Dynamics of phosphate in Shark Bay, Western Australia

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Abstract

Mass balances of carbon (C), nitrogen (N) and phosphate (P) for Shark Bay are briefly reviewed. P becomes depleted in the bay and appears to limit biomass. The net rate of P uptake in the bay is determined by sedimentation. Some preliminary data on concentrations of P and iron (Fe) in sediments are presented to distinguish differing mechanisms of P sedimentation.

Concentrations of both P and Fe in sediment decrease into the bay (7.59-0.65 μmol P g-1 and 11.41-4.71 μmol Fe g-1, respectively). 83-88% of total P in the sediments is inorganic P, 10-15% is organic P and 2% is adsorbed P. 90% of the inorganic P in Hamelin Pool sediments is in large shells and shell fragments. It is reasoned that if most of the P in sediments of the outer bay is also in larger fragments of calcium carbonate ($CaCO_3$), then the net rate of P uptake is directly related to the rate of community calcification of the bay and not necessarily to the rate of net community production, as stated earlier. Shark Bay remains as an important and exciting ecosystem to study interactions and mass balances of biologically labile materials.

Résumé

Les équilibres de masse de carbone (C), d'azote (N) et de phosphate (P) pour la Baie des Chiens Marins sont brièvement revus. Le P diminue dans la Baie et semble limiter la biomasse. Le taux net de levée du P dans la Baie est déterminé par la sédimentation. Certaines données préliminaires sur les concentrations en P et en fer (Fe) dans les sédiments sont présentées pour distinguer les mécanismes différents de sédimentation de P.

Les concentrations à la fois en P et en Fe dans le sédiment diminuent dans la Baie (respectivement 7.59-0.65 μmol P g-1 et 11.41-4.71 μmol Fe g-1). 83-85% de la totalité de P dans les sédiments est du P inorganique. 10-15% est du P organique et 2% est du P absorbé. 90% du P inorganique dans les sédiments de Hamelin Pool se trouve dans les grands coquillages et les fragments de coquillages. Nous pensons que si la majeure partie du P dans les sédiments de la Baie extérieure se trouve également dans de plus grands fragments de carbonate de calcium ($CaCO_3$), le taux net de levée du P est directement lié au taux de calcification de la communauté de la Baie et pas nécessairement au taux de la production nette de la communauté, comme on l'a formulé antérieurement. La Baie des Chiens Marins demeure un important et passionnant ecosystème pour étudier les relations mutuelles et les équilibres de masse des matériaux biologiquement labiles.

Introduction

Nearshore ecosystems are increasingly important as sites for studying marine biogeochemical cycles. Recycling and deposition of materials in nearshore

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benthic systems vary depending on the biological communities and the physical features of those ecosystems. Some coastal ecosystems trap terrigenous materials and other nearshore ecosystems act as sources or sinks of materials which are exchangeable with the sea. Understanding the dynamics of materials in coastal ecosystems is essential to predict and solve problems of coastal pollution, determine rates of cycling of anthropogenic compounds and even to quantify global elemental cycles.

P is a key compound in understanding the biological and geochemical processes in the world's oceans. P binds with C to form organic and inorganic components of plants and animals. There is little information on the interaction of C and P cycles in coastal ecosystems, especially in shallow tropical and subtropical seas. A major goal of my research in Shark Bay has been to identify some of the dominate biogeochemical processes that involve the interaction of C and P. Here I summarize earlier work, and present preliminary data indicating that the incorporation of P into $CaCO_3$ is the major sink for P in Shark Bay; I suggest that the net rate of P uptake in Shark Bay is not necessarily related to organic C production but may be directly related to the rate of calcification by the C:P ratio in shells.

Background

Shark Bay is a very large shallow basin. There is virtually no input of material from land; consequently nearly all of the material forming the sediments in the bay is a direct result of biological, chemical and physical processes operating within the bay over geological time (Logan and Cebulski 1970; Logan 1974). The salinity gradient in Shark Bay can be used to determine whether certain dissolved compounds in the water are produced or consumed within the bay. Concentrations of the major ions in seawater are too high to be affected by the activity of organisms, consequently salinity can be used to quantify physical processes such as the rate of evaporation of water and horizontal mixing. Even though biologically active compounds are recycled within the bay, perhaps many times, some compounds accumulate and form sediments. Sediments of Shark Bay include biogenic forms of C and P.

