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NUTRIENT STATUS AND PHOSPHORUS SPECIATION OF MANZALAH LAKE SEDIMENT, EGYPT

SUMMARY

Manzalah Lake is largest brackish water ecosystem (~1071 km^2) in the Mediterranean delta coast of Egypt. This study aims to determine the spatial and temporal distribution of nutrient, nitrogen (N) and phosphorus (P) and their forms, in the sediment of Manzalah Lake. Ammonia was the dominant nitrogen forms (188.57 ± 82.62 µg g^{-1}) followed by nitrate (5.51 ± 4.30 µg g^{-1}). The total P concentrations ranged from 817.2 µg g^{-1} to 1912.6 µg g^{-1} with a mean value of 1134.9 ± 240.86 µg g^{-1}. The rank order of P fractions in Manzalah Lake sediment was different among seasons, where the most abundant form was NaOH-P that participated with high percentage (average: 48.39%). Inorganic-P participated with a major fraction in formation of sedimentary phosphorus, amounting to 56.25 %. The order of inorganic P fractions was: Al-P> Ca-P > Fe-P > available-P with their average relative abundances of 8.60: 3.62: 1.93: 1.00. The sediments play an important role in the dynamic sink-source of nutrients, modifying the nutrient availability in water column. Abiotic factors such as salinity, pH and temperature, and functional ecosystem processes such as primary production and decomposition, can affect significantly the phosphorus concentration in the surface lake sediment more than external factors such as the sewage inputs in the transitional water ecosystems.

INTRODUCTION

The transitional water ecosystems have long been considered naturally eutrophic systems as a result of the physical, chemical and biological processes that take place in their shallow, well-mixed waters loaded by nutrient-rich sediment. Additionally, they are subjected to a wide range of disturbances from natural and anthropogenic sources (DE VICENTE *et al.*, 2003).

Transitional water ecosystems act as an ecological buffer system, protecting the marine environment. They act as a sink for the pollutants, when large amounts of nutrients (N and P) enter these stretches of water, repeated algal blooms are observed and the lakes become eutrophic (Gomez *et al.*, 1998).

Nutrient cycling throughout lakes is directly linked to processes operating within the lake and surrounding environs (Nesbeda, 2004). As a result, lacustrine nutrient conditions reflect both the natural processes and human activity and their effects on the lake (Pearce, 2000). Urbanisation and agricultural activity have led to widespread P enrichment of lakes water causing a range of environmental, social and economic problems at regional and local levels encompassed under the term eutrophication. Also, human influences can accelerate this process resulting in artificial anthropogenic eutrophication (Withers and Jarvie, 2008). In some cases as Manzalah Lake, sewage and other waste have been drained directly into water bodies, dramatically increasing the available phosphorus and nitrogen (Nesbeda, 2004).

Sediment can act either as a sink or as a source of phosphate. P exchange across the sediment–water interface is a complex topic with a long history of research. The importance of the chemical speciation and the quantification of the amount of sedimented and stored phosphate in P-recycling was soon stressed (De Vicente *et al.*, 2003). Complexity arises from the interaction of chemical, biological and physical processes that are involved in P-recycling (Boström *et al.*, 1982).

Phosphorus release from lake sediments is primarily governed by chemical processes that determine the kinetic diffusion between the sediments and the overlying anoxic water (De Montigny and Prairie, 1993; Pearce, 2000). P diffusion from lake-bottom sediments is also a function of the phosphorus forms present (Fe or Al complexes, precipitated minerals, etc.). The availability of species (such as Fe and Al) to bind with phosphorus and the capacity of phosphorus to be adsorbed onto sediments are, in part, determined by the local lithology, mineralogy, and sediment grain-size (Boström and Pettersson, 1982; Pearce, 2000). Biological activity also plays a key role in the mobility of phosphorus in lake bottom settings. Deposition of organic detritus transports nutrients into lake-bottom sediments and bacterial decomposition of organic matter affects the oxygen content of the sediments and overlying water (Nesbeda, 2004).

