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SPATIAL VARIABILITY OF PHOSPHORUS FRACTIONS IN SURFICIAL SEDIMENTS ALONG THE RIVER NILE, EGYPT: ENVIRONMENTAL IMPACT ASSESSMENT

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ABSTRACT :

In Egypt, the River Nile receives great quantities of agricultural, industrial, municipal and domestic wastes. Monitoring of phosphorus fractions and their speciation in the Nile sediments was the main objective of the present study. The work aimed also to assess possible chemical pollution and perceiving pollution sources along the Nile. Surface sediment samples were collected from 20 sites along the River Nile and its northern branches. The samples were analyzed for their chemical and physical characterization. Phosphorus fractionation was carried out using seven-step sequential extraction technique. Results of the phosphorus partitioning in the examined sediments decreased in the order HCl-P> residual P> NaHCO₃-IP> NaOH-IP> NaOH-OP> NaHCO₃-OP> H₂O-P. Phosphorus bound to water-soluble, NaHCO₃ and NaOH are readily available to the biosystem, especially higher plants. While P connected to the HCl and residual fraction are more strongly held into the sediment components and, therefore, unavailable to the biosystem.

Results also showed that P speciation is controlled by its source and geochemical behavior and the degree of pollution. The major part of P is hosted in the HCl extractable fraction followed by residual fraction, reflecting their natural association in the primary Ca-apatite and secondary Fe-and Al- phosphorus.

A significant part of P is associated with NaHCO₃-IP and NaOH-IP fractions, while NaHCO₃-OP and NaOH-OP are less important, Moreover traceable quantities of P are accompanied by H₂O-P fraction.

Phosphorus fractionation show a general marked enrichment along the Nile, with elevated levels of the environmentally-derived P close to the source of pollution.

INTRODUCTION:

Currently, the Nile stream receives enormous amounts of agricultural wastewater that carry various chemical pollutants related to the widespread use of fertilizers and pesticides. Besides, great quantities of industrial, municipal and domestic wastes and street dusts are drained, directly or indirectly, into the Nile. Phosphorus (P) input is a key factor in controlling the trophic state in fresh water. The movement of P from a terrestrial to an aquatic environment can, therefore, pose a threat to water quality. The accumulation of P in agricultural soils resulting from fertilizer, organic manure and sewage sludge applications might enhance the potential for P losses (Sibbesen, 1989). Because of the high P-retention capacity of most soils, vertical movement of P through the soil profile into drainage water is, generally considered of little importance (Sharpley and Menzel, 1987 and Sharpley *et al.*, 1994).

Eutrophication, caused by phosphorus enrichment, is a new environmental problem, since the closure of the Aswan High Dam in 1964, the flow regime of the river has changed from highly fluctuated to nearly constant. Accordingly, advanced eutrophication of surface water leads to problems with its use for fisheries, recreation, industry or drinking, due to increased of undesirable algae and aquatic weeds and oxygen shortages caused by their senescence and decomposition (Kotak *et al.*, 1993).

The form of P in agricultural runoff is dependent on the initial P sources, the hydrological pathway it follows from land to stream, and any physical, chemical or biological transformation that take place to the drainage network. Subsequent sedimentation and in stream transformation may further modify the form of P in fresh waters (Heathwaite, 1993).

Phosphorus in runoff and receiving waters is present primarily as ions of organic orthophosphate or associated with organic or inorganic colloidal and particulate materials. It exists in both dissolved and particulate states (Heathwaite, 1993).

Many sequential fractionation strategies have been developed to quantify different forms of P in soils. The method developed by Hedley *et al.* (1982) and Tiessen and Moir (1993) has been used for investigation of the forms and transformations of P in soil and sediments.

The objectives of this study is to estimate the distribution and speciation of P fractions in surficial bottom sediments from the River Nile

in Egypt aiming to recognize their environmental impact.

MATERIAL AND METHODS: Sampling:

A total of 20 samples (Fig. 1) were collected from the surficial bottom sediments along the Nile banks in Egypt and its northern branches (Damietta and Rosetta). This was carried out during the period of the winter draught in which the level of the Nile water is significantly dwindled. Accordingly, the surface bottom sediments along the Nile banks become very shallow and accessible to be sampled correctly.

The sampling sites were chosen to represent different flow regimes, namely high-energy and low energy. The high energy sites correspond to sites of high rate of flow and are characterized by active sediments. The low energy sites, show very low water velocity and are considered to be sites of accumulation where fine suspended matter are settled down and precipitated. At each sampling point, the top sediment layer (3 cm) was taken using a plastic scoop, mostly at a water depth of few centimeters. The collected sediment samples were placed in plastic bags and transported to the laboratory.

In the laboratory, samples were wet passed through a plastic sieve to remove the coarse materials, animal and plant remains. They were then air-dried and prepared for subsequent analysis. The pH values were measured in the sediment suspension (1:2.5), whereas electric conductivity (EC) was measured in 1:5 extract. Cations and anions were determined according to Black (1982). Inorganic carbonate was determined volumetrically using Major collins Calcimeter, whereas organic carbon content was measured by wet oxidation using Walkely-Black procedure (Dewis and Freitas, 1970). Sediment samples used for particle-size distribution were pretreated with H₂O₂ and HCl, dispersed over-night in Na-



hexametaphosphate, and then evaluated by the pipette method (Day, 1965).

Fig. (1): Map of the River Nile in Egypt and its northern branches (Damietta and Rosetta) showing the sampling sites.

Total Fe and Mn:

For the determination of total Fe and Mn content, air-dried samples were separated to the fine fraction (<60µm) using a nylon sieve. This size fraction is considered as most sensitive to metal accumulation (WHO, 1982).

The method described by Ure (1990) was used to determine the amount of total Fe and Mn in the collected samples. The concentration of these elements in the obtained digests were measured using Buck Scientific 210-Atomic Absorption Spectrophotometer.

