

Phosphorus Speciation in the Coastal Sediments of Khawr Ash Shaibah Al-Masdudah: Coastal Lagoon in the Eastern Red Sea, Kingdom of Saudi Arabia

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ABSTRACT

The total phosphorus concentrations and its speciation were studied in the surface sediment of Khawr ash Shaibah al Maftuhah. The distribution pattern of total phosphorus in the sediment showed east-west gradient indicating different depositional environment of the lagoon. The largest pool of the sedimentary phosphorus was apatitic phosphorus (57%) followed by refractory organic phosphorus (42%). The impact of loosely adsorbed and exchangeable phosphorus (0.9 % of total phosphorus) and Metal oxide Phosphorus (0.6 % of total phosphorus) on the budget of total phosphorus in the sediments was minor. The concentration of dissolved phosphorus in the upper water column is most probably buffered by apatitic phosphorus. The low concentration of metal oxide phosphorus is suggested to be influenced by the calcareous nature of the lagoon. Possible transformation between apatitic and refractory organic phosphorus is inferred from the correlation of both parameters. The correlation of refractory organic carbon with total phosphorus in the sediments suggests in situ production due to biological activities.

ID # (2738)

Received: 20/04/2013

In-revised: 17/09/2013

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KEYWORDS

Phosphorus, Marine, Coastal,
Sediment, Red Sea, Speciation.

أشكال الفوسفور في الرواسب الساحلية لخور الشعبية المفتوحة: لاجون ساحلي على شرق البحر الأحمر بالمملكة العربية السعودية

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المستخلص

تمت دراسة التركيز الكلي للفوسفور وأشكاله في الرواسب السطحية لخور الشعبية المفتوحة. أظهر نمط التوزيع للفوسفور الكلي في الرواسب التدرج من الشرق إلى الغرب مما يدل على البيئة الترسيبية المختلفة في البحيرة. الفوسفور الأباتيتي هو المكون الأعظم من أشكال الفوسفور المترسب (57 %) يليه الفوسفور العضوي المقاوم (42 %). تأثير الفوسفور السهل والقابل للتبادل (0.9 %) والفوسفور علي هيئة أكسيد العنصر (0.6 %) علي ميزانية الفوسفور الكلي في الرواسب كانت ضئيلة. تركيزات الفوسفور في طبقة المياه العلوية ربما يتم تنظيمها بواسطة الفوسفور الأباتيتي. التركيز المنخفض من الفوسفور علي هيئة أكسيد العنصر ربما يتأثر بالخاصية الكلسية للبحيرة. هناك إمكانية للتحويل المتبادل للفوسفور الأباتيتي والفوسفور العضوي المقاوم والتي يستدل عليها من العلاقة بين العاملين. العلاقة بين الفوسفور العضوي المقاوم والفوسفور الكلي في الرواسب تقترح إنتاج موضعي كنتيجة للنشاط البيولوجي.

رقم المسودة: (2738)

تاريخ استلام المسودة: 2013/04/20

تاريخ المسودة المعدلة: 2013/09/17

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الكلمات الدالة

الفوسفور، ساحل البحر، رواسب،
البحر الأحمر، الأشكال، توقعات

Introduction

Nutrients in seawater have an important role in controlling the primary productivity in the oceans that in turn has potential impact on the atmospheric carbon dioxide (McElroy, 1983). Phosphorus is one of nutrients that is considered as bio-limiting element on geological timescales (Smith, 1984); (Codispoti, 1989). Rivers are the major source of phosphorus to the oceans whereas the ultimate sink is marine sediments. The balance between two processes are the main factor controlling the level of phosphorus in seawater (Froelich *et al.*, 1982); (Ruttenberg, 1993).

The Red Sea has oligotrophic nature, so the concentration of nutrients is significantly low with highest values observed in the Southern Red Sea (Morcos, 1970); (Edward, 1987). Most of studies of phosphorus in the Eastern coast of the Red Sea were concentrated on the dissolved fraction in seawater (El-Rayis, 1998), (El-Rayis and Moammar, 1998), (El-Sayed, 2002); (Turki *et al.*, 2002); (Al-Farawati, 2010), & (El-Sayed, *et al.*, 2011). Little has been done on the forms of phosphorus in the marine sediments in the Eastern Red Sea. The phosphorus in marine sediment constantly interacts with dissolved phosphate ions in the water through adsorption/desorption and co-precipitation/dissolution processes. In this study, total sedimentary phosphorus was fractionated into four distinct pools:

- (i) Loosely adsorbed and exchangeable-associated phosphate.
- (ii) Iron and aluminum-associated phosphate.
- (iii) Calcium-associated phosphate/ apatite.
- (iv) Refractory organic phosphorus.