Erection of Aswan High Dam accompanied by considerable increase in population and consequently in man's activities constitutes the main cause of pollution in the Coastal Delta lakes. Since the sixties of the last century Manzalah Lake is suffering from pollution as it receives untreated sewage and industrial effluents from different drains. Eutrophication, as well as occurrence of metal and pesticide contaminants constituted in these lakes problems of increasing concern (Saad, 2003). Many studies were carried out concerning with water quality and the distribution of nutrient, heavy metals and pesticides as well as the effect of drains effluents on the environments of Manzalah (Khalil, 1990; El-Shebly, 1994; Zyadah, 1995; Ibrahim *et al.*, 1997; Abdel-Satar, 2001; Fathi *et al.*, 2001; Fathi and Abdelzahar, 2003; El-Enani, 2004; Shakweer, 2005; Yacoub *et al.,* 2005; Ali, 2008; Abdel-Satar, 2008). This notwithstanding, no study was carried out on the distribution of available nutrient on lake sediments and the composition of phosphorus chemical forms to show the effect of sediment on the distribution of nutrient in water column.

Our goal is to assess the nutrient availability in Manzalah lake sediment and to estimate the amount of phosphate stored in sediment and the composition of the different forms of phosphate using a sequential extraction procedure since the P exchange of sediment is a function of its binding forms.

MATERIALS AND METHODS

Site description

Manzalah Lake is the largest of the four brackish coastal lakes fringing the Nile Delta (about 60% of their total area) (Fig. 1). The lake is shallow with an average depth of about one meter. Most of the shallow areas of the lake are densely populated with rooted plants. The lake is transverse by a number of small islands of varying sizes dividing the lake into a number of inter-connected basins (Ibrahim *et al.,* 1997). The lake water quality is affected by the input of the drains and the direction of the prevailing wind. Now, the lake is considered as a sink for disposing industrial and human wastes (Abdel Baky *et al.,* 1998). The lake receives drainage water inflows through several inlets along the southern margin (Bahr El-Baqar, Ramsis, Hadous and El-Matariya) and connected with the Mediterranean via El-Gamil inlet that permitting exchange of water and biota. The annual mean salinity declined since 1921, from 16700 mg l^{-1} during 1921-1926 (Fouad, 1926), to 2770 mg l^{-1} during 2007 (Abdel-Satar, 2008). This declining pattern is attributed to an increase in inflow of agricultural drainage water and the restriction of water inflow in the El-Gamil Lake-Sea connection. So, the lake changed to eutrophic fresh water (Khalil and Awamri, 1988). Consequently; Manzalah Lake is highly dynamic aquatic ecosystem. There are continuous changes in physical, chemical, hydrological and biological properties since the early 1900's due to the increase in fresh water inputs and nutrient loading associated with the agricultural and land reclamation and urban waste disposal (Abdel-Satar, 2008). Some hydrographic feature of the studied lake was shown in Tab. 1.

Table 1- Abiotic feature of water column in Lake Manzalah from Abdel-Satar (2008)

Variable	***Winter***	***Spring***	***Summer***	**Autumn**
Temperature (^{o}C)	**19.8-22.0**	**20.6-23.0**	**27.8-30.5**	**25.1-26.8**
Transparency (cm)	**35-130**	**20-125**	**10-130**	**30-130**
Salinity (‰)	**2.01-3.19**	**2.25-3.61**	**2.50-4.41**	**1.40-3.02**
pH (bottom water)	**7.91-8.71**	**7.63-8.94**	**7.56-8.15**	**7.65-8.43**
DO (mg/l)	**2.52-11.80**	**0.68-11.98**	**1.20-6.50**	**2.60-7.60**
COD (mg/l)	**5.92-10.12**	**11.12-24.00**	**8.80-18.00**	**6.00-12.80**
Ca^{2+} (mg/l)	**35.27-85.77**	**40.08-116.23**	**24.05-64.13**	**20.03-32.06**
Mg^{2+} (mg/l)	**100.89-147.56**	**94.81-136.14**	**97.24-175.03**	**77.79-141.00**
NO_3^- (µg/l)	**46.10-169.00**	**16.41-321.29**	**26.14-182.62**	**95.74-257.24**
NO_2^- (µg/l)	**20.40-284.11**	**11.71-154.14**	**5.29-127.32**	**15.11-228.19**
NH_3 (µg/l)	**278.5-3398.5**	**217.0-7507.5**	**861.0-3059.0**	**196.0-6575.5**
Ortho Phosphorus (mg/l)	**0.044-0.815**	**0.095-1.467**	**0.041-0.290**	**0.118-0.960**
Fe (mg/l)	**0.673-2.900**	**0.415-1.677**	**0.218-1.528**	**0.280-2.128**
Mn ((µg/l)	**53.98-325.34**	**27.70-263.88**	**22.0-168.0**	**20.0-174.0**

