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Comprehensive Evaluation of Trace Metal Distribution and Pollution index in the Sediments of Coastal areas of Sindh, Pakistan

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ABSTRACT
Coastal areas of Sindh, Pakistan were selected in order to study the availability of heavy metals and their concentrations in the surficial sediments (<60µm). These soil samples were analyzed for Fe (Iron), Mn (Magnese), Cr (Chromium), Pb (Lead), Zn (Zinc), Cu (Copper), Co (Cobalt) and As (Arsenic) to examine metal concentrations in sediments. Assessment of anthropogenic pollution in sediments pollution index by Single-factor index analysis. Elemental concentration of Mn is highest in coastal sediments followed by Fe, Zn, Pb and As i.e. Mn > Fe > Zn > Pb > Co > Cu > As. This study revealed that local geology has not shown any significant influence on coastal sediments of the study area. The results of this study shows that Fe, Cr and As are the most serious pollutants in creek / beach sediments especially at Port Qasim industrial area and Ketti Bunder.
***Key words**: Distribution pattern, pollution index, trace metal*

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INTRODUCTION

Soil is not only a medium for plants to grow or a pool to dispose of undesirable materials, but also a transmitter of many pollutants to surface, ground and coastal water. So the accumulated pollutants in surface soils ultimately transported to different environmental components of coastal aquifers. Soil analysis offers advantages over water analysis for the control and detection of metal pollution in estuaries [7], although metal concentrations may also fluctuate over time [1].

Trace elements found in soils/sediments is immobilised in water and thus could be involved in absorption, co-precipitation, and complex formation [17]. Sometimes they are co-adsorbed with other elements as oxides, hydroxides of Fe, Mn, or may occur in particulate form [2]. Their concentrations in stream and coastal sediment compartments can be used to reveal the history and intensity of local and regional pollution [13]. Anthropogenic activities have greatly altered the geochemical cycle of trace metals, resulting in widespread environmental contamination [12]. The concentration in sediments depends not only on anthropogenic and lithogenic sources but also upon mineralogical composition and depositional environment of the sediments [20].

The coastal areas of Sindh present to the northern part of the Arabian Sea and specially the beaches of Karachi are among the best beaches in the world. The beaches of Karachi are almost bounded by the Hub River in the west and the Indus River in the east. The coast of Karachi can be divided into two parts; one lying on the west of the navigation channel of Karachi harbor, starting from Manora Island extending up to Cape Monze and ultimately to Makran coast beginning from Gadani beaches. The other part of the coastline is on the eastern side on navigation channel, which comprises of Clifton, Gizri and Ibrahim Haidari beaches. Discharge of toxic chemicals, over pumping of aquifer and contamination of water bodies with substance that promote algae growth are some of the today's major cause for water quality degradation.

It has been observed worldwide that the impact of anthropogenic perturbation is most strongly felt by estuarine and coastal environments adjacent to the study areas [14] as the coastal area receives significant amount of waste containing metal from municipal wastewater, garbage and industrial effluents. In the study area, heavy metals enter into aquatic ecosystems mainly from anthropogenic sources, such as industrial wastewater discharges, sewage wastewater and fossil fuel combustion [9].

The collection of soil samples for trace metals in the study area has been done to serve a basis for the planning of control strategies to achieve better environmental quality, and will as a key for an effective management of soil quality; similar extensive investigations of coastal soils have been carried out recently in many countries [23]. These soil samples were analyzed for Fe, Mn, Cr, Pb, Zn, Cu, Co and As to examine metal concentrations in sediment. Therefore, the study will attempt to evaluate the extent of heavy metal contamination from the surface to the bottom sediments and the degree to which heavy metals are influenced. The special distribution and the transportation procession of trace element in surficial sediments were studied to illustrate distinct pattern of the functional area and were plotted by Golden Software's SURFER program. The q-q plot made by SPSS, the single-factor model.

MATERIAL AND METHODS

A total twenty one samples of coastal sediments from same number of sites were collected during 2011-2012 (Figure 1) (Table 1). The estimation of the total metal concentration, from sediments was determined according to [16]. Sediment samples were taken at a depth of 0-15 cm which was quickly packed in air tight plastic bottles. Sub-samples of the material were oven dried at 500C for 48 hours and ground using mortal and pestle. Then the samples were sieved by <63 μm sieving net and 2 gm of sub-sediment sample were digested by using acids mixtures (HNO3 +, HCLO4 and HF) respectively, to obtain the total concentration of the metals in the sediments as been recommended by [2]. Precautions were taken to avoid contamination during drying, grinding and sieving. Cd, Co, Ni, and Pb concentrations were determined with Atomic Absorption Spectrophotometer.
For the single index factor analysis the mathematical expression is written as follows:

$P_{ij} = C_{ij} / S_j$

Where P_{ij} is the pollution index of the heavy metal *j* in the *i*-th functional area soil. C_{ij} is the measured contamination value of heavy metal *j* in the *i* -th functional area soil, and S_j is the background contamination value of heavy metal *j*.