Materials and Methods

(1) Study Area

The Al-Shoaiba area consists of two lagoons: Northern and Southern lagoons, also known as Khawr Ash Shaibah Al-Masdudah and Khawr Ash Shaibah Al-Maftuhah. This study was restricted to study phosphorus speciation in the sediment of Khawr Ash Shaibah Al-Maftuhah that covers an area of figure 1.

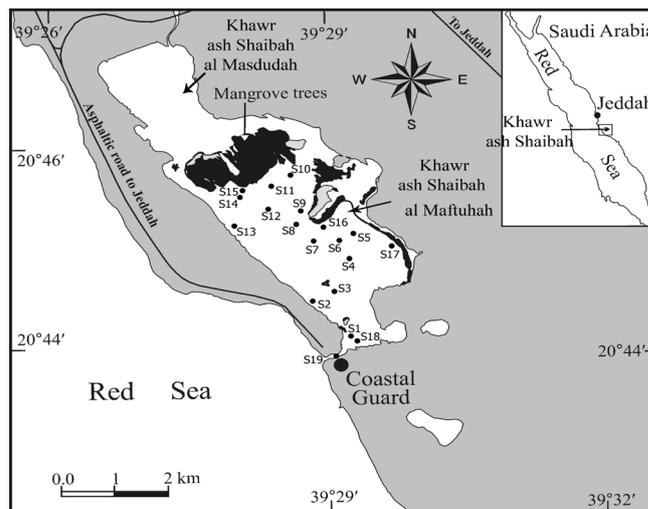


Figure 1: Geographical Positions of Sampling Stations in Khawr Ash Shaibah Al-Maftuhah.

The lagoon is located approximately 100 km South of Jeddah, close to Shoaiba desalination plant. Mangrove stands are spread along the Eastern and Northern parts. Water exchange is limited to a narrow inlet in the southern lagoon. Additionally, the lagoon suffers from the dry and hot climate and there is no rivers flow. As a result high salinity values were recorded, ranging between ~ 42 to 50 (Rasul *et al.*, 2010). Detailed study on the sediment types, sediment composition and mineralogy, turbidity levels, water quality and bathymetry was recently studied (Rasul *e. al.*, 2010).

(2) Sampling and Methods of Analysis

The surface sediment was collected using the Van veen grab from each station and stored in polythene bags, (figure 2).

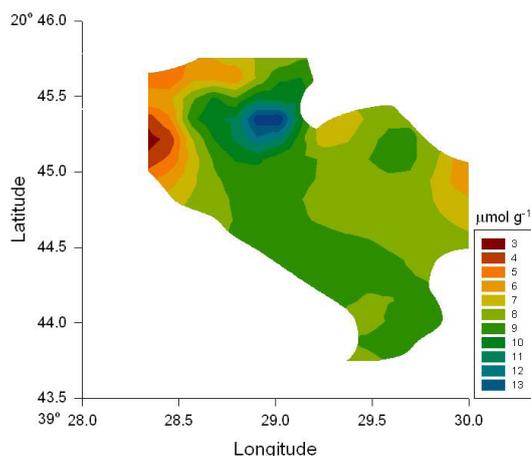


Figure 2: Surface Distribution of Total Phosphorus in the Sediments of Khawr Ash Shaibah Al-Maftuhah.

