Egypt. J. Chem. **55**, No.2, pp. 179 – 189 (2012)

Monitoring of Some Pollutants in Sediments of Damietta Estuary and Its Impacts on Coastal Share in front of Damietta Governorate

A. M. Hassan, M. H. Ali*, A. M. Kotb and G.G. Soliman**
*Faculty of Science, Al-Azher University, *National Institute of Oceanography and Fisheries and **Dara Petroleum Company, EGPC, Ministry of Petroleum,Cairo, Egypt.*

THE ANALYSIS of distribution pattern of heavy metals Fe, Mn, Zn ,Cu, Pb , Cd , Ni ,Cr, Co, Mo As, Al and Hg in sediment, of Damietta estuary and in front of Mediterranean coastal shoreline was carried out through four successive cruises (February to November 2008). The results revealed that, heavy metals in the Damietta Estuary were higher in concentrations than those of Mediterranean shoreline. This is due to the industrial and domestic waste discharges and return flow of agricultural drainage water. Furthermore, the heavy metals content decreased progressively while moving away from Damietta Estuary to Mediterranean shoreline which declared that heavy metals content of Mediterranean shoreline depends on its distribution pattern in Damietta Estuary. The order of the detected concentration of heavy metals in sediment samples in Damietta Estuary and Mediterranean shoreline concentration is Fe > Mn > Al > Zn > Cr > Pb > Ni > Co > Cu > As > Cd > Hg > Mo and Fe > Mn > Al > Zn > Cr > Ni > Co > Pb > Cu > As > Cd > Hg > Mo, respectively.

Recently, a number of studies have been analyzed and reported on the presence of trace metals in the sediment of the rivers and lakes in the world. Where the bottom sediment act as accumulator for these metals and the rate of accumulation depends mainly on the environmental parameters such as pH, temperature, salinity, hardness, dissolved oxygen…, etc. [1,2].

Heavy metal pollution in air, water, soil and plant systems is of major environmental concern on a worldwide scale with the rapid development of industry. Beside their natural occurrence, heavy metals may enter the ecological system through anthropogenic activities, such as, sewage sludge disposal, application of pesticides and inorganic fertilizers as well as atmospheric deposition [3].

Contamination with heavy metals may have devastating effects on the ecological balance of the aquatic environment and the diversity of aquatic organisms becomes limited with the extent of contamination [4].

Sediments are important sinks for various pollutants like pesticides and heavy metals play a significant role in the remobilization of contaminants in aquatic systems under favorable conditions and in interactions between water and sediments. The direct transfer of chemicals from sediments to organisms is now considered to be a major route of exposure for many species [5]. The release of trace metals from sediments into the water body and consequently to fish will depend on the speciation (*i.e.* metals may be precipitated, complexed, adsorbed, or solubilized) of metals and other factors such as, sediment, the physical and chemical characteristics of the aquatic system [6].

The assessment of environmental quality with respect to heavy metals in aquatic systems involves the measurement of a series of metals in water, sediments and living organisms [7,8] .

Thereafter, the main objective of the present study is to investigate the distribution of heavy metals in Damietta Estuary and Mediterranean shoreline sediment.

Material and Methods

Position of collecting samples

On the basis of ecological considerations, six stations were selected to cover Damietta estuary and other six stations were selected to cover the Mediterranean coastal line.

Location and characteristics feature of each station is given in the following Table and Figure.

TABLE 1. Location and characteristics feature of each station .

	Station No.	**Position**	
		Latitude	**Longitude**
Damietta Estuary	I	31°24'36.14"	31°47'12.49"
	II	31°25'5.55"	31°48'35.83"
	III	31°27'32.10"	31°48'6.77"
	IV	31°28'33.05"	31°49'39.26"
	V	31°30'12.78"	31°50'0.52"
	VI	31°32'3.11"	31°50'40.84"
Mediterranean coastal shoreline	VII	31°31'22.69"	31°52'2.29"
	VII	31°31'20.22"	31°54'5.80"
	IX	31°30'54.90"	31°56'50.27"
	X	31°29'41.62"	31°47'5.21"
	XI	31°29'11.09"	31°45'23.46"
	XII	31°28'29.13"	31°43'8.94"

