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A QUANTITATIVE APPRAISAL OF SEDIMENT CONTAMINATION AT KARACHI COAST, PAKISTAN

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ABSTRACT

Unsustainable industrialization and exponential growth of human population in the metropolis of Karachi is responsible for extensive pollution all long the Karachi coast. The major source of pollution is the unregulated and untreated discharges of domestic and industrial effluent that is not only responsible for coastal water pollution but are being deposited in the seawater sediments and disrupting the benthic biodiversity. This study covers an extensive 2 years pollution survey of Karachi coastal water sediments at ten sampling sites to evaluate physicochemical profile of the Karachi coastal water sediments. The pollution monitoring is further supplemented by GIS studies so as to determine the spatial distribution of pollutants in the sediments. The study revealed that pH of the sampling sites is mostly towards neutral to slightly alkaline whereas the dissolved oxygen concentration was fairly low that showed high concentration of organic pollution in the sediments. The BOD levels were also higher that further confirms the continuous deposition of organic load in the Karachi coastal water sediments. COD concentration in the sediments samples were exceptionally higher that confirms the dumping of untreated industrial effluents. Similarly, theconcentration of Oil and grease, phenol and cyanide have shown alarming trends. The concentrations of nutrient parameters (Total Kjeldahl nitrogen and phosphate) also represent heavy loads of pollution entering in to the sea through municipal and industrial effluents. The concentration of heavy metals was in the order of Ni > Pb > Cd > Cr > As at the sampling locations. The present research concluded that the coastal sediments show heavy pollution loads of chemical and metal pollution that is likely to hamper the costal ecosystems. There is a dire need that strict regulations be implemented to secure costal biodiversity of the region.

Keywords: Pollutant, Toxicity, Heavy metals, Karachi, Sediments, GIS

INTRODUCTION

Marine sediments performa significant role in regulating the aquatic ecosystem. The assessment of the sediments across the globe is likely to be done to evaluate and monitor their capability to accrue most of the toxicants in aquatic ecosystem (Singare *et al.,* 2012). The aquatic biodiversity is regulated through various physical and chemical factors that involve pH, temperature, dissolved oxygen, dissolved solids, metals and minerals (Bhatt and Srinivasan, 2019).Of which the heavy metals are extremely toxic in higher concentrations but at the same time are essential micronutrients for the growth of organisms if present in lower quantities (Mamboya, 2007). The coastal environment of a country is crucially important for the economic growth as it provides various resources, biodiversity and habitats but heavy loads of pollution mostly disrupts the coastal ecosystem that ultimately affects the food chain through the process of bio-magnification of pollutants (Meiaraj and Jeyapriya, 2019). Literature indicates that contaminated seafood directly influences human health specifically those with higher quantities of heavy metals (Fialkowski *et al.,* 2009; Lim *et al.,* 2008; Erdogrul, 2006).

Marine sediments act as a sink of industrial and municipal discharged pollutants in the sea that depends on the geological, hydrological, physicochemical and biotic factors interacting together in the sea (Liang *et al.,* 2018 and Fujita *et al.,* 2014). Up to 90% heavy metals load is due to the presence of sediments and suspended matter in aquatic ecosystem that retain contaminants (Amin *et al.,* 2009 and Zheng *et al.,* 2008). The coastal sediments have the ability to immobilize the heavy metals but not in permanent way as they can migrate to seawater under certain environmental conditions. However, the process of transmission and deposition is not yet completely understood (de Souza *et al.,* 2016;Dhanakumar *et al.,* 2015 and Zhao *et al.,* 2013).

The environmental deterioration cost due to water and sediment pollution is very high, affecting the whole food chain from aquatic species to human being and continue to obstruct the ecological balance and prevailing socioeconomic conditions in a region (El-Amier *et al.*, 2015).

Karachi is the most industrialized and populous city of Pakistan having an estimated population of 22 million. The coastline of Karachi is approximately 135km with an environmentally resource-abundant area but due to domestic, commercial and industrial contamination, the coastline is overwhelmed with heavy pollution load (Shahzad *et al.,* 2009).Various studies are conducted to evaluate the levels of pollution along the coastline of Karachi (Alamgir *et al.,* 2019; Ali *et al.,* 2019; Alamgir *et al.,* 2017; Jilani, 2018, Tariq *et al.,* 2016; Jilani, 2015; Khan *et al.,* 2012).However, the data on extent of pollution load in the sediments of Karachi coastal water is very limited.

This research aims to assess the extent of Physico-chemical pollutants in the coastal sediments of Karachi city so as to develop a baseline with regards to the spatial distribution of pollutants in the sediments. The study was conducted in 2016 and 2017 that involves extensive field surveys and sampling along 10 different locations along the Karachi coast. This study will be a useful guide for regulating environmental laws by strict monitoring of unregulated industrial and domestic discharge along the Karachi coast.

Methodology

Sampling

Karachi city is situated at 24.8607ºN and 67.0011ºE at the southern region of Pakistan comprising of a population of 14.91 million (Census 2017). However, unofficial reports suggested that the population of Karachi is more than 22 million. This megacity has four main industrial zones consist of about 10 thousand industrial units i.e. SITE (Sindh Industrial Trading Estate), the KIA (Korangi Industrial Area), LITE (Landhi Industrial Trading Estate) and WWI (West Wharf Industries). Most of the industries lack wastewater treatment facilities and are discharging untreated wastewater directly into the sea without knowing the serious repercussions emerging with an alarming threat (Khan *et al.,* 2012).With these formal industrial units, there exists a sizeable number of informal industries that contribute a huge burden of waste into the sea. Commercial and municipal wastewater also contaminates the Karachi coast. Pre-identified sampling sites along Karachi coast were chosen for this research. The sample locations are presented in Fig. 1.

Samples were collected every month for a period of 2 years (2016-2017). Sediments samples were collected in clean plastic bags and kept in an ice box for further transportation to the IES, University of Karachi.

Physico-chemical analysis of sediments samples

pH and dissolved oxygen (DO) were determined through HACH Sension 156 Multi-parameter probe. APHA (2005) methods were adopted for the analysis of BOD_5 (Biochemical oxygen demand), Chemical Oxygen Demand (COD) and cyanide. Oil and grease (n-hexane extract) was determined through gravimetric analysis as reported in APHA (2005). Phenol was ascertained by photometric analysis as directed in APHA (2005).