Sequential Fractionation of Sediment **Phosphorus:**

A modification of the methods of Hedley et al. (1982) and Tiessen and Moir (1993) was selected to extract the empirically defined pools of P. A 0.5g aliquot of air dried sediment sample (<2-mm) was placed in a 50-ml centrifuge tube and subjected to sequential fractionation. The reagents and conditions employed in the extraction procedure of the different fractions are summarized as follows:

- 1-Water-suluble (H₂O-P): Sample was extracted with 30ml of deionized water through 16 hours end-to-end shaking. After agitation, the tubes were centrifuged at 26 860 rpm for 15 min at 5°C; then, the supernatant was passed through a 0.22 μ m filter (Greenberg *et al.*, 1992).
- 2-NaHCO₃-soluble Inorganic P (NaHCO₃-IP): The residue from step 1 was extracted with 30 ml of 0.5 M NaHCO₃ (PH= 8.2) by 16 hours end-to-end shaking, centrifugation and filteration through a 0.22-µm filter.
- 3-NaHCO₃-soluble Organic P (NaHCO₃-OP): The filterate of step 2 was digested in an autoclave for 60 min. at 103.5 Kpa and 121 °C, with acidified ammonium persulfate.
- 4-NaOH- soluble inorganic P (NaOH-IP): The residue from step 2 was extracted with 30 ml of 0.1 M NaOH, by 16 hours end-to-end shaking, centrifugation and filtration through 0.22 μm filter.
- 5-NaOH- soluble Organic P (NaOH-OP): The filtrate from step 4 was digested in an autoclave for 40 min., at 103.5 Kpa and 121 °C with acidified ammonium persuflate.
- 6-HCl-soluble P (HCl-P): The residue remaining from step 4 was extracted with 30 ml of 1M HCl, by 16 hours end-to-end shaking, centrifugation and filteration through 0.22 μm filter.
- 7-Residual-P: The residue from step 6 was extracted with H_2SO_4 H_2O_2 (Tiessen and Moir, 1993).

The procedure described above was performed in duplicate on each composite sample from each replication. Orthophosphate P in the various filtrates and digests was determined colorimetrically following the method of Murphy and Riley (1962). The difference between the total and inorganic P in the extracts represents the organic P.

Data Analysis:

Simple correlation analysis was used to calculate the correlation coefficients between phosphorus forms and sediment characteristics.

RESULTS AND DISCUSSION:

The twenty surface samples collected from the bottom sediments of the River Nile were divided into four segments: segment No. I represents Upper Egypt, segment No. II represents Mid Egypt, segment No. III represents Great Cairo and segment No. IV represents the northern branches (Fig. 1).

The obtained data (Table 1) show that pH values were almost similar along the Nile banks in Egypt, ranging from slightly to moderately alkaline (7.14 to 8.04). However, EC and soluble cations and anions showed wide differences along the Nile stream. Electrical conductivity, soluble cations and soluble anions were higher in sediments as one proceeds northwards of the river stream. Sediments of segment No. IV contained the highest values of EC, soluble cations and anions, especially site No. 20 (Rosetta). Contrarily, sediments of segment No. I showed the lowest values of EC, as well as soluble cations and anions. Differences in organic C levels (Table 2), were also detected along the Nile banks. Organic carbon level fluctuated between 1.15% and 8.21%; the highest levels were determined in site No. 4 (Griga 1) and 14 (Shobra). This might be due to the disposal of industrial wastes. However, mean organic C levels increased slightly in the northwards of the river stream, especially in segment No. III.

					Soluble	Cations ar	nd Anions ((meq/L)		
Sampling sites	рН (H ₂ O 1:2.5)	EC dsm ⁻¹ (1:5)	Na	K	Ca	Mg	CI	HCO3	CO ₃	SO4
Upper Egypt (segment No.I)										
Aswan (No. 1)	7.45	0.46	0.49	0.89	2.37	0.99	1.75	1.70	0.60	0.64
Kom-ombo (Aswan) (No. 2)	7.77	0.55	0.77	1.95	1.87	0.99	2.50	1.33		1.67
Qena (No. 3)	7.43	0.78	0.49	1.11	4.59	2.10	1.50	4.70	0.80	1.29
Girga 1 (Sohag) (No. 4)	7.40	1.82	2.49	2.11	7.44	5.52	5.60	7.20		4.76
Girga 2 (Sohag) (No. 5)	7.69	0.60	0.79	0.58	3.66	1.51	2.50	2.80		1.24
Girga 3 (Sohag) (No. 6)	7.88	0.30	0.36	0.61	1.44	0.68	1.05	1.01	0.20	0.83
El-Sheikh-Yossef (Sohag) (No.7)	7.68	0.41	0.41	0.68	2.01	1.11	1.00	2.88		0.33
Tahta (Sohag) (No. 8)	7.39	0.32	0.33	0.49	1.66	0.66	1.00	1.70	0.40	0.04
Tema (Sohag) (No. 9)	7.38	0.88	1.51	1.33	3.73	2.11	3.32	3.50		1.86
Mean	7.56	0.68	0.85	1.08	3.20	1.74	2.25	2.98	0.50	1.41
Mid Egypt (segment No.II)										
El-Brgaia (El-Minia) (No. 10)	8.04	0.30	0.44	0.33	1.22	1.02	1.60	1.20		0.21
El-Fashn (Beni-Swaif) (No. 11)	7.57	1.53	2.82	1.50	7.88	3.83	9.00	5.20	0.16	1.67
Mean	7.81	0.92	1.63	0.92	4.55	2.43	5.30	3.20	0.16	0.94
Great Cairo (segment No.III)										
El-Massara (No. 12)	7.59	0.96	0.95	1.21	4.86	2.51	5.00	2.35		2.18
Cairo (No. 13)	7.38	0.70	0.69	0.88	4.15	1.56	4.23	2.45		0.60
Shobra A (No. 14)	7.83	0.30	0.61	0.21	2.05	0.53	1.88	1.12		0.40
Beni-Salama (No. 15)	7.60	0.48	0.56	0.80	2.22	1.34	1.00	3.80		0.13
Mean	7.60	0.61	0.70	0.78	3.32	1.49	3.03	2.43	-	0.83
Delta (segment No.IV)										
Banha (No. 16)	7.66	1.48	1.21	1.16	6.62	3.93	3.29	6.88		2.74
Mit-Ghmr (No. 17)	7.19	0.61	0.69	1.00	3.62	1.58	2.25	2.99	0.60	1.05
Damietta (No. 18)	7.63	1.51	1.72	2.23	6.93	3.05	6.00	5.10	0.40	2.43
Desouk (No. 19)	7.66	0.58	0.67	0.86	3.12	1.53	1.00	3.66	0.40	1.12
Rosetta (No. 20)	7.22	13.74	36.00	23.33	87.00	46.00	154.00	36.11	0.80	6.42
Mean	7.472	3.584	8.058	5.716	21.458	11.218	33.308	10.948	0.55	2.752

