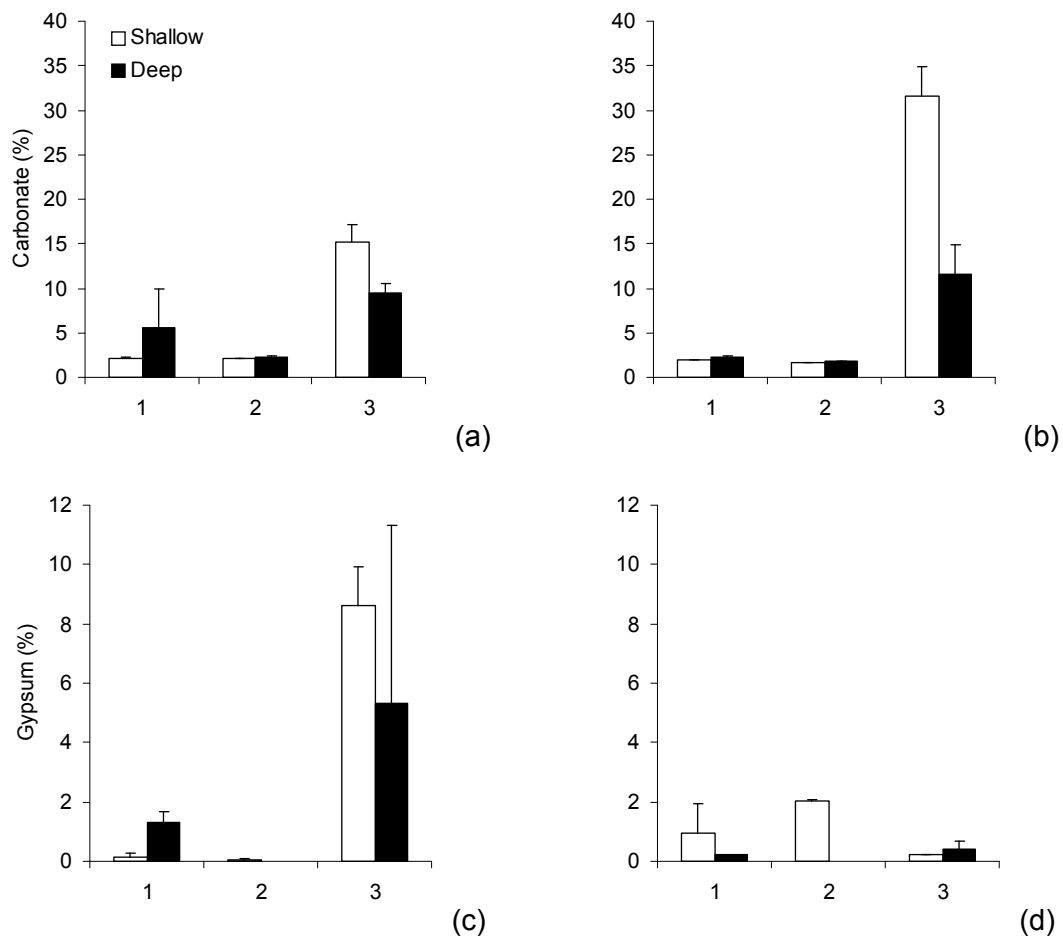
The concentrations of AVS followed a similar trend to the concentrations of ferrous iron, typically with higher values in deeper sites and in summer (Figure 3). Concentrations were particularly high at Long Point, and generally higher in the South Lagoon at Jack Point when compared to the North Lagoon at Pelican Point. The sedimentary buffering capacity of the sediments to sulfide was estimated as the ratio AVS/Fe(II) (Figure 3). The cold extraction of iron with 0.5 M HCl releases mostly iron that is highly reactive to dissolved sulphides, and therefore the ratio AVS/Fe(II) gives an indication of the saturation state of the Fe(II) buffer (Viaroli *et al.* 2004). The amount of Fe(II) extracted from non-reactive clay minerals using this low concentration of HCl and short extraction time (3 h) was assumed to be comparatively negligible (Leventhal and Taylor 1990; Raiswell *et al.* 1994). The results indicate that AVS is typically in the form of FeS, with no excess free sulfide being released in the water column and high residual buffering capacity potentially available. Only at Long Point the saturation state of Fe(II) reaches capacity, particularly in shallow sediments. Even then, it is unlikely that accumulation of dissolved sulfides will occur, as some additional iron may be locked in crystalline oxide phases, which are not extracted with cold HCl but readily converted to iron sulfides (Raiswell *et al.* 1994).



