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Note

Seasonal variation in heavy metal concentrations in sediment from Khalasi Estuary, Hormozgan, Iran

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ABSTRACT

The study aimed for a preliminary assessment of the distribution and levels of five heavy metals (Zn, Cu, Pb, Fe and Ni) in surface sediment of Khalasi Estuary, Hormozgan, Iran, collected from three stations during four seasons of the year, 2012-2013. The estuary does not receive domestic and industrial untreated wastewaters. The range of metal concentrations (mg g^{-1} dw) recorded were: Zn 0.051-0.164; Cu 0.016-0.061; Pb 0.001-0.460; Fe 2.541-6.537 and Ni 0.019-0.131. The spatial variation in concentrations and comparison among seasons indicated that there are significant differences in the concentrations of metals in sediment for all seasons. The results of correlation analyses showed that there is significant positive correlation for Fe-Total Phosphorus, Ni-Total Organic Matter, and Zn-Total Organic Matter and also significant positive correlation between levels of lead, copper and zinc metals with that of levels of silt and clay in the sediment. According to the guideline values, the concentrations of metals studied do not pose a threat to the ecology of the area.

Keywords: Heavy metals, Iran, Sediment, Total organic matter, Total phosphorus

Heavy metal contamination in the environment is of critical concern, because of the toxicity of heavy metals and their accumulation in organisms. Heavy metals in contrast to most pollutants are nonbiodegradable and they undergo a global ecological cycle. Many human activities such as mining, overuse of chemicals, industrial waste from ports and refineries have resulted in heavy metals contamination in coastal ecosystems. Contamination by trace metals could affect both oceanic water and those of the continental shelf and the coastal zone. Due to their influence on water, plants, animals and humans (Rabitti *et al.,* 1983), long term-monitoring of heavy metal contamination of sediments in the aquatic ecosystems is of considerable interest to both researchers and regulatory agencies.

Sediments play a key role in the geochemical and biological processes of marine ecosystems and act as sinks for metals and organics which enter the aquatic environment. Physicochemical factors which bring about the exchange of heavy metals between water and sediments include hydrodynamic effects, bioturbation in sediments, salinity of the interstitial water in sediments, season, temperature and dissolved oxygen (Soares *et al.,* 1999). However, influence of these factors such as season should be evaluated and taken into consideration to assure sufficient reliability on the spatial and temporal comparisons essential for bioindication. Accumulation of heavy metals in the upper sediment of the marine environment, pose threat to sediment-dwelling organisms and fish. Sediment analysis has been frequently used to identify sources of heavy metal in the aquatic environment (Stanley *et al.,* 2004). as this facilitates detection of heavy metals that are absorbed by particulate matter, which might escape detection using water analysis.

Heavy metal contamination in the sediment of Persian Gulf has been studied by many researchers (Abdolahpur Monikh *et al.* 2012; Safahieh *et al.* 2011; de Mora *et al.* 2004; Pourang *et al.* 2005). The uptake of heavy metals in the aquatic ecosystem is affected by grain size, partition coefficient (Kd), cation exchange, organic matter content and mineral constituents. However, in contrast to earlier reports, Pokorny (2000) suggests that elevated concentrations of metals do not necessarily pose a threat as they may never be released from the sediments and therefore may not be available for excessive plant uptake. The current study was aimed to determine the total content of heavy metals [*viz.,* Zinc (Zn), Copper (Cu), Lead (Pb), Iron (Fe) and Nickel (Ni)] in surface sediments of the Khalasi Estuary (Fig. 1); to evaluate the seasonal variations in their concentration; to assess the effect of concentration of total phosphorus (TP) and total organic matter (TOM) on the levels of heavy metals as well as to estimate the spatial distribution of heavy metals in the sediments of the study area.

