Metal Exchange Between Sediment and Water Column in Rosetta Estuary, Egypt

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Abstract: The present study was carried out to clarify factors affecting the dynamic distribution of heavy metals in the main River Nile Estuary (Rosetta Estuary) during the exchange between sediment pore water (PW) and overlying bottom water. Dissolved heavy metals were simply measured by pre-concentrated membrane filtered water samples and chelating onto chelex 100 cation-exchange resin. The surfacial bottom sediments were collected using a Van-Veen grab sampler. Direct measurement of the different trace metal concentrations were carried out in the interstitial waters, since the trace metals in the estuarine interstitial waters occur in concentrations well above the detection limit of suitable analytical instruments and give reliable data. The diffusive fluxes of different metals at the sediment-water interface were calculated using Fick's first law from concentration gradients in the interstitial waters and near-bottom waters. It was noticeable that all metals are fluxed from sediment to near bottom water, except few cases depending on environmental conditions of the sampling stations and type of sediments. Molecular diffusion within interstitial waters is of fundamental importance in affecting the exchange of dissolved constituents across the sediment-water interface. Hence, the considerable variability in these coefficients was due to seasonal variations in the temperature of near-bottom waters in addition to the differences in sediment porosity. Coefficients were found the highest in silty-clay sediments in summer and early autumn.

Key words: Fluxes · Interstitial waters · Pore water · Molecular diffusion and coefficients

INTRODUCTION

Sediments are the final destination of trace metals, as a result of adsorption, desorption, precipitation, diffusion processes, chemical reactions, biological activity and a combination of all those phenomena. Sediments is considered as an important sink for heavy metals, but when some physical disturbance occurs, or there is diagenesis and /or changes in pH or redox potential, they may become a source of metals, releasing them to the overlying water column [1].

It was becoming increasingly clear that, solute exchange across the sediment-water interface is an important process in regulating the water column distributions and global cycles of many elements [2-6]. Transport processes to be incorporated include not only molecular diffusion of solutes and gases, sediment accumulation for solids, due also enhanced diffusion of solutes and gas, mixing of solids due to bioturbation and move or current activity, non-local exchange processes caused by biota and gas bubble formation [7].

Due to the importance of Rosetta Estuary in regulations of the water quality between the River Nile and adjacent area of the Mediterranean Sea, the present study was carried out to cover the gap in information reganeling the factors effecting the dynamic distribution of heavy metals in the area of Rosetta Estuary due to the exchange between sediment pore waters and overlying bottom waters.

MATERIALS AND METHODS

Study Area: In the present study, 13 locations along the Rosetta Estuary as shown in figure 1 were selected to represent the Nile River Side (NRS), the estuary (Est) and its adjacent Sea Side (SS).

Dissolved heavy metals were simply measured by pre-concentrated of 5 liter membrane filtered water sample and chelating them onto chelex 100 cation-exchange resin in conjunction with flame atomic absorption spectro-photometry [8,9].