The sediment samples were dried in air, homogenized and powdered in an agate mortar. The extraction procedure used in this study is based upon the scheme developed by (Aspila *et al.*, 1976), and (De Lange 1992) for marine sediment with minor alteration. One gram of dried sample was extracted in 25ml of filtered low-phosphate seawater ($0.1\mu\text{M}$ phosphate) in a shaker at room temperature for 24h, which represented the loosely adsorbed and exchangeable phosphorus (P_{ex}). The residue from (P_{ex}) was washed with 30ml of Milli-Q water twice to remove any residual seawater. The residue from (P_{ex}) extraction was extracted with 25ml of 0.5 N NaOH solutions to give fraction of iron and aluminium-associated phosphorus ($P_{\text{Fe/Al oxides}}$). The residue from NaOH extraction was then extracted with 25ml of 0.5 N HCl, which represented calcium-associated and apatite phosphorus (P_{apatitic}). Total phosphorus (P_{T}) in sediment was determined by igniting 0.5g of sediment at 550°C in a muffle furnace and it was extracted with 0.5 N HCl after shaking for 16h. The residual refractory organic phosphorus (P_{org}) is then determined as the difference between total phosphorus and the sum of (P_{ex}), ($P_{\text{Fe/Al}}$) and (P_{apatite}). A centrifuged at 4000rpm was applied for the extracts for 10min. The supernatant in each extract was diluted with Milli-Q in 30 ml polypropylene vials to a final volume of 25 ml. The concentration of extracted phosphorus was analyzed using the molybdenum blue spectrophotometric method (Murphy and Riley, 1962).

Results and Discussion

The suitability of a phosphorus fractionation method for characterisation of phosphorus forms depends on the environment, the material to be studied, and on the type of material for which the method was originally designed. For instance, a high abundance of clay minerals, organic matter, and calcareous minerals may affect the ability of extraction procedures to distinguish between different phosphorus forms (Ruttenberg 1992). The sediments in the study area are typically poor in organic matter, but high in calcium carbonate (Rasul *et al.*, 2010). Thus, it was anticipated that calcium carbonate forms would be of major

importance. However, and as it can be seen below, the organic fraction is also shown to be a major fraction in the present study.

(1) Total Phosphorus (P_{T})

The concentration of total phosphorus in surface sediments of Khawr ash Shaibah Al- Maftuhah ranged between $2.53\mu\text{Mg-1}$ (St.S13) and $14.14\mu\text{Mg-1}$ (St. S8) with an average of $7.47\mu\text{Mg-1}$ (table 1).

Table 1: Concentrations of phosphorus species ($\mu\text{M g}^{-1}$) in the surface sediments of Khawr ash Shaibah al Maftuhah.

Station	P_{T}	P_{ex}	$P_{\text{Fe/Al oxides}}$	P_{apatitic}	P_{org}
S01	6.90	0.07	0.03	4.29	2.51
S02	8.99	0.06	0.05	4.68	4.20
S03	8.21	0.03*	0.03	4.36	3.79
S04	7.40	0.06	0.07**	4.43	2.84
S05	8.34	0.08	0.04	4.45	3.77
S06	7.94	0.08	0.06	4.78	3.02
S07	8.19	0.06	0.04	4.88	3.21
S08	14.14**	0.05	0.05	3.38	10.66**
S09	9.50	0.06	0.05	3.14	6.25
S10	7.13	0.07	0.04	2.58	4.44
S11	5.29	0.05	0.05	2.81	2.38
S12	9.95	0.04	0.04	3.5	6.37
S13	2.53*	0.04	0.02*	0.72*	0.75
S14	5.90	0.05	0.02	2.85	2.98
S15	3.58	0.05	0.04	3.17	0.32*
S16	5.68	0.06	0.04	4.4	1.18
S17	5.60	0.07	0.05	3.97	1.51
S18	9.47	0.05	0.05	7.01**	2.36
S19	7.16	0.13**	0.05	4.71	2.27
Mean	7.47	0.06	0.04	3.95	3.28
	± 2.55	± 0.02	± 0.01	± 1.16	± 2.38

(**High Values / *Low Values)

These values are close to the values reported for Edko Lagoon in the Mediterranean (Khalil, 2007), Burullus Lagoon and shallow waters of Mediterranean (Khalil, *et al.*, 2007) and Great Barrier Reef continental shelf (Monbet *et al.*, 2007); but lower than those reported for Maryout Lagoon in the Mediterranean (Abdallah, 2011). Dramatic gradients in the concentration of total phosphorus between Eastern and Western part of the Northern lagoon are evident (see figure 2). The surface concentrations decreased toward the western part indicating different depositional environments of phosphorus.

