Accumulation and Bioavailability of Heavy Metals (Cadmium, Chromium, Nickel, Lead and Zinc) in Water and Sediment Samples in the Musa Creek, Northwest Coasts of the Persian Gulf

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Accumulation and Bioavailability of Heavy Metals (Cadmium, Chromium, Nickel, Lead and Zinc) in Water and Sediment Samples in the Musa Creek, Northwest Coasts of the Persian Gulf

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Abstract

The current study aimed to investigate the total concentrations of heavy metals in water and sediment samples as well as their bioavailability in sediments of Musa Creek. Twenty samples including 10 sediments and 10 water samples were collected from 10 stations. The concentration of heavy metals was measured using inductively coupled plasma–mass spectrometry. The bioavailability of heavy metals was carried out by first step of Tessier sequential extraction method so called single extraction in the manuscript. The results showed that the mean concentrations of cadmium, chromium, nickel, and zinc in water samples was 0.17, 7.44, 43.80, and 8.85 mg/L, respectively. The concentration of lead was lower than the detection limit of the 0.1 mg/L. The positive correlation of heavy metals in water samples is due to their potential common source. The negative correlation of nickel with other elements in sediment samples indicates that, apart from the industrial activity in the region, the geogenic origin affects the concentration of metals. The factor analysis showed two components. The first component was lead, zinc, chromium, and cadmium with the common source (s) and nickel was the second component with geogenic origin. The high concentrations of heavy metals in the exchangeable phase of Tessier sequential extraction showed that the bioavailability of the elements in sediment samples, especially lead and zinc is at a high level that could be a serious threat to the aquatics of the region.

Keywords: Heavy metals, Musa Creek, Bioavailability, Single extraction

1. Introduction

Heavy metals, are among the most common and notable environmental pollutants [3,14]. A part of heavy metals is soluble after entering the environment. Some of these metals are also attached to suspended particles by weak bonds. Suspended particles containing heavy metals will gradually accumulate in sediments in case of deposition [18]. Sequential extraction methods have been designed to identify pollution sources, evaluate mobility and bioavailability of metals, identify metal bonding sites for evaluation of the mechanism of metal accumulation, contamination, and transportation, as well as for the detection of different forms of metal...
binding to sediment [6]. [23] investigated the distribution and speciation of cadmium, copper, lead, iron, and manganese in shallow sediments of Ginjo Bay in northeastern China using Tessier sequential extraction method. Sequential extraction experiments showed 39–61% of cadmium in the exchangeable phase. According to these results, cadmium is at a high-risk level in the environment, while copper and lead are at medium risk level [17].

2.1. Site description

The study area is located in the 30°27′18″/33″ to 30°30′12″/48″ N latitudes and 49°04′08″/39″ to 49°04′48″/87″ E longitudes. Figure 1 shows the map of the study area and the location of water and sediment samples in the region.

Musa Creek is the result of the joint operation of the hydrological and tectonic processes, which has been formed due to the low slope of the vast plain of Khuzestan. The lands in both sides of the Creek are extremely low, and much of it goes under the water during the rise of waves and tides in the Gulf. In the past, the formation of Musa Creek was attributed to local subsidence [12], and its formation was considered very young, but nowadays this region is attributed to sea level changes in Quaternary [9]. Due to the presence of quaternary young alluvial coatings, the geological knowledge associated with this area is very little and limited to the results of oil drilling and geophysical studies of regions beside it.

2.2. Sampling, preparation and analysis

Twenty samples including ten water samples and ten sediment samples were taken from 10 stations in the area. Samples were collected in the study area at intervals of 300 m (three replicates at each station). The sampling points were first registered using a Garmin® 12 channels GPS Global Positioning System. High density polypropylene bottles (previously rinsed with dilute nitric acid and then deionized water) were used for sampling. Electrical conductivity, pH and EC were determined on site by a calibrated multimeter. Water samples were filtered through a 0.45 μm Whatman filter paper and poured into polyethylene bottles and preserved with 2 mL nitric acid to prevent the precipitation of metals. The specimens were stored at 4 °C in the refrigerator after recording the specifications [13].