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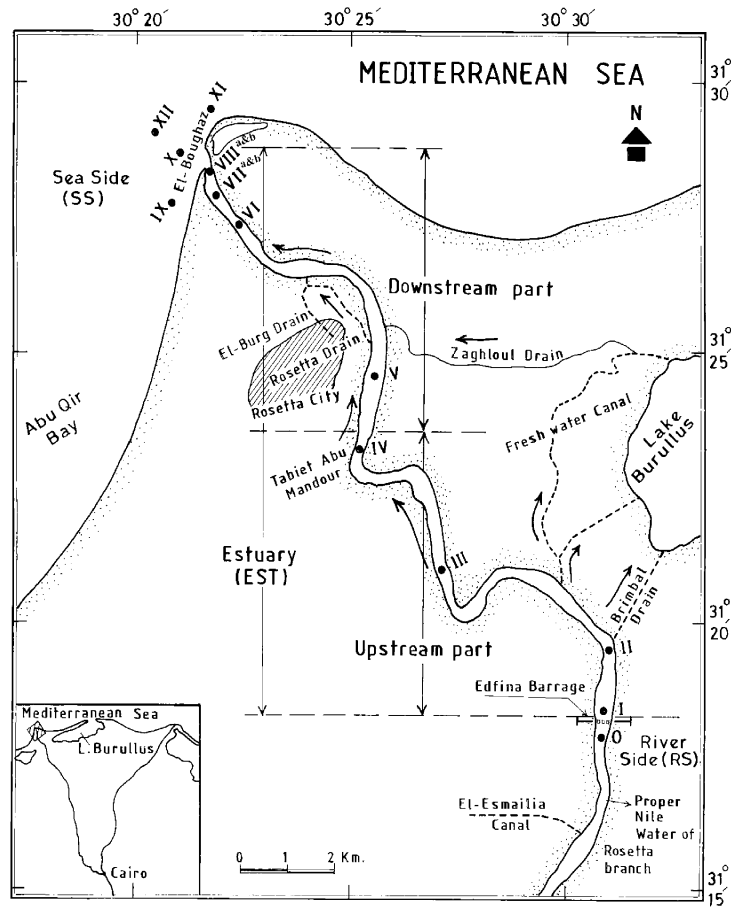
Fig. 1: Map showing the locations of sampling stations from Rosetta Estuary.

The surfacial bottom sediments were collected using a Van-Veen grab sampler. The sediment samples were then, preserved in plastic bags and kept frozen until the extraction of their pore water (PW) contents and further analyses.

In the present study, the choice of the techniques used for extracting the interstitial water from sediments was usually governed by the nature of sediments and available facilities as the following:

- In case of muddy sediments fractions, the squeezer technique was used [10]. The squeezer was lined with Teflon as recommended by Patterson and Settle [11]; (b)-centrifugation for finer sediments at 10.000 rpm for about 20 minutes [12,13]; and (c)-By filtration on a glass fibers filter, in case of coarse sediments.

Direct measurement of different trace metal concentrations were carried out in the interstitial waters, since the trace metals in the estuarine interstitial waters occur in concentrations well above the detection limit of suitable analytical instruments and give reliable data [14]. Method validation for some heavy metal measurements were performed based on ISO 17025 (Table 1), accordingly all the operated method were found satisfactory.

Flux Calculation: The diffusive fluxes of different metals at the sediment-water interface were calculated using Fick's first law from concentration gradients in the interstitial waters and near-bottom waters [15,16].

$$J_x = -D_s \, \Phi_0 \, (C_x - C_0) \, x'^{-1},$$

Whereas

J_x-diffusion flux at depth x ($\mu mol \ cm^{-2} \ s^{-1}$),

D_s-total sediment diffusion coefficient,

$\Phi_{0\text{-sediment}}$ porosity,

C_x-concentration [$\mu mol \ dm$-3] for $_x = x,$'

C_0-concentration [$\mu mol \ dm$-3] for $_{x=0,}$

$_x$ = sediment depth (5 cm) (the negative sense towards the sediment).

Table 1: Method validation for Iron, Manganese, Copper, Zinc and Cadmium based on ISO 17025

Metal	Limit of detection ppb	Recovery	Precision		Range	Linear range
	LOD ppm	Truness %	Repeatability %	Between day Variability%	ppm	ppm
Fe	0.006	98.6-102	0.965-1.723	1.25-3.265	0.5-30	0.0-35
Mn	0.005	96.5-100.6	1.256-2.433	1.76-2.98	0.4-25	0.05-30
Cu	0.007	95.8-106	0.746-0.597	1.56-2.142	0.5-5.0	0.0-12.0
Zn	0.003	99.2-99.9	1.53-0.045	4.44-0.23	0.1-2.5	0.0-3.0
Cd	0.009	92-99.9	1.71-1.527	5.0-1.086	0.05-1.5	0.0-2.0

Values of the total sediment diffusion coefficient were calculated using the equation [17].

$$D_s^{sed} = D_s^0 / \Phi_0\, F^{'},$$

Whereas
D_s^0-water diffusion coefficient at infinite dilution [cm^{2}s^{-1}] $F^{'}$-the modified [17] formation factor, corrected for viscosity and deviation from the Archie relation $F^{'} = \Phi^{-2.5}$

RESULTS AND DISCUSSION

The calculated flux values of some metals (Fe, Mn, Cu, Zn and Cd) from the grab sediment PW of Rosetta Estuary were listed in table 2 and represented in figure 2.

