CHARACTERIZATION OF PHOSPHORUS SPECIES DISCHARGED TO THE S.E MEDITERRANEAN BASIN FROM LANDBASED SOURCES

Mohamed A.R. Abdel-Moati

Oceanography Department, Faculty of Science, Alexandria University, Egypt - marabdelmoati@ hotmail.com

Abstract

Particulate phosphorus species were differentiated in water discharged to the SE Mediterranean basin. Despite the discharge of $1770x10^3$ MT y^{-1} of suspended matter to the SE Mediterranean, the area is still phosphorus limited. Variations in the quality of discharged water do not permit the appearance of a predominant phosphorus fraction. Iron bound phosphorus (P_{fe}) was enriched in the Nile discharge while elevated P_{org} levels were discharged from highly productive delta lakes and wastewater outfalls. Bioavailable phosphorus (P_{ex} and P_{org}) represents 16-67% of the particulate phosphorus pool.

Key words: Phosphorus, chemical speciation, coastal waters, Levantine basin

Introduction

Phosphorus is a key element in the biogeochemical cycles of the marine environment. Its availability in seawater is important in controlling its productivity. The SE Mediterrenean basin is the largest seawater body where primary production is phosphorus-limited. This unusual limitation may be due to inorganic processes adsorbing phosphorus onto labile iron hydroxides carried by Saharan dust and River Nile particulate matter. In estuarine or estuarine-like ecosystems, characterized by the transition from fresh to salt water environments, an understanding of the factors that regulate the biomass and production requires insight into the behaviour of the different forms of the targeted element rather than the total concentration. Since sequential extraction techniques are most promising for separating and quantifying various reservoirs, the aim of the present study is to evaluate the concentration levels of the main phosphorus forms in suspended matter and reconstruct a phosphorus input rate to the SE Mediterranean basin from landbased sources. It should help in understanding phosphorus biogeochemical cycling and its effect on the present day productivity.

Material and Methods

Water samples were collected from the major landbased sources discharging to the SE Mediterranean basin off the Egyptian coast. These include: Nile delta coastal lagoons opening to the Mediterranean (sites 1, 3, 5 and 7), a major sewage outfall off Alexandria city (site 2), the River Nile (site 4) and a major agricultural drain (site 6). Total phosphorus (P_{tot}) [1] and phosphorus forms [2] were determined on dried suspended matter obtained by centrifugation.The five steps SEDEX scheme was used to separate the following phosphorus pools: exchangeable + loosely-bound (P_{ex}); iron bound (P_{fe}); authigenic + biogenic apatite + $CaCO_3$ bound P (P_{au}); detrital apatite + other remaining inorganic phases (P_{det}) & organic (P_{org}) [2]. The method is suitable for measuring concentrations <0.005 wt %P. The method was tested for efficiency, specificity, matrix effect and reproducibility. Phosphate extracted from suspended matter was measured spectrophotometrically [3]. Simultaneously, suspended matter was tested for carbonate, organic content (Loss On Ignition) and chlorophyll a.

Results and Discussion

The amount and type of water discharged from the different landbased sources as well as its average TSM content are presented in Table 1. The SE Mediterranean waters off the Egyptian coast receives $18.3x10^9$ m^3 of fresh, brackish and wastewater (mainly sewage) annually from different landbased sources. About 20% of this amount are discharged from the Nile while 28% are derived from Lake Manzalah, the largest and most productive Nile Delta lake (Table 1).

Table 1. Amount and characteristics of water discharged to the SE Mediterranean.

Location	Landbased Discharge Points						
	L. Mariut	KBPS	L. Edku	R. Nile	L. Burullus	Gh. drain	L. Manzalah
TSM(mg/l)	26.9	53	87.7	138	113	105	31.5
POC/TSM %	79	68	33	53	32	26	83
Chl a (µg/l)	4.2	8.6	2.3	1.1	0.9	0.8	10.9
Discharge*	2.3	0.2	1.4	3.5	2.2	3.5	5.2
Water type	S+B	S	B	F	B	B	B
CO3/TSM %	18	31	54	44	62	58	22

KBPS= Kay Bey Pump Station *$x10^9 m^3 y^{-1}$ S=Sewage B=Brackish F=Fresh

The concentrations of different particulate phosphorus species as well as their contribution to P_{tot} are presented in Table 2. P_{ex} contributed to about 2-22% of P_{tot}. P_{ex} concentrations are proportionally related to particle size. Pex decrease gradually by increasing salinity seawards from landbased sources.Variations in P_{ex} concentrations depend on alteration in redox conditions and adsorption capacity. When semi-reducing conditions prevail, P_{ex} reached maximum levels. P_{ex} is the most bioavalable fraction especially when phosphorus concentration in the water column is low.