**Figure 3. Acid volatile sulfide (AVS) contents (per gram wet weight) during summer and winter in shallow and deep sediments collected from sites 1 (Pelican Point), 2 (Long Point) and 3 (Jack Point). Also shown is the ratio between AVS and ferrous iron.**

### 3.3. Carbonate and gypsum

The carbonate and gypsum content of sediments remained relatively low between Pelican Point and Long Point, but increased substantially in the hypersaline waters of Jack Point (Figure 4). For gypsum, precipitation in the South Lagoon was only evident in summer (Figure 4c). Although the data suggests higher carbonate content in shallow waters of Jack Point during winter, this trend is more likely to reflect small scale variability due to wind-forced inundation/evaporation along the shores of the lagoon. During winter, intense southerly winds during the collection period are likely to have pushed water at Jack Point to higher levels along the eastern shores, so that the shallow sample might have been in an area exposed during summer.

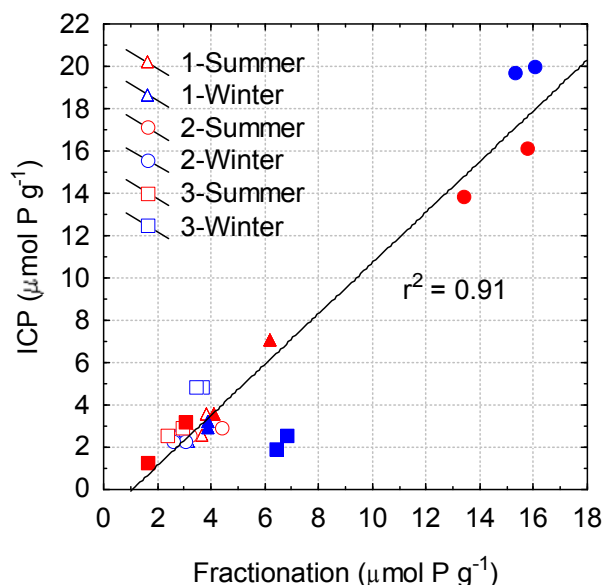


**Figure 4. Carbonate concentrations in summer (a) and winter (b), and gypsum concentrations in summer (c) and winter (d) at sites 1 (Pelican Point), 2 (Long Point) and 3 (Jack Point). Values are shown as the mean, error bars indicate standard deviation.**

### 3.4. Phosphorus

Total P content obtained from the fractionation experiments agreed well with values from ICP-AES, varying from 1.63 to 16.02  $\mu\text{mol P g}^{-1}$  dry weight (Figure 5). The influence of depth and season on P content and fractionation between phases varied with position along the salinity gradient (Figures 5 and 6). In the estuarine waters of Pelican Point, neither season nor depth were strong drivers of P dynamics. Long Point was also not greatly affected by seasonality, however deep sediments here had a very high P content driven by the accumulation of organic P. In the hypersaline waters of Jack Point, the relative contribution of organic P to total P typically decreased by half or more during winter, driven by an increase in P associated with oxides in shallow waters, and authigenic P in deeper waters. The latter were responsible for more than doubling total P concentrations between summer and winter.

Porewater phosphate concentrations increased along the salinity gradient, with a steep gradient observed during summer (Figure 7). While porewater phosphate accounted for up to 0.6% of total P in summer, it remained below 0.1% in winter. Concentrations were lowest at Pelican Point, but increased at Long Point concomitantly with high levels of organic P. Concentrations peaked in the deep waters of Jack Point during summer, but declined substantially during winter when the formation of an authigenic phase in the sediments was obvious.



