Assessment of Trace Metals Accumulation in Water and Surface Sediments of Chabahar Bay, Makran

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In this study the levels of trace metals in surface water and sediments, water physical characteristics (temperature, salinity and pH), water organic carbon (OC%), sediment organic matter (OM %) as well as sediment grain size distribution throughout the nine stations of Chabahar Bay were measured to assess as a consequence of natural and anthropogenic sources. The analyzed elements were arsenic (As), Barium (Ba), Iron (Fe), mercury (Hg), Potassium (K), lithium (Li), magnesium (Mg), Manganese (Mn), tin (Sn), strontium (Sr), thallium (Tl) and uranium (U). The samplings were performed from 3.8 to 13.6 m depths of Tiss, Konarak, Desalination Plant, Entrance of Chabahar Bay, Posm and Ramin during April 2012 (Pre-Monsoon).

Inductively Coupled Plasma Mass Spectrometry inductively (ICP-MS) was used to detect element levels. Sediment samples were exposed to wet sieving and Laser Particle Sizing determination.

Tin, lithium, potassium magnesium and iron levels were higher in the Konarak than other stations. Due to the high percentage of clay in coastal parts of Konarak, transferring pollution of desalination plants by water flow can be considered a threat in the future.

[Keywords: Trace and Rare Metals, Water, Sediment, Chabahar Bay, Oman Sea, ICP-MS]

Introduction

The water quality of aquatic environment could be main factor to control the state of health in both man and animal. Human activities have increased levels of metal ions and polychlorinated biphenyl compounds in marine ecosystem. Heavy metal pollution in the marine environment is determined by measuring its concentrations in water, sediments and living organisms. Sediment analyses plays a crucial role in assessing the degree of heavy metal pollution and resulting health risk associated with the food chain. Heavy metals such as Tl, Hg, As and Sn are regarded as being serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to negatively affect various organisms. Their concentrations in the global environment are significantly increasing and reaching levels of potential (lethal and sub lethal) toxicity for many living organisms. Concentrations of chemicals in sediments may be several orders of magnitude higher than in overlying waters.

Among the toxic trace metals, mercury (Hg) is one of the most serious contaminants in water, sediment, and biota at most parts of the world and its toxicity to humans has been well established. Mercury released into the aquatic ecosystems tends to stick to particles in the water, especially particles with higher organic matter contents, and finally settle down as bed sediments. Abundances of mercury in primitive upper mantle and seawater are estimated 0.5 and 0.05 ppb and for arsenic are 69 and 2.3 ppb, respectively.

Arsenic is notorious as a toxic element. Tin and its compounds are significant and controversial chemicals in the environment. Tin occurs naturally in the earth’s crust and seawater with a concentration of approximately 2–3 ppm and 0.01 ppb, respectively.

The Gulf of Oman is a strait that connects the Arabian Sea with the Strait of Hormuz, and offers the only entrance from the Arabian Sea and the Indian Ocean into the Persian Gulf. It also is an important (and vital) shipping route for the oil-producing countries in the Persian Gulf area. Chabahar Bay, which situates on the Makran Coastline in Sistan and Baluchestan Province, Southeast of Iran, is a free trade and industrial zone on the coast of the Gulf of Oman. The special importance of Chabahar Bay is due to its Ω shape and limited water circulation. The study area has humid climate, hot summers and...
moderate winters. Fishing and marine commerce are the main activities in the study areas. Due to increasing industrial activities in recent decades in this area, it is expected that it could influence on accumulating anthropogenic trace metals, in water and coastal marine sediments\textsuperscript{11,12,13}.

The main objectives of the present study were 1) to investigate trace metal distribution in water and surface sediments from the Chabahr Bay, Oman Sea, 2) to discover relationships between the elemental levels, organic matter, organic carbon as well as water different parameters, 3) to detect pollution source(s) and 4) to compare pollution levels with other marine ecosystems.

Materials and Methods
Chabahar Bay at southeastern Iran was suspected to heavy metals contamination due to natural processes and human activity. To assess pollution in the bay, 27 surface sediments and 27 surface water samples (Table 2) were collected from 9 stations in Chabahar Bay in the May 2012 (Figure 1). Geographical locations of the sampling stations are presented in Table 4.