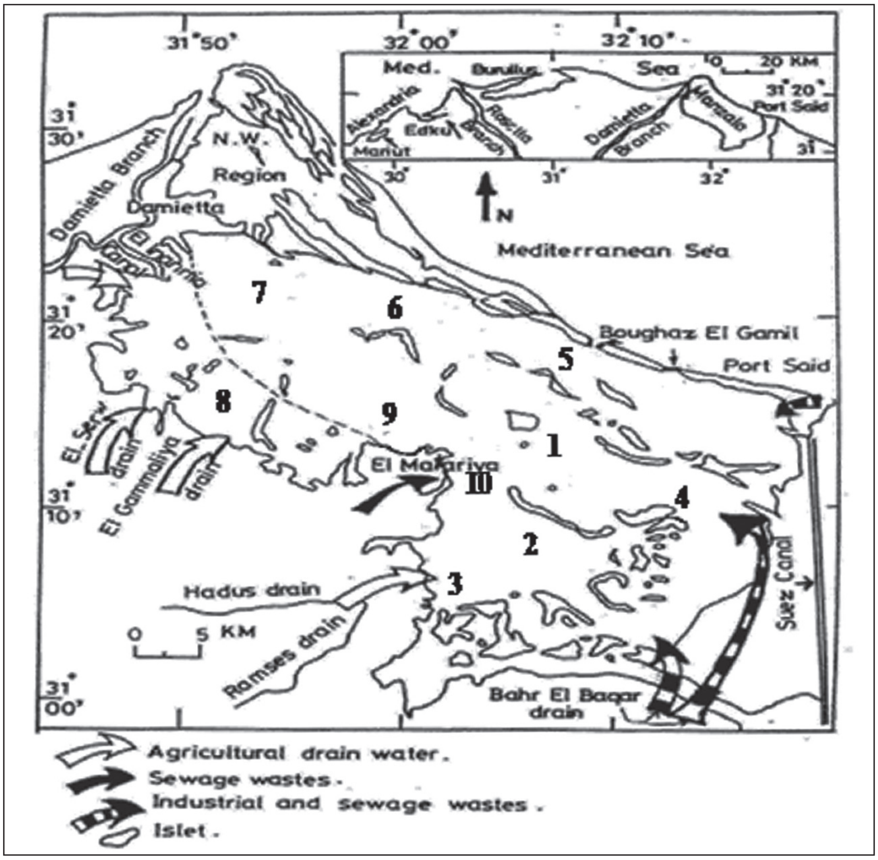

Fig. 1 - Map of Manzalah Lake showing sampling sites.

Sediment samples and procedure

Sediment samples were collected seasonally from ten sampling sites in 2007 using an Eckman sampling device from the top 20 cm layer (Fig. 1). Samples were air dried, homogenized by grinding and finally the exchangeable nitrite, nitrate and ammonia beside the P fractions were analyzed.

The concentrations of exchangeable ammonia, nitrite and nitrate were measured using KCl extraction and quantified directly by indophenol blue, modified Griess-Hosvay and hydrazine-$CuSO_4$ reduction methods, respectively according to American Society of Agronomy (1982).

Sediment P fractions were characterized using a modification of the sequential fractionation procedure of Paludan and Jensen (1995), begun within 24 h of sample collection. Phosphorus fractions identified by this procedure are operationally defined based on the extractant. Extractions were performed at room temperature using replicate subsamples of each sediment sample. To estimate weakly adsorbed P, 1 g of sediment sample was shaken in 1 M NH_4Cl for 1 h. Following centrifugation and filtration, bicarbonate dithionite (BD) was used to extract P adsorbed to oxidized Fe and Mn (Fe-P); soil pellets remaining from the previous extraction were shaken with 0.1M BD for 1 h. To estimate P associated with clay and Al oxides (Al-P), remaining soil pellets were shaken for 16 h with 0.1M NaOH. To extract Ca-bound P (Ca-P), remaining soil pellets were shaken with 1M HCl for 1 h, and then centrifuged and filtered as above. In each step, soil residues were washed twice by shaking for 2 min with extractant, followed by deionized water. The three extracts were then combined, filtered and stored for phosphorus analysis. Refractory organic P (Res-P) was estimated as the P remaining in each soil pellet following HCl-P extraction. Pellets were air-dried, ground with a mortar and pestle, and then oven-dried to a constant mass at 90 ^{o}C. Subsamples (0.2 g) were combusted for 16 h at 550 ^{o}C in a muffle furnace, and Res- P was extracted with 20 ml of 1M HCl in a block digester for 1 h.

