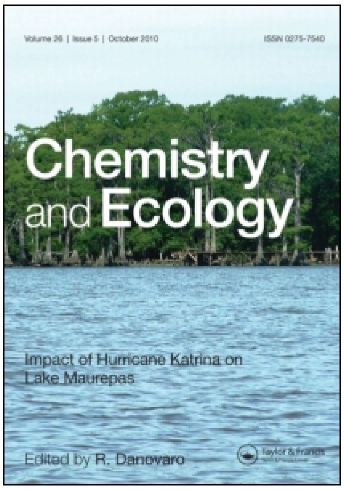

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

Phosphate enrichment in the northern Gulf of Aqaba: Regulation by carbonate sediments and impact on nitrogen elevation

M. Y. Rasheed[a]; S. A. Al-rousan[a]; M. I. Badran[a]
[a] Marine Science Station, University of Jordan Yarmouk University, Aqaba 7710, Jordan

To cite this Article Rasheed, M. Y. , Al-rousan, S. A. and Badran, M. I.(2005) 'Phosphate enrichment in the northern Gulf of Aqaba: Regulation by carbonate sediments and impact on nitrogen elevation', Chemistry and Ecology, 21: 3, 199 — 208
To link to this Article: DOI: 10.1080/02757540500151663
URL: http://dx.doi.org/10.1080/02757540500151663

Chemistry and Ecology
Vol. 21, No. 3, June 2005, 199–208

Phosphate enrichment in the northern Gulf of Aqaba: Regulation by carbonate sediments and impact on nitrogen elevation

M. Y. RASHEED*, S. A. AL-ROUSAN and M. I. BADRAN

Marine Science Station, University of Jordan Yarmouk University, PO Box 195, Aqaba 7710, Jordan

(Received 5 November 2004; in final form 25 April 2005)

The effect of carbonate sediment in regulating phosphate concentrations in sea water was investigated by laboratory incubation experiments using different sediment types. Incubation experiments were made with two types of sediments: uncontaminated sediment from a marine reserve and contaminated sediment with deposited phosphate powders. Fluxes of inorganic nitrogen and phosphate were estimated from linear regressions of solute concentrations over incubation periods. Ammonium and phosphate fluxes were about twofold higher in the uncontaminated sediment that had significantly lower organic carbon and total phosphate concentrations than in the phosphate-contaminated sediment. To test the effect of dissolved phosphate on increasing nitrogen fixation, additional incubation experiments were carried out using treated carbonate and silicate sediments with added dissolved phosphate (20 μM). Incubations were made under sterile conditions with $HgCl_2$ added to distinguish between biologically enhanced processes and pure physicochemical processes. The adsorption rate of phosphate onto carbonate sediment was about twice that onto silicate sediments. No nitrogen elevation either as ammonium or as nitrate was observed in the soluble phosphate enrichment incubations. In conclusion, this study demonstrates the importance of the regulation of soluble phosphate concentrations in carbonate sediment environments where the carbonate sediment acts as a buffering system keeping soluble phosphate concentrations at certain steady-state levels. The study also demonstrates the lack of evidence on enhancement of nitrogen concentrations due to the increase phosphate concentrations.

Keywords: Phosphate; Carbonate sediment; Gulf of Aqaba; Nutrients

1. Introduction

Phosphate pollution in waters of the Gulf of Aqaba, resulting from phosphate loss during shipment, has been a long ongoing concern since the mid-1970s [1, 2]. However, few studies have been undertaken to understand the phosphate behaviour in the local environment of the Gulf of Aqaba. Recently, a report prepared by the International Expert Team [3] supporting the fish farms in Eilat claimed that phosphate dust is not only a source of phosphate pollution but also increases the nitrogen availability in sea water, based on a hypothesis that phosphate enhances nitrogen fixation in nitrogen-deficient systems. This has no well-founded

---

*Corresponding author. Email: m.rasheed@ju.edu.jo

Chemistry and Ecology
ISSN 0275-7540 print/ISSN 1029-0370 online
http://www.tandf.co.uk/journals
DOI: 10.1080/02757540500151663

scientific grounds in the Gulf of Aqaba. Plankton studies have shown that the nitrogen-fixing blue-green alga, *Trichdesmuim* sp., exists in the upper 100 m waters of the Gulf of Aqaba mainly during summer and autumn [4, 5] where and when phytoplankton chlorophyll *a*, phosphate and nitrogen concentrations are low [4–7]. This indicates that nitrogen fixation in the Gulf of Aqaba, if it occurs, is driven by nitrogen deficiency rather than phosphate availability.