The sampling locations were 1) Tiss, 2) Konarak, 3) Desalination plant, 4) Entrance of Chabahar Bay, 5) Posm, and 6) Ramin. The selected sampling sites represent the most important harbors, desalination plant and industrial regions in Sistan and Baluchestan Province and they represent coastal areas that can have a relative higher pollution due to higher population. Sampling was performed in April 2012 (Pre-Monsoon).

![Fig. 1 — The location of the sampling site in the Chabahr Bay.](image-url)
Australia\textsuperscript{16}. Detection limit of TOC analyser was 50 ppb (5*10\textsuperscript{-6} %). The concentrations of TOC in all samples were higher than the detection limit. The recovery of methodology was 97±2%.

The limits of detection (three times of the standard deviation on the procedural blanks) for elements are reported in Table 1.

Statistical analyses of the data including correlation and regression calculations were carried out by using SPSS V19 and Excel. A Kolmogorov-Smirnov test was executed to analyse the normality of data distribution. Spearman correlations were calculated between elements concentrations in different stations.

**Results and discussion**

**Element levels in Water samples**

In this study arsenic (As), Barium (Ba), Iron (Fe), mercury (Hg), Potassium (K), lithium (Li), magnesium (Mg), Manganese (Mn), tin (Sn), strontium (Sr), thallium (Tl) and uranium (U) levels in water and sediments with maximum standard deviation of 10%, water physical characteristics (temperature, salinity and pH) and water organic carbon (OC%), sediment organic matter (OM %) as well as grain size distribution in the sediments throughout the nine stations at depths between 3.8 to 13.6 m in the Chabahar Bay were measured (Tables 2 and 4). Salinity, pH and water temperature were uniform on all stations and exhibited only a narrow variation. The range and averages of water physico-chemical characteristics were as Organic Carbon: 0.10-0.26-0.28% (Deeper parts of Konarak to coastal parts of Konarak and Tiss) (0.17±0.06) %, pH: 8.03-8.15 (8.1±0.04), Dissolved Oxygen: 3.12-4.77 (4.0±0.7) mg.L\textsuperscript{-1}, Temperature: 25.1-28.6 (26.6±1.2) °C and Salinity 36-37.3 (36.6±0.37) % (Table 2).

The variation of dissolved metal concentrations in seawater samples from the investigated area is summarized in Table 2 compared with the typical natural trace element concentration of water. The means of metal concentrations in water were: Hg: >0.1, As: 29±3, Ba: 7.6±1.2, Fe: 127±103, Li: 195±12, Mn: 5.4±2.4, Sn: >0.1, Sr: 8.4±0.3, Tl: 14±1, U: 3.2±0.1 ppb and K: 723±26, Mg: 1440±57 ppm. The relative amount of the metals in water sample is in the order: Mg<K<Li<Fe<As>Tl>Sn>Ba>Mn>

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<th>Elements</th>
<th>Water µg.L\textsuperscript{-1}</th>
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<th>Water µg.L\textsuperscript{-1}</th>
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Table 1 — The elements limits of detection (DL).

Table 2 — Elements concentrations (µg.L\textsuperscript{-1}), water organic carbons %, as well as water characteristics (pH, temperature (°C) and salinity (PSU)) in different station at Chabahar Bay.
As concentrations of mercury and tin in sea water were lower than detection limit of the instrument (0.1 µg L⁻¹), so comparing the results with natural mercury (0.05 ppb) and tin (0.01 ppb) levels in sea water was not possible. Anyhow, the mercury and tin concentrations were lower than their Cosmochemical Estimates Composition (CMC), which are 1.8 and 69 ppb, respectively.

The results demonstrated that arsenic level in the seawater follows a relatively uniform distribution (24 to 33 µg L⁻¹) with maximum level at coastal parts of Tiss. Arsenic levels in the water samples were approximately 10 and 20 orders of magnitude higher than the average arsenic concentration in sea water and open sea water, respectively (3 µg L⁻¹ and 1.5 µg L⁻¹).