Table (1): Selected chemical properties of the studied sediments

The total inorganic carbonates (Table 2) displayed relatively high variability throughout the examined sediments (0.78–7.24%); the highest value was determined in site No. 14 (Shobra) while the lowest one was found in site No. 15 (Beni-salama). The texture of the studied sediments differed from sandy to sand clayloam, where coarse sand fraction (>100 μ m) ranged from 5.75 to 73.02%, fine sand fraction (100-50 μ m) ranged from 5.22 to 61.02%, silt fraction ranged from 2.04 to 46.02% and clay content ranged from 2.04 to 34.08%. Distribution of the particle size fractions along the examined sediments showed consistent patterns about the precipitation of the fine fraction northwards in

the river stream as influenced by very low water velocity (Table 2).

Total Fe and Mn concentrations (Table 2) point to the abundance of both (4.34-9.97% and 985-3005 mg kg⁻¹, respectively). This is attributed to the lithogenic nature of the Nile sediments, which are extremely influenced by the composition of the parent rocks in the hinterlands particularly the Ethiopian basaltic plateau (Omer, 1996 and 2003). The spatial variability of Fe and Mn along the Nile is influenced by the flow regime. They are enriched in low-energy sediments (mean 7.03% and 2093 mg kg⁻¹, respectively) whereas their contents are depleted (4.92% and 984 mg kg⁻¹, respectively) in the high-energy site (No.7).

	00		Pa	article size d	listributio	n	Tota	(ppm)
Sampling sites	% %	In. C.%	Sand %	Sand %	Silt	Caly	F۵	Mn
	70	0 /0	> 100	100-50	%	%	10	WITT
Upper Egypt (segment No.I)								
Aswan (No. 1)	2.08	4.28	5.76	40.18	46.02	8.04	71533	1495
Kom-ombo (Aswan) (No. 2)	2.26	3.46	33.04	48.90	10.02	8.04	84565	1750
Qena (No. 3)	2.97	2.39	30.72	19.22	20.02	30.04	63635	1960
Girga 1 (Sohag) (No. 4)	6.40	6.60	31.30	26.54	8.08	34.08	51450	2150
Girga 2 (Sohag) (No. 5)	1.72	5.69	49.30	36.64	6.02	8.04	56420	2588
Girga 3 (Sohag) (No. 6)	1.15	6.61	58.90	31.02	2.04	8.04	74393	3005
EI-Sheikh-Yossef (Sohag) (No.7)	2.60	1.92	51.22	24.68	14.08	10.02	49200	985
Tahta (Sohag) (No. 8)	2.08	2.32	67.72	5.22	28.02	2.04	62205	2523
Tema (Sohag) (No. 9)	1.34	5.20	31.32	52.22	12.40	4.06	56908	2385
Mean	2.51	4.27	39.92	31.62	16.30	12.49	63367.67	2093.44
Mid Egypt (segment No.II)								
El-Brgaia (El-Minia) (No. 10)	1.30	4.92	62.72	5.22	30.02	2.04	60970	1928
El-Fashn (Beni-Swaif) (No. 11)	3.88	2.53	26.92	61.02	2.04	10.02	65715	2070
Mean	2.59	3.73	44.82	33.12	16.03	6.03	63342.50	1999.00
Great Cairo (segment No.III)								
El-Massara (No. 12)	2.55	6.18	28.04	35.88	6.04	30.04	63700	1715
Cairo (No. 13)	1.73	3.38	35.50	42.42	10.02	4.06	99690	2640
Shobra A (No. 14)	8.21	7.24	59.80	6.16	18.02	16.02	43388	1011
Beni-Salama (No. 15)	2.92	0.78	73.02	10.86	2.04	14.08	56973	1120
Mean	3.85	4.40	49.09	23.83	9.03	16.05	65937.75	1621.50
Delta (segment No.IV)								
Banha (No. 16)	2.62	1.83	11.54	44.39	20.05	24.02	59118	1249
Mit-Ghmr (No. 17)	3.59	3.73	39.20	14.74	44.02	2.04	79853	2200
Damietta (No. 18)	2.12	2.89	37.52	38.42	8.04	16.02	82450	1580
Desouk (No. 19)	1.78	2.81	25.22	52.68	20.05	2.05	76440	1629
Rosetta (No. 20)	3.26	2.67	29.40	46.50	14.08	10.02	53450	1341
Mean	2.67	2.79	28.58	39.35	21.25	10.83	70262.20	1599.80

Table (2): Organic and inorganic carbon percentages, particle size distribution and total iron and manganese contents in the examined sediments.

Phosphorus status along the Nile sediments:

The most important mechanism of phosphorus introduction into the aquatic environment is adsorption onto surfaces of sediment particals and other solid phases. This process is heterogeneous and takes place with different substances such as clay minerals, organic matter, hydrous oxides of Fe, Mn and Al, and carbonates (El-Sokkary, 1994). The relative importance of these substances for phosphorus adsorption is dependent upon both their ability and their abundance. Sediments do not consist of well-defined separate solid phases, but the phases participating are intermingled, and one phase may coat another. However,

distribution and variability of the various P fractions throughout the Nile sediments will be discussed in the following paragraphs:-

I- Water- Soluble Phosphorus (H₂O-P):

This fraction is usually considered to represent the most labile P in the soil and sediments (Yaobing Sui *et al.*, 1999).

The H₂O-P content of the studied sediments was significantly different through the examined segments, and even within the same segment (Table 3). The mean H₂O-P contents in the considered segments were 23.85, 13.64, 27.05 and 25.28 mg kg⁻¹ in the segments I through IV so, these sediments can be classified as P-rich (Tran *et al.* 1988).