Monthly sediment samples were collected in polythene bags by scuba diving between June 2012

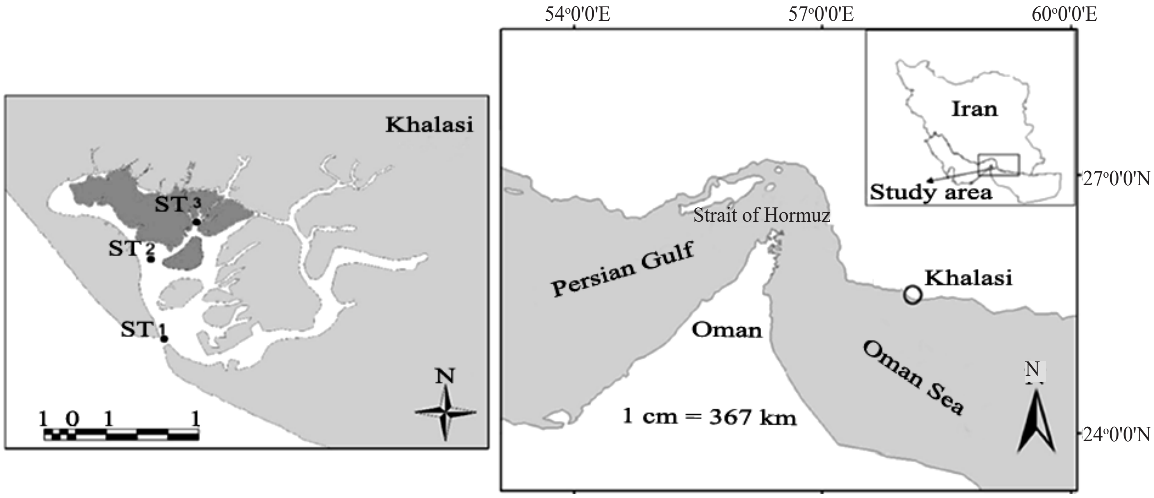

Fig. 1. Map of the Persian Gulf and location of the Khalasi Estuary as study area

and May 2013 at three stations (ST 1, ST 2 and ST3) in Khalasi Estuary (25°24`N-53°41`E; 28°57`N-59°15`E). Some portion of sediment samples were dried in a vacuum oven at 105ºC until constant weight, lightly ground in an agate mortar for homogenisation and prepared for analysis of heavy metal, TP and TOM content. As the metals are generally associated with below 63 µm particles and also to determine silt, sand and clay ratios using standard dry sieving techniques, sediments were passed through a 63-mesh stainless steel screen (Rae, 1997). An aqua regia digest (EPA method 3050B) which consists of a 3:1 ratio of HCl: HNO_3 was used to extract total P (TP). Total organic matter (TOM) of dried subsamples was determined as the difference between dry weight (80°C, 24 h) of the sediment and residue left after combustion at 450°C for 2 h (Parker, 1983). A CEM MSP 1000 microwave digestion system was used for wet digestion of samples. About 1 g of sediment sample was weighed and transferred to microwave digestion vessels, to which 7 ml of concentrated HNO_3 and 1 ml of H_2O_2 were added. Inductively coupled plasma mass spectrometry (ICP-MS, Hewlett Packard 4500) was used for the determination of total heavy metals (THM) in terms of Zn, Cu, Pb, Fe and Ni.

All reagents were of analytical reagent grade and standard solutions were obtained from Merck. The glassware was soaked in nitric acid solution (10%) for 24 h and washed with double distilled water before use. Standard reference material SRM 1645 (National Bureau of Standards) for sediment were used to check the accuracy and precision of analytical procedures. Percent recoveries were Zn: 102.1; Cu: 87.3; Pb: 106; Fe: 101.8 and Ni: 103.1.

One-way ANOVA and Duncan's multiple comparison tests were used to compare the concentration of heavy metals between stations. One way ANOVA with posterior calculation of lowest significant differences was used for comparison of four seasons. Pearson correlation coefficients were applied to examine the relationship between sediment metal content and sediment TP, TOM and THM content. The significance level was set at $\alpha = 0.05$.

Table 1 shows the seasonal variation in the concentration of Zn, Cu, Fe, Pb and Ni of sediment at Khalasi Estuary, Iran. As can be seen from Table 1, the distribution of metals is not homogeneous over the whole Khalasi Estuary and over the study period. ST1, ST2 and ST3 accumulated different amounts of the metals. Of all the heavy metals examined, Fe had the highest concentration. The Khalasi Estuary is far from industrial activities and does not receive domestic and industrial untreated wastewaters. However, ST2 was the most contaminated among the stations.