Jordanian phosphate powder is almost completely insoluble in sea water [2]. Evidence is provided by the comparable soluble reactive phosphate concentrations in the sea water at the phosphate-loading berth with other coastal stations in and even with offshore surface water (Jordan's National Monitoring Program, 1999–2003). Also, there is no elevation in the concentration of total inorganic nitrogen or of chlorophyll *a* at the phosphate-loading berth as compared with other coastal and offshore stations.

Carbonate sediments accumulate in the Gulf of Aqaba near coral reefs. They are made up from coral and mollusc fragments as well as shells of microbenthic fauna. These sediments are loose and unconsolidated in nature characterized by high porosity and permeability [8, 9]. Carbonate sediments are reported by several authors to have a strong regulatory effect on phosphate concentrations in sea water [10–12]. Even if phosphate is introduced in purely soluble form, carbonate sediment adsorbs soluble phosphate and establishes steady-state conditions where soluble phosphate concentrations are maintained at a certain level.

The objectives of this study were to investigate the fluxes of dissolved inorganic phosphate (DIP) and dissolved inorganic nitrogen (DIN) from carbonate sediments and the possibility of nitrogen fixation due to elevated phosphate concentrations, as well as to assess the regulatory effect of carbonate sediments on phosphate concentrations.

2. Materials and methods

2.1 *Sampling site*

Sediment cores for the first incubation experiment were collected from two sites on the Jordanian coast of the Gulf of Aqaba (figure 1). The first site was in front of Marine Science Station (MSS), a well-developed coral reef site and a marine reserve since the mid-1970s. In this area, the sediment is mainly carbonate composed of coral reef fragments, remains of foraminifera, calcareous red algae and sea urchins [8]. Silicate sediments also exist nearby. Samples of the MSS sediments were collected for the second incubation experiment. The second site was near the phosphate-loading berth (PLB). The PLB sediment is composed mainly of quartz and feldspar with high organic phosphorus content that fall out of raw phosphate powder during shipment.

2.2 *Incubation experiments*

2.2.1 Incubation experiment 1. The purpose of this experiment was to estimate the flux of dissolved inorganic nitrogen (DIN) and phosphate (DIP) from natural sediments from the two sites. Sediment cores for this incubation were collected by diving, using acrylic cylinders with an inner diameter of 9.5 cm and length of 40 cm and a sharp edge from the bottom. About 10 cm of sediment was collected, overlaid by about 30 cm of bottom waters. The cores were then covered by air-tight plastic lids with two sampling ports. The water above the sediment was kept homogeneous by continuous stirring using a 7-cm-diameter rotating disk that was

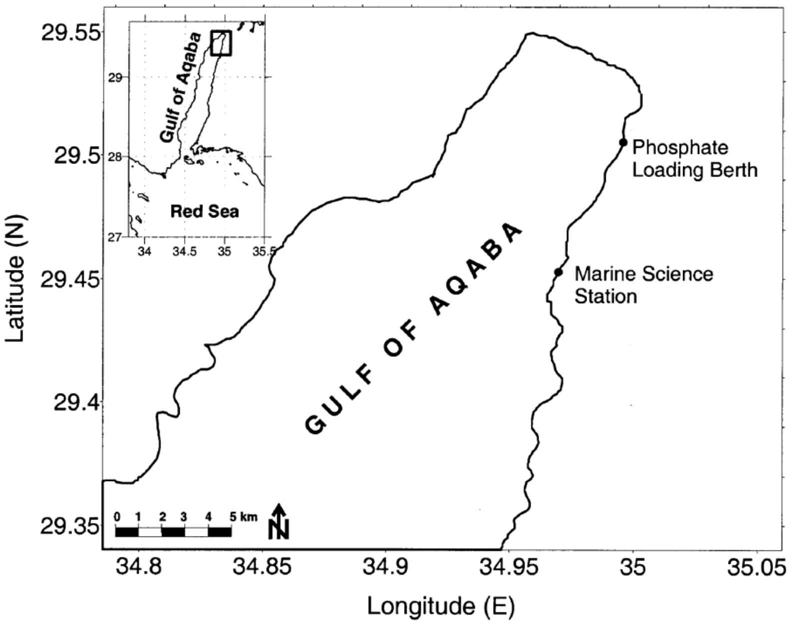

Figure 1. Location of the sampling sites.

placed 10 cm above the sediment. Aeration at a low rate by an air pump was used to keep the water's dissolved oxygen concentration near saturation. Three chambers were used for each site. Once stirring was started, the redox potential for the water above the sediment was recorded at different time intervals. For the analysis of inorganic nutrients (ammonium, nitrate, nitrite and phosphate), 50 ml of the overlaying water was withdrawn using a syringe at different time intervals (figure 2) and replaced with 50 ml of new sea water. The total incubation period was about 200 h.

