HEAVY METAL POLLUTION IN COASTAL SEA WATER OF NATHIA GALI, KARACHI (PAKISTAN)

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ABSTRACT

The metal pollution has been identified in the coastal regions of oceans and seas throughout the world. Karachi is located in the north eastern border of the Arabia Sea, lying between latitudes 24°48’ N and 66°59’ E longitude. The port and several industries are located in the Karachi city. Untreated or partially treated industrial and domestic waste waters are discharged directly or carried by several streams into the Karachi coastal water. The main sources of pollution in Karachi coastal water includes domestic and industrial waste; tanneries effluents; rainfall and associated pollutant from runoff; shipping and agricultural sources.

The present investigation was undertaken to know the levels of heavy metals (Mg, Fe, Mn, Cu, Ni, Zn, Cr, Pb, Cd, and Co) in surface and tide pools seawater of Nathia gali of Karachi coast. The concentration of Mg (1.01-7.47 g l⁻¹), Fe (0.27-1.05 mg l⁻¹), Mn (0.04-0.27 mg l⁻¹), Cu (0.05-0.43 mg l⁻¹), Ni (0.07-1.86 mg l⁻¹), Zn (0.09-1.77 mg l⁻¹), Cr (0.05-1.04 mg l⁻¹), Pb (0.43-0.62 mg l⁻¹), Co (0.24-0.52 mg l⁻¹) and Cd (0.03-0.2 mg l⁻¹) have been determined in the surface and tide pools seawater of Nathia gali coast of Karachi. The main sources of pollution are domestic and sewage outfall, direct discharge of factories and industrial effluents. The distribution of metals was not uniform in both surface seawater and tide pools seawater.

Key Word : Heavy metal, Surface seawater, Tide pools seawater, Nathia gali

INTRODUCTION

The metal pollution in the ocean is a major problem that is directly affecting the marine life and indirectly affects human health and resources. Karachi, being the natural seaport and the largest industrial city of Pakistan, located in the north eastern border of the Arabia Sea, lying between latitudes 24°48’ N and 66°59’ E longitude. In Karachi city there are about 200 million gallons sewage per day (909.05m3/day), sewage and waste water generates from industrial and municipal sources. The industrial and municipal waste inputs into the...
sea have sharply increased through the river Indus, Layari, Mali, Hub, and Windler. The most important large industries in Karachi involve metal and non metal manufacturing textiles, tobacco, food and beverages, chemicals, paints, rubber, paper and paper product, pharmaceutical and product of coals and oil that contributes approximately 99% of the total industrial pollution. That's why, the marine environment is feared to undergone a considerable trace metal contamination.

Some of such studies have been also reported by various workers in different parts of the world. Only fragmentary data are available pertaining to the specified areas. have reported the effect of Steel mill effluents on the Bakran and Gharo creeks. There is hardly any information on seasonal variation of trace metal concentration in this coastal area of Karachi. Khan and Saleem reported the trace metal (Zn Co Fe and Mn) in surface water of Karachi harbor. The main objective of present investigation was to know the levels of Cu, Mn, Zn, Ni, Mg, Fe, Cr, Pb, Cd, and Co seasonally in surface seawater and seaweed pools of the Karachi coast.

The present investigation was undertaken to know the levels of heavy metals (Mg, Fe, Mn, Cu, Ni, Zn, Cr, Pb, Cd, and Co) in seawater (surface and tide pools) of Nathia Gali of Karachi coast.

**MATERIAL AND METHODS**

The samples of seawater were collected at monthly intervals from surface and tide pools from Nathia Gali of Karachi coast. The water samples were filtered using 0.45 µm membrane (millipore) filter paper and acidified with 0.1 N HCl for further treatment. For the preconcentration of heavy metals the samples of seawater were chelated with ammonia pyrrolidine dithiocarbonate and then extracted with methyl isobutyl ketone (MIBK). The extracted sample was back extracted by evaporating the organic solvent and acidified with concentrated HCl. The atomic absorption spectrophotometer (Varian, Model AA-20) was used to analyze the heavy metals (Mg, Fe, Mn, Cu, Ni, Zn, Cr, Pb, Co and Cd). Reagent blank was treated similarly as samples using same volume of APDC, MIBK, acid and deionized water. All results are reported in mg l⁻¹ except Mg, which is in g l⁻¹.