(2)The Loosely Adsorbed and Exchangeable Phosphorus (P_{ex})

The loosely adsorbed and exchangeable phosphorus is shown to be related to bioavailability of phosphorus (Zhou *et al.*, 2001). Beside phosphate concentration, temperature and salinity has significant impact on the release of loosely adsorbed and exchangeable phosphorus. In Khawr ash Shaibah al Maftuhah, the (P_{ex}) concentration ranged between 0.03 and 0.13 μMg^{-1} and with average of 0.06 μMg^{-1} (see, table1). The highest (P_{ex}) concentration was observed in sediments collected from St.19 (0.13 $\mu\text{M g}^{-1}$) at the entrance of the lagoon. Apart of the highest value at the entrance of the lagoon, the distribution of (P_{ex}) showed decreases westward (figure 3).

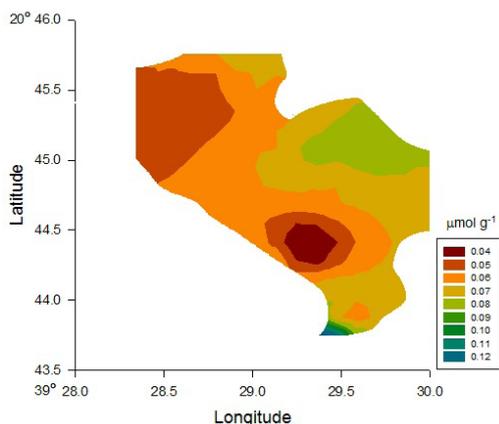


Figure 3: Surface Distribution of Loosely Adsorbed and Exchangeable Phosphorus in the Sediments of Khawr Ash Shaibah Al-Maftuhah.

The loosely adsorbed phosphorus represents about 0.9 % of the sedimentary inorganic phosphorus (table. 2). Percentage of (P_{ex}) ranged between 1% and 25% was suggested to be due to high degree of oversaturation (Penn *et al.*, 1995). It is also suggested that high concentrations of adsorbed phosphorus in the sediment is the main factor controlling algal blooms as the macrophytes effectively reduce the (P_{ex}) content in the bottom sediment (Guang-Wei *et al.*, 2006). The highest values observed at the entrance could be attributed to the absence of macrophytes and analogue marine plants due to high current speed. However, the values of sedimentary adsorbed phosphorus in Khawr ash Shaibah al Maftuhah indicate that this sedimentary phosphorus reservoir could be a minor contributor in the biogeochemical cycle of phosphorus in the study area.

Table 2: Percentage of Phosphorus Species (%) in the Surface Sediments of Khawr Ash Shaibah Al-Maftuhah.

Station	P_{ex}	$P_{Fe/Al\ oxides}$	$P_{apatitic}$	P_{org}
S01	1.0	0.4	62	36
S02	0.7	0.6	52	47
S03	0.4*	0.4	53	46
S04	0.8	0.9	60	38
S05	1.0	0.5	53	45
S06	1.0	0.8	60	38
S07	0.7	0.5	60	39
S08	0.4	0.4	24*	75**
S09	0.6	0.5	33	66
S10	1.0	0.6	36	62
S11	0.9	0.9	53	45
S12	0.4	0.4	35	64
S13	1.6	0.8	68	30
S14	0.8	0.3*	48	51
S15	1.4	1.1**	89**	09*
S16	1.1	0.7	77	21
S17	1.3	0.9	71	27
S18	0.5	0.5	74	25
S19	1.8**	0.7	66	32
Mean	0.9±0.4	0.6±0.2	57±16	42±17

(**High Values / *Low Values)

This low values are probably the results of the presence of high apatitic phosphorus contents in the sediment that buffer the concentration of the loosely adsorbed and exchangeable phosphorus (see below). This hypothesis is confirmed by plotting the concentrations of loosely adsorbed and exchangeable phosphorus and apatitic phosphorus that showed a positive correlation, (figure 4). However, although the correlation is positive, it is insufficient to explain the low concentration of the loosely adsorbed and exchangeable phosphorus. Other environmental parameters should be considered to solve the behaviour the loosely adsorbed and exchangeable phosphorus.