2.2.2 Incubation experiment 2. The purpose of this experiment was to estimate the adsorption rate of dissolved phosphate onto carbonate sediments compared with silicate sediments and to investigate the possibility of DIN elevation driven by DIP elevation in the sea water. Sediment for this experiment was collected from two shallow sites (5 m) in front of the Marine Science Station including carbonate and silicate sediments. The sediments were washed with tap water and dried, and 250–500 μm grains were separated by mechanical sieving. The incubation was done in the same manner as in experiment 1 with 10 cm of the treated sediments and sea water collected from about 0.5 m water depth. Eight chambers were used for this incubation, four for each sediment type. To each of the eight incubated chambers, 1 ml of concentrated potassium hydrogen phosphate was added, to yield a phosphate concentration of about 20 μM in the water above the sediments. Two carbonate and two silicate chambers were sterilized with 2 ml of saturated $HgCl_2$ solution to eliminate any biological activity including nitrogen fixation in the chambers and to limit the change in phosphate concentration to physicochemical action keeping biological factors aside.

The fluxes and adsorption rate of DIN and DIP were estimated from linear regressions of solute concentrations over incubation times.

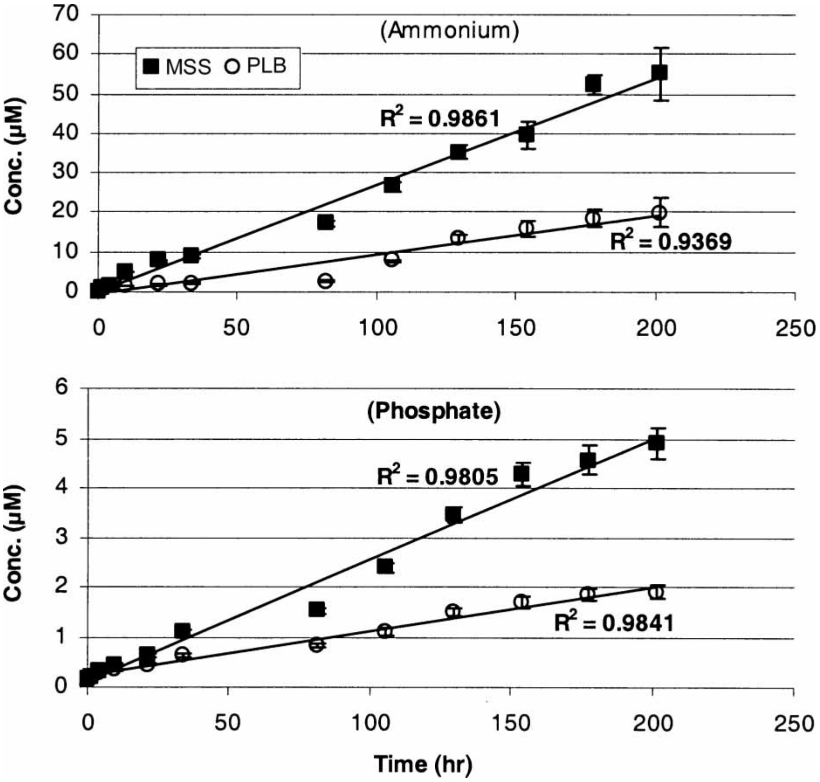

Figure 2. Changes in ammonium and phosphate concentrations in overlaying waters over 200 h of incubation with sediments collected from the MSS and PLB sites. Error bars represent the average of three incubation chambers.

2.3 *Analytical procedures*

The calcium carbonate content of the sediment was measured by complexmetric titration of calcium carbonate with 0.1 N of hydrochloric acid [13]. Organic carbon contents in the sediments were measured [14]. The ignition method was used for total phosphate determination in the sediment [15]. The redox potential for the water above the sediment surface was measured using a Mettler Toledo electrode. Inorganic nutrients (ammonium, phosphate, nitrate and nitrite) in the water were determined spectrophotometrically [16].