Estimates of net rates of organic and inorganic C, N and P uptake were made by constructing a water budget and by measuring the concentrations of those elements in sediments (Table 1; Smith and Atkinson 1983, 1984). The deposition of inorganic C as $CaCO_3$ shifts the pH of water in the bay about 0.15 pH units, from 8.25 in the oceanic region of the bay to 8.10 in Hamelin Pool. The shift in pH creates higher partial pressures of carbon dioxide gas (CO_2) in water than in air; thus CO_2 gas is released to the atmosphere. Shark Bay releases about as much CO_2 to the atmosphere each year as does the burning of petrol in all automobiles within Western Australia. N, as inorganic N compounds, is taken up in organic material. There is not enough N advecting or mixing into Shark

Table 1: Rates of net uptake and net production of C, N and P by Shark Bay (mmol m^{-2} d^{-1}). From Smith and Atkinson (1983).

Process	Rate
Org C Prod	1.2
Inorg C Prod	3.2
CO_2 gas evasion	2.0
net N uptake	0.030
oceanic N input	0.002
net N-fix	0.028
max N-fix	0.16
net P uptake	0.0037

Bay from the Indian Ocean to support the net sink of organic N in the sediments. The extra N in the sediments is assumed to be created by N-fixation. An estimate of N-fixation rate for the bay is about 0.028 mmol N m^{-2} d^{-1} and this rate represents a low value for benthic systems.

P, which is removed from the water by the growth of organisms, is buried in the sediments as organic P and inorganic P (Figure 1; Atkinson 1987). Other than the Indian Ocean there are no major external sources of P into Shark Bay.
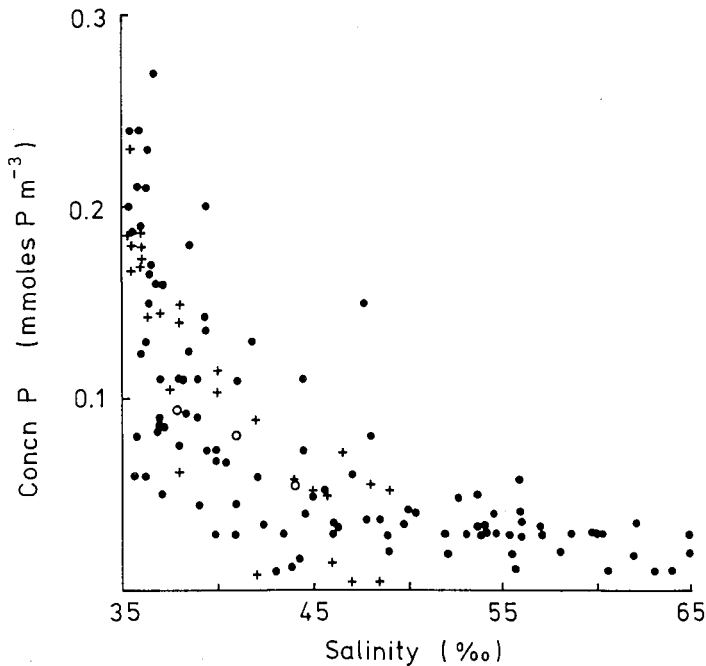
Figure 1: Concentration of disssolved P decreases into Shark Bay. (.) Hopeless Reach and Hamelin Pool, (+) Freycinet, (o) Lharidon. Reprinted from Atkinson 1987.

Figure 2: Total P in surface sediments versus the salinity at the sampling location. Symbols as in Figure 1. "C" represents the mean values for the core samples. Reprinted from Atkinson 1987.

Approximately ¼ of the P input from the Indian Ocean is by a slow net advection of water into the bay; the slow advection of water replaces water that evaporates. The remaining ¾ of the oceanic input is sustained by horizontal mixing down the gradient of P in the bay (Figure 1; Smith and Atkinson 1983). Horizontal mixing is created by reversing tidal currents.