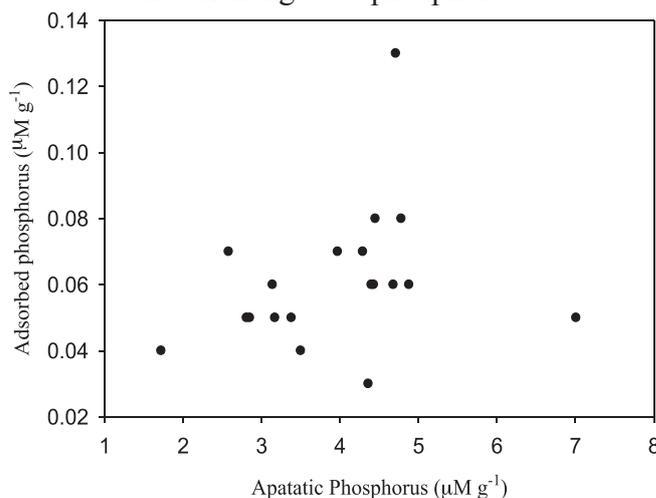


Figure 4: Correlation between of Loosely Adsorbed and Exchangeable Phosphorus and Apatitic Phosphorus in the Sediments of Khawr Ash Shaibah Al-Maftuhah.

(3) Metal Oxide Phosphorus ($P_{\text{Fe/Al oxides}}$)

The concentration of phosphorus bound to iron and aluminium oxides ($P_{\text{Fe/Al oxides}}$) is significantly low in Khawr ash Shaibah al Maftuhah. The fraction of phosphorus that is extracted by NaOH solution is used for estimation for short and long-term available phosphorus in the sediment particularly at the sediment-water interface in the presence of anoxic environment (Zhou *et al.*, 2001); & (Wang, 2008).

The ($P_{\text{Fe/Al oxides}}$) concentration in the sediment of Khawr Ash Shaibah Al- Maftuhah ranged between 0.02 and 0.07 μMg^{-1} with an average of 0.04 μMg^{-1} (see, table 1). The relative contribution of ($P_{\text{Fe/Al oxides}}$) to sedimentary inorganic P ranged between 0.3 and 1.1% with an average of 0.6% (see, table 2). The highest value of ($P_{\text{Fe/Al oxides}}$) was observed at St. 4 (.07 μMg^{-1}) whereas the lowest value was found in the farthest north at stations St. 13 and 14. The general distribution showed relatively higher values in the Eastern region in comparison to the Western region that could be attributed to the higher contents of clay minerals delivered by dormant wadis (figure 5).

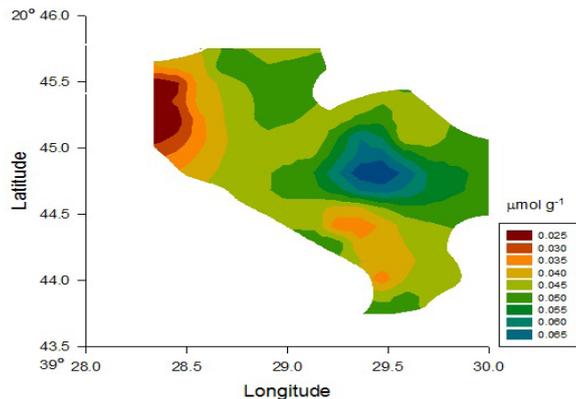


Figure 5: Surface Distribution Metal Oxide Phosphorus in the Sediments of Khawr Ash Shaibah Al-Maftuhah.

The distribution pattern of ($P_{\text{Fe/Al oxides}}$) is in parallel to the distribution pattern of the loosely adsorbed and exchangeable phosphorus (see, figure 4).

This iron and aluminium phosphorus fraction contributed 6%-23% of total phosphorus in the sediment in Burullus Lagoon and shallow waters of Mediterranean (Khalil, *et al.*, 2007), 43% in Maryout Lagoon in the Mediterranean (Abdallah, 2011) and 9%-13% in Edko Lagoon in the Mediterranean (Khalil, 2007).

The reported values of ($P_{\text{Fe/Al oxides}}$) from various basins have shown wide variability with higher values observed in eutrophic non-calcareous environments (Penn *et al.*, 1995). Since the nature of Khawr Ash Shaibah Al-Maftuhah is predominant with calcareous deposits, the contribution of ($P_{\text{Fe/Al oxides}}$) to the total phosphorus in sediment is anticipated to be minor as indicated from our data.