According to different standard marine water, almost all of the heavy metals concentrations at the sampling areas appeared within the normal range (Table 2).

Although arsenic level (69 ppb) was lower than its probable effect level (100 ppb), but was much higher than naturally arsenic level in seawater (2.3 ppb). The arsenic levels in all the stations were almost comparable. The results showed that arsenic in seawater might be originated from the natural source and salinity. From the correlation matrix (Table 3), we can deduce that the strongest correlations exists between Sr-U-Mg (0.91<r<1.00, P=0.01) and Fe-Mn-Ba (0.82<r<0.86, P=0.01) in water samples.

Arsenic, barium and thallium were significantly correlated with pH, uranium and magnesium were correlated with dissolved oxygen and temperature.

Minimum and Maximum (Mean concentration with the corresponding standard deviations) element levels in the sediments of all the sampling sites were as: As¹³: 9.5-21 (13.2±4.5), Ba: 98-134 (116±12), Mn: 465-905 (663±183), Li: 10-45 (24±12), Sr: 272-636 (474±221), Sn: <0.5±0.0, U: 1.2-3.2 (3.1±0.0) ppm, Hg: 11-24.5 (19.5±3.5) ppb, Fe: 1.2-3.2% (1.80±0.65), K: 0.6-1.8 (0.97±0.4), Mg: 0.6-2.1 (1.1±0.4) ppm.

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Sediment samples

Minimum and Maximum (Mean concentration with the corresponding standard deviations) element levels in the sediments of all the sampling sites were as: As¹³: 9.5-21 (13.2±4.5), Ba: 98-134 (116±12), Mn: 465-905 (663±183), Li: 10-45 (24±12), Sr: 272-636 (474±221), Sn: <0.5±0.0, U: 1.2-3.2 (3.1±0.0) ppm, Hg: 11-24.5 (19.5±3.5) ppb, Fe: 1.2-3.2% (1.80±0.65), K: 0.6-1.8 (0.97±0.4), Mg: 0.6-2.1 (1.1±0.4) ppm.

Precision was close to ±10% (SD) for all elements analysed in triplicate samples per station, which shows uneven sedimentation in the area. According to the Figures 2 and 3, metal contents in the sediments were observed in the order of Fe>Mg>K>Sn>U>Li>Ti>Hg. Organic matter with average of 3% varied from 2.25 (coastal parts of Tiss) to 8% (deeper parts of Konarak).

Minimum Hg level (11±1.4 ng g⁻¹ d.w) belonged to coastal Tiss sediments, which is comparable with that in continental crust of East China, 9 ppb²⁵. Maximum
mercury level (24.5±0.7 ng. g⁻¹ d.w) detected at coastal Posm sediments. The average mercury level in this study (18 ppb) was almost three and four times lower than that in earth’s mantle and earth crust (60 and 85 ppb), respectively. Mercury values in the analysed sediments were compared with Effect Range SQGs Guidelines (ERL (150 ng. g⁻¹), ERM (Effect-range-medium,710 ng. g⁻¹), TEL (Threshold Effect level,130 ng. g⁻¹), PEL(Probable – Effect – level,700 ng. g⁻¹), ISQG-Low (150 ng. g⁻¹) and ISQG-High (1000 ng. g⁻¹) from the American NOAA Organization. The results demonstrated that mercury concentrations in the sediment (18±4.1 ng. g⁻¹) appeared to be lower than TEL (130 ng.g⁻¹ d.w), thus there was no pollution risk for this element.

Tin concentrations (1.4±0.4 ppm) were more detected in harbors, such as coastal parts of Konarak and Ramin. Pollution sources at Ramin station with higher tin element in sediments and low clay and silt fractions should be seriously considered. Higher lithium, magnesium, Potassium and Iron concentrations were detected in the sediments of Konarak, which is an area with relatively more industrial activities. Thallium in all the stations was lower than the detection limit of the analyzing instrument (0.5 µg.g⁻¹); lower than that in the earth crusts (0.850 ppm) and in earth’s mantle (0.0041 ppm). Barium level (116±12 ppm), which was almost four times lower than that in earth crust (425 ppm), was relatively comparable in different sampling stations (Figure 3).