Iron (Fe): The calculated flux values of Fe fluctuated between-10.3 to-198.5μg/m^2.day during winter and spring, respectively with an annual average value of-78.9μg/m^2.day in the NRS,-46.4 to-1153.7μg/m^2.day at stations I and II during winter and autumn, respectively with an annual average-402.4μg/m^2.day in US; between-57.7 to-811.7μg/m^2.day at stations VIII and V during spring and winter, respectively, with an annual average-_361.9μg/m^2.day in DS and between-40.7 to-374.8μg/m^2.day at station XI during spring and summer, respectively, with an annual average-176.8μg/m^2.day in SS.

Manganese (Mn): The calculated flux values of Mn were found between-3.6 to-614.6μg/m^2.day during winter and spring, respectively with an annual average-159.3μg/m^2.day in the NRS, 33.9 to-913.8μg/m^2.day at stations II and III during summer and autumn, respectively with an annual average value of-149.6μg/m^2.day in US;-11.3 to-432.3μg/m^2.day at stations V and VII during autumn and summer, respectively, with an annual average-_114.5μg/m^2.day in DS and between-2.5 to-83.9μg/m^2.day at stations X and IX during winter and autumn, respectively, with an annual average-25.6μg/m^2.day in SS.

Table 2: Calculated flux values of iron, manganese, coper, zinc and cadmium (μg/m^2. Day) in grab sediment pore water of Rosetta Estuary, Egypt