Sampling sites	Н ₂ О-Р	NaHCO ₃ -IP	NaHCO ₃ -OP	NaOH-IP	NaOH-OP	НСІ-Р	Residual-P	Total-P
		1	•	ma P ka	⁻¹ sedimer	ht		1
Upper Egypt (segment No.I)								
Aswan (No. 1)	24.26	161.87	33.05	171.03	23.41	671.15	156.35	1241.12
Kom-ombo (Aswan) (No. 2)	13.96	169.15	62.97	118.22	41.25	697.94	150.03	1253.52
Qena (No. 3)	37.28	97.00	24.25	63.66	42.66	737.15	165.27	1167.62
Girga 1 (Sohag) (No. 4)	40.91	123.07	73.35	77.90	127.28	753.50	133.18	1259.19
Girga 2 (Sohag) (No. 5)	24.25	162.88	35.81	140.71	30.58	707.43	118.55	1220.21
Girga 3 (Sohag) (No. 6)	19.40	87.30	31.95	76.42	40.30	738.16	119.73	1113.26
El-Sheikh-Yossef (Sohag) (No.7)	20.01	81.57	42.35	78.21	84.98	589.99	113.95	1011.06
Tahta (Sohag) (No. 8)	15.16	136.38	26.76	154.05	78.14	689.29	152.83	1252.61
Tema (Sohag) (No. 9)	19.40	181.08	27.63	139.49	47.44	701.51	160.73	1277.28
Mean	23.85	133.37	39.79	113.30	57.34	698.46	141.18	1199.54
Mid Egypt (segment No.II)								
El-Brgaia (El-Minia) (No. 10)	13.94	141.23	17.08	67.32	28.92	650.37	147.54	1066.40
El-Fashn (Beni-Swaif) (No. 11)	13.34	120.65	33.72	77.00	78.01	591.23	161.53	1075.48
Mean	13.64	130.94	25.40	72.16	53.47	620.80	154.54	1070.94
Great Cairo (segment No.III)				-				
El-Massara (No. 12)	38.19	92.15	41.55	96.40	48.18	687.16	233.17	1236.80
Cairo (No. 13)	14.25	149.71	38.94	123.68	36.63	665.44	256.54	1285.19
Shobra A (No. 14)	40.31	135.16	69.92	93.36	136.82	676.66	225.74	1377.97
Beni-Salama (No. 15)	15.46	78.81	24.99	71.54	20.69	590.64	221.01	1023.14
Mean	27.05	113.96	43.85	96.25	60.58	654.98	234.12	1230.78
Delta (segment No.IV)							-	
Banha (No. 16)	35.76	150.03	59.14	106.44	39.49	658.26	205.34	1254.46
Mit-Ghmr (No. 17)	37.29	184.62	113.72	192.87	131.75	689.99	189.49	1539.79
Damietta (No. 18)	15.76	203.67	39.29	162.81	54.76	691.15	197.81	1365.25
Desouk (No. 19)	16.06	189.73	34.22	148.29	51.25	705.49	193.43	1338.47
Rosetta (No. 20)	21.52	131.24	40.39	133.70	72.99	727.38	218.68	1345.90
Mean	25.28	171.86	57.35	148.82	70.05	694.45	200.95	1368.75

Table (3): Fractions of phosphorus in the examined River Nile sediments

The highest H_2O -P values (27.05 mg kg⁻¹) was detected in segment III (Great Cairo), associated with high organic matter and clay contents. Besides, the sites of this sigment usually receives high levels of raw domestic, municipal and industrial wastes. On the other hand, the lowest H_2O -P value was detected in Mid Egypt segment (No. II), associated with relatively low organic matter and clay contents.

Water soluble-P represents a traceable percent of the total P (Table 4), where it ranged from 1.11 to 3.25% (mean 1.99%) in segment I, from 1.24 to 1.31% (mean 1.28%) in segment II, from 1.11 to 3.09% (mean 2.20%) in segment III and from 1.15 to 2.85% (mean 1.85%) in segment IV. Water soluble- P gives an indication of potential soluble-P movement with leaching and sometimes used as a measure of labile- P (Nishimoto *et al.*, 1977).

The general pattern of H_2O-P variability along the studied Nile sediments (Table 5) tends to be positively correlated with the organic carbon, inorganic carbonate, clay and silt in each segment (r=0.62^{**}, 0.41^{**}, 0.70^{**} and 0.20^{*}, respectively). Meanwhile, pH, sand fraction, total Fe and Mn were significantly and negatively related to H₂O-P. The correlation was insignificant between H₂O-P and electrical conductivity. Significant positive correlations were found between H₂O-P and each of NaHCO-OP, NaOH-OP, HCI-P, and total-P, (r=0.58^{**}, 0.44^{**}, 0.37^{**} and 0.38^{**}, respectively). In contrast, there was a significant negative correlation with NaHCO₃-IP fraction (r=-0.16^{*}).

II-Inorganic NaHCO₃-Phosphorus (NaHCO₃-IP):

The NaHCO₃-IP was found to be highly correlated with P uptake by plants (Menon *et al.*, 1984; Sharpley 1991) and thus usually assumed to be plant available (Cross and Schlesinger 1995).

The NaHCO₃-IP contents of the examined sediments were different within each segment and among segments. The mean NaHCO₃-IP contents of the studied sediments in all segments (No. I, II, III and IV, respectively) were 133.4, 130.9, 113.9 and 171.9 mg kg⁻¹. The relatively high concentration of NaHCO₃-IP recorded in segment IV may be attributed to industrial and agricultural draining into the Nile and reflect the widespread use of phosphate fertilizers. This was more pronounced in sites No. 16, 17 and 18 where the concentrations were 194.6, 203.7 and 189.7 mg kg⁻¹, respectively. Intermediate NaHCO₃-IP levels were observed in segment I (Upper Egypt) and segment II (Mid Egypt), where the mean concentrations were 133.4 and 130.9 mg kg⁻¹. This was particularly true, in Aswan (161.9 mg kg⁻¹), where sites are located very close to the outfall drains discharging agricultural and industrial wastes (e.g Kom-Ombo sugar plant).

When considered as a percent of the total P, the NaHCO₃-IP possessed small fractions, although variable in between the examined segments as well as within each segment, (Table 4). The average values were 10.99%, 12.23%, 9.26% and 12.56% in segments No. I, II, III and IV, respectively.