**RESULTS AND DISCUSSION**

The concentrations of heavy metals (Mn, Cu, Ni, Zn, Mg, Fe, Cr, Pb, Co and Cd) were estimated in seawater from the two stations (surface seawater and tide pools seawater) of Nathia Gali of Karachi coast. The data reveal that the high metal concentrations were found in the pre and post monsoon season. Magnesium concentrations are shown in Fig. 1 range from 2.04-5.67 g l⁻¹ for surface seawater and 1.01-7.47 g l⁻¹ for tide pools seawater. The highest Mg concentrations were found in surface seawater in period from October to December (5.03-5.67 g l⁻¹) and in tide pools seawater Mg was high in May (6.37 g l⁻¹) and June (7.47 g l⁻¹). Beg et al. reported the same concentration of Mg in seawater in the vicinity of Layari, Gulbai, Lauxmi, Habib Ocean, and Sandspit when compared to present results.
The concentration distribution of Fe is shown in **Fig. 2**. The concentrations of Fe in seawater ranged from 0.27-1.04 mg l⁻¹ for surface seawater and 0.30-1.05 mg l⁻¹ for tide pools seawater. The Fe concentrations were high in July both in surface seawater (1.04 mg l⁻¹) and tide pools seawater (1.05 mg l⁻¹). The high iron concentration in surface seawater is due to contamination from industries and other operations. The present results showed that Fe concentration were very low as compared to Rizvi et al. who studied the influence of effluents of steel mill on Bakran creek water. However the present result for the range of Fe concentration were similar to the range of Fe concentration observed by Khan and Saleem for samples collected from Karachi harbour. The distribution of Mn is shown in **Fig. 3** ranged from 0.06-0.19 mg l⁻¹ for surface seawater and 0.04-0.27 mg l⁻¹ for tide pools seawater. The high concentrations of Mn were recorded in surface seawater in April (0.19 mg l⁻¹) and in June in tide pools seawater (0.27 mg l⁻¹). The Mn concentrations were similar as found by Rizvi et al. for the steel mill effluent from Bakran creek, Karachi and Khan and
Saleem\textsuperscript{17} from Karachi harbour. Rao and Indusekhar\textsuperscript{28} reported low value of Mn in seawater of Saurashtra coast, (India) as compared to the present study and the Mn concentration were also high when compared with previous results obtained from Plymouth and the West Coast of Scotland\textsuperscript{9}.

The Cu concentration in seawater ranged from 0.05-0.43 mg l\textsuperscript{-1} for surface seawater and 0.08-0.34 mg l\textsuperscript{-1} for tide pools seawater (Fig. 4). The Cu concentrations were higher in surface seawater in month of July (0.43 mg l\textsuperscript{-1}) and in tide pools seawater in month of April (0.34 mg l\textsuperscript{-1}). The concentration of Cu were generally higher compared to the studies from Danish sounds and Kattegat, Baltic Sea\textsuperscript{21}, Bahrain, UAE (Western Arabian Sea) and Sultanate of Oman (Gulf), water\textsuperscript{12}, Northern North Sea\textsuperscript{5}, Saurashtra coast (India)\textsuperscript{28}, Kodiyakkarai coast (India)\textsuperscript{25}, Polish zone of Southern Baltic\textsuperscript{18}, Northern North Sea and Atlantic water\textsuperscript{5,22}. However the concentrations observed are in good agreement with previous study Rizvi \textit{et al.}\textsuperscript{32} from Karachi, Pakistan in which the influence of effluents of steel mill on Bakran creek studied. The greater concentration of Cu in coastal water is due to contaminated
river water inputs. Nickel concentrations are shown in Fig. 5. It range from 0.1-0.41 mg l$^{-1}$ in surface seawater and 0.07-1.86 mg l$^{-1}$ in tide pools. The highest concentrations of Ni were found in November (0.41 mg l$^{-1}$) in surface seawater where as in tide pools seawater the highest concentrations were found in March (1.86 mg l$^{-1}$). In general concentrations of Ni were also higher when compared to other similar studies $^{9,21,28}$.