Nutrients analysis such as Total Kjehldahl Nitrogen (TKN) and Total phosphate were estimated by distillation method followed by titrimetric analysis and spectrophotometric method using ascorbic acid, respectively.

Determination of heavy metals

The assessment of heavy metals was carried out by taking enough sample quantity in a china dish, oven-dried at 105˚C followed by addition of concentrated HNO_3. The samples were digested until convert to pale yellow or colorless. Followed by digestion, the addition of HNO_3 (5mL) and deionized water was ensured and filtration of content was done by using Whatman Filter paper no. 1. After this step, deionized water was used to make up the sample to 25ml in a volumetric flask. NOVA 60 (Merck) was then used for analysis of sample for heavy metals (As, Cr, Cd, Ni and Pb).

GIS methodology

The geo-statistical analysis was carried out in ArcGIS 10.1 version using Inverse Distance Weighted (IDW) tool through interpolation method. This tool was used to identify the distribution of physicochemical and heavy metal pollutants along the coastline. The process required vector data of boundary line of Karachi to analyze the geospatial spread followed by stated equation (Bhunia *et al.,* 2018). The points with closer distance were assigned with higher weighted impacts and vice versa.

$$Z(x_0) = \frac{\sum_i^n \frac{x_i}{h_{ij}^{\beta}}}{\sum_i^n \frac{1}{h_{ij}^{\beta}}}$$

Where,

$Z(x_0)$ = value for interpolation,

n = sample size,

x_i = i^{th}data value,

h_{ij} = distance between interpolated value and the sample data value, and

β = power of the weight

Multivariate analysis of variance

Multivariate analysis (MANOVA).of the given data set was also performed (Table 1).

Table 1.One way MANOVA table for 'k' treatments each replicated 'n' times presented in tabular form as:

	Sum of squares and product matrices	Degrees of freedom	Wilk's-Lambda	F approximation	P
Treatment	H	H=(t-1)	$\frac{\lvert R \rvert}{\lvert H+R \rvert}$	$F[ph,ab-c]$	
Residual	R	R=t(n-1)			
Total	TSum of above	t = tn-1			

Where square matrices H, R and T are $p \times p$ dimension, p representthenumber of variatesunder consideration. F is the test statistic approximation calculatedfromWilk_s-lambda and P is the probability.

RESULTS AND DISCUSSION

A neutral to alkaline pH of coastal sediments has been shown over the study time period i.e. 7.6-7.73 (2016) and 7.29-7.57 (2017) as displayed in Table 2. Whereas, the average sediments is high in 2016 i.e.7.66 as compare to2017 with minimum standard deviation (0.05).This suggests pH of coastal sediments is consistent in the year 2016, low coefficient of variation also confirm this result. A kind of related sediment findings have also been observed from the southeast coast of India (Santhanam and Premkumar, 2017).It is evident that highly alkaline pH is responsible for causing the mobilization of heavy metals from sediments that cause more serious pollution effects on marine species (Hong *et al*., 2011).

The DO concentrations found in coastal sediment samples were in a range of 1.54 to 1.92 in 2017 and 1.34 to 2.33 mg/kg in the year 2016 (Table 2). DO concentration decreases from 2016 to 2017 as both measure of statistics average and standard are minimum in the year 2016.This shows low DO concentrations during the study period is likely due to elevated levels of domestic and industrial effluents contamination which is confirmed by the sampling sites S-6 to S-10. However, global warming is one more reason of exceptionally low levels of DO in oceans throughout the world (Song *et al.,* 2019).

There exists municipal and industrial sources of pollutants that rise the BOD and organic pollution levels across coastal region (Kiran and Ramaraju, 2019).The range of mean BOD concentration around study area was 496.2 to 611.8 mg/kg (2016) and 451.3 to 608.1 mg/kg (2017). The estimated maximum BOD level was detected from S-7 in 2016**,** whereas, minimum from S-4 in 2016.Beside this both average value of BOD and coefficient of variation are minimum in 2016 reflecting that the level of BOD increases in 2017. As discussed earlier, lower DO levels (Table 2) represent the high loads of organic pollution in the studied samples of sediments. Low oxygen levels and high BOD load have inhibited the aquatic lives. Another study conducted in the same region i.e. Karachi, verified the high BOD concentrations in sediments i.e. 1645.3mg/kg reported by Alamgir *et al.* (2018).

Table 2 shows the results of COD concentration in the sampling sites. The mean minimum COD levels reported from S-8 i.e. 1275 mg/kg (2016) while mean maximum COD levels are reported from S-7 i.e. 2010 mg/kg.

Contrarily, the year 2017 shows considerably higher concentrations i.e. minimum COD level is 1933 mg/kg while maximum COD concentration is 2641 mg/kg. There is a great contribution of both biodegradable and non-biodegradable organic pollution in high COD content in the marine and coastal sediments. The present results corroborate the findings of Alamgir *et al.* (2019). However, Alamgir *et al.* (2019) showed elevated levels of COD as compared to the present findings.

Living organisms are adversely affected by lowest levels of cyanide as it is highly lethal but in the present study, cyanide analysis surprisingly show a concentration of 3.81 mg/kg from S-4 site in the year 2017. The mean cyanide concentrations are found to be 0.48 to 0.98 mg/kg and 0.53 to 0.93 mg/kg in 2017 and 2016, respectively. Moreover, the average concentration of COD increases in 2017 while the minimum value of standard deviation reflecting the presence of COD is consistent throughout the year. On contrary, the average of cyanide concentration increases with high variability in 2017. Therefore, Karachi shipyard waste, chemical industries' illegal dumping and many other tracks promote the cyanide presence at the coastal sediments of Karachi.

Oil pollution is not a new phenomenon at Karachi coast. Again, the reason is negligence and lack of strict regulatory actions against untreated industrial and municipal discharges at coastline and accidental oil spills as well. It is well-studied that oil degradation takes lots of time and resources to treat but the degradation rate is not easy to determine due to its intricate complexity and the composition of oil and other petroleum products (Zahed*et al.*, 2010). It can be seen in Table 2 that oil concentration was higher in the studied period. In India, a study reported relatively higher contents of oil and grease near thermal power plant i.e.62-86 mg/g (Jeyageetha and Kumar, 2016). The bacteria found in marine sediments are known for their pronounced role in oil degradation (Dwinovantyo *et al.*, 2016). The amount of oil and grease is quite alarming in the bottom deposits of Karachi coastal water. Oil and grease forms thin film over the sediment that prevents the entry of DO. Such condition is lethal for benthic biota.

