

**Seasonal fluxes of
phosphate across the
sediment-water interface
in Edku Lagoon, Egypt**

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Abstract

Edku Lagoon is a shallow, brackish, coastal wetland located in the north-western part of the Nile Delta. It suffers from a high level of eutrophication, owing to the heavy load of nutrients, especially phosphorus. The purpose of this paper was to study the flux rates of organic and inorganic phosphorus across the sediment water interface in Edku Lagoon. Both the organic and inorganic phosphorus of surface sediments, pore water and their concentrations in the water just above the sediments were used to calculate the flux rates and to derive the geochemical models. These suggest that, at present, the flux of inorganic and organic phosphorus is from water to sediments via the sedimentation of inorganic particles and organic matter. The results show that phosphorus deposition to the sediments exceeds the rate of inorganic phosphorus release from the sediments to the water column. In a steady state, the rates of organic phosphorus release more or less match the rates of deposition. These reflect the imbalance (accumulation) of phosphorus in the geochemical cycle in the lagoon and its highly eutrophic status. Efforts to control the eutrophication of Edku Lagoon have focused on reducing the phosphorus input.

The complete text of the paper is available at <http://www.iopan.gda.pl/oceanologia/>

1. Introduction

Sediments play an important role in phosphorus (P) cycling in shallow lagoon ecosystems, acting both as a sink and a source of P due to the continuous transport of chemical species across the sediment-water interface (Jorcin & Nigueira 2005). The P concentration in the water column in shallow lakes can thus be buffered by sediments (Zhang et al. 2001). Phosphorus releases from sediments can be an important factor in controlling the trophic state of aquatic systems, especially in shallow waters (Ingall & Jahnke 1997). It is commonly assumed that a major carrier for phosphate in sediments is organic matter, which acts as a source of nutrients to microbial communities (Faul et al. 2005, Ruttenberg 2009). The total decomposition of organic matter returns carbon (C), nitrogen (N) and P to their soluble forms. In anaerobic sediments, bacteria reduce nitrate to dinitrogen gas (N_2) and mineralize ammonium from organic matter. Thus, ammonium and phosphate may be released from the sediments to the overlying water, enhancing primary production in an amplified positive feedback (van Cappellen & Gaillard 1996).

As diagenetic processes depend on organic matter, temperature, oxygen availability and sediment grain size (Chapelle 1995, Asmus et al. 2000), benthic fluxes are influenced by these environmental factors (Wilson & Brennan 2004), leading to spatial and temporal variability in sediment-water nutrient exchanges in most coastal environments (Vidal & Morgu  1995). Other factors potentially influencing sediment phosphorus retention include the pH of the overlying water (by affecting the strength of ionic phosphate sorption to sediment solid surfaces), the quantity and quality of the organic-C input, inputs of P-bearing minerals, bioturbation epipelagic photosynthesis, rooted plant activity, concentrations of organic matter in sediment, reactive iron, dissolved sulphate and calcite, and other sediment characteristics (Wetzel 2001).

Edku Lagoon, one of the northern Nile Delta Lakes, receives vast inputs of terrigenous and anthropogenic nutrients (especially P and N compounds) from agricultural runoff, sewage and drain discharges. These nutritional conditions create a rich resource spectrum for algal growth and make the lake biologically productive. Previous studies conducted on the hydrography, biological and chemical characteristics of Edku Lagoon water and sediments (Hemeda 1988, Ibrahim 1994, Shata 2000, Zaghloul 2000, Okbah & Gohary 2002, Shakweer 2006, Khalil 2007) concluded that this lake suffered from a high level of eutrophication, due to the heavy load of nutrients. Phosphorus release studies of Edku Lagoon focused mainly on the total P form (Badr & Hussin 2010), whereas the release of soluble reactive phosphorus (SRP) and dissolved organic phosphorus (DOP) was often

ignored. In fact, DOP in lagoon ecosystems has been recognized as an important source of P for aquatic organisms (Edlund & Carman 2001, Kim et al. 2003). The objective of the present study was therefore to develop a model showing the mobility of inorganic phosphorus (IP) and organic phosphorus (OP) across the sediment-water interface. The model simulations show the interaction between the dissolved and solid phases of P and quantify the processes of sedimentation, adsorption/desorption, partitioning, mineralization, decomposition and diffusion taking place at the sediment-water interface.