Sediment samples were taken from a depth of 0–10 cm on the soft-bottom undisturbed parts with Ekman grab and were mixed thoroughly to make a composite sample.

The sediment samples were oven dried at 50 °C to a constant weight after removal of excess water. The...
dried samples were sieved to less than 2 mm in a plastic sieve and ground to fine powder using an agate and a pestle. Part of the ground sample was used to determine the total concentrations of metals as well as bioavailability, and the non-ground sieved portion was used to determine organic matter and pH. Samples were prepared and analysed according to the standard methods [22]; American Public Health Association (APHA) 2001).

For the total concentrations of heavy metals in sediment samples to be measured, one gram of powdered sediment was poured into a balloon, and 10 ml of nitric acid and perchloric acid was added in a ratio of 1:4. The digestion stage was then performed using a hot plate digester for 1 h and 3 h at 140 °C. After cooling the specimens under the hood, the volume of the samples was reached to 25 ml with double distilled water, and they were filtered using Whatman filter paper 42 [13].

Because the most mobile metals are extracted in the first fraction and continue in order of decreasing of mobility, so the only bioavailable part was done. For this part of single extraction analysis, about one gram of sediment was weighed using an electronic scale and used for analysis. These sediment samples were poured into 15-ml centrifugal tubes, and the same tubes were used until the end of the analysis stages. This analysis is as follows:

For this step, 1 g of sample is placed in a 50 mL tube. The sample is exposed to 1 mol Na OAc at pH 8.2 and shaken. The fraction is separated from the supernatant by centrifugation at 10,000 rpm, for 30 min. The supernatant is collected for lab analysis [21]. Measurements of heavy metals in all of the above samples were carried out by inductively coupled plasma–mass spectrometry ICP-MS after microwave acid digestion following Method 3051A (USEPA 1998) at the laboratory of Geological Survey and Mineral Explorations of Iran (GSI). All reagents were of Merck® Suprapure® grade.

Statistical analysis was performed by Spss16.

3. Results

3.1. Water samples

The descriptive indices of the heavy metals (µg/L), pH, EC (ms/cm) in the water are shown in Table 1. The results indicate that the concentration of cadmium in the range of 0.12–0.25 µg/L with an average of 0.17 µg/L. The average chromium concentration in water is 7.44 µg/L, a minimum of 4.90 µg/L and a maximum of 12 µg/L. The mean nickel concentration in water is 43.80 µg/L, which is in the range of 34.60–53.70 µg/L. The mean zinc concentration in water is 8.85 µg/L, which is in the range of 8.02–9.6 µg/L. The level of lead was lower than the detection limit of the device (0.1 µg/L). The mean pH of the region is 8.28 and in the range of 7.54–8.35. EC with an average of 71.92 milisiemens/cm is in the range of 69.40–73.40 milisiemens/cm.

The results of the correlation coefficient among measured factors in water are presented in Table 2. According to the above-mentioned results, among heavy metals, the highest correlation is between nickel and zinc (r = 0.861), chromium and nickel (r = 0.853), cadmium and nickel (r = 0.823), cadmium and zinc (r = 0.823). There is also no significant correlation among heavy metals, EC and pH.

3.2. Sediment samples

Table 3 shows the total concentration of heavy metals (mg/kg) and descriptive statistics in sediment samples as well as the single extraction analysis of heavy metals (µg/kg). As can be seen, the highest content was for chromium at station 6 (144 mg/kg). Whereas the lowest concentration was for cadmium at station 8 (0.19 mg/kg).

Regarding the single extraction results in Table 4, among the stations examined, the station 1 has the highest cadmium content (1.4 µg/kg) in the exchangeable phase. The level of chromium in the exchangeable phase is less than 1 µg/kg at all stations except station 9 and 10 (10 and 30 µg/kg, respectively).