Phosphorus analyses

The inorganic P (inorg-P) concentration of each extract was determined colorimetrically as orthophosphate by the procedure of Murphy and Riley (1962). Weakly adsorbed-P, Fe-P, and Al-P extracts were subsequently digested in an autoclave by wet oxidation, and organic P (org-P) concentrations in these extracts were calculated as the difference in inorg-P concentrations of digested and non-digested extracts. For Res-P extract, all P was considered to be org-P, but for Ca-P extracts, all P was considered to be inorg-P. Total P was calculated by summing all the inorganic and organic P concentrations.

RESULTS AND DISCUSSION

Nutrients play a decisive role for the environmental state of lakes, where the primary production of lakes is strongly limited by nutrient availability. Increased nutrient input therefore leads to enhanced lake productivity, with cascading effects on the remaining trophic levels and the interactions between them (Jeppesen *et al.*, 2005).

Table 2- Seasonal changes of exchangeable nutrient (μg g^{-1}) in Manzalah Lake sediment

Site	***Winter***	***Spring***	***Summer***	***Autumn***
		NH_3-N		
1	165.00	175.45	257.25	33.75
2	139.05	192.25	154.60	24.45
3	163.25	183.95	253.10	177.50
4	185.55	192.15	280.95	187.50
5	220.80	307.50	255.00	125.25
6	162.30	440.70	195.25	38.85
7	169.20	255.00	185.05	61.50
8	167.70	309.00	175.55	63.00
9	192.90	225.00	207.00	85.80
10	200.00	320.25	198.50	216.00
		NO_3-N		
1	10.257	2.943	3.257	3.457
2	19.770	2.400	6.685	7.057
3	23.141	3.086	6.542	7.343
4	5.914	2.314	4.071	4.628
5	5.743	2.886	3.914	4.343
6	7.086	3.200	3.543	7.143
7	7.571	2.171	4.742	4.943
8	3.828	2.057	3.314	3.571
9	10.771	1.828	1.686	5.428
10	6.210	2.743	4.028	4.743
		NO_2- N		
1	0.246	0.094	0.586	0.057
2	0.019	0.113	0.264	0.113
3	0.019	0.094	0.945	0.170
4	0.019	0.076	0.189	0.264
5	0.253	0.076	0.246	0.151
6	0.113	0.132	0.246	0.189
7	0.019	0.246	0.189	0.246
8	0.019	0.076	0.189	0.132
9	0.019	0.246	0.076	0.113
10	0.050	0.189	0.094	0.170

Nitrogen is primarily found in organic compounds and whose release is mainly induced by the decomposition of organic substances (Søndergaard, 2007). Ammonia was the dominant nitrogen forms in the studied lake sediment (Table 2), reached maximum in spring and summer (average: 0.260, 0.216 mg g^{-1}) with high significant seasonal variations ($P<0.01$) without any site differences ($P=0.80$). Ammonia itself is non-cumulative toxic substance, and the high levels of ammonia released by the sediment do not cause a problem with high dissolved oxygen (DO) percentage and low pH (Johnston and Minnaard, 2003). Contrarily, Manzalah Lake is characterized by low DO concentrations at the most sites reflecting ammonia toxicity particularly in hot seasons.

The exchangeable NO_3^--N concentrations are mostly higher than NO_2^--N values (Table 2). Both showed random distribution among different sites (P=0.43 and 0.82, respectively), with high significant temporal variation (P<0.01). In addition there is an increase in nitrate values in winter and autumn reflecting the oxidized conditions of lake sediment in cold seasons. In contrast, nitrite registered the highest values in summer thus reflecting the anoxic condition at the sediment-water interface (Johnston and Minnaard, 2003).