Mathematical models are valuable tools for integrating existing knowledge of relevant biogeochemical mechanisms and their interactions and for predicting the behaviour of P in lagoon ecosystems. Extensive work on the quantitative description of P release fluxes and processes has been conducted. The primary objective of this modelling exercise was to provide quantitative predictions of P dynamics for research and the management of eutrophication.

2. Material and methods

Study area

Edku Lagoon is a shallow, eutrophic, brackish, coastal wetland located in the north-western part of the Nile Delta, west of the Rosetta branch about 30 km east of Alexandria. It lies between latitudes $30^{\circ}12'30''\text{N}$ and $30^{\circ}16'17''\text{N}$, and longitudes $31^{\circ}18'41''$ and $32^{\circ}09'30''\text{E}$ (Figure 1). The lagoon is connected to the Mediterranean Sea through a narrow channel (Boughaz El-Maadyia). Satellite images from 2007 indicate that the total surface area of the lagoon is about 62.5 km^2 , 22 km^2 of which is open water; the remaining area (42.7 km^2) is covered by aquatic vegetation, islands and islets. According to these estimates, the open water area thus represents only 35% of the total surface area of the lake (Moufaddal et al. 2008).

Edku Lagoon receives huge amounts of drainage water from two main drains, namely El-Khairy (annual inflow $592 \times 10^6 \text{ m}^3$) and Barsik (annual inflow $348 \times 10^6 \text{ m}^3$), which open into the eastern basin of the lagoon (Badr & Hussin 2010). The water sources of El-Khairy Drain are from three drainage waters coming from El-Bousely, Edku and Damanhour sub-Drains, transporting domestic, agricultural and industrial wastes, as well as effluents from more than 300 fish farms. Barsik Drain transports mainly agricultural drainage water to the lagoon. These drainage waters mostly give rise to water movement through the lagoon from both east and south to the north. The north-western part of the lagoon also receives seawater through Boughaz El-Maadia from Abu Qir Bay, a shallow basin into which