| Region	Station	Fe Spring	Summer	Autumn	Winter	Averages	Mn Spring	Summer	Autumn	Winter	Averages	Cu Spring	Summer	Autumn	Winter	Averages	Zn Spring	Summer	Autumn	Winter	Averages	Cd Spring	Summer	Autumn	Winter	Averages
NRS	0	-198.5	-79.3	-27.5	-10.3	-78.9	-614.6	-10.9	-8.2	-3.6	-159.3	-0.62	-0.03	-0.32	0.54	-0.11	-8.35	-2.77	-6.53	-5.69	-5.83	-9.60	-1.39	-1.12	-0.79	-3.22
Upstream	I	-717.8	-184.5	-224.5	-46.4	-293.3	-117.2	11.5	0.2	-1.7	-26.8	-6.22	-1.13	-2.64	-0.18	-2.54	-172.82	-49.86	-50.14	-6.41	-69.81	-3.93	5.09	-1.75	0.07	-0.13
Upstream	II	-680.3	-369.6	-1153.7	-816.0	-754.9	-87.5	33.9	-5.7	-21.7	-20.3	-5.99	-3.31	-10.36	-5.16	-6.21	-92.75	-74.48	-189.19	-99.43	-113.96	-1.18	-2.71	-5.72	2.01	-1.90
Upstream	III	-123.7	-353.7	-315.8	-150.2	-235.8	-441.1	12.2	-913.8	-41.9	-346.1	-2.76	-0.57	-2.38	-1.68	-1.85	-42.09	-24.30	-162.93	-28.47	-64.45	-1.95	-1.96	-6.76	0.13	-2.64
Upstream	IV	-337.2	-811.4	-724.7	-723.2	-649.1	-77.1	-123.1	-480.1	-140.2	-205.1	-1.11	-7.88	-10.06	-5.98	-6.25	-3.61	-473.73	-216.28	-120.62	-203.56	-0.94	-3.68	-10.34	-2.22	-4.30
Upstream	Mean	-411.5	-359.7	-489.2	-349.2	-402.4	-180.7	-16.4	-349.8	-51.4	-149.6	-4.02	-3.22	-6.36	-3.25	-4.21	-77.82	-155.59	-154.64	-63.73	-112.95	-2.00	-0.81	-6.14	0.00	-2.24
Downstream	V	-684.7	-577.4	-179.9	-811.7	-563.4	-68.9	-246.0	-11.3	-27.7	-88.5	-2.49	-6.40	-1.22	-9.04	-4.79	-18.73	-63.72	-22.76	-123.73	-57.24	-1.39	-5.52	-2.61	-14.00	-5.88
Downstream	VI	-158.2	-718.8	-401.6	-334.5	-403.3	-50.0	-173.9	-86.1	-36.7	-86.7	11.48	-5.22	-8.44	-2.51	-1.17	-42.83	-68.53	-112.88	-69.59	-73.46	0.01	-1.76	-2.80	0.52	-1.00
Downstream	VII	-88.3	-413.2	-257.6	-315.3	-268.6	-120.0	-432.3	-21.8	-13.4	-146.9	-2.16	-5.40	-2.50	-1.19	-2.81	-16.28	-137.05	-31.58	-47.75	-58.16	-1.80	-0.38	-2.61	0.03	-1.19
Downstream	VIII	-57.7	-321.2	-222.4	-248.2	-212.4	-36.7	-112.7	-28.3	-366.2	-136.0	-1.05	-2.18	-2.28	-1.63	-1.79	2.71	-35.45	-36.62	-53.67	-30.76	-0.73	-0.92	-1.12	-0.83	-0.90
Downstream	Mean	-247.2	-507.7	-265.4	-427.4	-361.9	-68.9	-241.2	-36.9	-111.0	-114.5	2.76	-4.27	-4.41	-1.78	-1.92	-18.78	-76.19	-50.96	-73.68	-54.90	-0.98	-2.14	-2.29	-3.57	-2.24
Sea Side	IX	-246.8	-243.7	-211.4	-96.4	-199.6	-50.5	-20.8	-83.9	-2.6	-39.5	-4.13	-0.87	-2.49	-0.47	-1.99	-28.63	-26.44	-19.87	-19.04	-23.49	0.06	-4.58	-0.95	0.28	-1.30
Sea Side	X	-62.5	-349.4	-177.8	-98.7	-172.1	-40.4	-16.3	-53.4	-2.5	-28.1	-1.63	-2.01	-1.41	-0.54	-1.40	-21.07	-12.35	-35.83	-17.11	-21.59	-1.51	-2.62	-0.77	0.24	-1.16
Sea Side	XI	-40.7	-374.8	-115.9	-98.4	-157.5	-19.4	-9.8	-11.6	-6.3	-11.8	-1.72	-2.14	-1.83	-1.12	-1.70	-2.74	-18.18	-32.97	-25.60	-19.87	-1.08	1.96	-2.53	-1.28	-0.73
Sea Side	XII	-110.1	-249.7	-183.8	-168.0	-177.9	-47.6	-19.0	-20.6	-4.2	-22.8	-0.93	-2.25	-3.08	-1.04	-1.83	-21.91	-50.82	-52.45	-64.00	-47.29	-0.95	-1.61	-0.39	-0.44	-0.85
Sea Side	Mean	-115.0	-304.4	-172.2	-115.4	-176.8	-39.5	-16.5	-42.4	-3.9	-25.6	-2.10	-1.82	-2.20	-0.79	-1.73	-18.59	-26.95	-35.28	-31.43	-28.06	-0.87	-1.71	-1.16	-0.30	-1.01