Phenolic compounds mainly pollute the sediments through marine based and land based sources of contamination. Phenolic compounds and the related substances are seemed to be highly toxic to aquatic species because of their endocrine disruption properties (Ramos *et al.,* 2009). In our study, the mean annual phenol concentration was in a range of 3.76 to 5.81 mg/kg for the year 2016 and 4.17 to 5.05 mg/kg for 2017. The coastal contamination sources of phenols are mainly industrial effluents from steel manufacturing, petroleum, chemical industries, pharmaceutical, paper and pulp mills, paints, metal industries etc. (Navarro *et al.,* 2008). In Karachi coastal water the prominent sources of phenol could be the petroleum refineries, effluent form Pakistan steel mills and the effluent of other industrial units.

The mean minimum value of total phosphate for the two consecutive study years was from sampling site S-1 where 7.16 mg/kg was found in the year 2016 whereas the maximum value recorded in 2017 from S-9 i.e. 9.14 mg/kg. In the study area, one of the typical sources of phosphate are inorganic fertilizers that have extensively used for agriculture purposes in the suburbs of Karachi. The presence of phosphate fertilizers and phosphoric acid contamination due to industrial discharges, cause high levels of phosphorus at the Gulf of Gabes sediments, Tunisia(Ayadi *et al.,* 2014). Eutrophication is another consequence of excessive phosphate adversely affect the marine ecosystem, which with abnormal algal growth intoxicate the marine life (Roy *et al.,* 2013).Point sources of phosphates can be managed by physical, chemical and biological method for treatment whereas remediation methods for non-point sources involve constructed wetlands, riparian belts and buffer zones (Sumathi and Vasudevan, 2019).It is also perceived that the average concentration of Phenol and Phosphate increase in 2017,having low variability but the average concentration of oil and grease decrease in 2017 with low variability.

The Total Kjehldahl Nitrogen (TKN) in sediment samples were found to be in a range of 65.37 (S-7) and 70.36 mg/kg (S-6) in 2017 but the maximum and minimum concentrations in 2016 were set up as 64 (S-10) and 73.04 mg/kg (S-1). El-Amier *et al.,* (2015) noticed the less significant nitrogen amounts i.e. 31.6 mg/kg from Egypt. The major cause of TKN in coastal sediments of Karachi is likely to be the untreated municipal sewages.

Heavy metal, a great ecological concern, enters in the ecosystem through natural and anthropogenic sources. These toxic metals release directly to the aquatic bodies through atmospheric deposition, domestic and agricultural run-off and industrial discharges (Förstner and Wittmann, 2012). Literature specifies the toxicity of heavy metals on living organisms as they are able to disrupt the normal functions and have ability to transform the properties of water and exposed them to lifelong threats (Yılmaz and Sadikoglu, 2011).

Organic Arsenic (As), a highly toxic form, formed by interaction of sulfur and organic matter in the effluent discharged to the sea. Organic As is considered to be the one having high affinity form complexes with the stated compounds and create thio-arsenic species (Sharma and Sohn, 2009).ASTDR, (2019) presents the toxicity ranking of arsenic in the 'Substance Priority List' as it is the first among hazardous substances. In Karachi coast sediments samples, mean levels of As were observed between 0.07-0.15 mg/kg in 2017 and 0.08-0.14 mg/kg in 2016. However, the minimum concentrations over the year increase gradually. In Saudi Arabia, a similar study showed As levels of 1.65 mg/kg from sediments of Al-Khobar coastline (Alharbi *et al.,* 2017). Anthropogenic sources are the major culprits of As concentrations in the environments that include smelting and mining activities, glass manufacturing and cancer drugs, agricultural sources like fertilizers and fossil fuel combustion (Mandal and Suzuki, 2002).These could also be the possible sources of As except mining for the present study.

Table 2. Descriptive statistics of physicochemical analysis of the sediment samples at Karachi coast (2016 & 2017).

	Parameters (mg/kg)	**Min**	**Max**	**Mean**	**Stand. Dev**
2016	pH	7.6	7.73	7.66	0.05
	DO	1.34	2.33	1.73	0.28
	BOD	496.2	611.8	560.3	35.66
	COD	1275	2010	1527.8	206.39
	Cyanide	0.53	0.93	0.648	0.135
	Oil and grease	35.01	52.55	45.6	6.07
	Phenol	3.76	5.81	4.57	0.74
	Phosphate	7.16	8.66	7.89	0.523
	TKN	64	73.48	70.39	3.378
	As	0.08	0.14	0.09	0.019
	Cr	0.11	0.16	0.14	0.018
	Cd	0.07	0.16	0.11	0.028
	Pb	2.68	4.49	3.46	0.623
	Ni	5.33	8.21	7.49	0.831
2017	pH	7.29	7.57	7.417	0.08
	DO	1.54	1.92	1.71	0.13
	BOD	451.3	608.1	520.56	44.78
	COD	1933	2641	2275.8	264.63
	Cyanide	0.48	0.98	0.694	0.184
	Oil and grease	36.36	43	40.3	2.03
	Phenol	4.17	5.05	4.74	0.289
	Phosphate	7.99	9.14	8.66	0.318
	TKN	65.37	70.36	67.27	1.983
	As	0.07	0.15	0.08	0.025
	Cr	0.06	0.08	0.07	0.007
	Cd	0.08	0.12	0.09	0.015
	Pb	3.02	4.19	3.63	0.37
	Ni	7.44	8.41	7.88	0.309

Table 3. Multivariate Tests[a]

Effect		Value	F	Hypothesis df	Error df	Sig.
Intercept	Pillai's Trace	.999	25042.448[b]	14.000	217.000	.000
	Wilks' Lambda	.001	25042.448[b]	14.000	217.000	.000
	Hotelling's Trace	1615.642	25042.448[b]	14.000	217.000	.000
	Roy's Largest Root	1615.642	25042.448[b]	14.000	217.000	.000
Sites	Pillai's Trace	.953	1.903	126.000	2025.000	.000
	Wilks' Lambda	.340	2.011	126.000	1672.032	.000
	Hotelling's Trace	1.237	2.113	126.000	1937.000	.000
	Roy's Largest Root	.553	8.891[c]	14.000	225.000	.000

Note: Author's calculation

a. Design: Intercept + Sites; b. Exact statistic; c. The statistic is an upper bound on F that yields a lower bound on the significance level.