### Table 1. Descriptive indices of measured parameters in water samples (µg/L).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Average</th>
<th>Max</th>
<th>Min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.17</td>
<td>0.25</td>
<td>0.12</td>
</tr>
<tr>
<td>Cr</td>
<td>7.44</td>
<td>12.0</td>
<td>4.90</td>
</tr>
<tr>
<td>Ni</td>
<td>43.80</td>
<td>53.70</td>
<td>34.60</td>
</tr>
<tr>
<td>Zn</td>
<td>8.85</td>
<td>9.6</td>
<td>8.02</td>
</tr>
<tr>
<td>Pb</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>pH</td>
<td>8.28</td>
<td>8.35</td>
<td>7.54</td>
</tr>
<tr>
<td>EC</td>
<td>71.92</td>
<td>73.40</td>
<td>69.40</td>
</tr>
</tbody>
</table>

ND: Not determined.

### Table 2. Correlation coefficient among measured parameters in water samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>EC</th>
<th>pH</th>
<th>Zn</th>
<th>Ni</th>
<th>Cr</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd</td>
<td>0.364</td>
<td>0.052</td>
<td>-0.822</td>
<td>0.822</td>
<td>0.647</td>
<td>1</td>
</tr>
<tr>
<td>Cr</td>
<td>0.130</td>
<td>0.2600</td>
<td>-0.776</td>
<td>0.852</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.432</td>
<td>0.2722</td>
<td>-0.861</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.275</td>
<td>0.246</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>0.184</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Correlation is significant at the 0.01 level (two-tailed).

*Correlation is significant at the 0.05 level (two-tailed).*
respectively). The concentration of nickel in the exchangeable phase is almost same for all stations, but the sample level taken at station 1 is 5.6 mg/kg.

Among the studied metals, lead has the highest concentration in the exchangeable phase, with the highest rate (111.9 mg/kg) in station 4 and the lowest rate (0.9 mg/kg) in station 8. The highest level of zinc in the exchangeable phase is 44.6 mg/kg at station 1.

The results of the correlation coefficient among sediment parameters are shown in Table 4. As it is shown, there is a strongly positive correlation between cadmium-chromium (0.831), lead-chromium (0.940), zinc-chromium (0.817), cadmium-zinc (0.791), lead-cadmium (0.903), and zinc-lead (0.804).

4. Discussion

4.1. Water samples

The concentration sequence of heavy metals in the water samples of the study area can be arranged in order lead < cadmium < zinc < chromium < nickel. At all stations, the concentration of lead was lower than the detection limit (0.1 μg/L). The present study shows that the concentration of nickel in the water samples is higher than that of other metals in water. On the one hand, the study area was a port which causes traffic of ships, vessels, discharge and loading of oil, and, on the other hand, the industrialization of the study area, the presence of petrochemical industries and refineries, the rate of nickel contamination is increased [25,27]. The high positive correlation coefficient (Table 2) between nickel and cadmium, as well as between zinc and chromium, this suggests common pollution source for these elements. Since nickel is an oil indicator, it is likely that a large part of the source of chromium, cadmium, and zinc will be from the oil of vessels in the region, the petrochemical wastewater, and the coloring of the bodies of ships and vessels. In a study carried out by [19] on a Khoshk river, a positive correlation was found among nickel, chromium, and zinc, which originated from a common source of gas station. Comparison of heavy metals (μg/L) in water with the other standards in Table 5 shows that cadmium, chromium, and zinc with an average concentration of 0.15, 7.46, and 2.19 μg/L are lower than the standard water for aquatics and the US Environmental Protection Agency standard (USEPA). Nickel with an average concentration of 43.80 μg/L is higher than the Canadian standard (25 μg/L) and the WHO standard (20 μg/L) and below the standard of the US Environmental Protection Agency (52 μg/L). Comparison of the concentrations of the elements in the water samples analyzed with the WHO standard shows that cadmium and chromium are below the contamination range. But the concentration of nickel appears to be higher than the standard limit. Also the average values of cadmium, chromium, nickel, and zinc were higher than the standard seawater.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Zn (ug/L)</th>
<th>Pb (ug/L)</th>
<th>Ni (ug/L)</th>
<th>Cr (ug/L)</th>
<th>Cd (ug/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water for aquatic life</td>
<td>100&lt;</td>
<td>50</td>
<td>ND</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Canada standard [7]</td>
<td>30</td>
<td>7</td>
<td>25</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>WHO [2]</td>
<td>ND</td>
<td>10</td>
<td>20</td>
<td>50</td>
<td>3</td>
</tr>
<tr>
<td>USEPA [2]</td>
<td>120</td>
<td>2.5</td>
<td>52</td>
<td>11-74</td>
<td>0.2</td>
</tr>
<tr>
<td>Sea water [10]</td>
<td>2</td>
<td>0.03</td>
<td>0.5</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>NOAA</td>
<td>81</td>
<td>8.1</td>
<td>8.2</td>
<td>50</td>
<td>8.8</td>
</tr>
<tr>
<td>Current study</td>
<td>8.58</td>
<td>ND</td>
<td>43.80</td>
<td>7.44</td>
<td>0.17</td>
</tr>
</tbody>
</table>