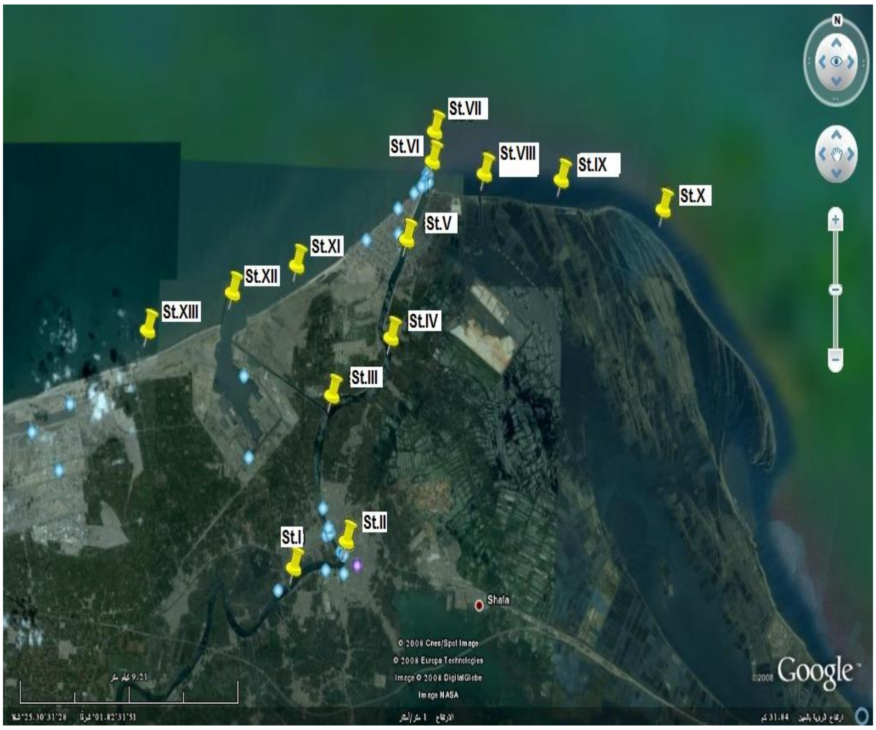

Fig. 1. A satellite map showing the sampling stations in Damietta Estuary and Mediterranean coastal shoreline .

Sampling program

Sediment samples were collected seasonally from the ponds under study during February 2008 until November 2008 and collected by using a stainless steel Ekman Dredge and transferred to polyethylene bags. About 50g of each well homogenized sample was air dried on plastic plates for several days in a clean dust free room, and finally oven dried at 85 °C until constant weight. The sediment analysis include some heavy metals (Fe, Mn, Zn ,Cu, Pb , Cd , Ni , Cr, Co, Mo As, Al and Hg).

Methods of analyses

Determination of heavy metals (Fe, Mn, Zn ,Cu, Pb , Cd , Ni ,Cr, Co, Mo As, Al and Hg) in sediment samples depend on the completely digestion of sediments.

Sediment samples were dried at 80 ^{0}C in oven and digested according to Kouadia and Trefry [9] method. The levels of Fe, Mn, Zn ,Cu, Pb , Cd , Ni ,Cr, Co, Mo As, Al and Hg in different digested samples were determined using ICP-400 model Perkin Elmer, USA.

Results and Discussion

According to Forstner, [10], the sediment existing at the bottom of the water column plays a major role in the pollution scheme of the river system by heavy metals. It reflects the current quality of the water system and can be used to detect the presence of contamination that doesn't remain soluble after discharge into surface water.

Iron values ranged between (4311 - 5604 µg/g) and (3687 - 7228 µg/g) in Damietta Estuary and Mediterranean coastal shore, respectively (Tables 2&3). The minimal values of iron were recorded during winter, which may be attributed to the mobilization of iron from sediment to overlying water at low pH and under the microbial activities [13]. The high values of iron were recorded during spring, which may be attributed to the increase in dissolved oxygen concentrations that was recorded during this season. It facilitate the oxidation of Fe^{+2} to Fe^{+3} thus increasing the precipitation of Fe(OH)3 to bottom sediment [14] .

Manganese exists in the soil principally as MnO_2 which is insoluble in water under reducing conditions [15].

Manganese values ranged between (375 – 636 µg/g) and (317 – 643 µg/g) in Damietta estuary and Mediterranean coastal shore, respectively (Tables 2&3). The results of manganese represented that, the high values of manganese were recorded during hot period (spring and summer). This may be attributed to the precipitation of Mn as MnO_2 under reducing conditions and high temperature of water and air during this period.

On the other hand, the lower values of manganese contents during cold period (winter and autumn), may be attributed to the dissolution of manganese oxides and hydroxides to overlying water under lower values of dissolved oxygen as well as air and water temperature[16].