Table 4. Output of Multivariate Analysis of variance of the sites.

Source	Dependent Variable	Type III Sum of Squares	Df	Mean Square	F	Sig.
Intercept	pH	13679.54	1	13679.54	266919.1	0
	DO	705.997	1	705.997	2231.882	0
	BOD	71727040	1	71727040	5469.104	0
	COD	8.42E+08	1	8.42E+08	1393.493	0
	CYANIDE	111.166	1	111.166	364.098	0
	OIL	433052.2	1	433052.2	3894.922	0
	PHENOL	4881.804	1	4881.804	3772.559	0
	PHOSPHATE	16184.7	1	16184.7	7289.695	0
	TKN	1131857	1	1131857	16895.51	0
	As	1.921	1	1.921	344.953	0
	Cr	2.814	1	2.814	939.601	0
	Cd	2.69	1	2.69	472.763	0
	Pb	3035.117	1	3035.117	2501.908	0
	Ni	14241.31	1	14241.31	11111.5	0
Sites	pH	1.22	9	0.136	2.644	0.006
	DO	3.872	9	0.43	1.36	0.207
	BOD	333403	9	37044.78	2.825	0.004
	COD	6673007	9	741445.2	1.227	0.279
	CYANIDE	1.501	9	0.167	0.546	0.84
	OIL	1715.268	9	190.585	1.714	0.087
	PHENOL	40.215	9	4.468	3.453	0.001
	PHOSPHATE	32.641	9	3.627	1.634	0.107
	TKN	1742.749	9	193.639	2.89	0.003
	As	0.036	9	0.004	0.722	0.689
	Cr	0.018	9	0.002	0.651	0.753
	Cd	0.074	9	0.008	1.446	0.169
	Pb	44.482	9	4.942	4.074	0
	Ni	26.872	9	2.986	2.33	0.016

Table 5. Output of one way ANOVA of sampling sites.

SITE	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
F-VALUE	223.13	172.35	155.31	182.45	119.91	114.83	141.3	191.05	136.73	136.73
P-VALUE	0	0	0	0	0	0	0	0	0	0

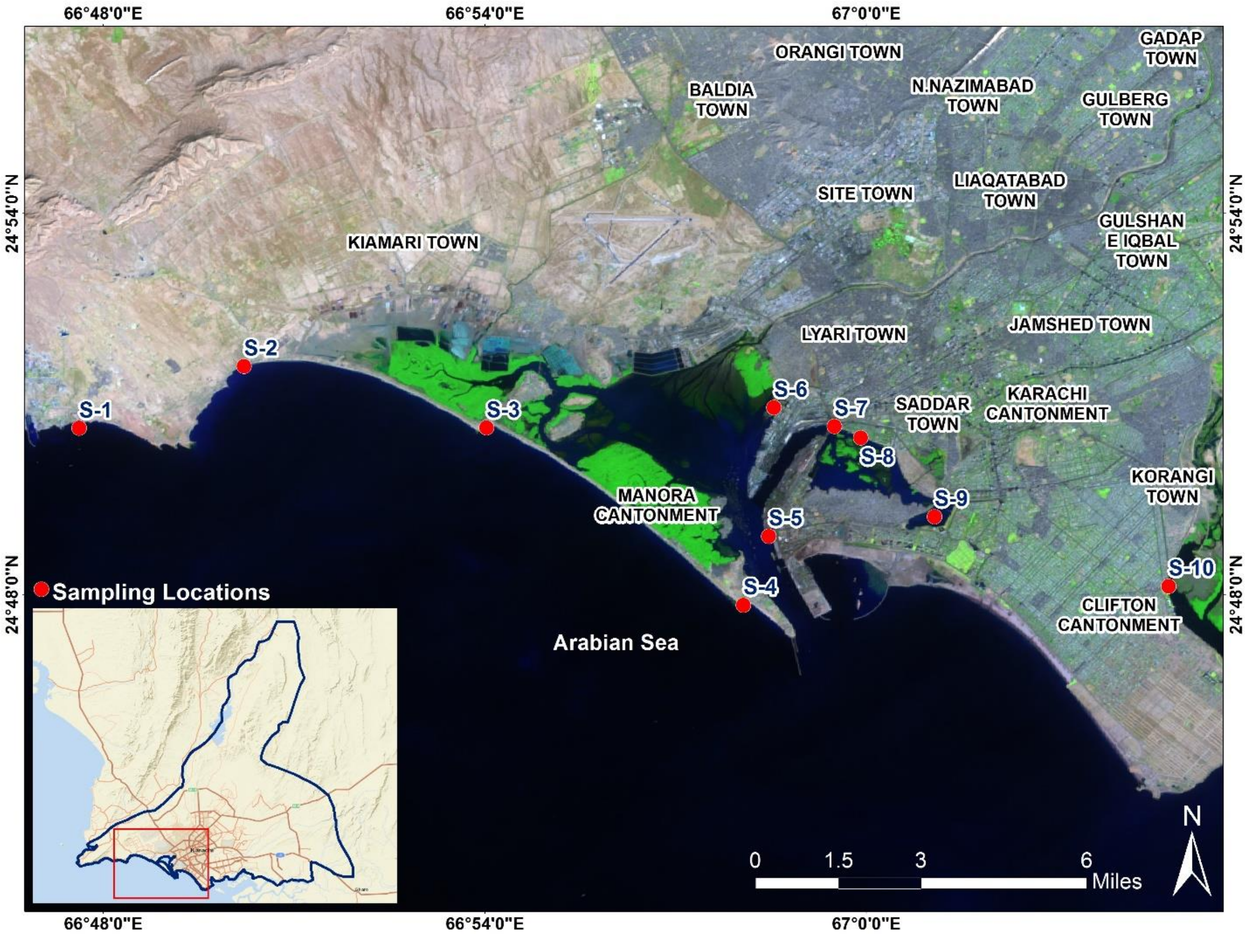

Fig. 1. Study area map represents sampling sites.