(-ve) = from sediment to overlying water
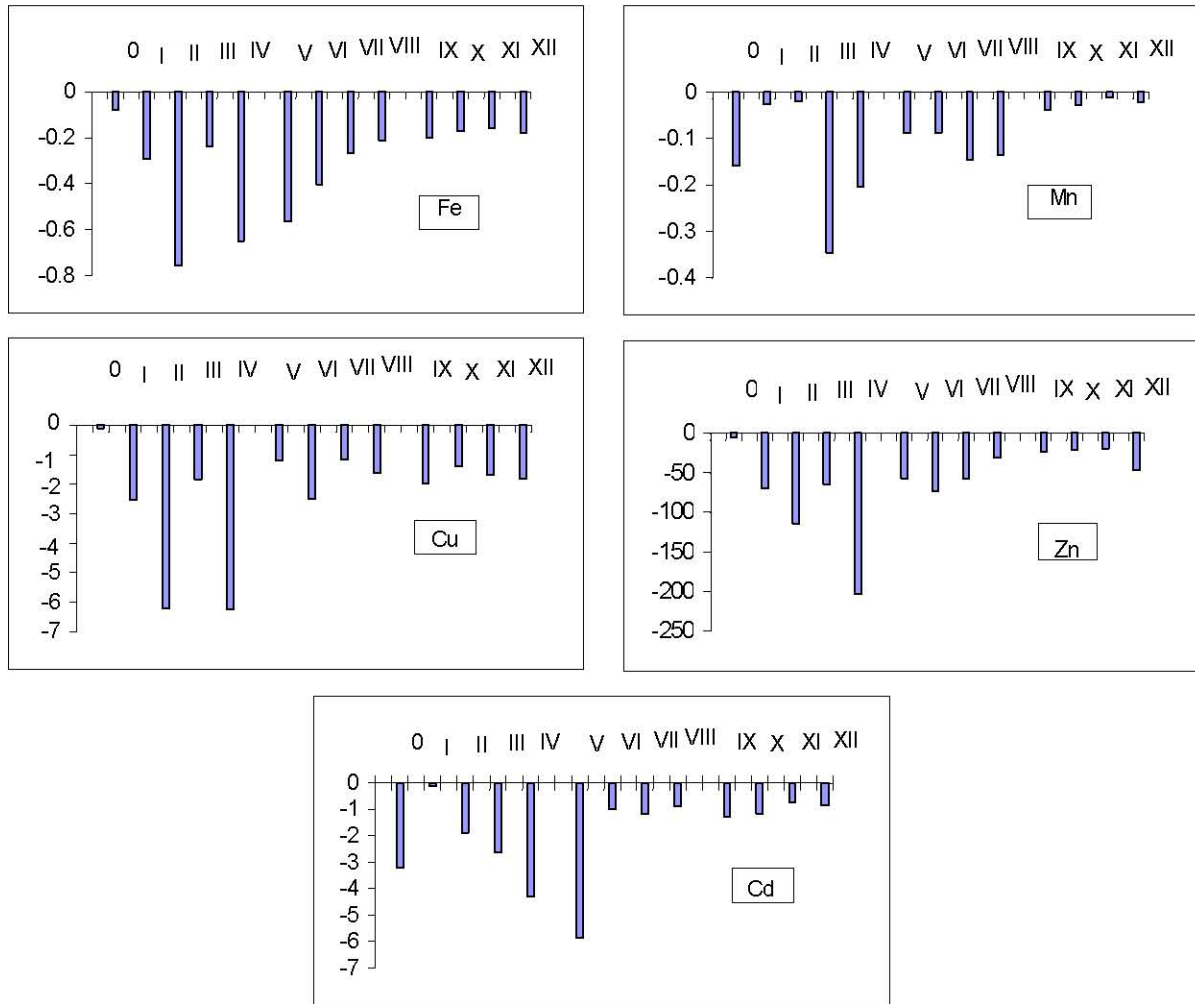
Fig. 2: Diffusion coefficient values of metals ($\mu g/m^2/day$)

Copper (Cu): The calculated flux values of Cu fluctuated between 0.54 to-0.62$\mu g/m^2$.day during winter and spring, respectively with an annual average-0.11$\mu g/m^2$.day in the NRS,-0.18 to-10.36$\mu g/m^2$.day at stations I and II during winter and autumn, respectively with an annual average-4.21$\mu g/m^2$.day in US;-1.05 to-11.48$\mu g/m^2$.day at stations VIII and VI during spring, with an annual average-_1.92$\mu g/m^2$.day in DS and between-0.47 to-4.13$\mu g/m^2$.day at station IX during winter and spring, respectively, with an annual average-1.73$\mu g/m^2$.day in SS.

