



Evaluation of Groundwater Quality for Heavy Metals by Using Chemical Indices Approach in Karachi, Pakistan

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Abstract

Freshwater consumption has been increased because of population growth and economic development. At the same time, depletion and contamination of groundwater is subject of great concern. Karachi is the industrial hub and serves as the economic backbone of Pakistan. The research aims to investigate the heavy metal pollution in the groundwater of Korangi Industrial Area, one of the largest industrial estates in Karachi. Eighteen representative locations were selected to collect groundwater samples and study the concentrations of heavy metals Cr, Fe, Ni, Cu, Zn, and Pb. Pollution load index, Nemerow's pollution index, and geo accumulation index approaches were used to interpret the basic data. The average concentrations of the measured heavy metals were 354.67 $\mu\text{g.L}^{-1}$, 694.33 $\mu\text{g.L}^{-1}$, 39.2 $\mu\text{g.L}^{-1}$, 12.89 $\mu\text{g.L}^{-1}$, 9.5 $\mu\text{g.L}^{-1}$, and 6.17 $\mu\text{g.L}^{-1}$ for Fe, Zn, Cu, Pb, Cr, and Ni, respectively. The results showed that groundwater quality in the study area is poor and mainly contaminated by Pb and Fe.

Keywords: Geo accumulation index, Heavy metals, Industrial effluent, Korangi industrial estate, Nemerow's pollution index, Pollution load index.

Introduction

Water is essential for all living creatures, and proper management of this renewable natural resource is a key aspect of sustainable development [1]. Groundwater resources are unevenly distributed and are under stress because of natural and anthropogenic factors [2]. There is a need to develop more sustainable practices and monitoring systems to protect these resources. The consumptive uses of groundwater for domestic, agriculture, and industrial sectors put huge pressure on natural systems in terms of quality and quantity [3]. Although, the groundwater resources are less vulnerable and protected by unsaturated zone or topsoil [4]. However, groundwater becomes vulnerable in areas with

high population density, industrial and agriculture practices, and intensive human use of the land. Industrial activities have the potential to contaminate groundwater bodies by releasing chemicals or wastes into the environment, either intentionally or unintentionally [5].

Heavy metals pollution is a well-known worldwide problem because of its toxicity, bioaccumulation, and environmental persistence [6]. Their discharge in water bodies can destroy the aquatic biota or transfer to humans through the food chain.

There are numerous potential sources of groundwater pollution, so it is often hard to

find the exact source of pollutants. Regarding heavy metal pollution, industrial wastewater is the major source of groundwater contamination [7]. Ignoring and mismanagement to handle industrial effluent is the most significant environmental problem, especially in the developing countries of the world [8]. In several megacities of developing countries, industrial waste is discarded into the soil and water bodies indiscriminately without considering the after-effects [9]. The story is not different in the case of the city of Karachi.

Over the last few decades, population and demographic distribution in Karachi have been changed dramatically. According to the 2017 census current population of Karachi is around 16 million, and nearly 5 million people live in slum areas without proper sanitation systems [10]. The city is a commercial and financial hub, plays an important role in the country's economy. Karachi has built several industrial zones such as Bin Qasim Industrial Zone, Federal B Industrial Area, Karachi Export Processing Zone, Korangi Creek Industrial Park, North Karachi Industrial Area, Pakistan Textile City, S.I.T.E Industrial Area, West Wharf Industrial Area, and Korangi Industrial Area.

Korangi industrial estate (KIE), Karachi is one of the biggest industrial estates (8500 acres) in Pakistan. This estate has been in operation since 1970. Two hundred thousand to three hundred thousand employees work in this industrial estate. It generates a revenue of Rs. 270 million per day. This industrial estate serves as the pillar of Pakistan's economy.

Anthropogenic sources of pollution and their impact on groundwater are reported from different areas of Karachi [11-15]. This will further intensify the demand for potable water for the city. This is also reflected in industrial effluent infiltrations worldwide.

Groundwater pollution due to heavy metal ion contamination of the Korangi Industrial area (KIA) is reported as a burning issue by earlier researchers [16, 17]. The presence of industrial zone and demand for fresh water is equally important; therefore, it is necessary to check and monitor the wastewater discharge in terms of its quality to protect the groundwater contamination. The current study evaluates the groundwater quality regarding heavy metals in and around the groundwaters of KIE by using chemical indices approaches.

Materials and Methods

Study Area

The study area (KIA) is situated in Korangi District, Karachi, Pakistan lied between 24°, 83' to 24°, 84' N and 67°, 1' to 67°, 11' E (Fig. 1). KIA is one of the major industrial areas and hosts almost 4500 industries, trading, and commercial units, including textile, pharmaceutical, chemical, steel, automobile, etc.

Sampling Approach

Eighteen representing points in the study area were selected for groundwater samples. One-litre polyethylene bottles were used to obtain samples. Samplings were done carefully to avoid any deterioration of water quality. The bottles were washed and rinsed with distilled and groundwaters before being used. The samples were acidified immediately with 1.5 mL concentrated nitric acid for metal preservation.

Trace Metal Analysis

The techniques stated in the book "Standard Methods for the Examination of Water and Wastewater" [18] for heavy metals were followed, and the instrument was spectrophotometer DR - 2800 UV VIS, HACH USA.