**Figure 5. Comparison of total P concentrations determined by ICP-AES and the modified 4-step SEDEX fractionation procedure for sites 1 (Pelican Point, triangles), 2 (Long Point, circles) and 3 (Jack Point, squares). Summer samples are marked in red, and winter samples in blue. Symbols for shallow samples are hollow, while symbols for deep samples are filled.**

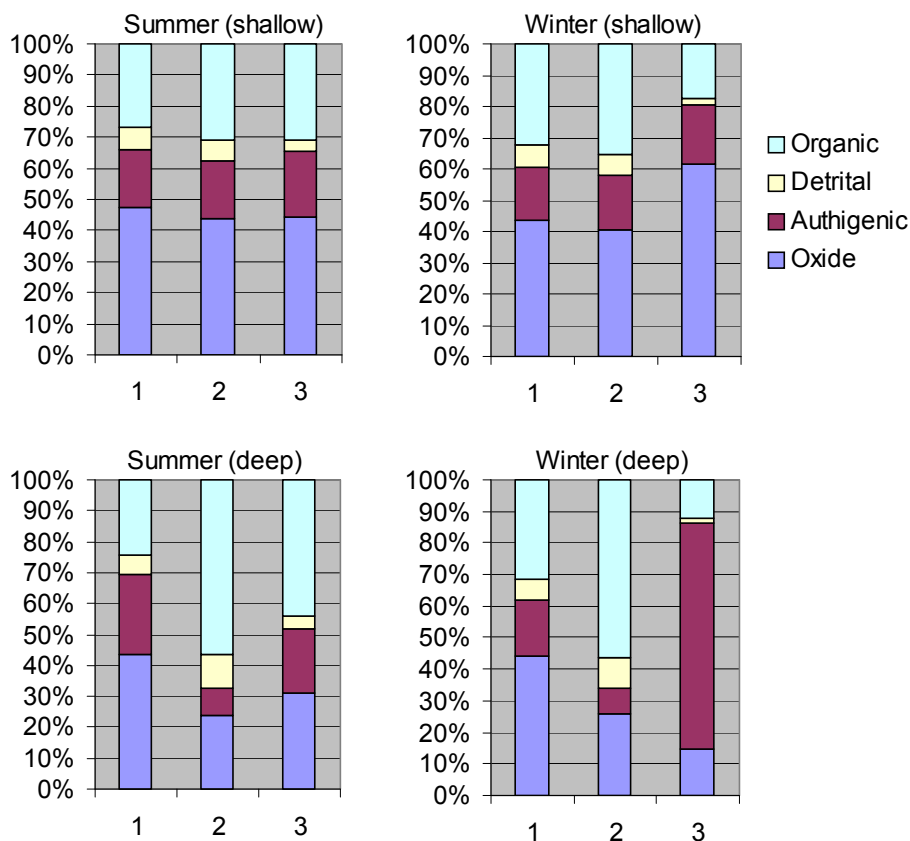


Figure 6. Phosphorus fractionation during summer and winter in shallow and deep sediments collected from sites 1 (Pelican Point), 2 (Long Point) and 3 (Jack Point).

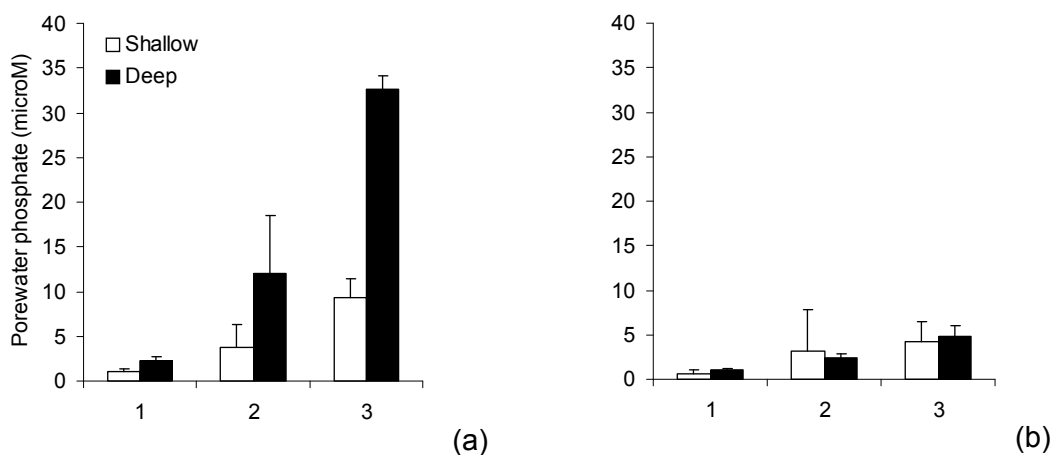


Figure 7. Porewater phosphate concentrations in summer (a) and winter (b) at sites 1 (Pelican Point), 2 (Long Point) and 3 (Jack Point). Values are shown as the mean, error bars indicate standard deviation.