The concentration of Zn in surface seawater ranged from 0.09-0.77 mg l$^{-1}$ and in tide pools seawater ranged from 0.08-1.77 mg l$^{-1}$ (Fig. 6). The highest concentrations of zinc in surface seawater were found in November (0.77 mg l$^{-1}$) and in tide pools seawater the highest concentrations of Zn were found in July (1.77 mg l$^{-1}$). The concentrations of Zn were very high than the values recorded from Bahrain, UAE (Western Arabian Sea) and Sultanate of Oman (Gulf) water $^{12,28}$ also reported low values of Zn in seawater of Saurashtra coast, India. Pragatheeswaran et al. $^{25}$ observed low

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**Fig. 5**

**Fig. 6**

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concentrations of Zn in Kodiyakkarai coast of India as compared to the present study. The concentration of Zn was higher when compared with the results of Korzeniewski and Neugebauer\textsuperscript{18} observed from Polish zone of Southern Baltic. The concentration distribution of Cr is shown in Fig. 7. It range from Cr 0.33-1.04 mg l\textsuperscript{-1} in surface seawater and 0.045-0.54 mg l\textsuperscript{-1} in tide pools seawater. The Cr concentrations were high in surface seawater in February (1.04 mg l\textsuperscript{-1}) and in tide pools seawater Cr concentrations were high in June (0.54 mg l\textsuperscript{-1}).

The concentrations of Pb in seawater ranged from 0.43-0.62 mg l\textsuperscript{-1} for surface seawater and 0.49-0.6 mg l\textsuperscript{-1} for tide pools seawater (Fig. 8). The highest Pb concentrations were found in surface seawater in March (0.62 mg l\textsuperscript{-1}) and in tide pools seawater Pb was high in June (0.6 mg l\textsuperscript{-1}). The Pb concentrations were high in comparison with the results of Kremling\textsuperscript{19} who studied the Pb concentrations in European shelf waters and Mart \textit{et al.}\textsuperscript{22} who studied the Pb concentrations in North sea, Norwegian sea, Barents sea and eastern Arctic Oceans. The range of Pb concentrations were also very high than the range of concentrations observed from Northern North Sea\textsuperscript{5} from Polish zone of Southern Baltic\textsuperscript{18}.

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The distribution of Pb is shown in Fig. 9. It range from 0.25-0.45 mg l\textsuperscript{-1} in surface seawater and 0.24-0.52 mg l\textsuperscript{-1} in tide pools seawater during the study period. The highest concentrations of Co in surface seawater were found in February (0.45 mg l\textsuperscript{-1}) and in tide pools seawater in January (0.52 mg l\textsuperscript{-1}). Rao and Indusekhar\textsuperscript{28} reported lower value of Co in seawater of Saurashtra coast, India. The range of Co concentration observed are similar to results observed by Rizvi \textit{et al.}\textsuperscript{32} from Bakran creek, Karachi that is influenced by effluents from steel mill. The concentrations of Co were also similar to results observed by Khan and Saleem\textsuperscript{17} from the Karachi harbour. The Cd concentrations in seawater ranged from 0.03-0.15 mg l\textsuperscript{-1} for surface seawater and 0.04-0.2 mg l\textsuperscript{-1} for tide pools seawater (Fig. 10). The highest concentrations of Cd in surface seawater were found in November (0.15 mg l\textsuperscript{-1}) and in tide pools seawater in June (0.2 mg l\textsuperscript{-1}). The present results of Cd were high as compared to the results of Danish sounds and Kattegat,
Baltic Sea\textsuperscript{21}. The ranges of Cd concentrations were very high than the concentrations obtained from Bahrain, UAE (Western Arabian Sea) and Sultanate of Oman (Gulf) water\textsuperscript{5,12} reported low concentrations of Cd in the Northern North Sea as compared to present study. The concentrations of Cd were higher in the present study when compared with the results of Korzeniewski and Neugebauer\textsuperscript{18} observed for Polish zone of Southern Baltic.