Phosphorus has been recognized as the most critical nutrient limiting marine productivity. One of the most important factors determining the phosphorus concentration of the overlying water is the phosphorus release from the sediments. Such release may have a significant impact on water quality and may result in continuing eutrophication (Aydin *et al.*, 2009). The present results showed that, the inorganic-P fraction was abundant in the sediment comprising 51.02, 68.73 and 55.02 % of the total sedimentary phosphorus in winter, summer and autumn, respectively (Fig. 2). In contrast spring showed the increase in the contribution of organic forms (50.21 %) and reflected the increase in inorganic P release to the overlying water. This is achieved by the decrease in average total-P concentrations (1006.08 µg g^{-1}) in sediment and increases the ortho phosphorus in the overlying water (Table 1). Also, these results are confirmed by the increase in the standing crops of phytoplankton (5289.8 x10^4 mm^3 l^{-1}) in spring compared with other seasons (1832.4, 4227.4 and 2308.9 x 10^4 mm^3 l^{-1} in winter, summer and autumn, respectively) (Abd El-Karim, 2009).

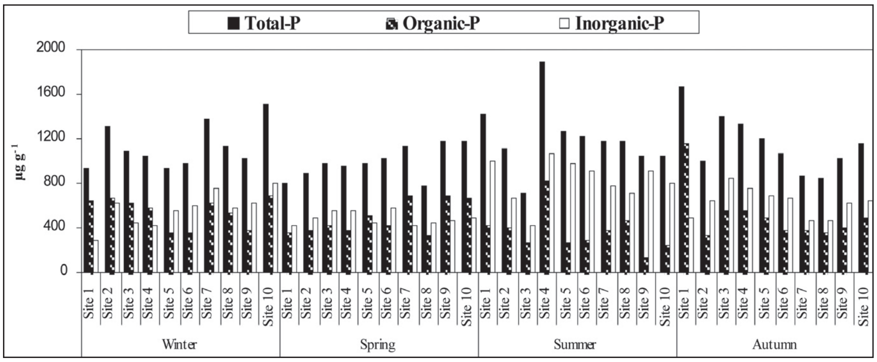

Fig. 2 - Total phosphorus and the relative contribution of each organic and inorganic P-fraction in Manzalah Lake sediment.

The study of phosphate regeneration is essential in lakes eutrophication. However, not all of the phosphorus fractions can be released from the sediments and rendered to eutrophication. Thus, to assess the risk of eutrophication in aquatic systems, it is necessary to know not only the total phosphorus content in the sediments but also the contents of different phosphorus fractions (Aydin *et al.*, 2009). It is now widely accepted that the accessibility of the various elements for biota uptake depends strongly on their specific chemical forms and binding sites. Despite their proximity in the average total P concentrations at the different seasons, P fractions showed different distribution patterns (Fig. 3), where the relative abundances of phosphorus forms follow the order: NaOH-P (42.60 %) > BD-P (16.85 %) > Res-P (16.76 %) > HCl-P (12.04 %) > NH_4Cl-P (11.74 %), NaOH-P (48.45 %) > BD-P (17.29 %) > HCl-P (14.56 %) > NH_4Cl-P (11.70 %)> Res-P (8.00 %), NaOH-P (54.29 %) > BD-P (15.97 %) > HCl-P (14.01 %) > NH_4Cl-P (9.89 %) > Res-P (5.83%) and NaOH-P (48.24 %) > BD-P (15.61 %) > HCl-P (12.35 %) > Res-P (12.62 %) > NH_4Cl-P (11.17 %) in winter, spring, summer and autumn respectively.

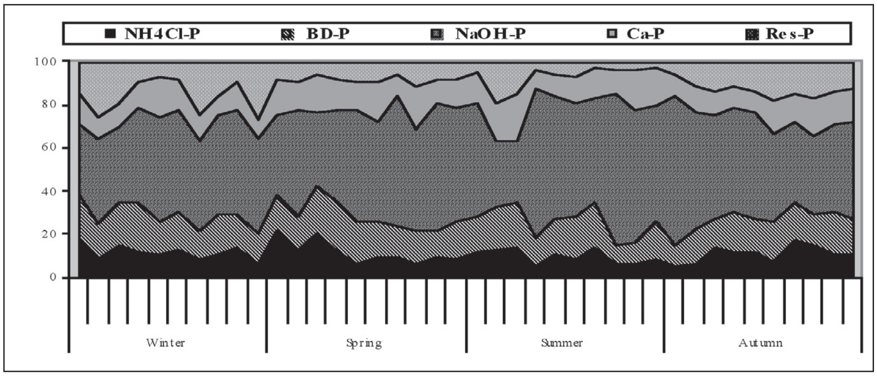

Fig. 3 - Relative contributions of each phosphorus forms to the sum during different seasons in Manzalah Lake sediment.