ND: No Data.

Table 3. Descriptive indices, total (mg/kg) and bioavailable contents (μg/kg) of heavy metals in sediment samples.

|  | Average | Max   | Min   | S-10 | S-9 | S-8 | S-7 | S-6 | S-5 | S-4 | S-3 | S-2 | S-1 | HM |
|---|---------|-------|-------|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|---|
| Ni | 0.27    | 0.34  | 0.19  | 0.22 | 0.21| 0.19| 0.20| 0.35| 0.31| 0.27| 0.34| 0.33| 0.25| Cd(t) |
| Cr | 0.37    | 1.4   | 0.0   | 0.0  | 0.1 | 0.0 | 0.7 | 0.0 | 0.2 | 0.2  | 0.0 | 1.1 | 1.4 | Cd(Sin) |
| Cd | 128.36  | 144   | 119   | 127.6| 124 | 122 | 119 | 144 | 127 | 126 | 136 | 130 | 128 | Cr(t) |
| Pb | 4.67    | 30    | 0.7   | 30   | 10 | 0.8 | 0.9 | 0.9 | 0.8 | 0.8 | 0.9 | 0.7 | 0.9 | Cr(Sin) |
| Zn | 81.4    | 90.8  | 79.0  | 79.3 | 84.3| 74.8| 90.8| 80.3| 79.0| 79.5| 81.5| 84.4| 80.2| Ni(t) |
| 2.77 | 5.6   | 0.9   | 2.8   | 2.9 | 2.6 | 2.3 | 3.1 | 0.9 | 3.1 | 3.4 | 2.4 | 5.6 | Ni (Sin) |
| 12 | 16.6   | 9.3   | 10.32 | 9.75 | 9.3 | 8.54| 16.6 | 11.2| 12.1 | 15.8 | 13.7 | 12.8 | Pb(t) |
| 41.07 | 111.9 | 0.9   | 12.3 | 8.8 | 0.9 | 26.6 | 27.7 | 55.3 | 111.9 | 70.9 | 31.9 | 64.4 | Pb(Sin) |
| 39.46 | 49.4  | 30.9  | 39.5  | 38.3 | 30.9 | 38.0 | 45.9 | 49.4 | 37.9 | 42.6 | 41.8 | 40.3 | Zn(t) |
| 13.88 | 44.6  | 0.8   | 0.9   | 0.8 | 0.8 | 0.9 | 5.4 | 6.8 | 24.9 | 29.6 | 24.1 | 44.6 | Zn(Sin) |