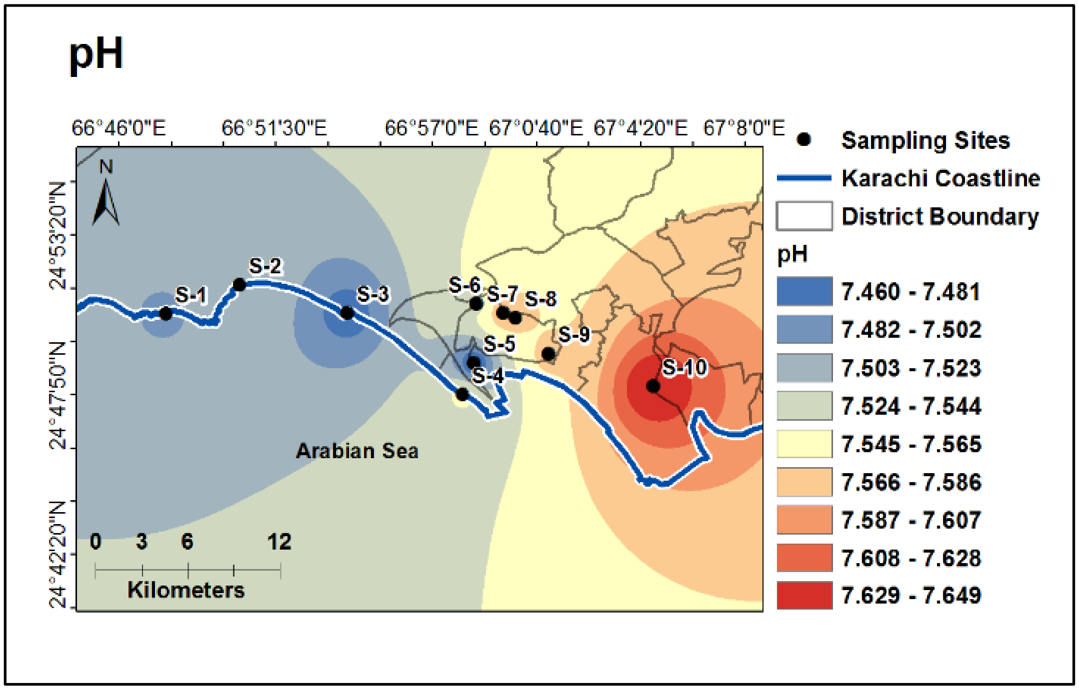

Fig. 2. Two years (2016-2017) average concentration of Physical parameter (pH) based on GIS.

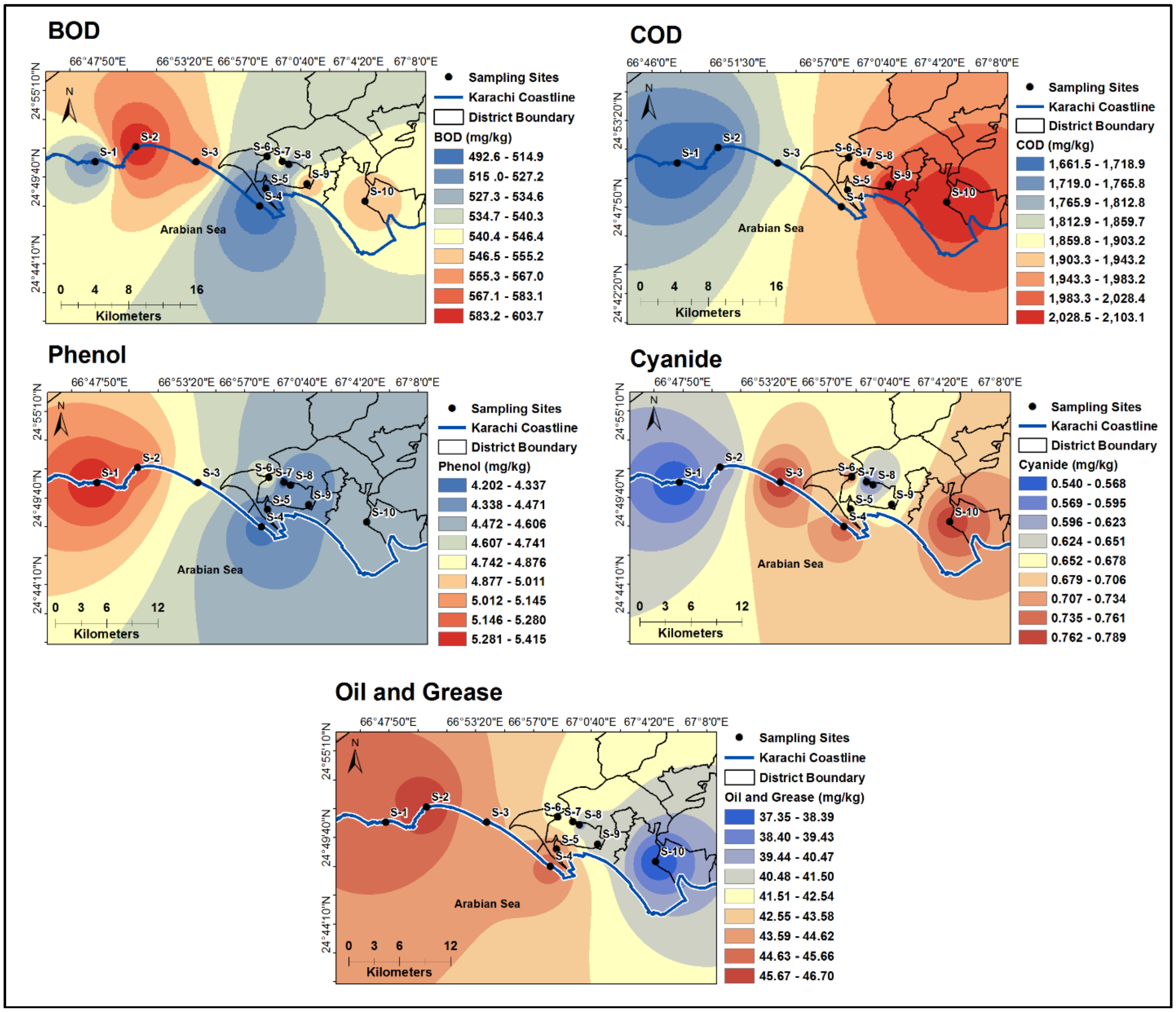

Fig. 3. Two years (2016-2017) average concentration of Chemical parameters (BOD, COD, Phenol, Oil and grease and Cyanide) based on GIS.