NaOH-P is exchangeable including P bound to metal oxides, mainly of Al (Kaiserli *et al.*, 2002), and was once used for the estimation of available P in the sediments under anoxic conditions and was an indicator of algal available P (Zhou *et al.*, 2001). This fraction recorded very high percentage of total sedimentary phosphorus (48.39%) in Manzalah Lake compared with different lakes in Egypt exposed to different pollution sources e.g Mariut Lake (28.56 %) (unpublished data), Qarun Lake (18.88%) and Wadi-El-Rayan Lakes (15.69 %) (Abdel-Satar and Sayed, 2009). It can be released for the growth of phytoplankton when anoxic conditions prevail at the sediment–water interface (Kozerski and Kleeberg, 1998). The decrease of DO was achieved in the Manzalah Lake water especially in hot seasons (Table 1), so that the NaOH-P contribution to the overlying water was high. The significant positive relationship (r=0.9, n=40) between the amounts of P released from the sediments and those in the NaOH fraction, indicated that NaOH was the main fraction that can release P easily.

BD-P represents the redox-sensitive P fraction, mainly including P bound to Fe-hydroxides and Mn compounds (KOZERSKI and KLEEBERG, 1998). In occasional DO depletion, BD-P was also released from the anaerobic sediments and acted as an internal P source to the overlying water (KLEEBERG and KOZERSKI, 1997). BD-P showed low concentrations in spring (average: 174.0 µg g^{-1}) with the flourishing of phytoplankton and increase in temperature. Therefore, BD-P form in Manzalah sediments acts as another source of phosphorus under anaerobic condition. So, the information on the different chemical forms of phosphorus in aquatic sediment is useful in understanding whether that sediment acts as an adsorber or source of phosphorus (TIYAPONGPATTANA *et al.,* 2004).

The decrease in the contribution of residual organic *phosphate* in summer (6.37 %) compared with other seasons may be due to the increase in decomposition rate of organic matter through the mineralization (PETTICREW and AROCENA, 2001; SØNDERGAARD, 2007). However, preservation of phosphorus in sediments depends on several factors including the nature of phosphorus compounds supplied to the sediment/water interface, sedimentation rate, bioturbation, or irrigation by bottom current, bottom-water oxygen content, diagenetic processes (i.e., formation of authigenic phosphorus-bearing mineral such as carbonate fluorapatite). Because these parameters vary in different sedimentary environments, burial flux of phosphorus may vary depending on the type of depositional environment (CHA *et al.*, 2005; AVILES *et al.*, 2006).

The most abundant form of inorganic phosphorus in sediment was Al-bound phosphorus (Fig. 4), where Al-P contributed greatest percentage of total inorganic sedimentary P in summer and autumn (62.64 and 59.29%, respectively) compared with winter and spring (56.74 and 48.33%, respectively) (Fig. 5). This may be attributed to the decrease in pH in summer and salinity in autumn (Table 1). The changes in environmental conditions such as pH or redox potential could be the main driving force for phosphate release and variations of phosphate removal efficiencies over seasons (PETTICREW and AROCENA, 2001). The binding of P to metal oxides is influenced by pH and competition from competing anions. Metal oxides (e.g. of Al) have variably charged surfaces that generally carry a net positive charge at low pH and a net negative charge at high pH. Also, the decrease in salinity may stimulate phosphate adsorption to metal oxides (HOU *et al.,* 2009). Thus, associations between metal oxides and anions such as phosphate are facilitated in freshwater at low pH (Paludan and Morris, 1999). This is also confirmed by the increase in the average concentrations of Fe-P in summer compared with other seasons (Fig. 5).