Zinc values ranged between (32.3 - 67.7 µg/g) and (27.1-53.8 µg/g) in Damietta Estuary and Mediterranean coastal shore, respectively (Tables 2&3). Zinc distributed in sediment in a similar trend as Mn, however, the higher values of Zn were recorded during summer and lower ones were recorded during winter, this indicates that, Mn is probably one of the geochemical support phases of Zn, where Zn associated with Mn, co-precipitate or adsorbed manganese oxide or hydroxide [17].

TABLE 2. Range and mean values of heavy metals in sediment at Damietta Estuary during 2008 .

Parameters	Winter		Spring		Summer		Autumn	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Iron µg/g)	4311 5334	4711	5187 5604	5390	5070 5334	5227	4605 4910	4766
Manganese (µg/g)	375 535	484	464 636	550	526 625	579	444 553	507
Zinc (µg/g)	32.30 65.64	46.82	38.18 57.10	50.05	44.16 67.68	54.97	36.97 55.89	47.15
Copper (µg/g)	7.80 16.70	12.87	6.37 20.28	10.83	10.03 16.04	13.36	7.95 15.44	10.86
Lead (µg/g)	10.92 23.40	19.05	21.65 27.19	23.92	24.60 31.19	27.45	20.76 26.21	23.06
Chromium (µg/g)	24.30 33.60	30.40	25.29 36.15	32.19	24.10 35.60	31.77	22.17 30.58	28.71
Cobalt (µg/g)	10.50 15.69	13.29	14.50 15.95	15.18	14.60 17.80	16.52	13.10 15.12	14.23
Arsenic (µg/g)	1.87 2.66	2.35	2.43 3.98	3.11	3.40 4.21	3.81	2.63 3.63	3.11
Cadmium (µg/g)	2.33 5.84	4.79	1.44 2.34	1.85	2.14 3.10	2.64	1.63 2.39	2.01
Nickel (µ/g)	11.79 18.78	16.12	14.43 23.40	18.48	16.80 23.60	20.52	14.02 20.46	17.51
Aluminum (µg/g)	39.10 58.60	50.49	44.85 67.99	56.12	48.70 58.70	53.80	43.12 56.88	49.35
Mercury (µg/g)	1.62 1.81	1.74	1.12 1.61	1.33	1.39 1.87	1.59	1.12 1.56	1.31
Molybdenum (µg/g)	1.12 1.23	1.18	0.97 1.43	1.16	1.27 1.71	1.45	1.00 1.41	1.17

TABLE 3. Range and mean values of heavy metals in sediment at coastal line of the Mediterranean Sea during 2008 .

Parameters	Winter		Spring		Summer		Autumn	
	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Iron µg/g)	3489 4189	3946	4026 7228	4892	4156 4875	4600	3687 5378.	4261
Manganese (µg/g)	317 382	350	461 643	533	483 535	510	427 525	468
Zinc (µg/g)	27.10 33.30	29.57	37.51 50.60	42.07	41.50 53.76	47.14	36.34 46.85	40.05
Copper (µg/g)	4.90 7.30	6.00	6.51 10.59	7.52	5.35 9.35	7.62	5.32 8.95	6.79
Lead (µg/g)	8.47 11.30	9.67	8.89 13.66	11.20	10.50 16.40	12.58	9.02 13.50	10.67
Chromium (µg/g)	19.30 24.90	21.87	24.14 29.64	26.61	21.50 28.90	25.68	20.72 26.16	23.48
Cobalt (µg/g)	8.90 11.30	9.92	11.60 14.91	13.08	12.60 15.70	14.10	10.86 13.74	12.20
Arsenic (µg/g)	1.35 1.81	1.62	2.04 3.34	2.63	2.47 3.64	2.90	2.15 3.13	2.48
Cadmium (µg/g)	1.58 2.25	1.95	1.40 2.51	1.84	1.69 2.78	2.21	1.39 2.37	1.81
Nickel (µ/g)	10.98 13.11	12.08	14.04 25.09	18.35	13.58 24.30	20.78	13.22 22.17	17.57
Aluminum (µg/g)	29.80 40.30	34.43	43.29 64.09	52.33	41.80 52.60	46.93	39.46 51.92	44.56
Mercury (µg/g)	0.92 1.66	1.41	1.10 1.45	1.26	1.10 1.74	1.44	0.99 1.38	1.21
Molybdenum (µg/g)	0.87 1.08	0.98	0.95 1.26	1.09	1.00 1.59	1.31	0.88 1.22	1.08