3. Results

3.1 *Sediment properties*

As expected, sediments at the first MSS site were characterized by high calcium carbonate concentrations (table 1) as this site has plentiful coral reef communities that can be the main source of carbonate sand. Sediments from the second MSS site were composed mainly of silicate sand. In the PLB, the sediment was contaminated with the phosphate deposits, as reflected in the high TP content of 13.6%. No important differences in organic carbon contents either between MSS and PBL sediment or between the sieved carbonate and silicate sediments were found.

Table 1. Basic chemical characteristics of sediments used in the incubation experiments.

	MSS	PLB	Sieved carbonate (MSS)	Sieved silicate (MSS)
$CaCO_3$ (%)	76.5	11.8	84.5	3.20
OC (g kg^{-1})	2.74	3.10	1.30	1.10
TP (g kg^{-1})	0.04	135.7	0.03	0.03

3.2 *Incubation experiments*

The time-dependent changes of incubation experiment 1 showed a progressive efflux for both ammonium and phosphate from the sediment to the water column, resulting in increased water column concentrations in both variables and for sediments from both investigated sites (figure 2). The elevation rates of both variables were higher in the MSS sediment incubation chamber than in the PLB chamber. The average daily efflux rates over a 200 h period from MSS carbonate sediment to overlying waters were about twofold higher than that of the PLB sediment for both ammonium and phosphate (figure 3).

Nitrate and nitrite concentrations increased in the overlying waters progressively during the first 2 days of incubation, and then started to decrease gradually until they reached steady-state concentrations of about 1.5 and 0.9 μM for nitrate and nitrite, respectively (figure 4). The redox potential in the overlying waters show similar changes to those of the nitrate and nitrite concentrations, indicating the dependence of the three variables on water oxygen concentrations. At the end of the incubation, the concentrations of nitrate and nitrite as well as the redox potential values in the overlaying waters were lower in the MSS chambers than in those of the PLB. The decrease in the three variables over the experimental period was higher in the case of MSS sediment than in the PLB sediment.

The nitrate concentration in the second incubation exhibited a similar behaviour to that in incubation experiment 1, as it increased initially (0–32 h), then decreased gradually at a rate of about 0.40 μM d^{-1} in both carbonate and silicate chambers (figure 5). The concentrations of DIP decreased gradually in the four incubation chambers (figure 6). The adsorption rate in the carbonate chambers calculated from DIP decrease was higher than that in the silicate chambers (0.48 ± 0.11 and 0.28 ± 0.11 mmol m^{-2} d^{-1} for carbonate and silicate, respectively). By the end of this incubation, DIP concentrations in the chambers decreased to 9 and 13 μM in the carbonate and silicate sediments, respectively.

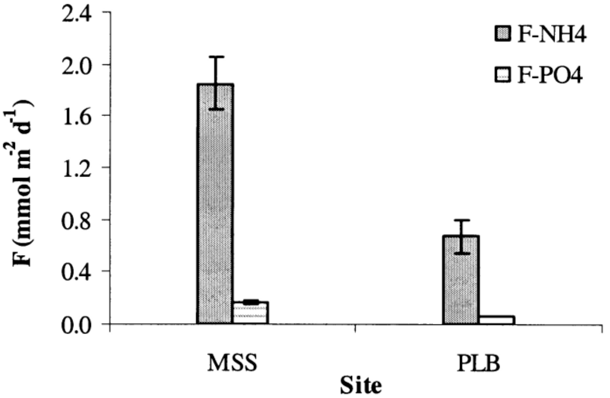

Figure 3. Average efflux rate (mmol m^{-2} d^{-1}) of ammonium and phosphate to overlying waters from sediments collected from the MSS and PLB over 200 h of incubation. Error bars represent the average of three incubation chambers.