Comparision of environmental condition of heavy metals with Sediment Quality Guidelines (SQGs) showed that Zn, Cu, Pb, Fe and Ni of the sediment in the study area in spring are unpolluted, in fall and summer are moderately polluted and in winter are moderately polluted and in few cases heavily polluted. Pollution levels based on the New York Sediment Criteria and Provincial Sediment Quality Guidelines for metals had the effect range low (ISQG-L) and high (ISQG-H). ISQG-L level indicates the sediment contaminants do not have adverse effects on aquatic organisms in the area. Analysis of variance and Duncan's multiple tests, showed significant differences in the concentrations of metals in the sediment during the four

Table 1. Level and standard error of heavy metal concentration (mg g^{-1} dry weight) in the sediment from Khalasi Estuary during the spring, summer, fall and winter seasons of 2012-2013

Stations	Seasons	Zn	Cu	Pb	Fe	Ni
ST1	Spring	0.067[a*]	0.036[b]	0.001[a]	5.686[c]	0.052[a]
	Summer	0.052[a]	0.016[a]	0.089[c]	4.626[b]	0.076[b]
	Fall	0.083[b]	0.035[b]	0.171[d]	2.813[a]	0.080[b]
	Winter	0.108[c]	0.042[b]	0.023[b]	6.410[d]	0.083[b]
ST2	Spring	0.114[b]	0.022[a]	0.460[d]	6.100[c]	0.062[b]
	Summer	0.066[a]	0.031[a]	0.072[b]	2.541[a]	0.034[a]
	Fall	0.115[b]	0.043[b]	0.024[a]	6.537[c]	0.101[c]
	Winter	0.164[c]	0.061[c]	0.428[c]	4.901[b]	0.131[d]
ST3	Spring	0.051[a]	0.017[a]	0.002[a]	3.105[a]	0.032[b]
	Summer	0.100[c]	0.026[b]	0.026[b]	3.706[a]	0.040[b]
	Fall	0.075[b]	0.025[b]	0.003[a]	6.393[b]	0.072[c]
	Winter	0.104[c]	0.035[c]	0.181[c]	3.364[a]	0.019[a]

[*]Different superscript letters show differences among seasons

seasons. The concentrations of Zn and Cu in ST1, ST2; Pb in ST3; Fe and Ni in ST1 showed significant increase during winter in comparison to other seasons. However, the levels of Fe and Ni in ST3 were significantly higher in the fall, than in the other seasons. This indicates that the metals are not strongly bound with the crystal structure of minerals present in sediment; thus dilution due to rain can largely affect metal concentrations in the sediment. The reasons for seasonal variation in metal concentrations within the stations are mainly dependent upon the local anthropogenic activities and hydrological regimes of each station (Soares *et al.,* 1999; Abdolahpur Monikh