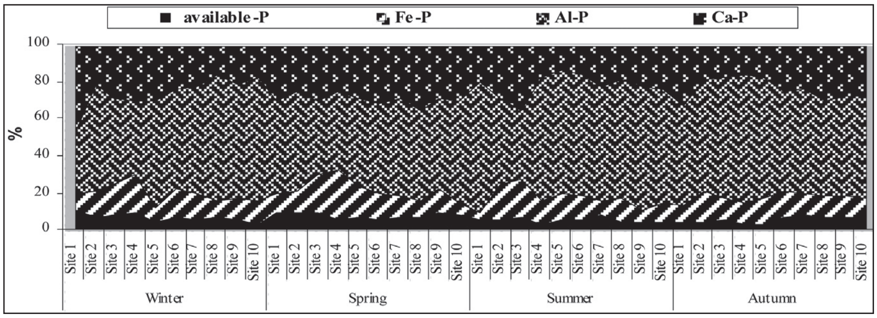

Fig. 4 - Relative contributions of each inorganic phosphorus fraction to the sum in Manzalah Lake sediment.

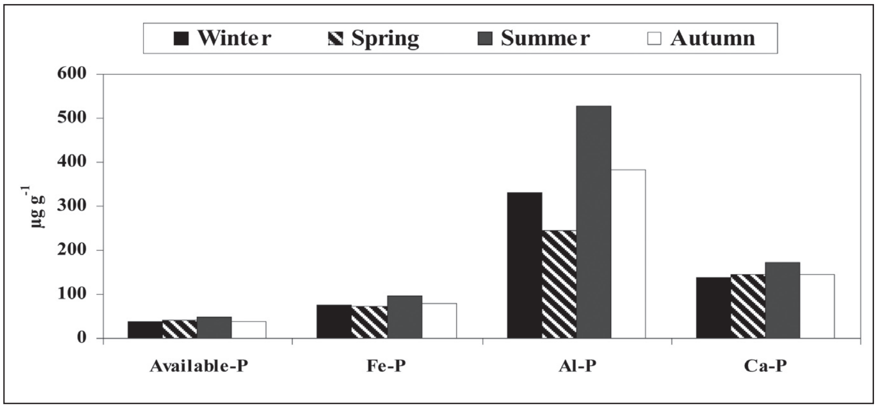

Fig. 5 - The average concentrations of inorganic phosphorus forms in different seasons.

Inorg-P associated with Ca^{2+} and Mg^{2+} phases registered the second contribution to inorganic P in all seasons that is deemed as a relatively stable fraction of inorganic P (Wang *et al.*, 2006, 2008). The average concentrations of Ca-P was relatively increased in summer compared with other seasons (Fig. 5), which probably results from the fact that the adsorption–desorption equilibrium was affected by temperature, where the increase in temperature stimulate the mineralization of organic matter in the sediment. During microbial decomposition, organic P may be transformed into fluorapatite (Anshumali and Ramanathan, 2007; Katsaounos *et al.,* 2007; Hou *et al.,* 2009). Available-P that includes the inorganic dissolved P in the pore water (Kaiserli *et al.*, 2002) recorded the lowest contribution to the inorganic P fractions

Although some sites exposed to drains effluents, there is no significant difference (*P*>0.05) in phosphorus species and the inorganic P fractions within sites except BD-P (*P*=0.05) and inorganic Fe-P (*P*=0.005), where the highest concentrations of Fe-bound P were recorded at site 4, indicating that the discharge of municipal wastewater has a significant influence on the accumulation of Fe-bound P in local sediments (Cyr *et al.*, 2009; Hou *et al.*, 2009). So that, the chemical co-precipitation of Phosphate, biological and hydrological processes control the Phosphorus concentration in the surface sediment more than external factors such as the sewage inputs.

CONCLUSIONS

From the previous results we can concluded that ammonia was the dominant nitrogen forms followed by nitrate in the lake sediment. Abiotic factors such as salinity, pH and temperature play important roles in the adsorption and desorption of phosphorus more than external factors such as the sewage inputs. The speciation of total phosphorus in different forms is necessary for the understanding of phosphate exchange mechanisms by sediments, its potential removal from the water column and the availability of phosphorus for primary producers. Up to 56.25 % of the phosphorus load originating from Manzalah Lake sediment was in inorganic P form and the most abundant form of phosphorus was NaOH-P that participated with high percentage (average: 48.39 %). The results declared that the rank order of P fractions in Manzalah Lake was different in different seasons but the order of inorganic P fractions was the same and was: Al-P> Ca-P > Fe-P > available-P with their average relative proportion 8.60: 3.62: 1.93: 1.00%.

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