Copper values ranged between (6.37 - 20.28µg/g) and (4.90 - 10.59 µg/g) in Damietta Estuary and Mediterranean coastal shore, respectively (Tables 2&3). The lower value of copper was recorded during winter, which may be attributed to the mobilization of copper from sediment to overlying water at low pH and under the microbial activities [18,19]. The high value of copper was recorded during spring, which may be attributed to the precipitation of copper from the water column as CuS and also due to adsorption on the suspended matter or the complexation with organic matter [20]. On the other hand, the annual average values of copper in the Mediterranean shoreline showed lower values than that recorded in the Damietta Estuary. This mainly attributed to the great amounts of domestic and agricultural runoff which accumulate on the bottom sediment of Damietta Estuary.

Lead values ranged between (10.92-31.19 µg/g) and (19.30 -29.64 µg/g) in Damietta Estuary and Mediterranean coastal shore, respectively (Tables 2&3). The increase of lead concentrations during spring and summer attributed to adsorption of lead onto organic matter which descended to the bottom sediment especially with high temperature[21].

Chromium and cobalt showed similar distribution trends as lead, their values were between (22.17-36.15 & 10.50 -17.80 µg/g) and (19.30 -29.64 & 8.90 - 15.70 µg/g) in Damietta Estuary and Mediterranean coastal shore for Cr and Co, respectively (Tables 2&3). The results revealed that, the values of both chromium and cobalt concentrations were decreasing during cold seasons (winter and autumn) and increased during hot seasons (summer and spring).

Arsenic values ranged between (1.87 - 4.21µg/g) and (1.35 – 3.64 µg/g) in Damietta Estuary and Mediterranean coastal shore, respectively (Tables 2&3). The highest value of arsenic was recorded during summer, which may be attributed to adsorption of arsenic by clayey minerals, suspended matter and surface microorganisms which descended to bottom sediment especially with high temperature [22], while the minimum values of arsenic were recorded during winter, which may be attributed to the mobilization of arsenic from sediment to overlying water at low pH and under the microbial activities [23,24].

Cadmium values ranged between (1.44 - 5.84 µg/g) and (1.39 - 2.78 µg/g) in Damietta Estuary and Mediterranean coastal shore, respectively (Tables 2&3). Minimum value of cadmium was recorded during autumn while the maximum value was recorded during winter, where the pH affects the mobilization of Cd[25].

Nickel and Aluminum showed similar distribution trends. Ni values ranged between (11.79 -23.60 and 10.98 -25.09 µg/g) in Damietta Estuary and Mediterranean coastal shore, respectively whereas Al values were (39.10 - 67.99 & 29.80 - 64.09 µg/g) (Tables 2&3). The increase in Ni and Al concentrations during hot seasons (summer and spring) may be due to their adsorption onto organic matter which descended to the bottom sediment especially with high temperature [26].

Mercury values ranged between (1.12- 1.87µg/g) and (0.92- 1.74 µg/g) in Damietta Estuary and Mediterranean coastal shore, respectively (Tables 2&3). The minimum value of mercury was recorded during winter, which may be attributed to the mobilization of elements from sediment to overlying water at low pH and under the microbial activities [27].

Molybdenum values showed the same trend as Ni, Al and Hg and ranged between (0.97-1.71 µg/g) and (0.87-1.59 µg/g) in Damietta Estuary and Mediterranean coastal shore, respectively, (Tables 2&3).

Conclusion

It is clear from the above mentioned results that heavy metals in the Damietta Estuary were higher in concentrations than those of Mediterranean shoreline, this is due to industrial and domestic waste discharges and returns flow of agricultural drainage water. Furthermore, the heavy metals content decreased progressively while moving away from Damietta Estuary to Mediterranean shoreline which declared that heavy metals content of Mediterranean shoreline depends on its pattern of distribution in Damietta Estuary.

The trends of detected heavy metal were Fe > Mn > Al > Zn > Cr > Pb > Ni > Co > Cu > As > Cd > Hg > Mo and Fe > Mn > Al > Zn > Cr > Ni > Co > Pb > Cu > As > Cd > Hg > Mo in Damietta Estuary and Mediterranean shoreline, respectively.

References

1. **Elewa, A.A., Sayyah, S.M. and Fouda, A.,** Distribution of some pollutants in Lake Nasser and Nile River at Aswan. (M. El-Raey (Ed.)) *Regional Symp. Environ. Stud. (UNARC), Alexandria.* (1990).