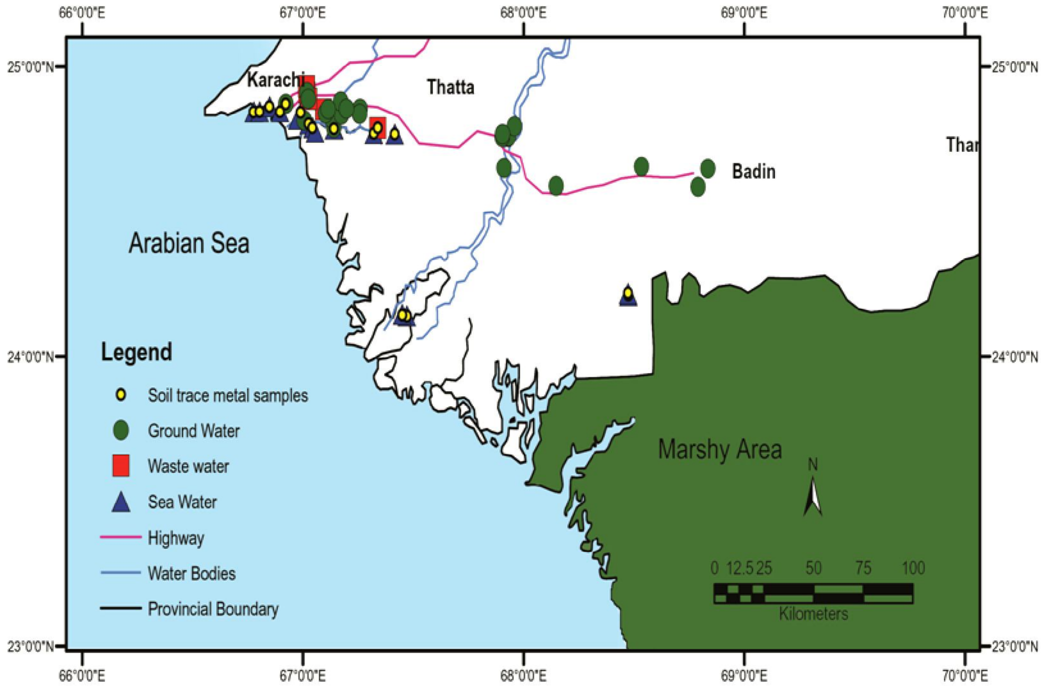


Fig 1: Map of the study area

Table No. 1: Sampling Sites during the Present Study

Sample No.	X	Y	Name of Locations
1	68°47'4.26"E	24°21'0.15"N	Qazi Muhammad, 1 Runn of Kutch
2	67°11'5.43"E	24°55'2.46"N	Qazi Muhammad, 2 Runn of Kutch
3	67°27'9.47"E	24° 8'20.63"N	Main keti Bandar (East)
4	67°27'9.59"E	24°8'0.43"N	Keti bandar 1
5	67°27'6.97"E	24°7'.78"N	Keti bandar 2
6	67°34'8.22"E	24°7'7.58"N	Port Qasim JT
7	67°33'9.03"E	24°78'7.37"N	Steel mill, Bin Qasim
8	67°3'9.91"E	24°78'7.63"N	Mazar Russian Beach, Back side of Steel Mill, Bin Qasim
9	67°14'0.41"E	24°78'4.84"N	Ibraheem Hyderi ,Korangi
10	67°02'7.72"E	24°80'3.22"N	Sea View, Hyper Star Building, Clifton
11	67°0'4.47"E	24°78'9.71"N	Sea View, Floating Ship, Clifton
12	66°58'11.15"E	24°48'13.99"N	Main Manora
13	66°58'17.29"E	24°47'48.93"N	Manora beach 1
14	66°56'41.81"E	24°48'56.98"N	Manora beach 2
15	66°98'3.42"E	24°8'3.36"N	Native Jeti Bridge, Left Side, Kemari
16	66°55'23.30"E	24°49'57.74"N	Main Sandspit
17	66°52'26.79"E	24°51'22.07"N	Main Hawks bay
18	66°50'54.48"E	24°51'40.73"N	Hawaks Bay 1
19	66°89'7.76"E	24°84'5.01"N	Hawaks Bay 2
20	66°77'5.79"E	24°84'5.51"N	Paradise Point 1
21	66°80'9.69"E	24°84'5.73"N	Paradise Point 2