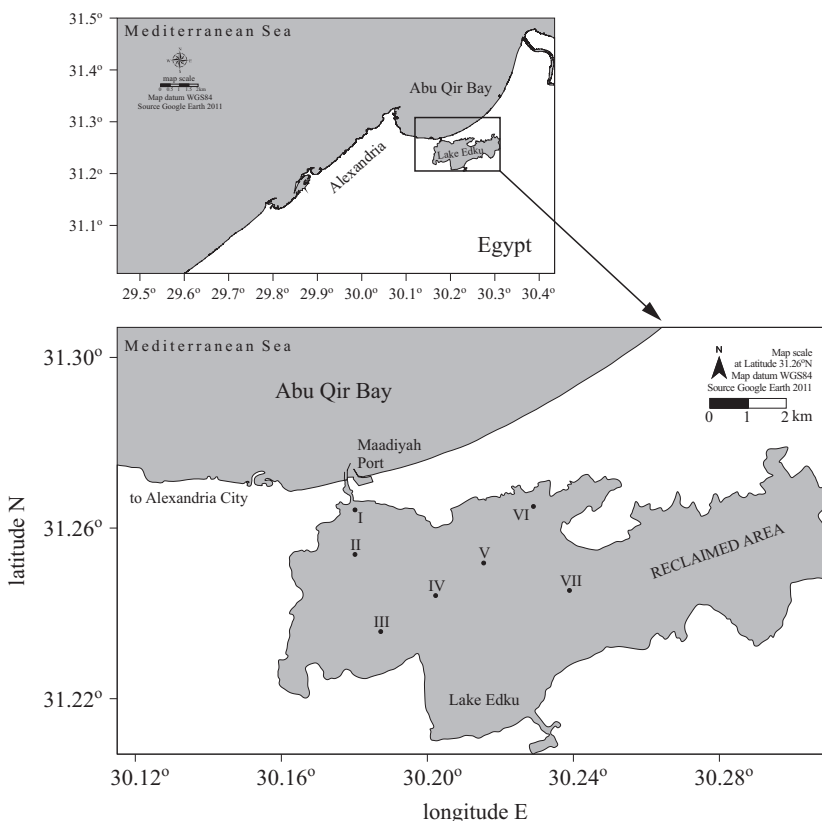


Figure 1. The study area and the locations (defined by Roman numerals) of sediment and water samples

considerable amounts of raw industrial wastes from several factories are discharged through El-Tabia Pumping Station at an average flow rate of $2 \times 10^6 \text{ m}^3 \text{ d}^{-1}$. The residence time (J) of the lagoon water in each season is 26, 54, 33 and 21 days for autumn, winter, spring and summer, respectively, with an annual average of 34 days (Badr & Hussin 2010).

Sampling and analysis

Surface sediment and the overlying water samples were collected seasonally from seven sampling sites (Figure 1). Sediment samples were put into polyethylene vials filled to the brim to prevent the entrapment of air bubbles, and immediately stored in an ice box to avoid post-oxidation. Water samples were collected in 1 L plastic bottles, from which 250 mL samples were immediately frozen for the determination of P forms.

Samples of overlying water were passed through $0.45 \mu\text{m}$ Millipore filters and stored at 4°C until analysis. Sediment samples for pore water

analysis were centrifuged for 30 minutes at 3000 rpm to separate particulate matter. Water temperature was measured using a simple thermometer graduated to 0.1°C; the pH was measured using a pocket pH meter (201/digital pH meter). Dissolved oxygen was determined using Winkler's method (Strickland & Parsons 1972). Water and pore water chlorosity were measured according to Mohr's titrimetric method. The dissolved inorganic and organic P in pore water and overlying water were determined photometrically (Strickland & Parsons 1972). The sediment samples were analysed following Folk's (1974) technique to determine the mean grain size. Total organic C was determined by the dichromate wet oxidation method of Walkley & Black (1934). Total, inorganic and organic P was determined according to Aspila et al. (1976). The water content and the porosity were also determined.

Model computations

The measured water and sediment properties data were used to calculate the fluxes of P forms to and from the surficial bottom sediments of Edku Lagoon. The model computations were conducted on the basis of the model calculations stated by Rifaat et al. (2012), namely,

$$F_s = U_s C_g \rho_s (1 - \emptyset) \text{ g cm}^{-2} \text{ yr}^{-1} \quad (\text{flux to sediment}),$$

$$F_d = -\emptyset D_s (\partial c / \partial z) \quad (\text{desorption flux}),$$

$$F_a = \emptyset V (K + 1) C_{\text{water}} \quad (\text{adsorption}).$$

The flux to sediment was calculated using the equation given in Lerman (1979):

$$F_s = U_s C_g \rho_s (1 - \emptyset) \text{ g cm}^{-2} \text{ yr}^{-1}.$$

Fick's first law was used to calculate the desorption flux from the surface sediment to the bottom water (Berner 1980); the equation was adapted by Andrieux-Loyer et al. (2008) thus:

$$F_d = -\emptyset D_s (\partial c / \partial z).$$

The adsorption of phosphorus onto sediment from bottom water was calculated using the equation from Lerman (1979):

$$F_a = \emptyset V (K + 1) C_{\text{water}}.$$

The flux of phosphorus to the bottom water due to the mineralization of organic matter was calculated using the decay rate computed from Rothman & Forney (2007), and the flux due to the dissolution of carbonate particles was calculated using the dissolution rate given by Lerman (1979).