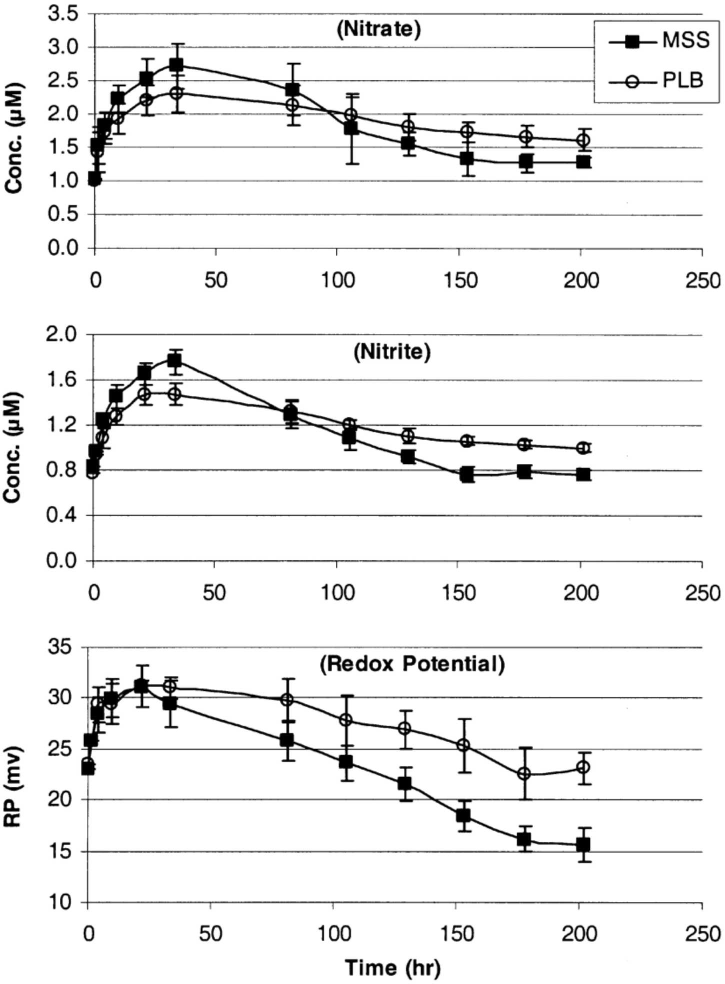

Figure 4. Changes in redox potential, nitrate and nitrite concentrations in overlaying waters over 200 h of incubation with sediments collected from the MSS and PLB sites. Error bars represent the average of three incubation chambers.

4. Discussion

4.1 *Nutrient fluxes from sediment*

Flux estimations show an apparent difference between the two sites (figure 3). High ammonium and phosphate fluxes were encountered in the case of the Marine Science Station carbonate sediment as compared with the sediment from the PLB, although the latter had higher organic carbon and phosphate concentrations (table 1). In general, material fluxes from sediments depend mainly on the rate of organic matter degradation, which results in mineralization of organic carbon, nitrogen, phosphorus and silicon to inorganic forms. As indicated by the redox potential profiles, the incubation conditions initially were relatively oxic with high oxygen concentrations that started to decrease, leading the incubations towards a less oxygenated state. Oxic respiration of organic matter can supply nitrate and nitrite for the water column [17, 18], whereas in sediments with a low oxygen concentration, ammonium can be supplied from nitrate reduction. Phosphate remains soluble under anaerobic conditions [19], and some