RESULT AND DISCUSSION

Distribution of trace metal concentration

Contour maps of surface metal concentrations provide a simple and effective manner of presenting results of contamination investigations [4]. These maps are drawn by using SURFER software. The interpolation method used is kriging and it is done following the recommended application for a uniformly spaced numerical data set given by [21].

In the study area, heavy metal distribution in the coastal sediments exhibits three trends. Maximum values were detected in the innermost area close to Ketti Bundar, in the surroundings of port Bin Qasim and in the axial areas. Major elements (Fe, Mn, Cr, Cu, Pb, Zn and As) best reflect these trends (Fig. 2 a - e, g & h). Iron and manganese content has a peak at station no. 8 and 5 in the transect between Ketti Bundar and port Bin Qasim (Fig. 2 a & b). On the contrary, the distribution pattern of the majority of the trace elements follows only one or two of these trends. For example, Cr and Zn show highest values towards south east and south west part of the study area (Fig. 2 c & g). Copper, lead and cobalt is distributed in different way (Fig. 2 d, e & f) with the exception that distribution pattern of copper showing common pattern with both lead and cobalt. While Mn and As has shown somewhat similar distribution pattern (Fig.2 b & h) as both of these element are concentrated in the south east region of the study area at station no. 7, 8 and 9.

The Fe content showed a very high value in the inner part of the port Bin Qasim harbor (1130, 1078 and 878 μg^{-l}), but, excluding these value, mean values are approximately 190 μg^{-l} (see Fig.2a). While the Mn, maximum concentrations (912, 718 and 688 μg^{-l}) are located at coastal belt of Karachi (i.e., Ibrahim Hyderi, Hyper star building and Floating ship) corresponding to sandy areas (see Fig. 2b). Other author Shrader et al., 1977, have found highest concentrations of Mn in the sand fractions. This phenomenon is most probably attributable to Mn oxide coatings on the sand grains. It is expected that in the study area in the presence of Mn inside the calcite in the sediments indicates the accumulation of these sediments under oxic conditions [5]. Ward et al. (1995) have also found this type of association Ca ± Mn, and they suggest this phenomenon as a result of co-precipitation of a calcite-manganese phase. The distribution pattern of Mn revealed that coastal area of Karachi has highly elevated in manganese concentration (Fig.2b). So, the higher concentration of Mn is found in Karachi due to origin of the marine environment.

The contour pattern of Cr shows high values at Ibrahim Hyderi (35μg^{-l}) (Fig.2c). However, at few locations samples has a low detectable value. The anomalous distribution of Cr is attributed to its occurrence is due to release of industrial waste water discharge into stream and coastal sediments.

Cu has same distribution pattern (Fig. 2d) as of Co and Pb. The occurrence of Pb content showed a high value in the inner part of the port Bin Qasim harbor (37 and 36 μg^{-l}), but, excluding these value, mean values are approximately 17.6 μg^{-l} (Fig. 2e). This may be attributed to release of lead adsorption by marine sediments [19]. The high content of this metal in sediments have been sourced from either Pb released from death and decay of marine organisms and / or through precipitation. There is little evidence that Pb is readily lost from soil profiles by leaching. Most heavy metals, including Pb, remain in an insoluble or stable form in surface layers of sediments after application of sewage sludge. So it can be presume that in the study area the source would be geogenic from the run of sediments. By contrast, Co content (Fig.2 f) shows high values 17.9 μg^{-l} in Kemari (Native Jetty) with a minimum at Ketti Bunder (4.2 μg^{-l}). In the study area, Co tends to be co-precipitated with iron oxides and especially with manganese oxides [11]. Distribution pattern of Zn also showed the high trends in stations located in south west site of coastal area i.e., Kemari and Manora harbor (598 and 587 μg^{-l}) (Fig. 2 g), but, excluding these value, mean values are approximately 174 μg^{-l}. These stations were probably affected by industrial waste which is loaded from the industrial outlets that were located along coastline.