The detailed method of computations is given in Rifaat et al. (2012). The geochemical model of IP and OP in Edku Lagoon is presented in Figure 2: it shows the fluxes of phosphorus across the sediment/water interface. The model is based on primary mechanisms regulating phosphorus behaviour in sediments, including sedimentation, adsorption/desorption, oxidation, decay and diffusion.

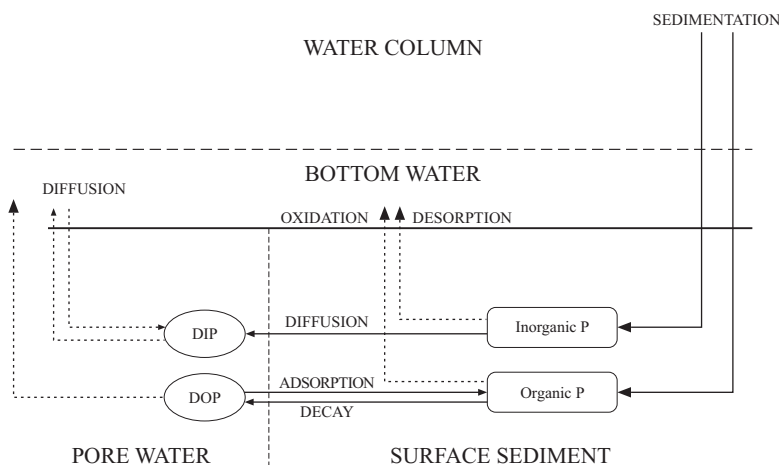


Figure 2. Model of phosphorus consumption in Edku Lagoon

3. Results

The physical and chemical properties of the lagoon bottom water, pore water and surficial bottom sediments are summarized in Tables 1 and 2. The chlorosity of the bulk water of the lagoon remained at nearly the same level (average 0.76 g Cl L^{-1}) during the warm seasons (spring and summer). But in the cold season, winter, the chlorosity of this water rose noticeably to nearly double the warm-season value (1.89 g Cl L^{-1}). The chlorosity of the pore water was high in winter and low in the warm seasons owing to the influent water from drains. Generally, the temperature increased progressively from winter (minimum temperature) to spring and summer (maximum temperature) but dropped in autumn. In general, the pH of the lagoon water during the four seasons was more or less the same, except in summer and autumn. The high values of dissolved oxygen (DO) in winter (9.4) were due mostly to the increase in solubility of oxygen in winter and to the decrease in activities of the indigenous organisms. In summer, the DO concentration fell to a lower level. Dissolved iron (DFe) was low in autumn and winter but high in spring and summer. Generally, the dissolved iron concentration in the pore water of the surface sediments

Table 1. Seasonal average chemical properties of Edku Lagoon bottom water and pore water

Parameter	Units	Winter	Spring	Summer	Autumn
bottom water					
temperature	°C	16.6	17.5	29.9	20.5
chlorosity	g L ⁻¹	1.89	0.9	0.63	2.34
pH		8.53	8.59	8.31	8.17
transparency	cm	84	84	63	63
suspended solids	mg L ⁻¹	80	96.8	67.7	67.9
dissolved oxygen	mg O ₂ L ⁻¹	9.4	8.3	4.2	6.7
dissolved Fe	μM	0.64	2.43	2.67	0.9
total Fe	μM	15.73	10.45	14.66	20.75
DIP	μM	2.83	8.24	2.35	2.86
DOP	μM	1.97	2.33	1.75	1.17
pore water					
chlorosity	g L ⁻¹	3.03	0.95	0.74	0.68
dissolved Fe	μM	5.63	12.38	4.25	3.96
DIP	μM	17.43	5.68	11.94	4.12
DOP	μM	8.42	27.58	4.62	3.06