## 4. Discussion

In the estuarine part of the North Lagoon, a strong marine influence and higher flushing brought by proximity to the Murray mouth guarantee small salinity fluctuations of only  $\sim 10 \text{ g L}^{-1}$  throughout the year. As a consequence, changes in sedimentary phosphorus concentrations and composition with season and depth are relatively negligible. Most phosphorus in the sediments occurred associated with oxide-phases (40-50%) or in organic forms (20-35%). The presence of ferric iron suggests mildly reducing conditions and some adsorption onto Fe(III)-oxyhydroxides. However, given that the optimal ratio for adsorption is considered to be  $\text{Fe/P} \sim 10$  (Golterman 2001), phosphorus in the oxide-phase was always in excess of measured Fe(III), the latter accounting for less than 50% of the oxide-bound phosphorus concentrations. This excess of phosphorus, here and in other parts of the Coorong, indicates that besides amorphous and poorly crystalline Fe(III)-oxyhydroxydes, crystalline phases (e.g. goethite and hematite) might also play an important role in regulating phosphorus concentrations at these high salinities. These crystalline minerals are not readily extracted with the acidified hydroxylamine used for iron extractions, but dissolve in the dithionite used to extract phosphorus (Poulton and Canfield 2005; Raiswell *et al.* 1994; Wallmann *et al.* 1993). As crystalline iron oxides are more resistant to microbial reduction and less reactive towards dissolved sulfide than their amorphous counterparts (Lovley and Phillips 1986; Poulton and Canfield 2005), a large proportion of the oxide-associated phosphorus is thus likely to be relatively stable in the sediments.

Although similar conditions occur further down the salinity gradient in shallow waters of Long Point, deep sediments at this site were anaerobic and covered by extensive microbial gelatinous mats during both summer and winter. Phosphorus concentrations reached extremely high values and appeared mostly in organic forms (50-60%), with only a small fraction bound to oxide-phases (<25%). In these sediments, iron was mostly reduced to FeS, suggesting high rates of sulphate reduction.

The most pronounced changes in phosphorus dynamics with season were seen in the South Lagoon. Sediments in this part of the Coorong were depleted of Fe(III) and rich in carbonate and gypsum, suggesting a link between phosphorus availability and mineral precipitation. Salinity at Jack Point typically varies between 2 and 5 times values in seawater (DEH, unpublished data), and a decline in alkalinity and calcium concentrations relative to chloride indicates the effective precipitation of carbonates from the water column (Ford 2007). The high rates of evaporation in the South Lagoon ensure high concentrations of calcium and bicarbonate in the water column, which exceed the solubility product of carbonate potentially leading to precipitation and a decrease in pH as alkalinity is consumed:



Although supersaturation of carbonate occurs in the water column, precipitation might be hindered by high concentrations of  $\text{Mg}^{2+}$  (up to  $6 \text{ g L}^{-1}$ ; DEH, unpublished data) and dissolved organic carbon (up to  $35 \text{ mg L}^{-1}$ ; Ford, 2007) resulting in adsorption to carbonate surfaces and slowing crystal growth (de Leeuw and Cooper 2004; Zhang and Dawe 2000). In the sediments, the precipitation of carbonate can be further enhanced by the production of bicarbonate during the oxidation of organic matter ( $\text{CH}_2\text{O}$ ) when sulphate is used as the terminal electron acceptor:



Phosphorus co-precipitates with carbonate as dissolved phosphate adsorbs to the surface of calcite crystals and is latter incorporated into the structure of the crystal as growth proceeds (Rodriguez *et al.* 2008). Apatite was not detected in the sediments through XRD analysis (Gabriel Palmer and Michael Angove, personal communication), ruling out the direct formation of crystalline Ca-P minerals. However, laboratory experiments suggest that crystallization of apatite occurs at very long time scales of 10-100 years following the initial precipitation of amorphous Ca-Mg-P precipitates (Gomez *et al.* 1999; Guldbransen *et al.* 1982).

In summer, two drivers would favour benthic carbonate precipitation: (1) intense biological activity leading to higher rates of sulphate reduction (Caumette *et al.* 1994), and (2) higher temperatures, as the solubility of carbonate decreases with temperature (Rodriguez *et al.* 2008). However, an increase in benthic fluxes of phosphate (Haese *et al.* submitted), coupled to high phosphate concentrations in porewaters (up to 34  $\mu\text{M}$ ) and the low importance of the authigenic-P phase in the sediments (<30%), suggest little sequestration of phosphorus by carbonate during this time of the year.