There was no significant variations observed in Mg and Pb concentrations between months (F = 1.22 and F= 0.91) and stations (F = 0.08 and F=0.21) where as significant variations observed in Fe, Co and Cd concentrations between months (F = 5.34, F=7.26 and F= 6.11 respectively) and stations (F = 3.92, F=5.53 and F=4.8 respectively). The Mn concentrations showed significant variations between months (F=2.85) but there were no significant variations found between stations (F=0.01). The differences in concentrations of Cu, Ni, Zn and Cr were significant between stations (F =13.51, F= 6.96, F= 5.06 and F= 3.94}

![Graph](image1)

**Fig. 8**

![Graph](image2)

**Fig. 9**
respectively) where as not significant between months (F= 0.52, F= 1.10, F=1.33 and F= 0.5 respectively).

The correlation between heavy metals in seawater showed that there were mostly positive and insignificant correlation found in between concentration of metals where as positive and significant correlation was found in between the concentration of Mg and Fe ($r^2 = 0.704$), Mg and Mn ($r^2 = 0.580$), Mg and Cd ($r^2 = 0.836$), Fe and Zn ($r^2 = 0.574$) and Fe and Cd ($r^2 = 0.794$). It is also noted that there was no relationship observed between surface seawater and tide pools seawater metal concentrations except Fe, Mn, Co and Cd showed positive and significant correlation ($r=6.96$, $r= 0.579$, $r= 0.761$ and $r=0.799$ respectively).

The present concentrations of metals (Mn, Cu, Zn, Ni, Mg, Fe, Pb, Cr, Cd and Co) estimated were high when compared with the natural composition of seawater\textsuperscript{16,31}. The overall concentrations of total metals estimated were same in the present study when compared with the results of the previous study observed from different coasts of Karachi\textsuperscript{17,26,32}.

The concentrations Mg, Mn, and Cu were low in surface seawater as compared to tide pools seawater. It may be due to evaporation, untreated industrial, domestic, sewage waste input, mixing, upwelling and use of metals in biological activity. The results of the present work showed that there was great seasonal; variation found in heavy metal concentrations that, is due to upwelling of seawater. The high concentrations of most of the metals found in summer and low in winter northeast season. The order of heavy metal distribution was in the following descending order Mg> Fe> Zn> Cr >Pb, Ni>Cu>Co > Mn > Cd in surface seawater and Mg>Zn>Ni> Fe> Pb>Cr>Co>Cu> Mn > Cd in tide pools seawater.

**CONCLUSION**

The present results indicate that the water is heavily polluted. This is due to, direct discharge of industrial and domestic waste, industrial coolant waters, along the coast, by Layari river input and river-born trace metal, erosion of the shores and the bottom, diffusion from shelf sediment and deposition of atmospheric particulate\textsuperscript{32,33}. High concentrations of Cu, Zn, Cr, Pb and other metals in seawater of coastal areas are
also due to harbour activities such as dredging and cargo handling, the dumping of ship waste and other coastal activities. Ansari, et al., 2001 also reported that the concentration of Cu, Ni, Zn, Pb, Cr and Cd were high in sludge samples of industrial area. Considering these facts, the present data contributes as big information. Coastal areas where heavy metal pollution is high such as the present study, needs special attention because continuous pollution inventories will have adverse effect in terms of increase in toxicity levels of the marine food chain, stress on marine plants and animals, ill effect on health of inhabitants, such as fisher men and bathing tourist. Immediate remedial action is therefore required to combat pollution in marine environment of Karachi coast.

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