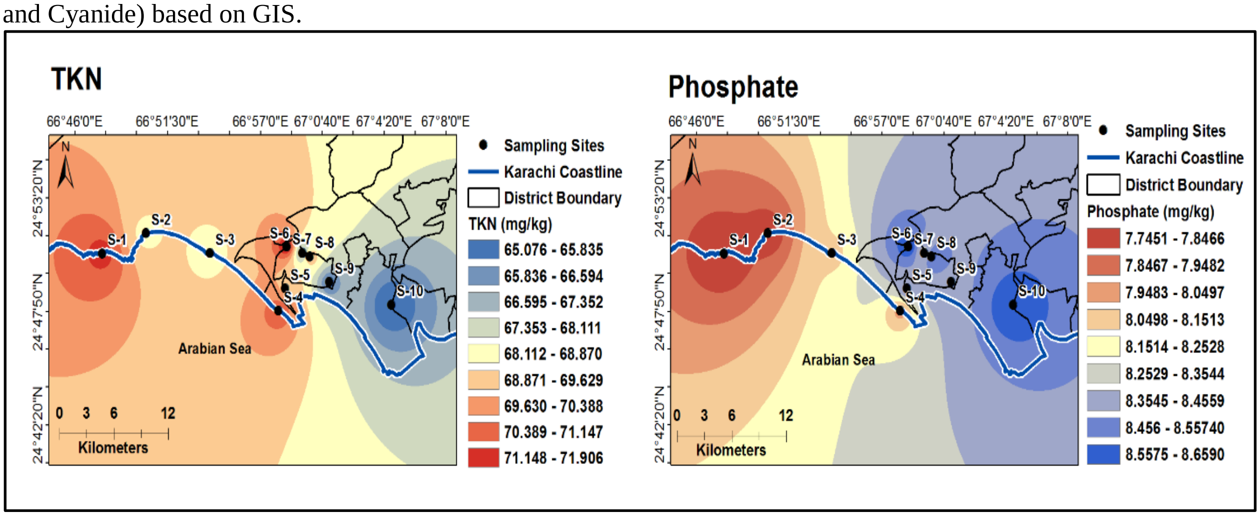

Fig. 4. Two years (2016-2017) average concentration of nutrients (TKN and Phosphate) based on GIS.

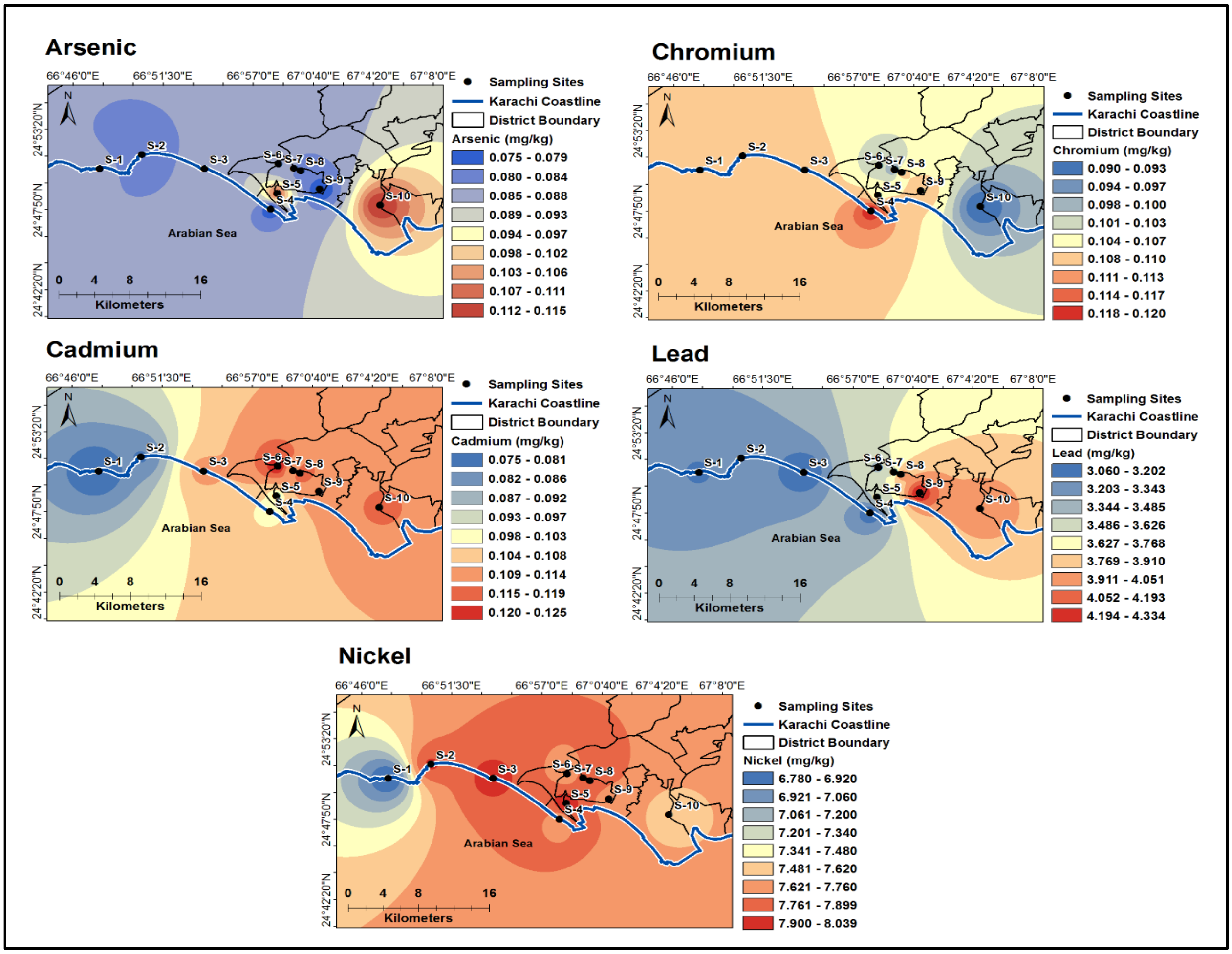

Fig. 5. Two years (2016-2017) average concentration of heavy metals (As, Cr, Cd, Pb, Ni) based on GIS.