Zinc (Zn): The calculated flux values of Zn showed variation between-2.77 to-8.35$\mu g/m^2$.day during summer and spring, respectively with an annual average-5.83$\mu g/m^2$.day in the NRS,-3.61 to-473.73$\mu g/m^2$.day at station IV during spring and summer, respectively with an annual average-112.95$\mu g/m^2$.day in US;-2.71 to-

137.05$\mu g/m^2$.day at stations VIII and VII during spring and summer, respectively, with an annual average-_54.90$\mu g/m^2$.day in DS and between-2.74 to-64.0$\mu g/m^2$.day at stations XI and XII during spring and winter, respectively, with an annual average-28.06$\mu g/m^2$.day in SS.

Cadmium (Cd): The calculated flux values of Cd were found between-1.12 to-9.60$\mu g/m^2$.day during autumn and spring, respectively with an annual average-3.22$\mu g/m^2$.day in the NRS, 5.09 to-10.34$\mu g/m^2$.day at stations I and IV during summer and autumn, respectively with an annual average-2.24$\mu g/m^2$.day in US; 0.52 to-14.0$\mu g/m^2$.day at stations VI and V respectively, during winter with an annual average-_2.24$\mu g/m^2$.day in DS and between 0.28 to-4.58$\mu g/m^2$.day at station IX during winter and summer, respectively, with an annual average-1.01$\mu g/m^2$.day in SS.

From the data of the present study it is noticeable that, all metals were fluxed from sediment to near bottom water, except few cases, depending on the marine environment at the sampling locations and type of sediments. The distribution Coefficient values of metals were not only, correlated to organic substances but also with other sorption-active surface. Toxicological effects often may inversely correlated with parameters such as iron oxyhydrate. There are strong effects of grain size composition, the influence of suspended matter concentration in aquatic system, which is even more important, if the kinetics of sorption and desorption are too slow for reaching equilibrium in a given time of interaction [18]. Particle-reactive elements were removed fast; distribution coefficients between sediment and water were found high, principally in winter.

The transformation of reactive components in solid matter, so called diagenesis, involves changes of element partition between solid and dissolved phases. The sequence of factors and events, which affect the release of biogeochemically active elements in estuaries, can be described according to Elbaz-Poulichet *et al.* [19] as follows:

- A dynamic environment, where strong chemical gradients occur in the pore water of fine grained sediments rich in organic matter and sulfides;
- A frequent change of river morphology, involving resuspension of these sediments, which leads to an oxidation of sulfide minerals whereby, solubility of typical heavy metals, is increasing.

The intensity of metal mobilization (sometimes also readsorption) depends on stability of either inorganic or organic complexes. Inorganic complexation by chloride ions is typical for cadmium, remobilization of cadmium first needs oxidation of sulfidic forms, than complexation by chloride ions can take place; intensity of readsorption is mainly controlled by the concentration of suspended particulates.

Compared to the relative strong effects during the oxidation of sulfide minerals, in particular iron sulfide, in anoxic sediments, suspended matter is usually varied between oxic and suboxic conditions, the latter characterized by Fe-carbonate minerals, whereas trace metals are still present in part as sulfides.

After deposition and during storage in reduced coastal sediments, adsorbed metals may transferred to sulfidic bonding forms. During erosion processes, oxidation can take place involving remobilization of a certain proportion of the sediment-associated metals, which may subsequently be reabsorbed in part to particulate matter. Under marine conditions, the extent of adsorption will mainly depend on the intensity of both complexation by chloride and competition with cations like Mg^{2+}, Ca^{2+} and Na^+. Such oxidative events are relatively short compared to the longer periods of reduced conditions during deposition. However, it can be expected that through repeated but irregular cyclic processes of erosion and deposition a significant release of metals from sediments will take place [19].