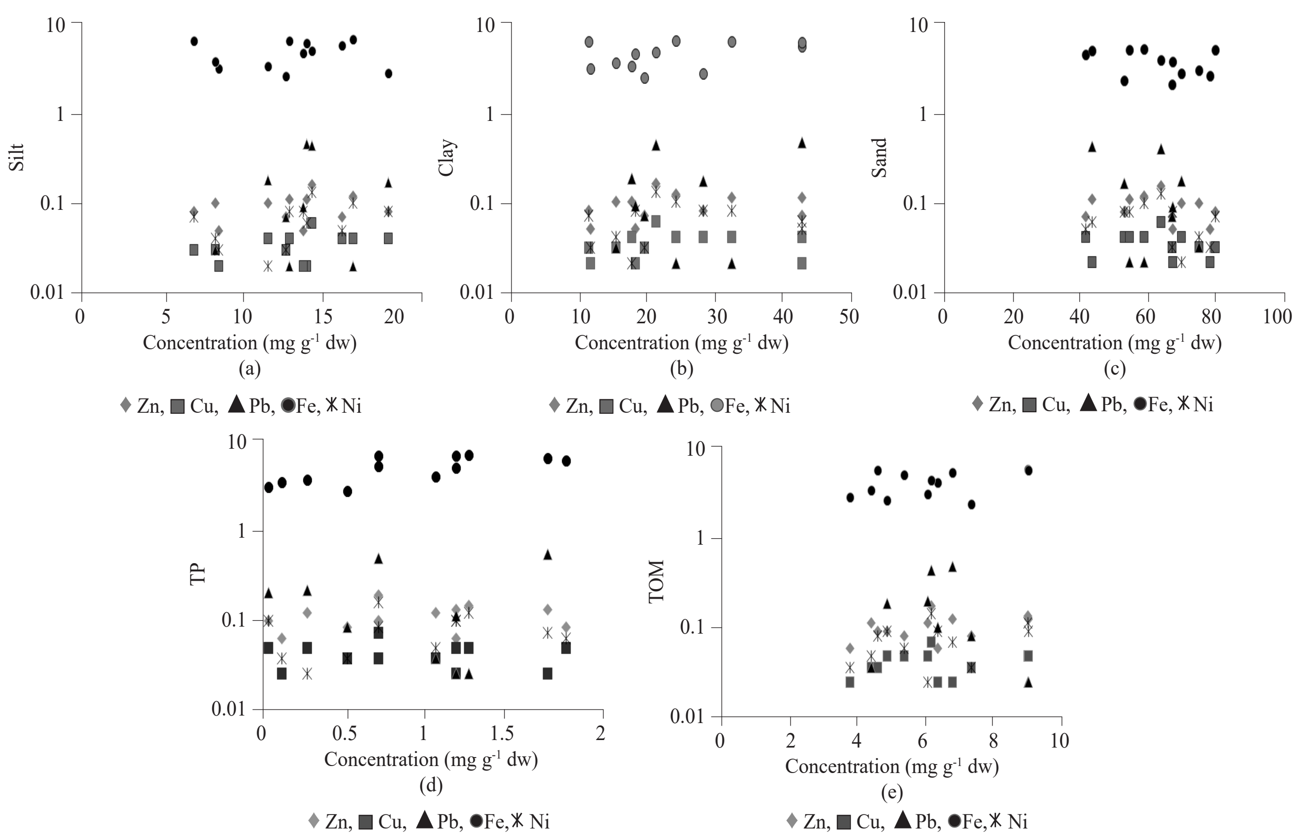

Fig. 2. Relationship between metal concentrations in sediment and a) Silt, b) Clay, c) Sand, d) Total phosphorus (TP) and E) TOM in three stations along Khalasi Estuary, Hormozgan, Iran. dw = dry weight

et al., 2012). Results of the present study are similar to the observations on seasonal variations in heavy metal distribution in sediments from Ondo coastal sediment, Nigeria (Asaolu *et al.,* 1997). Pearson's correlation coefficients among TP, TOM, silt, clay and sand with heavy metals in the sediments studied are presented in Fig. 2. TP had a significant positive correlation with Fe ($r = 0.72$, $p<0.01$). Moderately high correlation ($p<0.05$) was found between TOM and Ni ($r = 0.75$) and Zn ($r = 0.69$). There were no significant relationship between the content of the rest of the metals and the levels of TP and TOM in the sediment. This finding indicates that TP and Fe in sediments could be from the same sources. Guo *et al.* (2010) showed that there was significant positive relationship between TP contents and the levels of Cu, Cd, Pb, Zn and As in sediment. Also, Abdolahpur Monikh *et al.* (2012) reported on the concentration order of heavy metals in sediment from Musa Estuary (Persian Gulf) to be Ni >Co > Cu > Pb > Cd. As organic matter can be bound with some fractions of heavy metals, it can affect the metal bioavailability and concentration of sediment (Eimers *et al.,* 2002). Hence we assumed a correlation of the sediment organic matter with sediment metal, levels for different stations. The results obtained in this study are in agreement with reported data of Zhang and Wang (2007), on heavy metal in sediment and their relationship with the content of TOM. Correlation matrix (Fig. 2) revealed the existence of a weak and nonsignificant correlation between heavy metal concentration and sand. Pb, Cu and Zn showed a positive correlation with silt ($p<0.01$) and clay ($p<0.05$). Sudhanandh *et al.* (2011) reported that finer sediments have a larger surface area, which allows heavy metals and other contaminants to be adsorbed easily. However, some of the studied heavy metals showed negative correlation with sand particles which presumably may have low surface area. In conclusion, the results of the present study can be used as baseline information to monitor metal contamination in Khalasi Estuary. This study demonstrated that seasons play a significant role in metal accumulation, as metals in the wet seasons showed greater concentration than those from dry seasons. Regression analysis showed that some heavy metals have a positive relationship with TP, TOM and silt-clay concentrations. We recommend that the form and extent of metal bioavailability in this area should be evaluated further.