Arsenic (As) shows high value at Ketti Bunder (6.1 μg^{-l}) (Fig.2h). In many locations concentration of this elements have below 0.001 μg^{-l}. This element has very low detectable values in 70.2% samples collected or found at below the decimal limit, maximum concentrations of this element is found in the surroundings of the harbour area. In the study area the occurrence of As is associated with sedimentary rocks of marine origin, fossil fuels, industrial wastes, agricultural use, and irrigation practices [8].

Except Cu, Co, As and Mn, most of the metals studied shows different pattern. High concentrations of heavy metals are found in stations located in south eastern part or in the central region of the study area. This result may be due to decrease water current in these parts that causes reduce chemical interactions between metals and sediment such as: suspended solid absorption, surface sediment sorption and rate of re-deposition which is responsible an increase metals concentration. Moreover, sediment particles size is a significant parameter in effecting the heavy metal concentration because fine particles have high ability to absorb soluble heavy metals

from aquatic area and deposit them to the bottom sediment [15]. The distribution pattern may also relate to particle size because these stations which are reported more fine particles composition mostly by silt and clay. This has also been reported by Zubair A, 1993 in their study that coastal sediments have high composition of silt and clay.

Number of researchers reported that silt and clay in sediment play significant role in deposition and entrapment of pollutants during adsorption process [15]. Zn and Cr also showed the high trends in stations located in south east site of coastal area; these stations were probably affected by industrial waste which is loaded from the industrial outlets that were located along coastline. The content of As, Zn and Pb decreased from mangrove line to coastlines. The concentration of As, Zn and Pb peaked at Ketti Bunder, Kemari and port Bin Qasim because these stations are influenced both the mangrove sedimentation and industrial waste which is loading from coastline. Several researchers suggested that sediment of mangrove forests act as trap for chemical contaminates because their sediment contain high percentage of silt and clay that increase metals adsorption in these stations [22]. This is also true in our study area.

The distribution pattern of these metals shows that the fine-grained sediments are concentrated at the mouth of the estuary and near the shore of the coastal area, where the hotspots of trace metals are situated (Fig. 1a, b, c, d & e). This indicates that fine particles might be a major carrier for transporting trace metals from the upstream source area to the coastal zone. The grain size of sediments is a reflection of the hydrodynamic processes and the deposition conditions in a coastal region.

From this study it infers that the physical properties (e.g. grain size) of sediments may affect the concentration of trace metals in estuaries and coastal areas. In the study area within estuarine, the clay content of the sediments increases in the direction of the sea. On the other hand, at the coastal area, the clay content of the sediments decreases along the direction of the ocean [26]. This pattern reflects a typical sediment transport mechanism in river delta regions [10] and this is in agreement with the numerical modelling of the transport of sediments by tidal currents [6]. This demonstrates that the sediment transported into the estuarine is mainly accumulated from the Indus river outlets.

Therefore it can be say that physical transportation is not the only way to control the pattern of trace metals in the estuary and coastal mixing zone, but it also be the most important factors controlling the spatial variations of the trace metals in sediments included grain size, the chemical condition (e.g. sorption, adsorption of trace metals, flocculation, etc.) of the sedimentary environment, and anthropogenic pollution [25]. So, in the study area, the distribution of trace metals between solution and particulate materials is strongly affected by the changes in the chemical property of particles in estuaries and their surroundings of coastal area.

Elemental concentration of Mn is highest in coastal sediments followed by Fe, Zn, Pb and As i.e. Mn > Fe > Zn > Pb > Co > Cu > As. The sediments from industrial discharge sites have the highest concentrations of Fe, Mn and Zn. Mean Pb concentration is highest in port Bin Qasim and Steel Mill wastewater discharge point.

This study revealed that local geology has not show any significant influence on coastal sediments of the study area. This is due to alluvial deposits of sand, silt, gravel and clay where the large numbers of unconfined aquifers occurs, there is no effect of geology in chemical composition of coastal aquifers of the study area. Furthermore the hydrological pathways of these aquifers also demonstrate that the coastal aquifers of the study area are not influenced by the local geology.