Molecular diffusion within interstitial waters is of a fundamental importance in affecting the exchange of dissolved constituents across the sediment-water interface. Hence the considerable variability in diffusive coefficients found in the present study may coincided principally with seasonal variations in the temperature of near-bottom waters and to the differences in sediment porosity. Diffusive fluxes were the highest in silty-clay sediments during summer and early autumn. [20] found that, Mn fluxes is strongly correlated not to temperature, but to the average primary productivity. Whereas, Sholkovitz. and Mann [21] suggested that, the temperature dependence of dissolution reaction is primarily responsible for the seasonal variations in fluxes Elderfield et al [22] justified that, temporal variations in interstitial water profiles are most likely when bioturbation rates are low.

Otero and Macias[23] pointed out the idea that, higher temperatures lead to an increase in the activity of sulphate-reducing bacteria, which in turn leads to an increase in alkalinity and sulfides condition consequently it leads to the removal of metals from the interstitial water. In contrast, in the soils colonized by plants, the oxidation of metal sulphides during summer lead to a decrease in pH and an increase in the metal concentrations in interstitial water.

Cadmium fluxes indicated that, it may taken place either into or out of sediments. Colbert *et al.* [24] pointed out that, correlation between Cd flux and sulphate reduction indicated that anaerobic microbial degradation was the major process controlling both the sign and the magnitude of cadmium fluxes.

The distribution of Cd in the study area were found higher than the expected values, they appeared to be dominated by natural physical and biogeochemical processes.

The recyclable element, eg. Manganese and cobalt are those, which are typically controlled by redox processes. Biologically active elements are easily taken up

by organisms; half life are somewhat longer than of the recyclable elements. With biologically active elements, prediction about their behaviour may become difficult. On one hand, association with dissolved organic matter and colloids may increase the residence time of metals in the water column; on the other hand, there are typical effects of filtering and aggregation by organisms, which make residence time of these elements substially shorter than the average flushing time of the larger estuaries [25].

It was concluded that, all metals were fluxed from sediment to near bottom water, except few cases, depending on the marine environment at the sampling locations and type of sediments. The distribution Coefficient values of metals were not only, correlated to organic substances but also with other sorption-active surface. Molecular diffusion within interstitial waters is of a fundamental importance in affecting the exchange of dissolved constituents across the sediment-water interface. Hence, the considerable variability in these coefficients was due to seasonal variations in the temperature of near-bottom waters and to the differences in sediment porosity. Diffusive fluxes were the highest in silty-clay sediments during summer and early autumn.

REFERENCES

1. Ramirez, M.S. Massolo, R. Frache and J.A. Corea, 2005. Metal speciation and environmental impact on sandy beaches due to El Salvador Copper mine, Chile. Marin pollution Bulletin, 50: 62-72.

2. Nixon, S.W., J.R. Kelley, B.N. Furnas, C.A. Oviatt and S.S. Hale, 1980. Phosphorus regeneration and the metabolism of coastal marine bottom communities. In: Marine benthic dynamics, K.R. Tenore and B.C. Coull, editors, University of South Carolina Press, pp: 219-242. northwest Pacific Ocean off Washington. Limnology and Oceanography, 30: 81-92.

3. Zeitzschel, B., 1980. Sediment-water interactions in nutrient dynamics. In: Marine benthic dynamics, K. R. Tenore and B. C. Coull, editors, University of South Carolina Press, pp: 195-218.

4. Codispoti, L.A. and J.P. Christensen, 1985. Nitrification, denitrification and nitrous oxide cycling in the eastern tropical South Pacific Ocean. Marine Chemistry, 16: 277-300.

5. Jones, C.J. and J.M. Murray, 1985. The geochemistry of manganese in the northwest Pacific Ocean off Washington. Limnology and Oceanography, 30: 81-92.

6. Sarva, M.P., Z.A. and M.R. Ahmad, 2010. Heavy Metals Dyanamics and Source In Intertidal Mangrove Sediment of Sabah, Borneo Island. Environment Asia, 3: 79-83.

7. Chanton, J.P. and J.W.H. Dacey, 1991. In Trace Gas Emissions by Plants, 1st ed. pp: 65-92, Academic Press, Inc.

8. Riely, J.P. and D. Taylor, 1964. Chelating resins for the consentrations of trace elements from sea water and their analytical use in conjunction with Atomic Absorption Spectrophotometry. Analytica Chemica Acta, 40: 479-485.