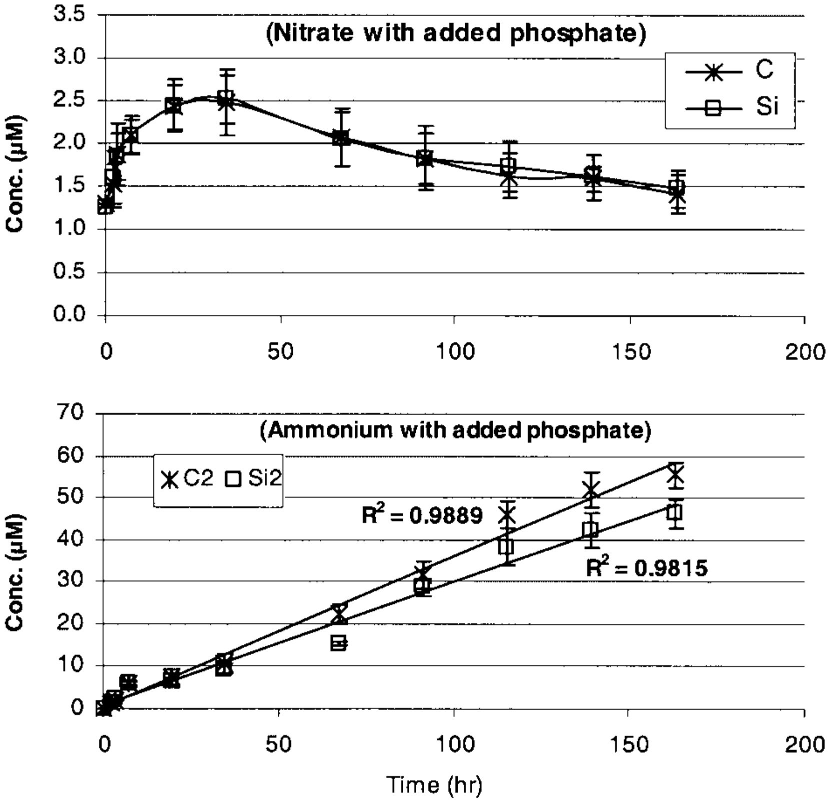

Figure 5. Changes in ammonium and nitrate concentrations in overlaying waters over 200 h of incubation with natural carbonate sediments and addition of soluble phosphate. Error bars represent the average of two incubation chambers.

iron oxyhydroxides which bind phosphate are converted to iron sulphides during sulphate reduction, which consequently results in free phosphate [20].

In addition to the chemical properties, mineralization of organic matter in the sediments depends also on the physical prosperities of the sediments such as permeability and mineralogy [8, 9, 21, 22]. The quality and quantity of degraded organic materials can also have some

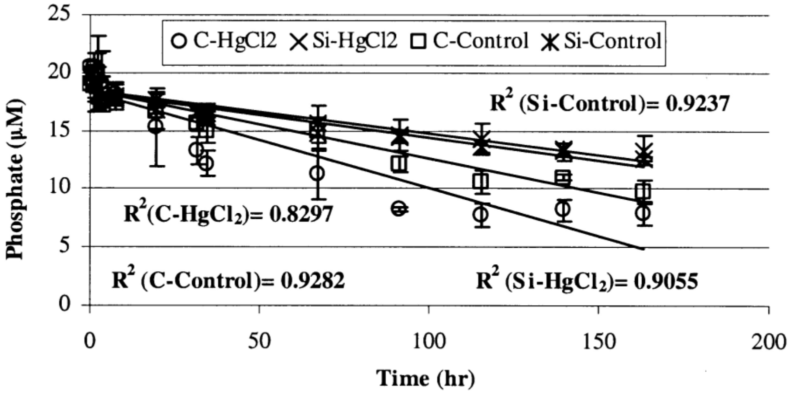

Figure 6. Phosphate adsorption on carbonate (C) and silicate (Si) sediments over 200 h of incubation under natural and sterile conditions (with added $HgCl_2$). Error bars represent the average of two incubation chambers.

effects [23]. The paradoxically higher ammonium and phosphate fluxes encountered in the MSS sediments than in the PLB sediments may be attributed to the type of organic materials in both sediments. MSS hosts a marine reserve with flourishing coral community including corals themselves and other living organisms accompanied with corals, as it is considered one of the most diverse and complex biological communities [24]. Organic materials produced from coral reef are generally degradable, as they are considered labile and fresh materials [25]. Within coral reef areas, phytoplankton density and chlorophyll *a* concentrations are relatively high [26, 27], and the decomposition of the detritus derived from phytoplankton is relatively fast [28, 29]. Accordingly, high degradation rates of organic deposits and high fluxes of inorganic materials are expected in the MSS sediment compared with PLB sediments. The PLB sediments are composed mainly of very fine mined phosphate deposits originating from the raw PLB [2]. These deposits have a high fraction of non-degradable refractory materials that result in low mineralization and fluxes.

4.2 *Phosphate regulation in carbonate sediment*

Phosphate enrichment may impact primary production as it is considered a limiting nutrient in some regions [30]. In tropical and subtropical regions where carbonate sediments are dominant at the shelf [8], phosphate regulation by adsorption on carbonate grains is well documented [10, 31–33]. It was demonstrated that the adsorption of phosphate on carbonate grains is a fast process, depending mainly on phosphate concentrations in addition to salinity and temperature [34]. Phosphate can also be trapped within the crystal lattice of carbonate granules [11, 12]. The second incubation experiment showed that adsorption of phosphate onto carbonate sediment was higher than on the silicate sediments under both sterile and non-sterile conditions (adsorption rates were 0.48 ± 0.11 and 0.28 ± 0.05 for carbonate and silicate sediment, respectively). To this effect, and taking into account that sediments in the coastal areas of the Gulf of Aqaba are mainly carbonate sediments, one may conclude that carbonate sediment may act as a buffer regulating phosphate concentration in the sea water by adsorption of dissolve phosphate.