An interesting result of earlier work is that the concentration of inorganic P and total P in the sediments decreases as the residence time or salinity of the water increases (Figure 2; Atkinson 1987). Presumably the decrease in the concentration of P in the sediments is a result of a decreasing input of P into the bay and a depletion of P in organic and inorganic matter (Atkinson 1987). The change in the C:P molar ratio of organic matter in sediments and autotrophs ranges from 100:1 in the oceanic part of the bay to 10,000:1 in Hamelin Pool (Atkinson 1987). This dramatic decrease in the concentration of P in the water,

sediments, and autotrophs is an indicator that P limits the development of biomass in the bay. Because P limits biomass, factors ultimately controlling biomass can be elucidated by determining dominate mechanisms of P sedimentation. The large changes in the concentration of P in the water column and sediments is unique and is useful to study mechanisms of P sedimentation in shallow subtropical ecosystems.

In coastal sediments with high content of organic matter (10-20%), such as upwelling areas, the concentrations of P in sediment pore water determine the relative concentrations of P in different sediment components. As organic matter remineralizes in the sediments, P is released into interstitial pore waters, creating high concentrations of P. The interstitial P reacts with inorganic constituents in the sediment including clays, Fe, aluminium (Al) and Ca to form P containing minerals. P can be adsorbed or desorbed rapidly from particle surfaces. P minerals are eventually formed by long-term solid-state diffusion of adsorbed P into lattice structures of particles (Froehlich 1988). Some P can be lost from the sediment by diffusion or bioturbation to the overlying water column (Figure 3A). The sediments of Shark Bay do not have high concentrations of organic matter (only 0.5-2.0% by weight) and sedimentation of organic material is relatively low (Atkinson 1987). The bay is also shallow with strong tidal currents, so sediments get reworked by physical and biological processes. Under these conditions in
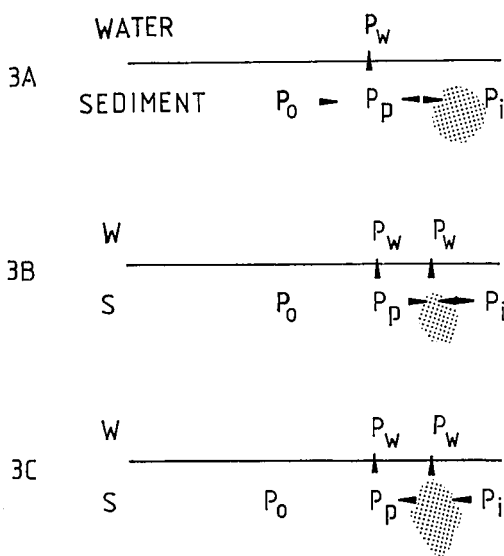

Figure 3: Possible dynamics of P in Shark Bay sediments. **3A:** Organic P (P_o) controls the inorganic P (P_i) sink via concentrations of interstitial P (P_p). P_p efflux to water (P_w). **3B:** P_i sink buffers P_p and P_w by adsorption and desorption from mineral surfaces (the dots). **3C:** P_i desorbs to P_p and P_w as shell fragments breakdown. See text for explanation.

Shark Bay, high interstitial concentrations of P are unlikely; instead, the concentration of P in the water column may be buffered by resuspended particles from sediments. Fast adsorptive-desorptive reactions in concert with long-term solid-state diffusion of P into the lattice of particles could "control" the concentration of inorganic P in the water (Figure 3b). This mechanism is common in many estuaries and represents an inorganic control of concentrations of P in the water column (Froehlich 1988); the buffering exchange rates often depend on the size and mineralogy of the sediment particles. Another likely possibility for Shark Bay sediments is that most P is coprecipitated with $CaCO_3$ or $CaPO_4$ of shells, tests, and bones. When the shells are broken down to fragments over millenia, P is released back to the water column or readsorbed onto the smallest particles in the sediment (Figure 3c). In this latter scheme, the deposition of P is biogenically controlled, not physically or chemically controlled. It is biogenically controlled because inorganic P, the dominant sink for P, is created by organisms, and the amount of P in the sediments depends on the nature of shells and bones, not on the concentration of P in interstitial water or the concentration of the overlying water.

The preliminary data presented here indicate that Fe, Al adsorption reactions are not buffering the concentration of P in the water column but the P deposition is directly linked to $CaCO_3$ production by the C:P ratio of inorganic biogenic material.

Methods

I used three approaches to obtain data on the dominate mechanism of P deposition in Shark Bay.