Table 2. Geochemical parameters of surface sediments

Parameter	Units	Winter	Spring	Summer	Autumn
mean size	Φ	6.11	5.31	4.99	5.49
density	g cm ³	1.5	1.5	1.5	1.5
porosity	%	0.52	0.52	0.52	0.52
organic matter	%	10.9	9.8	9.2	9
Fe	%	4.3	3.7	3	3.8
IP	μg g ⁻¹	734	717	658	717
OP	μg g ⁻¹	257	266	193	215

was much higher than that in the overlying water. The minimum soluble inorganic phosphate level (DPP) was recorded in the winter season (low influent water). A high level of soluble organic phosphate (DOP) was recorded in spring; this seems to be connected with the increase in the OP loading from the drainage basin in spring. In general, the DPP level in the pore water of the surface sediments was higher than that of the overlying water during most of the seasons except spring. The average sediment grain sizes in winter, spring, summer and autumn were 6.1, 5.3, 5 and 5.5Φ respectively. There was no distinct difference in the distribution of the organic matter content between the four seasons. A high average level was

recorded in winter (10.9%), and a lower one (9.1%) in autumn. Sediment phosphorus followed the opposite trend to P in water; IP in sediment was high in winter ($734 \mu\text{g g}^{-1}$) and low in summer ($658 \mu\text{g g}^{-1}$).

The geochemical models of IP and OP in Edku Lagoon are presented in Table 3. All the movements of phosphorus from water to sediments take place by two processes: sedimentation of inorganic particles and organic matter. The IP flux from water to lagoon sediments (sedimentation of inorganic particles) during the four seasons is much the same, with an average flux rate of $3.31 \times 10^{-4} \pm 0.15 \times 10^{-4} \text{ g cm}^{-2} \text{ yr}^{-1}$ and a relatively higher value in winter. OP flux rates (sedimentation organic matter) peak in spring at $2.2 \times 10^{-8} \text{ g cm}^{-2} \text{ yr}^{-1}$.

The reactions releasing phosphates from sediment to bottom water are desorption and oxidation of organic matter. The model desorption flux of IP shows that the maximum value ($7.5 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$) is recorded in winter. Both spring and winter show the highest release of OP to the bottom water ($2.1 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$ and $2.4 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$ respectively).

Table 3. Flux rates of inorganic and organic phosphorus for the four seasons

Processes	Autumn	Spring	Summer	Winter
sedimentation (IP)	3.37×10^{-4}	3.4×10^{-4}	3.1×10^{-4}	3.4×10^{-4}
sedimentation (OP)	1.6×10^{-8}	2.2×10^{-8}	1.5×10^{-8}	2.0×10^{-8}
desorption	5.9×10^{-9}	5.8×10^{-9}	6.4×10^{-9}	7.5×10^{-9}
oxidation (OP)	1.5×10^{-9}	2.4×10^{-9}	1.5×10^{-9}	2.1×10^{-9}
adsorption		5.4×10^{-9}		8.4×10^{-10}
diffusion (pore water)	4.3×10^{-9}	5.2×10^{-9}	2.7×10^{-9}	5.1×10^{-9}
decay	6.4×10^{-10}		6.6×10^{-10}	
diffusion (IP)	9.6×10^{-11}		1.2×10^{-9}	3.2×10^{-10}
diffusion (OP)	2.3×10^{-10}	3.4×10^{-9}	3.5×10^{-10}	9.0×10^{-10}
diffusion (pore water)		4.4×10^{-10}		

Sediments contributed phosphorus to pore water by three processes: decay of organic matter, adsorption from pore water to sediment, and diffusion to pore water (Figure 2). The IP diffusion flux models exhibit a seasonal variation throughout the year, increasing during winter and spring ($5.1 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$ and $5.2 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$ respectively), but decreasing during summer ($2.67 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$). OP liberation from the sediment to pore water depends on the diffusion and decay of organic matter. These processes seem to be reversed in spring and winter (Table 3). In autumn and summer, owing to the decay of organic matter, the sediment acts as a source of OP to pore water.