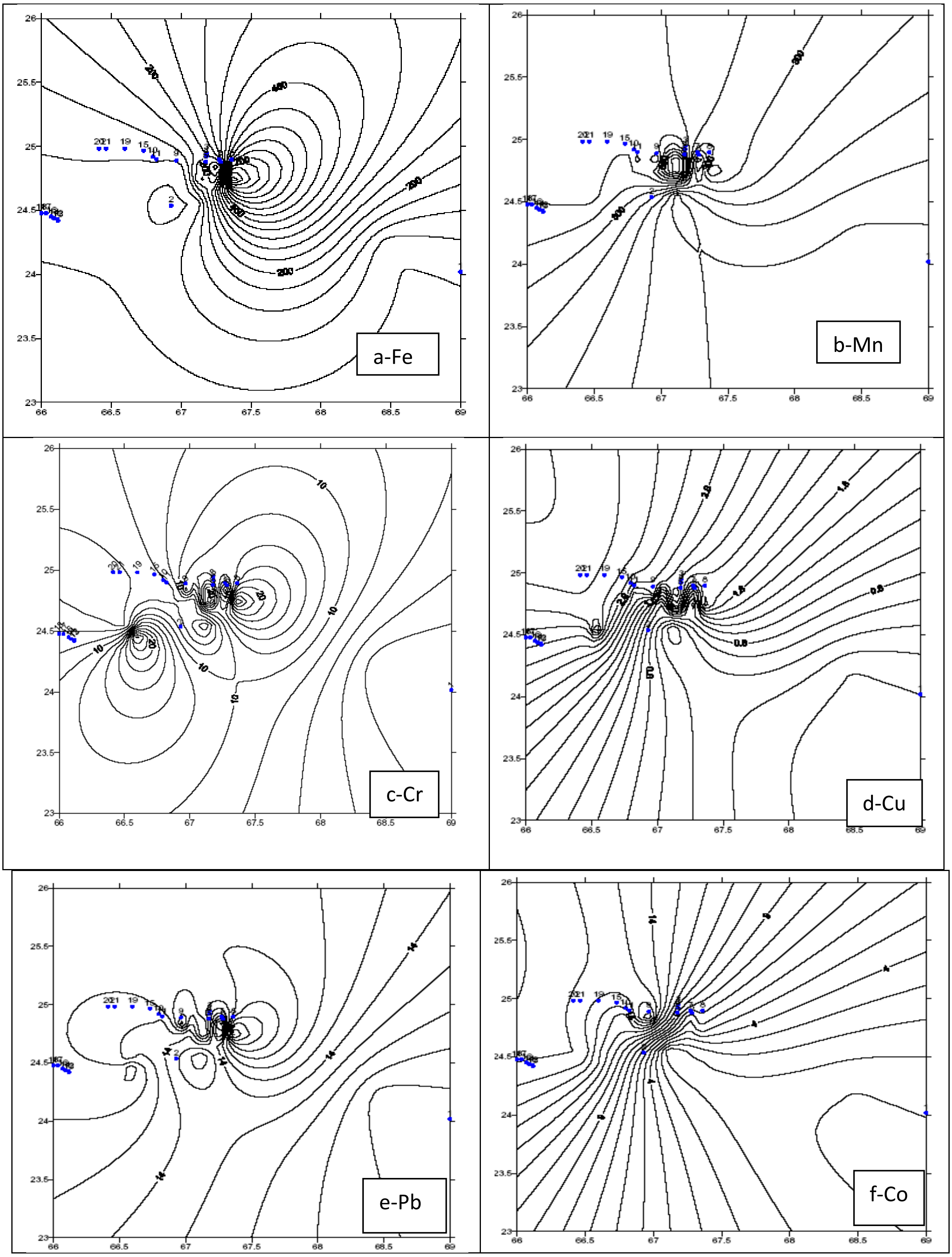
Heavy Metals Pollution

The primary purpose of sediment quality guidelines (SQGs) are to protect aquatic biota from the harmful and toxic effects related with sediment bound contaminants and is a useful tool for evaluating potential for contaminants within sediment to induce biological effects.

Single-factor index analysis

The pollution indexes of the heavy metals in each region are calculated and shown in Table 3, respectively. The single factor index evaluation method is employed to get real quantitative information of key pollution elements and excessive multiples, which is one of the most current methods used in evaluation of the degree of heavy pollution in soil. Heavy metal contaminants Fe, Mn, Cr, Cu, Pb, Co, Zn and As are numbered as 1 to 8, respectively. According to the value of P_{ij}, this can be determine which kind of pollutants exceeds and the excessive multiple in different area in the coastal belt of the province, and further determine what are the most serious pollutants and most serious regions of the pollution. According to the related information, the grading standard of single-factor is shown in Table 3.