One approach was to measure Fe and P in three cores, one core from the oceanic region of the bay, one from the metahaline region and one from the hypersaline (see "C" in Figure 2). If Fe and P covary, both vertically within each core and horizontally between cores, then it would be good initial indication that P might be precipitated as Fe minerals. Cores were collected by pushing a 8 cm diameter, 50 cm long PVC tube into the sediment. The core was removed from the PVC tube and sliced into 2 cm sections. Each section was frozen immediately in a field freezer.

Sections were dried in a laboratory at 60°C, ground to a fine powder and then extracted in 1N HCl. The supernatant of the extraction was filtered through GF/C filters. Fe was measured using Atomic Absorption Spectrophotometry and P was measured colorimetrically using the molybdate sulphuric acid reaction (Strickland and Parsons 1968).

The second approach was a serial extraction of the core samples to determine which chemical fraction contained most of the P. The extraction distinguished several chemical forms of P: 1) adsorbed P; 2) Fe- and Al- P; 3) organic P; and 4) inorganic P in $CaCO_3$. The serial extraction was briefly as follows (Biggs and Strom 1983). A 0.5 g sample of powdered sediment from a core was placed

in a flask. The sediment was extracted in 0.5 N NaOH for 1 hour; this fraction represents Fe- and Al- bound P. The sediment slurry was filtered through GF/ C filters; then the filtrate was analyzed for P colorimetrically after adjustment of the pH to 4-7. The sediment sample was then washed with citrate-diothionite solution. Any P adsorbed back onto $CaCO_3$ during the first step is remobilized in this step. The filtrate was also analyzed for P. This fraction also included any free $Fe(OH)_2$. The next two steps were acid extractions, 0.5 N and 1.0 N HCl, liberating $CaPO_4$ and $CaCO_3$, respectively. The remaining sediment was redried, oxidized at 550°C and then extracted in 1 N HCl. This last fraction represents organic P.

The third approach was to determine if the amount of P per gram of sediment changes as a function of the size of the sediment particles. If adsorption of P from the water column or interstitial water is significant, then the fine fraction would be expected to have larger amounts of P. Likewise, if desorption of P dominates, then the fine fraction would have the least P, and the larger shells and shell fragments would contain most P. A 8 cm diameter core was collected from Hamelin Pool on 29 December 1987, 1 km offshore from Boolagorda Station in 3 m of water. The core was separated into a top section (1-10 cm) and a bottom section (12-30 cm); the sections were frozen. In the laboratory each section of core was dried at 60°C. The dried sediment was then shaken through Edecot sieves of the following sizes: 0.25 μm, 1.0 μm, 3.35 μm. This procedure left 4 size classes of sediment: 0.0-0.25 μm, 0.25-1.0 μm, 1.0-3.35 μm, and greater than 3.35 μm. Subsamples from each size class were ground to a fine powder (0.2 mm screen) in a Culatti grinder and then extracted in 1N HCl for inorganic P.

Results

Fe decreased from 11.41 μmol Fe g-1 ($\pm$ 1.62) in the oceanic core, to 8.50 μmol Fe g-1 ($\pm$ 2.35) in the metahaline core and 4.71 Fe ($\pm$ 1.29) in the hypersaline core. There were also significant vertical changes in the concentration of Fe within each core, which created large ranges and standard deviations (Table 2; Figure 4).

P also decreased from 7.57 μmol P g-1 ($\pm$ 0.43) in the oceanic core to 2.41 μmol P g-1 ($\pm$ 0.27) in the metahaline core and 0.65 μmol P g-1 ($\pm$ 0.10) in the hypersaline core. Unlike Fe, there were no significant vertical changes of P within each core. Consequently the ranges and standard deviations were relatively small (Table 2; Figure 4). Fe changed horizontally throughout the bay by 2.4 fold while P changed 11.7 fold.

Results of the serial extraction for all three cores showed that less than 2% of P was adsorbed, 10-15% was organic P and the remaining 83-88% of P was included in the acid soluble fraction as $CaPO_4$ and $CaCO_3$. These results are consistent with earlier results (Atkinson 1987).

Table 2: Total inorganic Fe and P in three cores: oceanic region, metahaline region and hypersaline region. Values in μmol g^{-1}. Data are shown in Figure 1.