The ammonium and nitrate concentrations in the set of incubations in the second experiment designed to test the effect of dissolved phosphate on nitrogen fixation were similar to those in incubation experiment 1, where there was no elevation of soluble phosphate concentration. This provides evidence of a weak or no effect of soluble phosphate in enhancing nitrogen fixation. The International Expert Team [3] claimed speculatively that the main source of both phosphate and nitrogen pollution in the northern Gulf of Aqaba is mainly Jordanian phosphate powder lost during shipment. This needs significant revision because it goes against scientific evidence. However, more work is still needed to support and quantify phosphate sequestration on carbonate sediments and to study the long-term steady-state conditions that result from such a phenomenon.

Acknowledgements

Thanks are due to Khalid Al-Trabeen and Ala Al-Tahan for their help in the lab. We would like to thank Abdullah Al-Momany for helping in sample collections. This work has been funded by the Marine Science Station, Aqaba-Jordan.

References

[1] M.H. Freemantle, N. Hulings, M. Mulqi, E.C. Watton. Calcium and phosphate in the Jordanian Gulf of Aqaba. *Mar. Pollut. Bull.*, **9**, 79–80 (1978).

[2] Abu-Hilal. Phosphate pollution in the Jordan Gulf of Aqaba. *Mar. Pollut. Bull.*, **16**, 281–285 (1985).

[3] International Expert Team. Evaluation of Pollution in the Gulf of Eilat. Report for Ministers of Infrastructure, Environment and Agriculture, Israel (2001).

[4] N. Gordon, D.L. Angel, A. Neori, N. Kress, B. Kimor. Heterotrophic dinoflagellates with symbiotic cyanobacteria and nitrogen limitation in the Gulf of Aqaba. *Mar. Ecol. Prog. Ser.*, **107**, 83–88 (1994).

[5] D. Lindell, A.F. Post. Ultraphytoplankton succession is triggered by deep winter mixing in the Gulf of Aqaba (Eilat), Red Sea. *Limnol. Oceanogr.*, **40**, 1130–1141 (1995).

[6] M.I. Badran. Dissolved oxygen, chlorophyll a and nutrients: Seasonal cycles in waters of the Gulf Aqaba, Red Sea. *Aquat. Ecosys. Health Manag.*, **4**, 139–150 (2001).

[7] M. Rasheed, M.I. Badran, C. Richter, M. Huettel. Effect of reef framework and bottom sediment on nutrient enrichment in a coral reef of the Gulf of Aqaba, Red Sea. *Mar. Ecol. Prog. Ser.*, **239**, 277–285 (2002).

[8] M. Rasheed, M.I. Badran, M. Huettel. Particulate matter filtration and seasonal nutrient dynamics in permeable carbonate and silicate sands of the Gulf of Aqaba, Red Sea. *Coral Reefs*, **22**, 167–177 (2003).

[9] M. Rasheed, M.I. Badran, M. Huettel. Influence of sediment permeability and mineral composition on organic matter degradation in three sediments from the Gulf of Aqaba, Red Sea. *Est. Coast. Shelf Sci.*, **57**, 369–384 (2003b).

[10] J. Dekanel, J.W. Morse. The chemistry of orthophosphate uptake from sea water into calcite and aragonite. *Geochim. Cosmochim. Acta*, **42**, 1335–1340 (1978).

[11] W. Balzer, B. Bodugen, F. Pollehne. Benthic degradation of organic matter and regeneration of nutrients in shallow water sediments off Mactan, Philippines. *Philippine Scient.*, **22**, 30–41 (1985).

[12] F.S. Sugai. Temporal changes in the sediment geochemistry of two southeast Alaskan fjords. *Deep Sea Res.*, **34**, 913–925 (1987).

[13] G. Muller. *Methods in Sedimentary Petrology*, Hafner, New York (1967).

[14] H.E. Gaudette, W.R. Flight. An inexpensive titration method for the determination of organic carbon in recent sediments. *J. Sedim. Petrol.*, **44**, 249–253 (1974).

[15] J.M. Andersen. An ignition method for determination of total phosphorus in lake sediments. *Water Res.*, **10**, 329–331 (1976).

[16] J.D.H. Strickland, T.R. Parsons. *A Practical Handbook of Seawater Analysis*, 2nd ed. Fish Research Board of Canada Bulletin, Ottawa, p. 311 (1972).