Chromium, a heavy metal with frequent uses in metallurgical industries(in the production of metal and alloy), chemical industries, tanneries and foundries (Dhal *et al.*, 2013).This study documented the Cr concentration in a range of0.06 to 0.08 mg/kg in 2017but was increased in 2016 i.e.0.11 to 0.16 mg/kg. Contrarily, the Cr levels at Morocco were far higher than our study i.e. 150.97 mg/kg due to various sources (natural + anthropogenic)(Omar *et al.*, 2015). Rahman and Singh (2019) stated few disruptions in living organisms by Cr as renal failure and tubular necrosis but Cr has mutagenic and carcinogenic effects as well. In Karachi, a large number of tanneries are situated in Korangi Industrial area. The major source of Cr in the sediments of Karachi coastal area could be the effluent generated from tanneries. Such effluent ultimately finds its way to the Karachi costal area without any treatment. It is found from the empirical analysis that the average concentration of TKN, As, Cr and Cd showed a decline in 2017. Subsequently, the TKN, Cr and Cd based on coefficients of variation show a consistency. On contrary, a significant changes is found in the variability of As.

A slight variation in Cd concentration can easily be seen at sediment analysis of Karachi coast i.e. in 2016, the mean minimum concentration was found to be 0.07 mg/kg and maximum 0.16 mg/kg but in 2017, it was in a range of 0.08-0.12 mg/kg. The monthly highest concentration was found from the S-10 sample i.e. 0.359 mg/kg in 2016. Neighboring country also present comparable coastal pollution situation in which 3.8 mg/kg Cd was quantified (which is much higher than our results) from east coast sediments in Tamil Nadu, India (Harikrishnan *et al.*, 2017). Moving towards the sources of sediment pollution, we found that Cd can enter through various anthropogenic activities such as Ni-Cd batteries, fertilizers, stabilizing, mining, incineration and fossil fuel combustion. Cd causes respiratory system and bones toxicities including pulmonary edema, pneumonitis, bronchitis, anemia and osteoporosis (WHO, 2010).

The average concentration of Pb is presented in Table1, in a range of 2.68-4.49 mg/kg in 2016 and a slight higher levels in 2017 i.e. 3.02-4.19 mg/kg. Considering the health effects of PB, these concentrations are enough to cause disruption in the food chain affecting not only coastal species but human being as well. A similar situation can also be seen at Red sea coast, Egypt where 3.9 and 10.9 mg/kg concentrations of Pb were found (Uosif *et al.*, 2016).

The present study identified the Ni concentrations in the sediments of Karachi coast is far exceeding the permissible limit i.e. in 2016 it is highest with 8.21mg/kg (S-5) and lowest 5.33 mg/kg (S-1) but in 2017, it is in a range of 7.44 (S-7) to 8.41 (S-3) mg/kg. Omar *et al.*, (2015) quantified that up to 79.89 mg/kg Ni in Moroccan coastal sediments but the reasons were geographical location and the natural sources of Nickel. A recent coastline study conducted at Karachi, also specified the life of aquatic species threatened by higher levels of nickel (Ali *et al.*, 2019).

Pollutants distribution based on GIS

The distribution of pollutants in this two year research is based on interpolation tool of GIS to map the average concentration of each parameter. Fig 2 to 5 show the maps of all physical, chemical, nutrients and heavy metals pollution distribution in the study area. The highest pH average of all the studied years was found from the site S-10 i.e. Creek Avenue (Fig. 2) and change in pH cause variation in the metal release and sequestration rates from the sediments (Atkinson et al., 2007).DO shows lowest 2 years-average values for S-2 (adjacent to Jamali Goth) due to a reason that this location receives high organic debris and effluents from nearby suburbs (Somar goth, Ismail Mubarak Goth, Ramzan goth etc.), restaurants and picnic spots (Hawks bay beach) that cause lowering of dissolved oxygen and highest BOD i.e. 604.15 mg/kg as seen in Fig. 3. For COD, heavy loads of pollution can be observe at the sampling site S-9 near Boat basin whereas oil/grease and phenol depict for S-2 (46.73 mg/kg) and S-1 near Arabian road (5.42 mg/kg), respectively. The sources of aforesaid parameters are the various industrial releases, ships activities, petroleum industries and oil spills in nearby locations because of the two industrial areas i.e. SITE and KIA. The sampling site adjacent to Arabian road receives effluent from Kemari, nuclear power plant and fertilizer industry. Cyanide average maximum concentration was 0.79 mg/kg from Kakapir adjacent area (Fig. 3)mainly due to industrial discharges from SITE industrial area that comprised of organic chemical, electroplating and metal industries and informal sectors that release cyanide in the effluent.Highest mean phosphate and TKN concentrations have been reported as 8.66 mg/kg and 71.92 mg/kg from Karachi Fish harbor adjacent area (Fig. 4) because of metabolic waste produced by fishes in this zone.

For heavy metals assessment, the trends show higher levels of As from Creek Avenue i.e. S-10 (0.115 mg/kg) and Cr from Manora i.e. S-4 (0.12 mg/kg)as illustrated in Fig. 5. Cadmium from Karachi fish harbor i.e. S-6 (0.125 mg/kg) was reported as it is mainly released in sewage sludge whereas, Pb from Boat basin i.e. S-9 (4.34 mg/kg) was assessed. The highest Ni pollution at Kemari Basin estimates an average of 8.04 mg/kg due to industrial effluent, port sewage and pollution from ships. Each heavy metal has shown to be in a higher concentration for different sampling locations due to different sources of effluent discharge in the sea. The elevated levels of heavy metals disturb marine ecosystem and aquatic life as higher discharges continues from industrial activities, effluent of petroleum products, desalination plants and domestic wastewater (Pitchaikani *et al.*, 2016; Viji and Shrinithivihahshini, 2017).