(4) Apatitic Phosphorus (P_{apatitic})

Apatitic phosphorus was among the most stable P forms in the sediments in oxic and anoxic environments, and therefore not easily released to the upper water column (Salomons and Gerritse, 1981); (Jensen *et al.*, 1995); (Gonsiorczyk *et al.*, 1998). The (P_{apatitic}) in the sediment of Khawr Ash Shaibah Al-Maftuhah ranged between 1.72 and 7.01 μMg^{-1} with a mean of 3.95 μMg^{-1} (see, table 1). On the other hand, the relative contribution of (P_{apatitic}) to sedimentary inorganic phosphorus ranged between 24% and 89% with an average of 57% representing the largest phosphorus reservoir in the sediment of Khawr ash Shaibah al Maftuhah (figure 6), (see table 2).

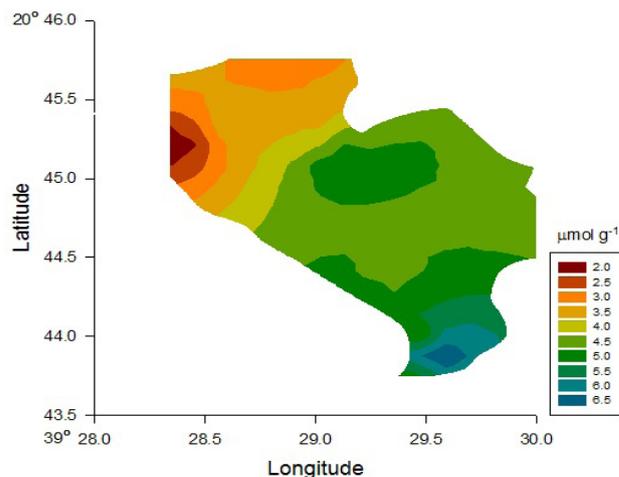


Figure 6: Surface Distribution of Apatitic Phosphorus in the Sediments of Khawr Ash Shaibah Al-Maftuhah.

The apatitic phosphorus fraction contributed to 50%-73% of total phosphorus in the sediment in Burullus Lagoon and shallow waters of Mediterranean (Khalil, *et al.*, 2007), 22% in Maryout Lagoon in the Mediterranean (Abdallah, 2011) and 49%-55% in Edko Lagoon in the Mediterranean (Khalil, 2007).

Possible of transformation between apatitic and refractory organic phosphorus through formation of some phosphorus-containing authigenic minerals has been reported (Ruttenberg, 1990); (Ruttenberg & Berner, 1993); & (Delaney, 1998). Although in this study, the authigenic apatite phosphorus was not distinguished from detrital apatite phosphorus. The correlation between the two major fractions (*i.e.* apatitic and refractory organic phosphorus) is shown in (figure 7).

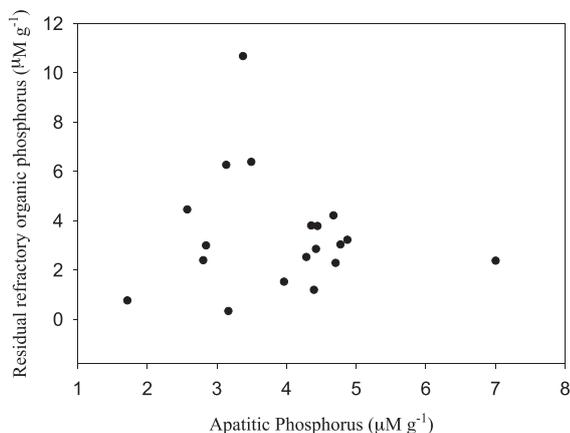


Figure 7: Correlation between of Refractory Organic Phosphorus and Apatitic Phosphorus in the Sediments of Khawr Ash Shaibah Al- Maftuhah.

In case of existent of transformation between the two fraction, the relation should show a negative and strong correlation. Although the regression line has a negative direction as it should be, the correlation was very weak suggesting that the transformation through formation of some phosphorus-containing authigenic minerals could occurs but at limited levels.

(5) Residual Refractory Organic Phosphorus (P_{org})

Refractory organic phosphorus concentration in Khawr ash Shaibah al Maftuhah sediments ranges from 0.32 to 10.66 μMg^{-1} (see, table 1). It was accounted of 42% of total sedimentary phosphorus and was the second largest pool of sedimentary phosphorus (see, table 2). Low concentrations of refractory organic phosphorus were found in the southern region, and concentration increases systematically northward (Figure 8).