2. **Soltan, M.E.,** The distribution of some metals in the various grain size fractions of Nile River sediments, *Delta J. Sci.* **18**(1), 62-78 (1994).

3. **Haiyan, W. and Stuanes, A. O.,** Heavy metal pollution in air-water-soil-plant system of Zhuzhou City, Hunan Province, China. *Water, Air, and Soil Pollution*, **147**,79–107 (2003).

4. **Suziki, K.T., Sunaga, H., Aoki, Y., Hatakeyama, S., Sumi, Y. and Suziki, T.,** Binding of cadmium and copper in the mayfly *Baetis thermicus* larvae that inhabit in a river polluted with heavy metals. *Comp. Biochem. Physiol.* **91**(C), 487-492 (1988)

5. **Zoumis, T., Schmidt, A., Grigorova, L. and Calmano, W.,** Contaminants in sediments: remobilization and demobilization. *Sci. Total Environ.* **266**, 195–202 (2001).

6. **Stumm, W. and Morgan, J.J.,** Aquatic *Chemistry. An Introduction Emphasizing Chemical Equilibrium in Natural Waters.* 2*nd* ed. John Wiley & Sons N. Y. 780pp. (1981).

7. **Samecka-Cymerman, A. and Kempers, A. J.,** Concentrations of heavy metals and plant nutrients in water, sediments and aquatic macrophytes of anthropogenic lakes (former open cut brown coal mines) differing in stage of acidification. *Sci. Total Environ.* **281**, 87–98 (2001).

8. **Sanchez Lopez, F. J., Gil Garcia, M.D., Martinez Vidal, J. L., Aguilera, P.A. and Frenich, A.G.,** Assessment of metal contamination in Donana National Park (Spain) using crayfish (*Procamburus Clarkii*), *Environ. Monitoring and Assessment,* **93**, 17–29 (2004)

9. **Kouadia and Trefry, J. H.,** Sediment trace metal concentration in the Ivory Coast, West Africa. *Water, Air and Soil Pollution,* **32**, 145-154 (1987).

10. **Forstner, U.,** Chemical forms and reactivities of metals in sediment, In: *Chemical Methods for Assessing Bio-available Metals in Sludges and Soils.* (R., Leschber, R.D. Davis, and P. L'Hermite, (Ed.)), El-Sevier, London, 1-30 (1985).

11. **Elewa, A.A., Sayyah, S.M. and Fouda, A.,** Distribution of some pollutants in Lake Nasser and River Nile at Aswan. (M. El-Raey, (Ed.)), *Regional Symp. Environ. Stud. (UNARC), Alexandria* (1990).

12. **Soltan, M.E.,** The distribution of some metals in the various grain size fractions of River Nile sediments, *Delta J. Sci.* **18**(1), 62-78 (1994).

13. **Elewa, A.A. and Goher, M.M.,** Environmental factors affecting the precipitation and dissolution of Fe, Mn, Zn, Cu, Pb and Cd in River Nile at Damietta branch. *Bull. Fac. Sci., Zagazig Univ.* **21**(2), 114 – 136 (1999).

14. **Hassouna, A.F.A.,** Some analytical study on sediments on Lake Nasser, River Nile and Aswan Dam Zone Reservoir. *M. Sc. Thesis,* Fac. of Sci., Al-Azhar Univ. (1989).

15. **Sawary, C.N. and Mecarty, P.L.,** *Chemistry for Sanitory Engineers* 2nd ed., Tosho Printing Co., LTD., Tokyo, Japan (1967).

16. **Elewa, A.A.,** Distribution of Mn, Cu, Zn, and Cd in water and sediment of River Nile at Aswan. *Egypt. J. Appl. Sci.* **8** (2), 711 – 713 (1993).

17. **Bertin, C. and Bourg, A. C. M.,** Trends in the heavy metal content (Cd,Pb,Zn) of river sediments in the drainage basin of smelting activities. *Wat. Res.* **29**(7), 1729-1736 (1995).

18. **Elewa, A.A. and Goher, M.M.,** Environmental factors affecting the precipitation and dissolution of Fe, Mn, Zn, Cu, Pb and Cd in River Nile at Damietta branch. *Bull. Fac. Sci., Zagazig Univ.* **21**(2), 114 – 136 (1999).