Phosphorus co-precipitation with calcium is potentially inhibited in summer by competing dissolved organic matter exudates from algal and microbial mats (Berner *et al.* 1970), and concurrent mineralisation of this organic matter acting to lower pH values and partially dissolve amorphous Ca-Mg-P precipitates (de Jonge and Villerius 1989; Lopez and Morgui 1992). Although these changes are unlikely to affect the large carbonate reservoir in the sediments, they might increase the solubilisation of freshly deposited amorphous phases and shift the balance from a calcium sink for phosphorus, to organic and oxide phases (Gomez *et al.* 1999; Moutin *et al.* 1992).

Another contributing factor might be the high salinities of up to 200  $\text{g L}^{-1}$  observed at the end of summer, as carbonate precipitates in a relatively narrow range of salinities, varying from 2.5 to 4 times values in seawater (Lazar *et al.* 1983). Gypsum precipitates at salinities >3.5 times seawater (Lazar *et al.* 1983), and its presence at high levels is further evidence of the very high salinities at this time of the year. Gypsum precipitated during summer might form a thin crust at the sediment surface that prevents efficient exchange with the water column (Caumette *et al.* 1994), further enhancing the role of benthic communities in regulating biogeochemical processes in the sediments. We indeed observed the formation of a multilayered microbial/mineral crust during summer in the very shallow and exposed shores of the South Lagoon.

As phosphorus-limitation might occur in the South Lagoon intermittently (Ford 2007; Haese *et al.* submitted), the higher availability of phosphorus during summer through higher mineralization of organic phosphorus and lower rates of incorporation into mineral precipitates could act to fuel primary productivity, particularly benthic if algal mats are active during this time of the year to intercept fluxes from the sediments to the water column. In contrast, more favourable conditions for the formation of Ca-Mg-P precipitates might occur during the colder months of the year as a result of a comparatively lower salinity during the wet season, potentially lower levels of dissolved organic matter in sediment porewaters, and higher pH values. The absence of apatite, however, suggests no long-term accumulation of Ca-P phases in the sediments, the latter being partially redissolved during summer. These factors would explain the lower availability of phosphorus in porewaters during winter, concomitant with a decrease of phosphorus in organic forms (<20%) and an increase in phosphorus associated with authigenic minerals (up to 73%).

## 5. Conclusions

The mechanisms regulating phosphorus availability along the Coorong lagoons are deeply influenced by changes in salinity. In estuarine waters, phosphorus concentrations are controlled by association to oxides, and thus oxidation/reduction conditions in the sediments. Towards the middle of the North Lagoon, extensive microbial mats were observed in deeper waters, trapping large amounts of phosphorus in organic forms. At these comparatively low salinities (<70  $\text{g L}^{-1}$ ), cyanobacteria might play an important role by fixing nitrogen from the atmosphere and pushing

the system to phosphorus-limitation. In this case, management scenarios should consider the potential for phosphorus locked into iron and organic phases to be released to the water column through changes in redox conditions.

In the hypersaline waters of the South Lagoon, phosphorus is sequestered in Ca-P phases during winter. This sink is, however, not permanent and is partially redissolved during summer, potentially as a result of increased biological activity during this time of the year, leading to higher phosphorus availability to fuel primary productivity. The decision-making process to reduce eutrophication in this part of the Coorong through management actions thus needs to take into consideration the interplay between salinity levels (influencing the abundance of N<sub>2</sub>-fixing organisms), groundwater inputs (increasing nitrogen availability) and seasonality (regulating phosphorus availability).

The significance of the seasonal changes observed in this work needs to be further validated by replicated measurements within seasons and over a larger area of the lagoons. The use of microsensors to define pH and redox profiles in the sediments would be very useful to test some of the hypothesis raised, as would laboratory experiments on the co-precipitation of phosphorus with calcium in hypersaline conditions, and to determine the limiting nutrient for phytoplankton growth. Future work should also consider the role of microbial/mineral crusts, potentially associated with gypsum precipitation, in regulating the transfer of nutrients between the sediments and the water column.

## 6. References

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