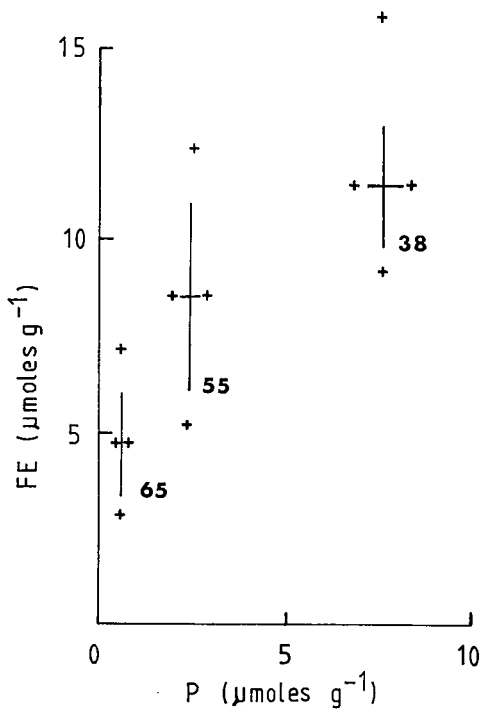| Parameters	Cores		
	38‰	55‰	65‰
Fe:			
mean	11.41	8.50	4.71
sdev	1.62	2.35	1.29
n	16	15	12
max	15.88	12.50	7.08
min	9.21	5.14	2.83
P:			
mean	7.59	2.41	0.65
sdev	0.43	0.27	0.10
n	16	15	12
max	8.39	2.84	0.79
min	6.77	1.96	0.53

Figure 4: Concentration of Fe and P in the inorganic fraction of Shark Bay sediments. (The oceanic core is 38‰, the metahaline core is 55‰ and the hypersaline core is 65‰, see Table 2.) Lines represent standard deviations of the means: "+'s" represent values for maxima and minima.

Table 3: Amounts and proportions of sediment in each size class for Hamelin Pool core (mm).

	Wt (g)	%
Core (1-18 cm)		
0.0-0.25	29	6.4
0.25-1.0	108	24.0
1.0-3.35	142	31.6
3.35+	171	38.0
total	450	100.0
Core (18-33 cm)		
0.0-0.25	51	10.8
0.25-1.0	105	22.1
1.0-3.35	102	21.6
3.35+	215	45.5
total	473	100.0
Intertidal Sand		
0.0-0.25	68	22.0
0.25-1.0	183	59.4
1.0-3.35	10	3.3
3.35+	47	15.3
total	308	100.0
Beach Sand		
0.0-0.25	33	10.9
0.25-1.0	148	48.3
1.0-3.35	45	14.6
3.35+	80	26.2
total	306	100.0

Table 4: Acid soluble (1N HCl) and organic fractions in the Hamelin Pool core. Weights in mg.

Sample	Initial Wt.	Acid Soluble Wt.	%	Organic Wt.	%
(1-18 cm)					
0.0-0.25	595.9	489.0	82.1	8.2	1.38
0.25-1.0	476.4	473.0	99.3	2.7	0.57
1.0-3.35	607.5	603.5	99.3	2.7	0.44
3.35+	471.5	469.3	99.5	1.7	0.36
(18-23 cm)					
0.0-0.25	498.3	424.5	85.2	6.1	1.22
0.25-1.0	515.2	510.5	99.1	2.8	0.54
1.0-3.35	492.8	489.6	99.4	2.0	0.41
3.35+	678.2	674.7	99.5	2.0	0.29

The size fractions of the Boolagorda core revealed the most interesting results. 40% of the sediment weight was comprised of shells greater than 3.35 mm and

about 68% of the sediment was shell fragments greater than 1.0 mm. Most of the intertidal and beach sand, having been sorted by wave energy, were comprised of smaller particles (Table 3). 99% of the three larger size fractions (>0.25) was inorganic whereas 85% of the smallest size fraction (0.0-0.25 mm) was inorganic (Table 4). The smallest size fraction had more organic material than the largest size (1.3% compared to less than 0.6% organic matter; Table 4).

The exciting result was that over 80% of the total inorganic P in the core was in the shell fragments greater than 3.35 mm and over 92% of the total inorganic P was in fragments greater than 1.0 mm. Only about 1% of the total P in the sediment was in the smallest size fraction, less than 0.25 mm (Table 5). Consequently, the largest size fraction had 20 fold more P with respect to Ca than the smallest size fraction (Table 6).