Multivariate (MANOVA) and Univariate (ANOVA) analysis of variance

The univariate (ANOVA) and multivariate (MANOVA) methods are used to explore the statistical significance of intergroup differences. For the ANOVA, the null hypothesis tested is the equality of the means of the dependent variable throughout the groups. Whereas in MANOVA, the null hypothesis tested is the equality of mean vectors on multiple dependent variables all through the groups. This study investigates the statistical significance difference of the chemical among the sites under the study using MANOVA. It is important to verify model assumptions of MANOVA through Pillai's Trace, Wilks' Lambda, Hotelling's Trace and Roy's Largest Root test.

The null and alternate hypotheses used are:

H0: There is no difference in the average levels of chemical elements under consideration

H1: There are differences in average levels of chemical elements under consideration

Based on the overall multivariate test the null hypothesis is rejected as the P-values on all testing is less than $\alpha =$ 5%. Therefore, the null hypothesis is rejected and it is concluded that there is differences in average levels of chemical components among the site where the atmospheric samples were collected. Table 3 represents the multivariate tests. Table 3, indicates that that all intercepts sum of squares are significant. Furthermore, the sum of squares of pH, BOD, Phenol, TKNS, lead and Nickel are significant resulting reject the null hypothesis that mean effect of these chemical are not same on each sites. Table 3 represents the Output of Multivariate Analysis of variance of the sites. Therefore, the output of MANOVA shows that sampling sites sediments are polluted because of high concentration of PH, BOD, Phenol, TKNS, lead and Nickel which dissolved oxygen concentration.

Additionally, univarite ANOVA is applied to each site in order to further investigate due to which paired of chemical mean are significantly different. The null hypothesis is simply defined as follows:
H_0: all chemicals mean are equal
H_a: at least two chemicals mean are not equal

The output of one-way ANOVA for each site is presented in Table 4, the P-value of F-test for each site is less than the level of significant rejecting the null hypothesis. Therefore, it is found that at least two pairs of mean are insignificant. Furthermore, individual 95% CIs for Mean Based on Pooled Standard Deviation identifying that BOD and COD are insignificant. This suggested that the BOD levels and COD concentration may be one of the reasons of pollution of sampling sites. As these sampling sites consist of the coastal areas Karachi where the organic load and untreated industrial effluents are disposed of.

In the next step cluster analysis of data is performed which is one of most important quantitative method for assessing similarities of sampling sites under consideration (Romesburg, 2004). The illustrations exhibit in Fig 6 where clusters have been joined at each phase of the analysis and the distance between clusters at the time of joining (Cornish, 2007). Cluster analysis grouped the sites into clusters on the basis of similarities within a group, showing two groups. Cluster I comprises of S1 and S3 (located downstream nearest Arabian Sea of the study area) and cluster II contains sections S4 – S10 (located upstream/ far from the Arabian sea of study area). Moreover, the S-2 which is located up stream of the Arabian sea, Jamali Goth significantly different from other sites.

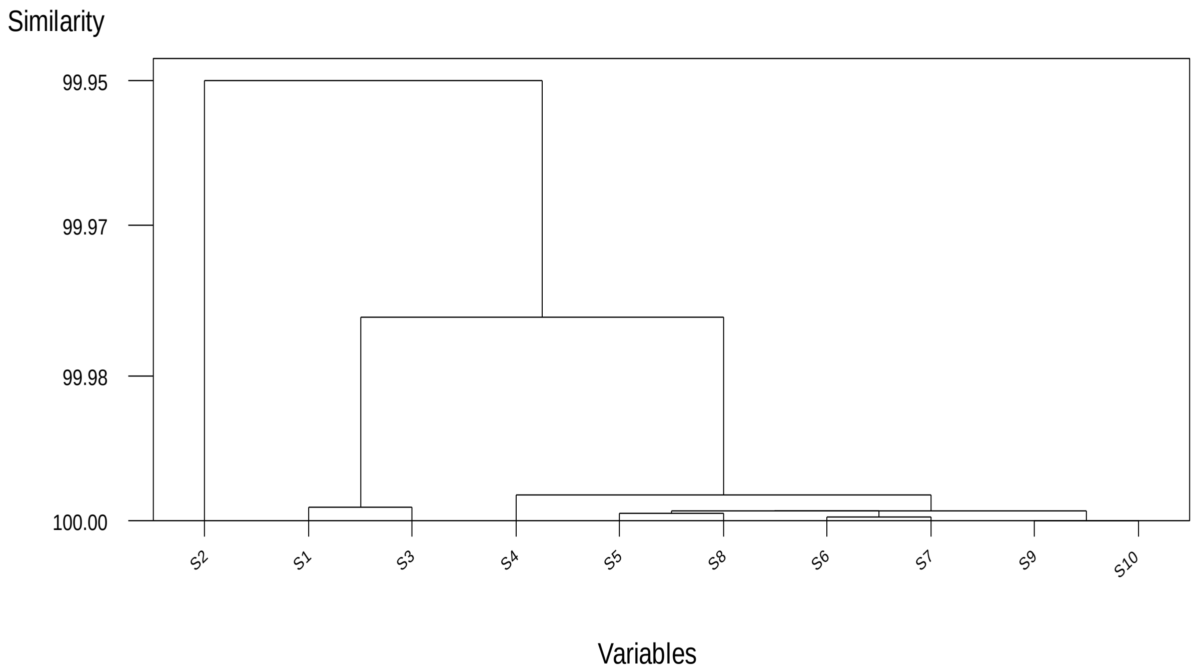

Fig. 6. Dendogram derived from unweighted pair group of 10 sampling sites along the Karachi coast.

Conclusions

This study concludes that the coastal sediments of Karachi are contaminated with municipal and industrial discharges responsible for toxicity of heavy metals in the ecosystem. Contaminated sediments are the source of environmental pollution that affects humans, aquatic life and the environment. The coastal pollution profile indicates that sediments are adversely affected by the low levels of dissolved oxygen, excessive organic pollution load and inorganic nutrients that requires strict action against illegal dumping and effective remediation strategies.

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