Arsenic concentration in all the stations was comparable. As specified in figure 2, the maximum arsenic concentration was found at deeper parts of Posm and Tiss. This element with an average concentration of 13.2 µg. g⁻¹ d.w was over than threshold effect level (7.24 µg. g⁻¹ d.w) and even over than Effect Range Low (ERL, 8.2 µg g⁻¹ d.w), but it was lower than probable effect level (41.6 µg. g⁻¹ d.w). Arsenic levels were higher than that in the sediments of the Persian Gulf and south parts of the Caspian Sea. High levels of arsenic contamination in are such as Bangladesh and India with natural origin, can explain high As levels in the north parts of Oman Sea. Marine currents could shift natural pollution to the Oman Sea. The sediments of Chabahar Bay are rather uncontaminated than west coast of India in the Arabian Sea.
anthropogenic sources, but natural sources can play basic role in their intrinsic levels.

Nowadays lithium is utilized in military industries and rechargeable batteries, which are becoming a common replacement for the lead acid batteries. Minimum Lithium, the strategic element, was 10 ppm at Tiss station and deeper parts of Posm. Maximum Li level (45 ppm) which was detected at coastal parts of Konarak, was 2 and 35 times higher than that in earth crust (20 ppm) and in fertile mantle rocks (1.3 ppm) reported by Seitz and Woodland27. The mean Potassium concentration in the sampling area (970 ppm) was almost four times higher than that in ocean floor basalts (260 ppm)24, 28 (Figure 3).

Uranium (2.2±0.8 ppm) was relatively higher in the sediments of coastal parts of Ramin, Konarak and deeper parts of Posm and was comparable with that in earth crust (2.7 ppm). Maximum manganese at Tiss (850-905 ppm) and Entrance of Bay (913 ppm) was comparable with that in earth crust (950 ppm). Maximum strontium level at Tiss station (794-815 ppm) was almost two times higher than that in earth crust (370 ppm). Magnesium (1.1±0.4 %) and Iron (1.8±0.6 %) were lower than those in earth crust (2.33 and 5.63 %, respectively) (Figure 3).

There were positive significant correlations between Fe, Li, Sn, Mg and K (0.64<r<0.98, 0.05<P<0.01). Uranium negatively correlated to manganese (r=0.63). Arsenic from one side negatively correlated to Li, Mg and K (-0.86<r<-0.65) and on other side positively correlated to strontium (r=0.88).

Organic matter was significantly correlated to silt and clay (0.7 and 0.64, respectively p<0.1), while was negatively correlated to sand (-0.77, p=0.05). In this study there were no significant correlations between organic matter, depth and sediment grain size and elements levels in the sea sediments, except for Barium and Clay fraction.

Statistical analysis Q-Q plot demonstrated that almost all data was normally distributed. Spearman correlation matrix between elements, organic matter, depths and corresponding sediment grain sizes, Table 5 — Spearman correlation matrix between the element levels, organic matter, depths and corresponding sediment grain sizes. (E: Elements, D: Depth)

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The results of Principal Component Analysis with Varimax Rotation Method showed three principal components or groups of elements in the sediments explaining 78 % of the total variation: Factor 1 (expressing 57 % of total variance) includes Ba, Li, Mg, K and Fe; Factor 2 (explaining 19.5 % of total variance) includes Hg, As and Sr; Factor 3 (Mn, U and Sn) explaining 11.6 % of total variance.

The data obtained in the present investigation showed that there were no significant correlations between the element levels in water and sediment samples.

**Conclusion**

Higher Sn, Li, K, Mg and Fe levels in the Konarak stations than other stations could be due to local harbor, dock, boat repair stations and also desalination plant activities. Due to the high percentage of clay in coastal parts of Konarak, transferring Pollution of desalination plants by water flow can be considered a threat in the future.

High As concentration in the sediment samples shows that the application of SQGs developed for other regions may not be suitable for use in the area, due to the naturally high background concentration of some metals present in the sediment. However high As level in the sediment indicates that more detailed and extensive investigations is required to legislate preventive laws, however special attention regarding to industrial developments and relevant inputs in this area is recommended.

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**References**