*HM (heavy metals), T(total), Sin(Single extraction).
4.2. Sediment samples

According to Table 3, the high positive correlation coefficient between chromium-cadmium, zinc-lead, as well as among cadmium-lead and cadmium-zinc, and a high positive correlation between lead-zinc, can be due to the close and common sources of these elements. The negative correlation coefficient between nickel and other heavy metals may be due to a different source of nickel in the sediments of the study area. Since the elements contained in the sediment can also be geogenic, it is likely that most of this element is naturally originated. But the nickel in the water samples originates from the industrial activities in the area and showed the positive correlation with other metals. In addition, the high percentages of fine-grained sediments, such as clay and silt confirm the presence of high concentrations of heavy metals and high retention of metals [8]. Factor analysis was done in order to identify associations among heavy metals and their possible sources (Table 6). Two factors were extracted explaining 94% of the total variance. Factor 1 explained 70.976% of the total variance and had high positive loadings on Cr, Zn, Pb, and Cd, which are heavy metals commonly associated with common source and factor 2 explained 23% of the total variance with high loading of nickel which can be associated with a different source of above mentioned metals.

Hierarchical analysis on heavy metal concentrations of sediment samples at sampling stations shows that samples 4, 10, 5 and 1 located close to the coast (Fig. 2) tend to cluster together and it is likely that similar factors are affecting these stations. According to Fig. 1, samples 3 and 6 located at a higher depth are in the same situation, and the rest of the stations are relatively different in terms of distance and proximity to other sampling sites. Potasznik et al. obtained similar results in 2016 [26].

4.3. Exchangeable phase

With the results obtained in Table 3, lead and zinc elements are exchangeable. For this reason, there is concern about the concentration of lead in the environment, because it can create the risks associated with bioaccumulation in marine organisms over time. The release of lead and zinc in the single extraction is not only an emphasis on the high mobility of these metals at the stations, but also these elements enter the sea mostly by human and industrial activities, which according to the effects of these two elements on living organisms, environmental monitoring of these elements is very important. High mobility and bioavailability of lead and zinc cause them to be separated from the outer surface of sediments (desorption) under the physicochemical conditions (alkaline to neutral pH), and enter the seawater and thus, the food chain. Because the lead limit for aquatics is 50 µg/L, some of the stations examined contain larger concentration of this element. In a study by Pandey et al. on sediments of the Ganga River in India, a high concentration of lead was also found in unstable parts, which can be readily available [17]. Chromium and nickel are often present in phases with low mobility, including the residual phase [4,15,16]. Also [24], studied sediment samples by sequential extraction and showed that the concentration of zinc in the exchangeable phase was significant [24]. The study by Banat (2005) on Jordanian urban soil reported a small concentration of cadmium and chromium in the exchangeable phase [1]. Based on the results of the chemical separation test, the bioavailability of heavy metals is as follows: lead > zinc > chromium > nickel > cadmium. According to Table 4, low concentrations of lead in the stations studied have the highest bioavailability and indicate the geogenic origin of nickel and cadmium.

5. Conclusion

The present study shows that heavy metals in water samples have a common source due to petrochemical, oil industries in the region and wastes produced by these industrial activities. The concentration of heavy metals in sediment samples is higher than that of water samples due to the fine-grained clay and silt sediments in which storage conditions for heavy metals are high. The results of correlation and principal component analysis show the probability of different origin of nickel with the rest of the metals. The hierarchical analysis performed on the sediment samples showed that the stations along the coastline had similar conditions for the concentration of heavy metals compared to the rest of the stations. By determining the exchangeable phases, it is possible to predict the effect of pollution on the other medium (water) at
least in a short period, which can be considered as an appropriate method for monitoring of pollution in marine systems. Due to the increasing expansion of industries and increased levels of contamination, changes in the concentration of heavy metals may be observed. Therefore, the measurement and monitoring of the heavy metals concentrations should be carried out continuously. Since the studied area is an environment for aquatics such as fish that is the main food of the inhabitants of these areas, high mobility, and bioavailability of lead and zinc can be accumulated in aquatic tissues. The consumption of oral aquatics will lead to the introduction of these elements into the human food cycle.

Acknowledgements

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Appendix.

References