Significant negative correlation was found between NaHCO₃-IP and clay and organic matter contents ($r=-0.42^{**}$ and -0.16^* , respectively). On the other hand, significant positive correlation was found between NaHCO₃-IP and sand $(100-50\mu m)$, silt and total Fe (r=-0.34^{**}, -0.37^{**} and -0.43^{**}, respectively). Meanwhile, there were significant positive correlations between NaHCO₃-IP and other phosphorus fractions except NaOH-OP fraction where the correlation was insignificant (Table 5).

III-Organic NaHCO₃-Phosphorus (NaHCO₃-OP):

Organic P fraction extracted by NaHCO₃ in the examined sediments was significantly variable along the river stream (Table 3). In addition, NaHCO₃-OP displayed a general northward increase along the river stream. This may be attributed to several factors including organic matter and fine fraction contents. Organic P tended to be higher when either or both organic matter and fine fraction were greater. Other studies have pointed to similar trends (Harrison, 1987). Furthermore, it seems that organic P is associated with the disposal of industrial and municipal wastes in the river stream. Examples of this association are illustrated in sites No. 4, 12, 14, 16 and 17 which exist in areas known to be characterized by industrial activities. In addition, site no. 2 (at Kom-Ombo) which is located close to the outfall of the Kom-Ombo drain discharging industrial, municipal and domestic wastes.

The percentages of NaHCO₃-OP in total phosphorus showed low variability in the examined sediments being, in means 3.32, 2.37, 3.56 and 4.19% of segments I, II, III and IV, respectively (Table 4). The relatively high quantities of NaHCO₃-OP fraction were detected in the northern sites (segments III and IV). This confirms the above discussed trend concerned with pollution of the Nile stream northwards.

Table (4): Relative concentrations of phosphorus fractions (%) of total P in the examined River Nile sediments

Sampling sites	H₂O-P	NaHCO ₃ -IP	NaHCO ₃ -OP	NaOH-IP	NaOH-OP	НСІ-Р	Residual-P	Total-P
				3	/o	1		
Appen Egypt (Segment No.I)	1 05	12.04	2.66	12 70	1 90	E4 00	12.60	100
Aswan (No. 1) Kem embe (Aewen) (No. 2)	1.95	13.04	2.00	0.42	1.09	54.00	12.00	100
Cons (No. 2)	2.10	13.49	5.02	9.43	3.29	55.00 62.47	11.97	100
Girga 1 (Sobag) (No. 4)	3.19	0.31	2.00	5.40	3.00	50.84	14.10	100
Girga 2 (Sobag) (No. 5)	1 00	12 25	2 02	11 53	2 51	57.09	0.72	100
Girga 3 (Sohag) (No. 6)	1 74	7 84	2.33	6.86	3.62	66 31	10 75	100
El-Sheikh-Yossef (Sohag) (No 7)	1.98	8.08	4 19	7 74	8 41	58 41	11 28	100
Tahta (Sohag) (No. 8)	1 21	10.89	2 14	12.30	6 24	55.03	12 20	100
Tema (Sohag) (No. 9)	1.52	14.18	2.16	10.92	3.71	54.92	12.58	100
Mean	1.99	10.99	3.32	9.36	4.83	58.38	11.76	100
Mid Eavpt (segment No.II)								
El-Brgaia (El-Minia) (No. 10)	1.31	13.24	1.60	6.31	2.71	60.99	13.84	100
El-Fashn (Beni-Swaif) (No. 11)	1.24	11.22	3.14	7.16	7.25	54.97	15.02	100
Mean	1.28	12.23	2.37	6.74	4.98	57.98	14.43	100
Great Cairo (segment No.III)								
El-Massara (No. 12)	3.09	7.45	3.36	7.79	3.90	55.56	18.85	100
Cairo (No. 13)	1.11	11.65	3.00	9.62	2.85	51.77	19.96	100
Shobra A (No. 14)	2.93	9.81	5.07	6.78	9.93	49.11	16.38	100
Beni-Salama (No. 15)	1.51	7.70	2.44	6.99	2.02	57.73	21.60	100
Mean	2.20	9.26	3.56	7.82	4.92	53.24	19.02	100
Delta (segment No.IV)								
Banha (No. 16)	2.85	11.96	4.71	8.48	3.14	52.47	16.37	100
Mit-Ghmr (No. 17)	2.42	11.99	7.39	12.53	8.56	44.81	12.31	100
Damietta (No. 18)	1.15	14.92	2.88	11.93	4.01	50.62	14.49	100
Desouk (No. 19)	1.20	14.18	2.56	11.08	3.83	52.71	14.45	100
Rosetta (No. 20)	1.60	9.75	3.00	9.93	5.42	54.04	16.25	100
Mean	1.85	12.56	4.19	10.87	5.12	50.74	14.68	100

Table (5): Correlation matrix of phosphorus fractions and the sediments characteristics

	H₂O-P	NaHCO ₃ -IP	NaHCO ₃ -OP	NaOH-IP	NaOH-OP	HCI-P	Residual-P	Total-P
NaHCO ₃ -IP	-0.16*							
NaHCO ₃ -OP	0.58**	0.27**						
NaOH-IP	-0.09	0.79**	0.31**					
NaOH-OP	0.49**	0.01	0.72**	0.07				
HCI-P	0.37**	0.26**	0.17*	0.24**	0.09			
Residual-P	0.14	0.09	0.13	0.14	0.06	-0.12		
Total-P	0.38**	0.71**	0.64**	0.74**	0.42**	0.49**	0.44**	
OC %	0.62**	-0.16*	0.55**	-0.23**	0.80**	0.04	0.20*	0.25**
In. C %	0.41**	0.03	0.21**	-0.07	0.25**	0.50**	-0.18*	0.17*
PH	-0.21**	-0.16*	-0.28**	-0.49**	-0.31**	-0.23**	-0.27**	-0.45**
EC dsm ⁻¹	-0.01	-0.02	0.00	0.10	0.10	0.24**	0.25**	0.20**
Sand % > 100	-0.25**	-0.36**	-0.17*	-0.30**	0.13	-0.21**	-0.15	-0.38**
Sand % 100-50	-0.27**	0.34**	-0.10	0.21**	-0.31**	0.06	0.05	0.12
Silt %	0.20*	0.37**	0.28**	0.52**	0.14	0.05	-0.03	0.39**
Caly %	0.70**	-0.42**	0.13	-0.47**	0.14	0.23**	0.013	-0.07
Total Fe	-0.39**	0.43**	0.07	0.41**	-0.29**	0.10	0.24**	0.28**
Total Mn	-0.18*	0.12	-0.10	0.14	-0.12	0.44**	-0.33**	0.02

*,** = Significant at 0.05 and 0.01 probability levels, respectively.