Phosphorus associated with Ca appears either as detrital fluoroapatite of igneous and metamorphic origin (P_{det}) or other forms as biogenic skeletal debris and $CaCO_3$ incorporated phosphate (P_{au}) [4]. P_{det} showed a negative correlation with P_{au}. Organic matter oxidation and sulphide occurrence enhance $CaCO_3$ dissolution leading to low P_{au} and P_{det} contribution to P_{tot} at locations 1 and 2. The extraction method can not discriminate between apatite forms, e.g., fish bone debris from igneous apatite-P. In the present study, at least 30-50% of the suspended phosphorus pool represents an insoluble phase and is ignored when looking for water column phosphorus enrichment.

Table 2. Average concentrations of particulate phosphorus fractions (µmol g^{-1})

Form	Landbased Discharge Points						
	Lake Mariut	KBPS	Lake Edku	River Nile	Lake Burullus	Gharb drain	Lake Manzalah
P_{ex}	2.16±0.7 (22)	0.65±0.3 (7)	0.4±0.2 (6)	0.34±0.2 (2)	0.6±0.1 (7)	0.±0.1 (6)	0.88±0.6 (6)
P_{fe}	0.3±0.1 (3)	0.3±0.9 (3)	1.8±0.3 (23)	5.2±1.1 (35)	2.69±0.3 (33)	2.66±0.2 (31)	1.670.5 (12)
P_{au}	1.9±0.4 (19)	2.1±1.1 (22)	2.7±0.9 (35)	3.6±1.7 (24)	2.1±1.1 (26)	1.9±1.6 (22)	4.3±0.9 (31)
P_{det}	1.21±0.7 (12)	0.8±0.3 (8)	1.1±0.6 (14)	1.7±1.0 (12)	1.9±0.7 (24)	2.4±1.6 (28)	0.9±0.4 (6)
P_{org}	4.31±2.81 '44)	5.84±1.1 (60)	1.66±1.3 (22)	3.94±1.2 (27)	0.8±0.2 (10)	1.15±0.9 (13)	6.37±2.09 (45)
P_{tot}	10.5±2.1	10.3±3.6	7.8±1.9	14.8±3.3	8.3±1.5	8.7±1.1	14.8±2.8

**Number between paranthesis is the % from the sum of species*

The release of P associated with reducible iron oxide in the low oxygen (<2-3.5 mg/l) and pH 6.8-7.3 bearing water, opposite to Lake Mariut and sewage outfall, lowered the concentration of P_{fe}. On the other hand, ferric oxyhydroxide particles, formed under oxic conditions, have a high adsorption capacity for phosphorus. The Nile water characterized by fine-sized particles and high Fe levels showed the maximum concentrations of P_{fe} (5.2 ± 1.1 μmol g^{-1}). The well-oxygenated waters (>5.5 mgl/l) and pH (8.1-8.3) render the P_{fe} fraction to be insoluble and non- reactive in the water column. Such a release leads to highly eutrophic coastal areas as indicated by their elevated chlorophyll a levels (4.2 and 8.6 μg/L, respectively). The gradient of P_{fe} decline at the mixing zone with seawater was much more pronounced than that of P_{au} and P_{det}. A high linear correlation (R^2= 0.74, $p<0.001$) appeared between total inorganic phosphorus and P_{ex} indicating that sequestering mechanisms, other than adsorption on compounds, are kinetically slow and unimportant and concern early diagensis for the inorganic phosphorus cycle.

P_{org} (range 0.8 ± 0.2 to 6.37 ± 2.9 μmol g^{-1}) is the most heterogenous phase due to its continuous modification by degradation processes constituting between 10 and 60% of Ptot. The coincidence between chlorophyll a concentrations and P_{org} suggested that most of the organic phosphorus is derived mainly from phytoplankton with little originating from macrophytes or that changes in phytoplanktonic growth and productivity are related to P_{org} remineralization. Organic phosphorus and organic carbon showed a significant correlation (R^2=0.85, p<0.001) suggesting a common origin. Most of previous studies did not clearly observe such a relationship since P_{org} is calculated by substraction from the P_{tot} [5]. For the coastal sediments off Alexandria, P_{org} makes up about 20.9±3.72% of P_{tot} with a mean concentration of 6.9±3.37 μmol g^{-1}[6]. P_{org} showed no clear trend in relation to salinity variations along the mixing zone.