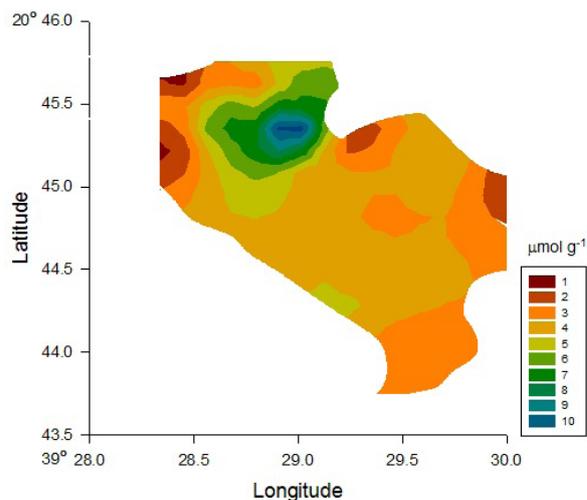


Figure 8: Surface Distribution of Refractory Organic Phosphorus in the Sediments of Khawr Ash Shaibah Al-Maftuhah.

The maximum concentrations ($10.66\mu\text{Mg}^{-1}$) of refractory organic phosphorus were found in the North Eastern region. The maximum concentrations were found in Northern coastal stations (S8 and S9). This maximum is in agreement with the maximum organic carbon content based on the study by (Rasul, *et al.*, 2010). However, the spatial distribution of refractory organic phosphorus is scattered and showed variability in the lagoon. The percentage of refractory organic phosphorus measured in the sediments of Khawr Ash Shaibah Al-Maftuhah is almost similar to that found by (Koch *et al.*, 2001) and it was attributed to the impact of mangrove on the sediments.

The correlation between the concentration of refractory organic phosphorus and calcium carbonate content for sediments from Florida Bay was negative and strong indicating in situ biological production by sea grass and algae. The percentage of calcium carbonate was not determined in the present study. However, the distribution pattern of the refractory organic phosphorus in Khawr Ash Shaibah Al- Maftuhah, (see, figure 8), is almost inverse the distribution pattern of the percentage of calcium carbonate in Khawr Ash Shaibah Al- Maftuhah by the study of (Rasul, *et al.*, 2010), indicating in situ biological production of refractory organic phosphorus. On the other hand, the correlation of total phosphorus and refractory organic phosphorus is positive and

strong indicating that a significant proportion of sedimentary phosphorus is produced by in situ biological activities (figure 9).

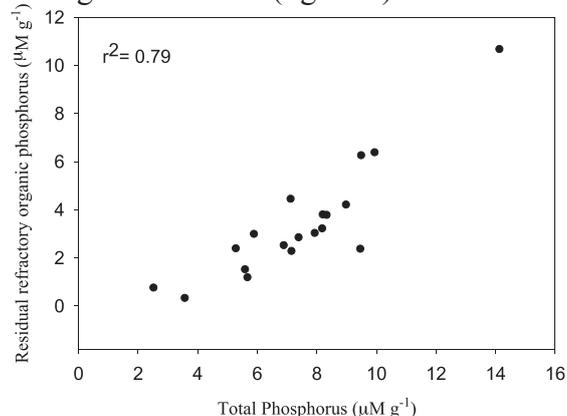


Figure 9: Correlation between of Refractory Organic Phosphorus and Total Phosphorus in the Sediments of Khawr Ash Shaibah Al-Maftuhah.

Conclusion

The total phosphorus concentrations and its speciation were studied in the surface sediment of Khawr Ash Shaibah Al-Maftuhah Lagoon. Highest concentrations of total phosphorus were evident in the Eastern part. The majority of phosphorus was concentrated in two forms; apatitic phosphorus (57%) and refractory organic phosphorus (42%). The most important form that possibly controls the concentrations of dissolved phosphorus is apatitic phosphorus. The high correlations between apatitic and refractory organic phosphorus suggested transformation process of apatitic phosphorus to organic phosphorus and vice versa.

Acknowledgement

This project was funded by the Deanship of Scientific Research (DSR), King Abdulaziz University, Jeddah, Kingdom of Saudi Arabia, under grant No.(301/150/431). The authors, therefore, acknowledge with thanks (DSR) technical and financial support. Map of the area was prepared by Dr. Ramadan Abo Zaid.

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