The obtained values of correlation coefficients (Table 5) show that NaHCO₃-OP fraction was significantly and positively correlated with organic carbon, inorganic carbonates and silt contents ($r=0.55^{**}$, 0.21^{**} and 0.28^{**}) respectively. Meanwhile, there are significant and positive correlations between NaHCO₃-OP and other phosphorus fractions, NaOH-IP ($r=0.31^{**}$), NaOH-OP ($r=0.72^{**}$) and total P ($r=0.64^{**}$). This is in agreement with the previously mentioned explanation.

IV-Inorganic Hydroxide-Extractable Phosphorus (NaOH-IP):

The IP extracted by 0.1 M NaOH is considered as P associated with Fe and Al components (Hedley *et al.*, 1982, Tiessen *et al.*, 1984 and Wager *et al.*, 1986) through chemisorption to their surfaces (Ryden *et al.*, 1977). Williams *et al.* (1971) indicated that some Ca-P may also be extracted by NaOH.

The NaOH-IP contents estimated in the examined sediments are given in Table (3). Significant differences were found among the examined sediments along the Nile. The amount of NaOH-IP, on the average, increased markedly northward where the mean contents for segments II, III and IV are 72.2, 96.3 and 148.8 mg kg⁻¹, respectively; segment I is an exception with a mean value of 113.3 mg kg⁻¹. Sites exhibiting the highest pollution level are those having the highest amounts of NaOH-IP: Mit-Ghmr (102.87 mg PKg⁻¹), Damietta (162.8 mgPKg⁻¹), Desouk (148.29) and Cairo (123.68), this implies that the NaOH-IP content is significantly influenced the anthropogenic activities along the Nile.

High values of NaOH-IP follow the elevated concentrations of total Fe and Mn in the examined sediments. The higher concentrations in sediments from lower-energy sites indicate that the major part of the Fe and Mn-bearing phases and the associated NaOH-IP is carried as a suspended load.

The NaOH-IP fraction (Table 5) was significantly and positively correlated with both fine sand fraction (100-50 μ m) (r=0.21^{**}), silt fraction (r=0.52^{**}) and total Fe (r=0.41^{**}), while it was significantly and negatively correlated with pH (r= -0.44^{**}), coarse sand fraction (>100 μ m) (r=-0.30^{**}) and clay fraction (r=-0.47^{**}). Otherwise, there was significant but positive correlations between NaOH-IP and other P fractions, HCI-P (r= -0.24^{**}) and total P (r=0.74^{**}).

The percentages of NaOH-IP of the total P in the examined sediments were relatively low and showed narrow variability among the studied segments. High quantities of NaOH-IP fraction were detected in sites located in the northern part of the Nile (segment No. IV, 10.87%), while relatively low quantities were detected in Mid Egypt (segment No. II, 6.74%) (Table 4).

V-Organic Hydroxide-Extractable Phosphorus (NaOH-OP):

The NaHCO₃- and NaOH-OP estimated by the Hedley procedure (1982), are found to be useful in characterizing the bioavailability of OP (Tiessen and Moir, 1993).

Significant differences in the NaOH-OP content were found among the examined segments and even within the same segment (Table 3), indicating that this fraction varied among the studied sediments. Primarily, the NaOH-OP fraction was greater than the NaHCO₃-OP fraction in all the examined sediments.

Sites located in the northern part of the Nile stream contained significantly higher NaOH-OP than the other sites. As the case for NaOH-IP, a general northward increase was reported for the NaOH-OP through segments II, III and IV (mean = 53.5, 60.6 and 70.1 mg kg⁻¹, respectively); segment I is also an exception with a mean value of 57.3 mg kg⁻¹. A frequent coherence was observed between high contents of NaOH-OP and the polluted sites, where elevated values were detected in Mit-Ghmr (131.57 mg kg⁻¹) Shobra (136.82 mg kg⁻¹) and Girga 1 (127.28 mg kg⁻¹).

The obtained values of correlation coefficients (Table 5) show that NaOH-OP fraction was significantly and positively correlated with total P ($r=0.42^{**}$), organic carbon ($r=0.80^{**}$) and inorganic carbonate ($r=0.25^{**}$) contents, while, significantly but negatively correlated with soil reaction ($r=-0.31^{**}$), fine sand fraction (100-50 µm) ($r=-0.31^{**}$) and total Fe content ($r=-0.29^{**}$).

The NaHCO₃ and NaOH-OP of the examined sediments are present primarily as ions of organic orthophosphate or in association with organic or inorganic colloidal and particulate material. It exists in both dissolved and particulate states. Dissolved organic P is generated from residues of organic matter and organic biomass (Heathwaite, 1993).

When considered as a percentage of the total P, the NaOH-OP possessed small fraction, and showed distribution pattern through the studied sediments. At the same time, the concentration of NaOH-OP was slightly higher than the detected NaHCO₃-OP fraction (Table 4). The mean percentage between the studied segments was comparable.

VI-Dilute Hydrochloric Acid Extractable Phosphorus (HCl-P) : The HCl-P is thought to represent the primary mineral fraction of P such as apatite (Williams *et al.*, 1980; Tiessen *et al.*, 1984; Tiessen and Moir, 1993). Since the P fraction that remained after the NaOH extraction is insoluble (Tiessen and Moir, 1993), the HCl-P is assumed to be of low bioavailability.

Results of the HCl-P partitioning in the examined sediments are given in Table (3). The HCl-P is the most abundant fraction of P (mean 620.8-698.4 mg kg⁻¹) in the examined sediments. The HCl-P values are predominant over the other seven extractions accounting for approximately 50-60% of the total P.

Data in Table (3) also show that there was no significant differences in the mean values of HCl-P where values obtained for all extracts were relatively comparable, being ranged from 620.8 to 684.5 mg PKg⁻¹. The highest value was detected in segment No. I followed by segment No. IV, III and No. II, respectively (Fig. 1). However, a significant difference was found to be affected by the site activity, where HCl-P ranged from 584.99 mg PKg⁻¹ in high energy site (Site No. 7) to 753 mg kg⁻¹ in low energy site (site No. 4).