19. **Osman, M.A., Ali, M.H.H., Mohamed, M.A.M. and Al-Afify, A.D. G.,** Assessment of agriculture drainage water quality to be used for fish farm irrigation. *Journal of Nature and Science,* **8**(2), 1-15 (2010)

20. **Nather Khan, I.S.A. and Lim, R.P.,** Distribution of metals in Linggi River Basin (Malaysia) with Reference to pollution. *Aust. J. Mar. Fresh Water Res.* (42), 409 – 422 (1991).

21. **Berg, H., Kiibus, M. and Kautsky, N.,** Heavy metals in Tropical Lake Kariba, Zimbabwe. *Water, Air, and Soil Pollution,* **83** (3/4), 237-252 (1995).

22. **Tessier, A., Couraard, Y., Camphell, P.G.C. and Aullair, J.C.,** Modeling Cd partitioning in oxic lake sediments and Cd concentrations in the freshwater bivalve Anodonta grandis. Limnol. *Oceanogr.* **38**, 1-17 (1993).

23. **Elewa, A.A. and Goher, M.M.,** Environmental factors affecting the precipitation and dissolution of Fe, Mn, Zn, Cu, Pb and Cd in River Nile at Damietta branch. *Bull. Fac. Sci., Zagazig Univ.* **21**(2), 114 – 136 (1999)

24. **Osman, M. A., Ali, M.H.H., Mohamed, M.A.M. and Al-Afify, A.D.G.,** Assessment of agriculture drainage water quality to be used for fish farm irrigation. *Journal of Nature and Science,* **8**(2), 1-15 (2010).

25. **Vasllikiotis, G., Samindiou, G.V. and Fytianous, K.,** *Map Technical Report. Series No. 45, UNEP, Athens:* 219 –235 (1990).

26. **Mantoura, R.F.C.,** The complexation of metals with humic materials in natural waters. *Estuarine and Coastal Marine Science,* **6**, 387-408 (1978).

27. **Elewa, A.A. and Goher, M.M.,** Environmental factors affecting the precipitation and dissolution of Fe, Mn, Zn, Cu, Pb and Cd in River Nile at Damietta branch. *Bull. Fac. Sci., Zagazig Univ.* **21**(2), 114 – 136 (1999).

(*Received* 30/4/2012 ;
accepted 18/6/2012)

رصد بعض ملوثات فى رسوبيات مصب دمياط وتأثيره على الشريط الساحلى امام حافظة دمياط

على مصطفى على حسن ، محمد حمدى حسن على* ، احمد محمد قطب و جمعة جابر سليمان**
كلية العلوم – جامعة الأزهر ،* المعهد القومى لعلوم البحار والمصايد و** شركة دارا للبترول – وزارة البترول – القاهرة – مصر .

يعتبر نهر النيل واحد من أهم المعالم الجغرافية المميزة لقارة إفريقيا و يمتد من دائرة عرض 4° جنوبا إلي 31° شمالا حيث يمر بكثير من التغيرات المناخية. يعتبر نهر النيل من أطول انهار العالم حيث يبلغ طوله 6700 كم و يبلغ ارتفاع النهر عند المنبع حوالي 5120 مترا فوق مستوي سطح.

ومن هذا المنطلق تم تجميع عينات الدراسة من فبراير 2008 حتى نوفمبر 2008 تم جمع العينات من خلال 6 محطات تم اختيارها داخل مصب فرع دمياط ممثلة لمختلف الأماكن فى المصب بالإضافة إلى6 محطات لشاطىء البحر الأبيض المتوسط عند مصب فرع دمياط حيث تم تجميع عينات تم تجميع عينات الروسبيات من جميع المحطات موسميا"

أظهرت الدراسة أن تركيزالفوسفات الكلى و العناصر الثقيلة فى الروسبيات (الحديد -المنجنيز- النحاس - الرصاص - الكادميوم - الزنك - الكروميوم- الكوبالت- الزرنيخ -النيكل- ألومنيوم- الزئبق- الموليبدينوم) يعتمد على كمية ونوعية المخلفات الصناعية التى تصرف فى مصب دمياط . حيث أوضحت الدراسة أن تركيز هذه العناصر تزداد فى محطات النهر بينما كانت تقل تدريجيا كلما ابتعدنا عن النهر إلى البحر.

- ويكون ترتيب تركيز العناصر الثقيلة فى النهر كالاتى :

Fe > Mn > Al > Zn > Cr > Pb> Ni > Co > Cu > As > Cd> Hg > Mo

- ترتيب تركيز العناصر الثقيلة فى البحر كالاتى :-

Fe > Mn > Al > Zn > Cr > Ni > Co > Pb > Cu > As > Cd > Hg > Mo