9. Abdullah, M.I. and L.G. Royel, 1974. Study of the dissolved and particulate trace elements in the Bristol Channel. Journal of Marine Biological Association U.K., 54: 581-597.

10. Manheim, F.T., 1966. Ahydraulic squeezer for obtaining interstitial water from consolidated and unconsolidated sediments. U.S. Geological Survey Professional, 550: 256-261.

11. Patterson, C.C. and D.M. Settle, 1975. The reduction of orders of magnitude errors in lead analyses of biological materials and natural waters by evaluation and controlling the extent and sources of industrial lead concentration introduced during sample collecting, handling and analysis. Proc. 7th IMR. Symp. La Fleur, P.D. (ed.). NBS Spec., pp: 422.

12. Klump, J.V. and C.S. Martens, 1981. Biochemical cycling in an organic-rich coastal marine basin. II-Nutrient sediment-water exchange processes. Geochemica Cosmochimica Acta, 45: 101-121.

13. Klump, J.V., 1987. Biological cycling in an organic-rich coastal marine basin 5. Sedimentary nitrogen and phosphorus budgets based upon kinetic models, mass balances and the stoichiometry of nutrient regeneration. Geochemica Cosmochimica Acta, 51: 1161-1173.

14. Duinker, J.C., 1976. The analysis of estuarine interstitial waters for trace metals. Proceedings on the Biogeochemistry of estuarine sediments. UNESCO/SCOR workshop held in Melreux, Belgium, 29 Nov.-3 Dec., pp: 43.

15. Bolalek, J. and B. Graca, 1996. Ammonium nitrogen at water-sediment interface in Puck Bay (Baltic Sea), Estuarine Coastal Shelf Science, 43: 767-779.

16. Feuillet-Girard, M., D. Gouleau and G. Blanchard, 1997. Joassard Nutrient fluxes on an intertidal mudflat in Marennes-Oleron Bay and influence of the emersion period, Aquatic Resources, 10: 49-58.

17. Krom, M.D. and R.A. Berner, 1981. The diagensis of phosphorus in a near shore marine sediment Geochim, Cosmochim, Acta, 45: 207-216.

18. Schoer, J. and U. Förstner, 1984. Chemical forms of artificial radionuclides and their stable counterparts in sediments. Proc Int Conference of Environmental Contamination, London, pp: 738-745.

19. Elbaz-Poulichet, F.F., J.M. Martin, W.W. Huang and J.X. Zhu, 1987. Dissolved cadmium behaviour in some selected French an Chinese estuaries. Consequences on cadmium supply to the Ocean. Marine Chemistry, 22: 125-138.

20. Hunt, C.D., 1983. Variability in the benthic Mn flux in coastal marine ecosystems resulting from temperature and primary productivity. Limnology and Oceanography, 28: 913-923.

21. Sholkovitz, E.R. and D.R. Mann, 1984. The pore water chemistry of $^{239-240}$Pu and ^{137}Cs in sediments of Buzzards Bay, Massachusetts. Geochemica et Cosmochimica Acta, 48: 1107-1114.

22. Elderfield, H., N. Luedtke, R.J. Caffrey and M.C. Bender, 1981. Benthic flux studies in Narragansett Bay. American J. Sci., 281: 768-787.

23. Otero, X.L. and F. Macias, 2002. Spatial and seasonal variations in heavy metals in interstitial water of salt marsh soils. Environ. Pollution, 120: 183-190.

24. Colbert, D.D., K.H. Coale, W.M. Berelson and K.S. Johnson, 2001. Cadmium flux in Los Angeles Along Beach Harbours and Sites along the California continental Margin. Estuarine, Coastal and Shelf Science, 53: 169-180.

25. Santschi, P.H., S. Carson and Y.H. Li, 1982. Natural radionuclides as tracers for geochemical processes microcosms and Narragansett Bay, pp: 96-109. Zn G.D. Grice and M.R. Reeve [eds.], Marine microcosms: Biological and chemical research in experimental ecosystems. Springer.