The P contents extracted by dilute hydrochloric acid from the studied sediments are most probably of pedogenic origin. This is supported by (i) the large HCl-P values are usually assigned to calcium phosphates predominating over other P forms (Chang and Jackson, 1957) and (ii) the pronounced increase in the amount of P extracted directly by dilute HCl may be attributed to solubility of Caphosphates (Lindsay, 1979). So, the elevated levels of HCl-P might be attributed to the pedogenic Ca- phosphates, while sites having depleted HCl-P values may be ascribed to a low content of lithogenic apatite.

The obtained data also indicate that the major part of P is hosted in the HCl-P fraction, reflecting their natural association with the Cacontaining minerals and their high exchangeable fraction.

The percentage of the HCl-P fraction of the total P in the examined sediments (Table 4) was generally high. It shows a distinctive partitioning pattern in the examined sediments, ranging from 54.1 to 66.3%, 55.0 to 61.0%, 49.11 to 57.73% and from 44.8 to 54.0% for segments I, II, III and IV, respectively.

Values of correlation coefficients (Table 5) show that HCl-P fraction was significantly and positively correlated with both total P ($r=0.49^{**}$), inorganic carbonates ($r=0.50^{**}$), clay ($r=0.23^{**}$) and total Mn ($r=0.44^{**}$) contents.

VII-Residual Phosphorus (Residual- P):

The residual-P was considered to be entirely inorganic, consisting of very recalcitrant and occluded Fe- and Al- associated P, because organic residues are very unlikely to remain after extraction with concentrated HCl (Tiessen and Moir 1993). Sediments of the four segments differed appreciably in residual-P values. Segment No. III (Great Cairo) was higher (mean 234.12 mgPKg⁻¹) than the other segments in residual-P (Table 3) being in the order: IV, II and I. We postulate that some residual-P in these sediments is probably Ca-P, which was not removed because all extractants prior to the I M HCl solution were alkaline. However, this Ca-P may act as a reserve for readily available P. When the readily available P is withdrawn, Ca-P in residual fraction may be mobilized to replenish the available P (Table 3). This explanation is further strengthened by the slight decline of residual P in the sediments, possessing high calcite content and thus probably more Ca-P. Accordingly, the local differences in the residual-P of the examined sediments are most probably of lithogenic origin. On the other hand, the occurrence of high levels of residual-P in segment No. III may be due to anthropogenic origin.

The residual-P represents an intermediate percent of the total phosphorus (table 4) where its mean values ranged from 11.76% in Upper Egypt (segment No. I) to 19.02% in Great Cairo (Segment No. III). The mean percentage of both Mid Egypt and Delta segments are markedly comparable.

Residual-P fraction (Table 5) was highly significantly and positively correlated with total P (r=0.44^{**}), total Fe (r=0.24^{**}) and organic carbon contents (r=0.20^{*}), while it was significantly and negatively correlated with total Mn (r= -0.33^{**}).

VIII- Total Phosphorus (Total- P):

Significant difference in the total phosphorus content (the sum of the seven extracts) was observed among the studied sediments (Table 3). The mean total phosphorus contents were 1199.54, 1070.94, 1230.78 and 1368.75 mg Pkg⁻¹ for Upper Egypt, Mid Egypt, Great Cairo and Delta, respectively (Fig. 1).

The results show that total- P in the sediment taken from high- energy site (No. 7) is significantly lower than that from low-energy sites (table 3 and figure 1). Such compositional pattern of the high energy site, reflects their natural status and represents the uncontaminated lithogenic phase of the Nile sediments. Phosphorus concentration in this sediment can be, accordingly, regarded as a background level for the examined sediments. As a result of its immobility under surficial conditions and its incorporation in the suspended matter, total- P is co-precipitated with the accumulating sediments at the lowenergy sites. Therefore, these sits are considered to be more sensitive to the possible chemical pollution along the Nile.

The generally high content of total- P is attributed to the lithogenic nature of the Nile sediments as well as anthropogenic impacts. The spatial variability of total- P along the Nile is influenced significantly by the flow regime, where they are enriched in low- energy sediments.

Samples collected from Mid Egypt displayed most of the P minimal values (Table 3 and Fig. 1). On the other hand, samples collected from other segments exhibited most of the P maxima; one sample (No. 15) is an exception being shifted from the above mentioned trend. This site is located in the western-north side of Great Cairo (segment No. III) and shows the lowest pollution status within this segment.

The obtained values of correlation coefficients (table 5) show that total- P was highly significantly and positively correlated with organic carbon (r= 0.25^{**}), silt fraction (r= 0.39^{**}) and total Fe (r= 0.28^{**}). Otherwise, there were significant but negative correlations between total-P and coarse sand fraction (>100µm) (r= - 0.38^{**}).

To confirm the previously discussed elevated levels of total phosphorus as controlled by the possible pollution sources, the effect of sediment composition and flow regime on phosphorus variability should be avoided. This goal has been achieved by calculating the enrichment factor (EF) (c.f. Musashino, 1993, Hassan et al., 1999). The EF defined as the ratio of P concentration in the sample to its concentration in the background sample (concentration of P at the high- energy site No. 7). Values of EF greater than one indicate that sources other than natural solid particles are involved. As shown in Table (6), significantly higher values of EF are reported reflecting anomalous P enrichment. It is observed that the local anomalous behavior of P is confirmed, being the highest values of EF along the Nile.