All the phosphorus contributions from pore water to bottom water occurred through two processes: diffusion to bottom water and diffusion to pore water. The diffusion flux of IP from pore water to bottom water was high in summer ($1.2 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$), whereas in spring the direction was reversed, with diffusion taking place from bottom water to pore water. The diffusion flux of OP varied seasonally with the highest diffusion flux in spring ($3.4 \times 10^{-9} \text{ g cm}^{-2} \text{ yr}^{-1}$).

4. Discussion

Owing to concentration differences in the sediment layers, phosphorus is transferred between the aerobic and anaerobic layers and is exchanged between sediment particles and pore-water. The phosphorus is desorbed from sediment particles to pore water in the anaerobic layers, whereas it is absorbed from pore water to the sediment in the aerobic layers. These processes allow P recycling in sediments, where the sediments act as a reservoir regulating P dynamics in Edku Lagoon.

According to Wang et al. (2003), particulate organic and exchangeable P fluxes are downward from the aerobic layers to the anaerobic layers, whereas dissolved P diffuses upwards from the anaerobic layers to the aerobic layers. A portion of the dissolved P in the aerobic layers is released into the overlying water. As a result of burial processes, phosphorus is lost into deeper sediments in that the sediment-water active layer moves upwards.

There are several reasons driving P release from the sediment, such as diffusion, wind-induced water turbulence, bio-turbulence, gas dilution, attached algae and rooted aquatic plants (Wetzel 2001). Release of phosphate from sediment to pore waters can be due to (1) microbial degradation of organic matter (Canfield et al. 2005); (2) polyphosphate accumulating species (Schulz & Schulz 2005, Diaz et al. 2008); (3) desorption from iron oxides when iron reduction takes place (Paytan & McLaughlin 2007) and (4) dissolution of P-containing mineral forms during subsequent alteration (Baturin & Dubinchuk 2003).

The present study indicated that there was no sharp difference in the sedimentation model of inorganic particles between the four seasons. The relatively higher sedimentation in winter ($3.4 \times 10^{-4} \text{ g cm}^{-2} \text{ yr}^{-1}$) was partially due to the oxicity of the sediment surface, where the bottom water dissolved oxygen reached $9.4 \text{ mg O}_2 \text{ L}^{-1}$. This indicates strong adsorption of dissolved phosphate to solid iron oxyhydroxides. In winter, the overlying water was oxygen-rich, and Fe was in the Fe (III) form, which forms an insoluble phosphate compound. When the sediment surface is oxidic, strong adsorption of dissolved phosphate to solid iron oxyhydroxides limits phosphorus efflux by preventing phosphate diffusion into the water

column from deeper, reduced, sediment. Under anoxic conditions, iron oxyhydroxides reductively dissolve, and phosphate is released into the water column. The apparent success of the classical model resulted in the widespread attribution of P mobilization incidents to sediment redox conditions for a variety of situations and time scales (Prairie et al. 2001, Gächter & Müller 2003).

The high IP desorption flux from sediment to bottom water was modelled in the winter season. It is widely recognized that wind-induced mixing processes in winter play an important role in the overall release of P from the sediments. As is commonly observed in shallow lagoons, the movement of boats and a moderate wave height in Edku Lagoon are enough to induce resuspension of the bottom sediments. The IP desorption flux from resuspended and reductive dissolution can result in a large contribution to the total nutrient load in the lagoon water (Haggard et al. 2005). Studies in a shallow, wind-exposed lake in Denmark (Sondergard et al. 1992) showed that the phosphorus loads induced by resuspension could be 20–30 times greater than that released from undisturbed bed sediments. As such, sediment feedback could represent a potential source of P to the overlying lake waters, which in turn have a significant impact on the recovery of such a system, especially in shallow lakes (Savchuk 2002).

The maximum fluxes of IP from sediment to pore water occurred in winter and spring. This indicates that during the period of lower temperatures, oxygen availability increases in pore water due to its enhanced solubility (Moutin 1992), which in turn activates IP release from sediment to pore water (Bally et al. 2004).