The sum of all extracted P phases was not significantly different from P_{tot} (<6%). Carbonate rich samples showed lower differences between the sum of species and P_{tot} (<1-3%). Generally, the concentrations of the P fractions derived for the SE Mediterranean are low compared to those in other estuaries.

About 1770x10^3 MT y^{-1} of suspended matter are discharged to the SE Mediterranean.Most of this material drifts eastward to Tena Bay via longshore currents. Low speed currents along the Egyptian coast (range 11-50 cm s^{-1}) permit the fast settling of this material to the bottom.

References

1. Aspila K.I.; Agemian H. and Chan A.S., 1976. A semi- automated method for the determination of inorganic, organic and total phosphate in sediments. *Analyst,* 101 : 187-197.
2. Ruttenberg K.C., 1992. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnology & Oceanography*, 37 (7): 1460-1482.
3. Strickland D.H. and Parsons I., 1972. A practical handbook of seawater analysis. *Fisheries Research Board of Canada, Ottawa*, 310 pp.
4. Andrieux F. and Aminot A., 1997. A two-year survey of phosphorus speciattion in the sediments of the Bay of Seine (France). *Cont. Shelf. Res.*, 17 (10) : 1229-1245.
5. Mach D.L.; Ramirez A. and Holland H.D., 1987. Organic phosphorus and carbon in marine sediments. *Am. J. Sci.*, 278 : 429-441.
6. El-Sammak A.A., 1994. Preservation of organic phosphorus in shelf sediments west off the Nile delta, Egypt. *Fresenius Envir Bull.*, 3 : 528-533.

Introduction

The Aegean Sea is an area of high seismic activity associated with important geothermal gas venting in shallow waters ranging from 2 to 120 m depth (1). Fluids from the vents, bacteria, and particles produced in the vent ecosystem are advected by currents and create a plume that spreads laterally at a level of neutral buoyancy. The geochemical cycling and biological production in these shallow hydrothermal systems is still largely unknown, particularly with respect to their importance in the production and export of particulate organic material. The present paper reports on the chemical composition of the settling material collected in particle interceptor traps deployed along the SE coast of Milos (Aegean Sea, Figure 1), in one area known for its extensive geothermal activity in the seabed (A) and in another presumed to be free of any major vent influence (B). The distributions of aliphatic and aromatic hydrocarbons and sterols, as source and maturity chemical indicators, were determined in order to contribute to a better understanding of the above processes.

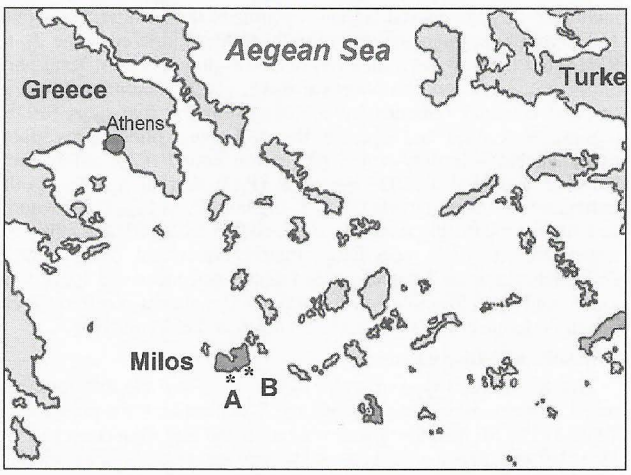

Fig. 1. Map of the Aegean Sea showing the location of the moorings. Site A is located in the vent zone off Paleohori Bay and site B beyond the influence of the submarine vents. Both moorings were located approximately 1 nautical mile offshore, and separated by a distance of about 3.5 nautical miles.

Materials and Methods

Moorings were deployed from June to September 1996, to collect during consecutive periods of 12 days settling particles at 60m over a bottom of 90m depth. Collected particles (50 mg ± 0.1), stored at –20°C until they were processed in the laboratory, were freeze dried and extracted (3 times) by sonication with 5 ml of dichloromethane and spiked with cholestane, deuterated pyrene and 5α-androstan-3β-ol as analyte surrogates. The organic extracts were concentrated by rotary evaporation to 1-2 ml, dried over anhydrous N_a2SO_4, and fractioned by column chromatography (5 x 20 mm) with 0.5 g of 3% water-deactivated alumina. Four fractions were collected: (I) 6 ml of