Locations	H_2O-P	NaHCO ₃ -IP	NaHCO ₃ -OP	NaOH-IP	NaOH-OP	HCI-P	Residual-P	Total-P
					[%] 0			
Opper Egypt (segment No.I)	4 24	1 09	0.79	2.10	0.00	4 4 4	1.07	1 22
Aswan (No. 1) Kem embe (Aewen) (No. 2)	0.70	1.90	0.70	2.19	0.20	1.14	1.27	1.23
Come (No. 2)	0.70	2.10	1.49	1.51	0.49	1.18	1.32	1.24
Qena (No. 3) Cirro 1 (Cohor) (No. 4)	1.80	1.20	0.57	0.81	0.50	1.25	1.45	1.10
Girga 1 (Sonag) (No. 4)	2.04	1.51	0.37	0.97	1.50	1.28	1.19	1.25
Girga 2 (Sonag) (No. 5)	1.21	2.00	0.85	1.80	0.40	1.20	1.04	1.21
Girga 5 (Soliag) (No. 6)	0.97	1.07	0.75	0.90	0.47	1.25	1.05	1.10
EI-Sheikh-rosser(Sonag) (No.7)	0.70	4.67		1.07			4 42	4.04
Tanta (Sonag) (No. 8)	0.76	1.67	0.63	1.97	0.92	1.17	1.43	1.24
Tema (Sonag) (No. 9)	0.97	2.22	0.63	1.78	0.56	1.14	1.41	1.26
Mid Egypt (segment No.II)								
El-Brgaia (El-Minia) (No. 10)	0.70	1.73	0.40	0.86	0.34	1.10	1.29	1.06
EI-Fashn (Beni-Swait) (No. 11)	0.67	1.86	0.80	0.98	0.92	1.00	1.42	1.07
Great Cairo (segment No.III)								
El-Massara (No. 12)	1.91	1.14	0.98	1.23	0.57	1.16	2.05	1.22
Cairo (No. 13)	0.71	1.83	0.92	1.58	0.43	1.23	2.25	1.28
Shobra A (No. 14)	2.01	1.67	1.65	1.19	1.61	1.15	1.98	1.37
Beni-Salama (No. 15)	1.27	0.97	0.59	0.91	0.24	1.00	1.94	1.02
Delta (segment No.IV)								

Table (6): The calculated enrichment factor (EF) for phosphorus fractions in the studied sediments

Banha (No. 16)	1.79	1.84	1.40	1.36	0.46	1.12	1.80	1.30
Mit-Ghmr (No. 17)	1.86	2.26	2.66	2.46	1.55	1.17	1.66	1.52
Damietta (No. 18)	0.79	2.50	0.93	2.08	0.64	1.17	1.74	1.35
Desouk (No. 19)	1.08	1.61	0.95	1.71	0.86	1.23	1.92	1.33

In general, it may be stated that most of the investigated 20 sites display some degree of pollution. Sites exhibiting the highest pollution grade are located in Mit-Ghmr, Shobra, Desouk, Damietta, Rosetta, Banha and Cairo (sites No. 17, 14, 18, 20, 16 and 7, respectively). The severely polluted sites documented in segment No. IV, which are located at the northern part of the Nile, reflecting their industrial activities (e.g. the Soda, pesticide, chemical and phosphate fertilizer plants). The high levels of P confirm the suggested anthropogenic enrichment from outside the basin. Cairo and Shobra, which is adjacent to Cairo, are considered as the most polluted spots where the pollution sources include industrial, municipal and domestic wastes as well as the navigation activities.

Other sites possible pollution activities are: Aswan, Kom-Ombo, Girga, Tahta and Tema (sites Nos. 1, 2, 4, 5, 8 and 9, respectively) reflecting potentially high influence of the above mentioned hazards. The daily increasing navigation activites represent an additional source of pollution in the Nile stream.

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> التغيرات المكانية لصور الفوسفور في الترسيبات السطحية لنهر النيل في مصر : تقييم التأثيرات البيئية على عبد الجليل، عدلى عبد العزيز عمر *

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نظراً لأن نهر النيل في مصر قد تصله كميات مختلفة من المخلفات الزراعية والصناعية والبلدية لذا فقد استهدف هذا البحث دراسة ورصد صور الفوسفور (Fractions) المختلفة فى كل جزء من أجزاء النهر بالإضافة إلى تقييم الملوثات الكيماوبة المحتملة، وإدراك وملاحظة مصادر التلوث المختلفة.

تم جمع عينات الترسيبات النهرية السطحية من عشرين موقعاً مختلفاً بطول الوادى وكذلك فرعى دمياط ورشيد، كما تم تحليل العينات تحت الدراسة لمعرفة صفاتها الطبيعية والكيماوية، وكذلك الصور المختلفة للفوسفور باستخدام تقنية الاستخلاص المتتابع (٧ خطوات متتابعة). وأظهرت النتائج أن توزيع الصور المختلفة للفوسفور (Fractions) في الترسيبات النهرية تحت الدراسة يتبع الترتيب التالى :

HCI-P > residual P > NaHCO₃-IP > NaOH-IP > NaOH-OP > NaHCO₃-OP > H₂O-P واتضح من النتائج أيضاً أن الفوسفور الذائب في الماء والمستخلص بواسطة بيكربونات الصوديوم وكذلك المستخلص بهيدروكسيد الصوديوم سواء كان فوسفور معدني أو عضوى إنه أكثر تيسراً للنظام البيولوجي، وبخاصة النباتات الراقية بينما كان الفوسفور المستخلص بحامض الهيدروكلوريك المخفف، وكذلك الفوسفور المتبقى غير ميسر للنظام البيولوجي تحت ظروف الدراسة .

أظهرت النتائج أيضاً أن كميات الفوسفور فى كل جزء (Fraction) مرتبط بالمصدر الطبيعى والسلوك الجيوكيميائى للفوسفور وكذلك درجة التلوث، ويتضح ذلك من أن الجزء الأكبر من الفوسفور يستخلص بحامض الهيدروكلوريك ويليه الفوسفور المتبقى .

وكانت هناك كميات معنوية من الفوسفور المعدنى استخلصت بواسطة بيكربونات الصوديوم وكذلك بهيدروكسيد الصوديوم ، بينما كانت كميات الفوسفور العضوى المستخلصة بنفس محاليل الاستخلاص السابقة أقل معنوية، وكانت هناك كميات محسوسة مستخلصة بالماء .

ومن استعراض النتائج السابقة يتضح وجود ارتفاع معنوى لكميات الفوسفور بطول نهر النيل مع وجود زيادة فى مستويات الفوسفور والتى قد ترتبط إلى حد كبير بالمصادر البيئية للتلوث، وبذلك فإن المستوى المرتفع من الفوسفور فى رسوبيات نهر النيل يمكن أن يمثل أحد الأدلة التى يجب الاعتماد عليها فى تقييم درجة التلوث وتحديد مصادره المختلفة بطول النهر، الأمر الذى يساهم كثيراً فى وضع الاستراتيجية المناسبة للحد من تلوث نهر النيل .