References

Abdolahpur Monikh, F., Safahieh, A. R., Savari, A. and Doraghi, A. 2012. Heavy metal concentration in sediment, benthic, benthopelagic and pelagic fish species from Musa Estuary (Persian Gulf). *Environ. Monit. Assess.*, 185: 215-222. doi:10.1007/s10661-012-2545-9.

Asaolu, S. S., Ipinmoroti, K. O., Olaofe, O., Adeeyinwo, C. E. 1997. Seasonal variation in heavy metal distribution in sediments from Ondo state Coastal area. *Ghana. J. Chem.,* 3: 11-14.

de Mora, S., Fowler, S., Wyse, E. and Azemard, S. 2004. Distribution of heavy metals in marine bivalves, fish and coastal sediments in Persian Gulf and Gulf of Oman. *Mar. Pollut. Bull.*, 49: 410-424. doi:10.1016/j.marpolbul. 2004.02.029.

Eimers, M. C., Evans, R. D. and Welbourn, P. M. 2002. Partitioning and bioaccumulation of cadmium in artificial sediment systems: application of a stable isotope tracer technique. *Chemosphere,* 46: 543-551. doi: 10.1016/s004 5-6535(01)00156-4.

Guo, W. H., Liu, X. B., Liu, Z. G. and Li, G. F. 2010. Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin. *Procedia. Environ. Sci.,* 2: 729-736. doi.org/10.1016/j.proenv.2010. 10.084.

Parker, J. G. 1983. A comparison of methods used for the measurement of organic matter in sediments. *Chem. Ecol.,* 1: 201-210. doi.org/10.1080/02757548308070802.

Pokorny, B. 2000. Roe deer *Capreolus capreolus* as an accumulative bioindicator of heavy metals in Slovenia. *Web Ecology,* 1: 54-62. doi.org/10.5194/we-1-54-2000.

Pourang, N., Nikouyan, A. and Dennis, J. H. 2005. Trace element concentrations in fish, surficial sediments and water from northern part of the Persian Gulf. *Environ. Monit. Assess.,* 109: 293-316. doi:10.1007/s10661-005-6287-9.

Rabitti, S., Boldrin, A. and Menagazzo-Vitturi, L. 1983. Relationship between surface area and grain size in bottom sediments. *J. Sediment Petrol*, 53: 665-667.

Rae, J. E. 1997. *Trace metals in deposited intertidal sediment*. Cambridge: Cambridge University Press, UK, p. 16-30.

Safahieh, A. R., Abdolahpur Monikh, F., Savari, A. and Doraghi, A. 2011. Heavy metals concentration in mullet Fish, *Liza abu* from petrochemical waste receiving creeks, Musa Estuary (Persian Gulf). *J. Environ. Protection*, 2: 1218-1226. doi: 10.4236/jep.2011.29140.

Soares, H. M. V. M., Boaventura, R. A. R., Machado, A. A. S. C. and Esteves da Silva, J. C. G. 1999. Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): multivariate analysis of data. *Environ. Pollut.,* 105: 311-323. doi: 10.1016/s0269-7491(99)00048-2.

Stanley, R. H. R., Buesseler, K. O., Manganini, S. J., Steinberg, D. K. and Valdes, R. J. 2004. A comparison of major and minor elemental fluxes collected in neutrally buoyant and surface-tethered sediment traps. *Deep-Sea Research, Part I*: *Oceanographic Research Papers*, 51: 1387-1395. doi:10.1016/j.dsr.2004.05.010.

Sudhanandh, V. S., Udayakumar, P., Ouseph, P. P., Amaldev, S. and Narendra Babu, K. 2011. Dispersion and accumulation trend of heavy metals in coastal and estuarine sediments and its textural characteristics, a case study in India. *J. Hum. Ecol.,* 36(2): 85-90.

Zhang, M. K. and Wang, L. P. 2007. Impact of heavy metals pollution on soil organic matter accumulation. *Ying Yong Sheng Tai Xue Bao,*18(7): 1479-83.

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