[17] D.E. Hammond, P. Giordani, G. Montanari, A. Rinaldi, R. Poletti, G. Rovatti, M. Astorri, M. Ravaioli. Benthic flux measurements in NW Adriatic coastal waters. *Mem. Soc. Geol. Italy*, **27**, 461–467 (1983).

[18] W.M. Berelson, D. Heggie, A. Longmore, T. Kilgore, G. Nicholson, G. Skyring. Benthic nutrient recycling in Port Phillip Bay, Australia. *Est. Coast. Shelf Sci.*, **46**, 917–934 (1998).

[19] S.M. Libes. *An Introduction to Marine Biogeochemistry*, Wiley, New York (1992).

[20] E.E. Roden, J.W. Edmond. Phosphate mobilization in iron-rich anaerobic sediments: Microbial Fe (III) oxide reduction versus iron-sulphide formation. *Arch. Hydrobiol.*, **139**, 347–378 (1997).

[21] R.G. Keil, D.B. Montlucon, F.G. Prahl, J.I. Hedges. Sorptive preservation of labile organic-matter in marine sediments. *Nature*, **370**, 549–552 (1994).

[22] R.S. Adams, R.M. Bustin. The effects of surface area, grain size and mineralogy on organic matter sedimentation and preservation across the modern Squamish Delta, British Columbia: the potential role of sediment surface area in the formation of petroleum source rocks. *Int. J. Coal Geol.*, **46**, 93–112 (2001).

[23] E. Kristensen, S. Ahmed, A. Devol. Aerobic versus anerobic decomposition of organic matter in marine sediment: Which is faster? *Limnol. Oceanogr.*, **40**, 1430–1437 (1995).

[24] Y.I. Sorkin. Coral reef ecology. In *Ecological Studies*, G. Heldmaier, O.L. Lange, H.A. Mooney, U. Sommer (Eds), p. 464, Springer, Berlin (1995).

[25] G. Hulthe, S. Hulth, O.J. Hall. Effect of oxygen on degradation rate of refractory and labile organic matter in continental margin sediments. *Geochim. Cosmochim. Acta*, **62**, 1319–1328 (1998).

[26] G. Yahel, A.F. Post, K. Fabricius, D. Marie, D. Vaulot, A. Genin. Phytoplankton distribution and grazing near coral reefs. *Limnol. Oceanogr.*, **43**, 551–563 (1998).

[27] M.I. Badran, P. Foster. Environmental quality of the Jordanian coastal waters of the Gulf of Aqaba, Red sea. *Aquat. Ecosys. Health Manag.*, **1**, 75–89 (1998).

[28] S. Henrichs, A. Doyle. Decomposition of ^{14}C-labeled organic substances in marine sediments. *Limnol. Oceanogr.*, **31**, 765–778 (1986).

[29] C. Richter, M. Wunsch, M. Rasheed, I. Kotter, M.I. Badran. Endoscopic exploration of Red Sea coral reefs reveals dense populations of cavity-dwelling sponges. *Nature*, **413**, 726–730 (2001).

[30] J.W. Fourqurean, J.C. Ziemen, V.N. Powell. Phosphorus limitation of primary production in Florida Bay: Evidence from C:N:P ratios of the dominant seagrass *Thalassia testudinum. Limnol. Oceanogr.*, **37**, 162–171 (1992).

[31] E. Ingall, R. Jahnke. Evidence for enhanced phosphorus regeneration from marine-sediments overlain by oxygen depleted waters. *Geochim. Cosmochim. Acta*, **58**, 2571–2575 (1993).

[32] A. Bertuzzi, J. Faganeli, A. Brambati. Annual variation of benthic nutrient fluxes in shallow coastal waters (Gulf of Trieste, Northern Adriatic Sea). *Mar. Ecol. Pubbl. Stn. Zool. Napoli*, **17**, 261–278 (1996).

[33] F. Spagnoli, M.C. Bergamini. Water–sediment exchange of nutrients during early diagenesis and resuspension of anoxic sediments from the Northern Adriatic Sea shelf. *Water Air Soil Pollut.*, **99**, 541–556 (1997).

[34] F.J. Millero, F. Huang, X. Zhu, X. Lui, J.-Z. Zhang. Adsorption and desorption of phosphate on calcite and aragonite in seawater. *Aquat. Geochem.*, **7**, 33–56 (2001).