The source of IP in pore water could be partly due to its mineralization from the buried organic matter containing P. The other part could be derived from the release of adsorbed PO_4 onto the surface of clays and/or precipitated iron oxide, due mostly to the change in the redox potential of the retained interstitial water there and the dissolution of iron oxides.

Particulate and dissolved organic phosphorus forms undergo bacterial decomposition (mineralization) and the phosphorus is transferred into the soluble orthophosphate pool.

The IP concentrations in pore water generally exceeded bottom water soluble reactive phosphorus concentrations, suggesting chemical gradients supportive of P release throughout the year. Comparison of the seasonal variations in pore and bottom water IP concentrations showed that concentration gradients were reduced during the spring, when pore water IP ($5.68 \mu\text{M}$) concentrations were lowest and bottom water IP ($8.24 \mu\text{M}$) concentrations highest. Therefore, the benthic flux of IP in this season changed direction (downwards) from the overlying water to the sediment

pore water. IP peaked in winter, when the regeneration rate of IP diffusion from the sediments to pore water was greater than its rate of diffusion from the overlying water.

In spring the major part of the OP contributing to the sediment by the sedimentation of organic matter ($2.2 \times 10^{-8} \text{ g cm}^{-2} \text{ yr}^{-1}$) could be attributed to the increased volume of agricultural drain water effluents entering the lagoon.

The release of OP from the bottom sediment to the overlying water (oxidation of organic matter and release of OP) was high in spring and winter. The organic carbon content in the bottom sediment increased in winter (10.9%) and in spring (9.8%). Wang et al. (2008) pointed out that OP release from the sediments was enhanced by the presence of organic matter.

OP liberation from the sediment to pore water depends on the diffusion and decay of organic matter. These processes seem to be reversed in spring and winter when OP diffuses from the pore water to the bottom sediment (Table 3). In summer and autumn, on the other hand, the sediment acts as a source of OP to pore water owing to the decay of organic matter. Schulz & Schulz (2005), Arning et al. (2008) and Diaz et al. (2008) concluded that the release of phosphate from particulate material into interstitial waters was caused by the benthic regeneration of organic matter, the dissolution of fish debris, desorption from iron particles and the metabolism of polyphosphate storing species.

During downward and upward transport, sorption also takes place (Wang et al. 2003). Generally, the bottom conditions during the present study were aerobic, except in spring and winter, when mixing processes intensified, so that the bottom became well oxygenated (dissolved oxygen = 9.4 and 8.3 mg O₂ L⁻¹ respectively). Dissolved iron concentrations were high in winter and spring (5.6 and 12.8 μM respectively). Phosphorus was desorbed from sediment particles to pore water in the summer and autumn, whereas it was adsorbed from pore water to sediment under good oxygen conditions. These processes allow phosphorus recycling in sediments, where the sediments act as a reservoir regulating phosphorus dynamics in Edku Lagoon.

5. Conclusions

It can be concluded that phosphorus in Edku Lagoon is controlled by sedimentation, desorption, oxidation and diffusion. The capacity of the sediment to retain and release phosphorus can be an important factor as regards predicting its environmental impact. It has been shown in the present study that the deposition (sedimentation) of inorganic phosphorus

from the overlying water to the sediment exceeded the rate of inorganic phosphorus release (desorption and diffusion). In a steady state, the rates of organic phosphorus release (oxidation and diffusion) roughly match the rates of deposition. These reflect the imbalance (accumulation) of inorganic phosphorus in the geochemical cycle in the lagoon and indicate that the status of this lagoon is highly eutrophic. These conditions make the lagoon biologically productive. A major effort to control the eutrophication of Edku Lagoon has been directed towards reducing the phosphorus input. This change in phosphorus storage indicates that there is an overall gain and accumulation in the water column and sediments in the lagoon from one season to another. The use of fertilizers and pesticides has to be regulated, and agricultural legislation needs to be developed in harmony with an effective environmental policy, especially for the Nile Delta lagoons.

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