The results of this study shows that Fe, Cr and As are the most serious pollutants in creek / beach sediments especially at Port Qasim industrial area and Ketti Bunder where the pollution index of these metals are comparatively high as the normal value (Table 3). The phenomenon indicates that there are many factories in the industrial areas of Port Qasim and Landi Industrial The result of the study further demonstrates that heavy metal pollution index, showing a state of potential contamination with respect to chromium where municipal and industrial waste received from Korangi and Landi industrial area is discharging their waste at fishing harbor. While the samples collected from beach at Paradise point, Hawksbay and Ketti Bunder (close to creek) has not shown any significant impact with respect to other trace metals except for Arsenic which is due to accumulation of vertebrate animal in sea sediment.



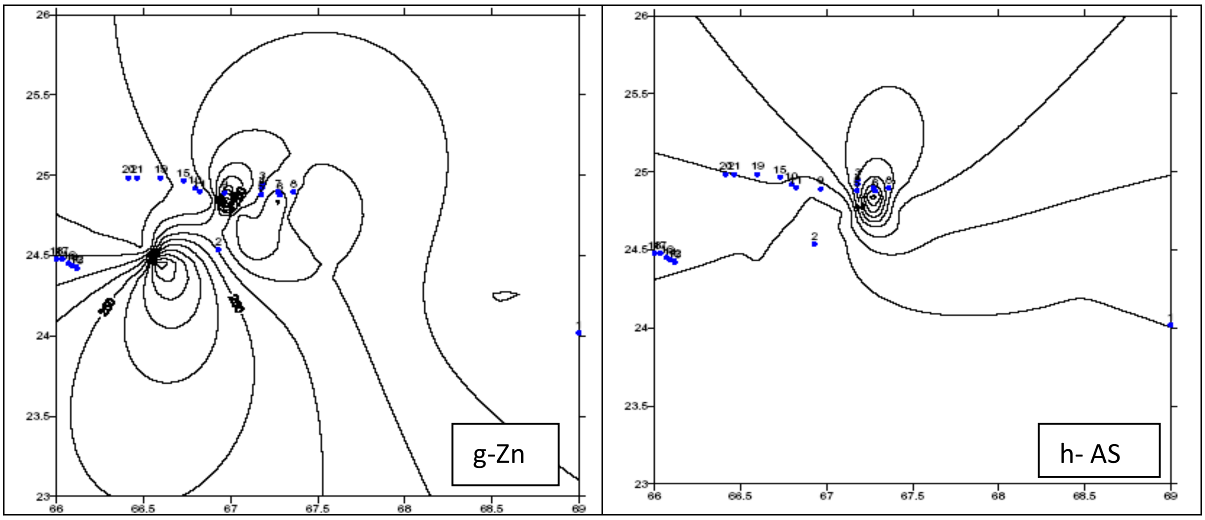


Table No. 2: The evaluation grading standards of the single factor index method

Sub -Index	$P_{ij} < 1$	$1 \le P_{ij} < 2$	$2 \le P_{ij} \le 3$	$3 \le P_{ij}$
Quality grade	clean	Potential Pollution	Slight pollution	Heavy pollution

Table No. 3: Pollution index of each heavy metal in the study area

Heavy Metals elements (mg^{-l})	Cr	Cu	Fe	Mn	Pb	Co	Zn	As
Contaminated Value (C_{1j})	0.3	0.9	56	57	2	4.5	24	4.7
Background Value (Sj)	0.3	0.9	9.2	48	2	4.2	18	1.7
Pollution Index (P_{1j})	1	1	6.1	1.2	1	1.1	1.3	3
Quality grade	Clean	Clean	Heavy pollution	Potential pollution	Clean	Potential pollution	Potential pollution	Heavy pollution

CONCLUSION

This study revealed that local geology has not show any significant influence on coastal sediments of the study area. This is due to alluvial deposits of sand, silt, gravel and clay where the large numbers of unconfined aquifers occurs, there is no effect of geology in chemical composition of coastal aquifers of the study area. samples collected from beach at Paradise point, Hawksbay and Ketti Bunder (close to creek) has not shown any significant impact with respect to other trace metals except for Arsenic**.** Except Cu, Co, As and Mn, most of the metals studied shows different pattern. High concentrations of heavy metals are found in stations located in south eastern part or in the central region of the study area. Elemental concentration of Mn is highest in coastal sediments followed by Fe, Zn, Pb and As i.e. Mn > Fe > Zn > Pb > Co > Cu > As. The results of this study indicated that Fe, Cr and As are the most serious pollutants in creek / beach sediments especially at Port Qasim industrial area and Ketti Bunder where the pollution index of these metals are comparatively high as the normal value.

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