Table 5: Amount of P in each size fraction for the Hamelin Pool core. The weighted average concentration of P in the sediment is shown on the last line. Note that this concentration is similar to concentrations shown in Figure 2 for high salinities.

Sample	μmol P g^{-1}	g	μmol P in fraction	%
(1-18 cm)				
0.0-0.25	0.0314	28.9	0.91	0.65
0.25-1.0	0.0914	108.3	9.90	7.1
1.0-3.35	0.0992	142.3	14.11	10.1
3.35+	0.6742	171.1	115.3	82.2
average	0.311			
(18-33 cm)				
0.0-0.25	0.0336	50.9	1.71	1.2
0.25-1.0	0.0687	104.5	7.2	5.0
1.0-3.35	0.1813	101.9	18.5	12.9
3.35+	0.5359	215.3	115.4	80.8
average	0.302			

Table 6: Ca and P in Hamelin Pool core. Weights are in μmol g^{-1}.

Sample	Ca	P	P/Ca (ppm)
(1-18 cm)			
0.0-0.25	7.041	0.0314	4.5
0.25-1.0	10.487	0.0914	8.7
1.0-3.35	6.335	0.0992	15.7
3.35+	7.661	0.6742	88.0
(18-23 cm)			
0.0-0.25	7.310	0.0336	4.6
0.25-1.0	8.641	0.0687	8.0
1.0-3.35	8.370	0.1813	21.7
3.35+	4.716	0.5359	113.6

Discussion

The preliminary results presented in this paper indicate that free Fe-P compounds are probably not a major sink for P. Even though concentrations of both Fe and P in sediment decreased from oceanic sediment to hypersaline sediments, that decrease can be simply explained by distance of the sediment, or site of deposition, from the oceanic source of new Fe and new P. Vertical changes in concentrations of Fe were not related to changes in P; likewise, horizontal changes in Fe (between cores) were 2.4 fold compared to changes in P of 11.7 fold. Further, results from the serial extraction revealed that there was little P in the Fe fraction. Nearly all P was bound in the $CaCO_3$ fraction. It is entirely possible that P could be bound as Fe compounds within shells (Sherwood et al. 1987), but vertical changes of Fe in each core without the concomitant changes in P indicates otherwise. The relationship between Fe and P in shells is not well understood and Shark Bay would be an excellent site to conduct further research on this topic.

Nearly all of the P in Hamelin Pool sediment was contained in larger shells and fragments of shells; this clearly indicates that the major source of P into the sediment is via biogenic $CaCO_3$, not by organic P compounds. As these shells breakdown, P must be lost by desorption back to the water column. If the sediments of the oceanic part of the bay also have more P in the larger fragments, then the ratio of P to Ca in the shells and bones of live organisms must decrease toward the inner bay to explain the horizontal decrease in concentration of inorganic P in the sediments. It is likely that most P is in the larger fragments of $CaCO_3$ throughout the bay because the relative proportions of adsorbed P, organic P and inorganic P did not change between oceanic sediment and hypersaline sediment. Changes in concentration of P in shells may be purely chemical, in which case the P to Ca ratio of shells from living animals is proportional to concentrations of P in water; or, it might be related to major shifts in the mineralogy of the shells, bones, and tests forming the sediment. This later case is entirely possible because of the large changes in species composition within the bay.

On the other hand, if the outer bay sediments have most P in the smallest size fraction, then adsorption of P may be the major reaction controlling the concentration of P in Shark Bay. Adsorption of P could be directly from the water column or from interstitial P.

If the outer bay sediments have most P in shell fragments, then the net rate of P uptake in Shark Bay is NOT related to net organic C production by the C:P ratio of organic material, as stated by Smith and Atkinson (1984), but would be directly related to the calcification rate of the system by the Ca:P ratio in shells etc. If this idea is shown to be correct then it would help explain why a number of tropical and subtropical systems that produce biogenic $CaCO_3$ become depleted in P.

Shark Bay remains as an important and exciting site to answer questions about the relationships between the deposition of P and the net production of biogenic material by communities of benthic organisms. The bay will continue to serve as a model ecosystem to study the interaction of biogeochemical cycles in coastal subtropical ecosystems.

Acknowledgements

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