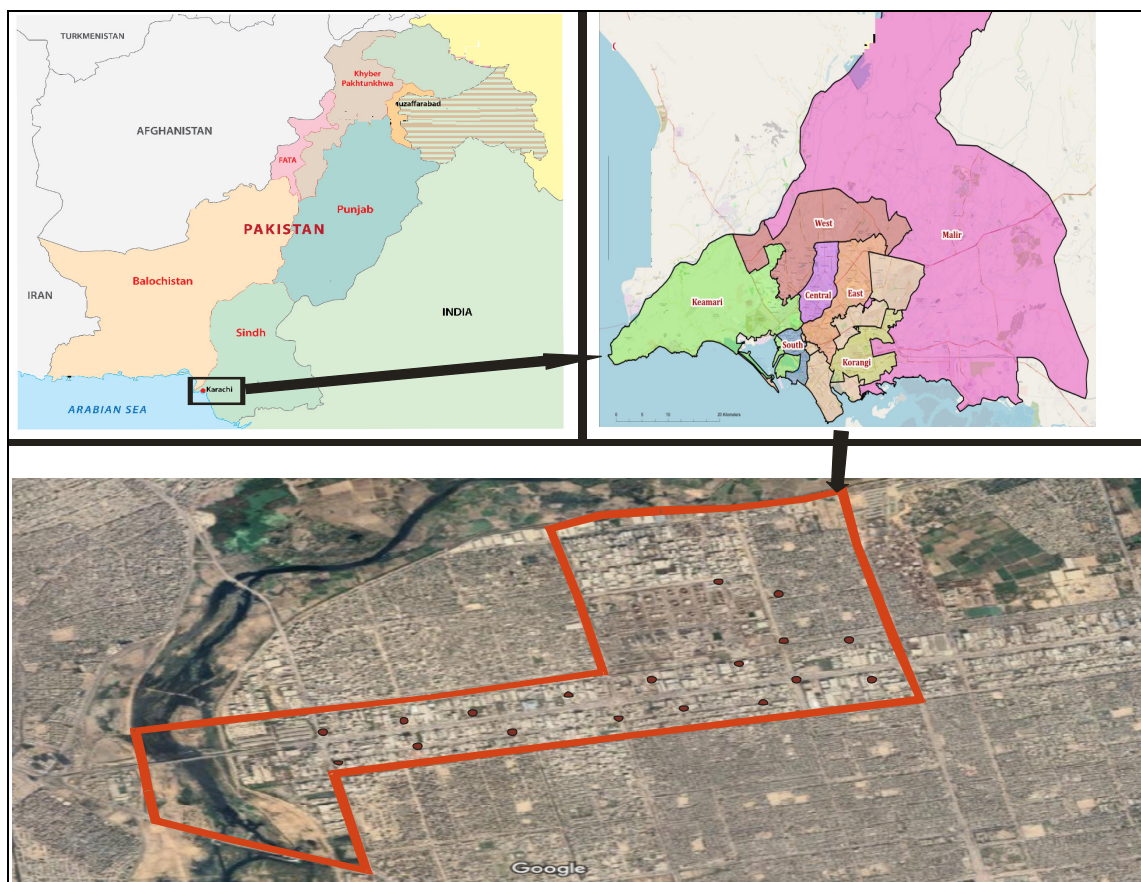


Figure 1. The location area of the research study (Korangi industrial estate, Karachi)

Statistical Analysis

MS Excel and Minitab version 11.12 were used for initial data recording, graphical presentation, and statistical analysis.

Chemical Indices

Nemerow's pollution index (NPI)

The NPI is enunciated by name that is also called the raw pollution index [19]. According to this index

$$NPI = \frac{C_i}{L_i}$$

Here, C_i = experimental concentration of i^{th} factor and
 L_i = allowable limit of i^{th} factor.

The NPI must be less than or equal to one [19].

The pollution load index (PLI)

The PLI was employed for determining the degree of pollution. The value of PLI less than one shows no pollution, whereas higher than one shows pollution.

Higher PLI values indicate high noticeable input from an anthropogenic source, and lower PLI values indicate no appreciable input. The amount of contamination in estuarine sediments was calculated by using formulae as follow,

$$CF = \frac{C_{\text{metal}}}{C_{\text{background}}}$$

$$PLI = n \sqrt{(CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)}$$

Here,

CF = contamination factor

C_{metal} = pollutant concentration in groundwater

$C_{\text{background}}$ = background value for the metals.

Geo accumulation index (I_{geo})

Contamination of heavy metal is calculated by I_{geo} method. It consists of seven grades, i.e., zero to six, which means the greater the number, the greater will be adulteration, calculated as:

$$I_{\text{geo}} = \log_2 \frac{C_n}{1.5 B_n}$$

Here,

C_n = concentration of metal in the enriched samples

B_n = background value

1.5 = a factor that minimizes the influence of positive variation in background values.

Results and Discussion

Heavy Metals Examination

The impact of anthropogenic heavy metal pollution was evaluated using NPI, PLI, and I_{geo} at 18 sampling sites of KIE. The current study indicates that these methods are convenient and valuable for the determination of contamination in groundwater.

Descriptive statistical analysis of heavy metals values generated and presented in Table 1. This data was compared with National Environmental Quality Standard, Pakistan (NEQS) and World Health Organization standards (WHO) in Table 2 [20]. The Fe range was 165 to 770 $\mu\text{g.L}^{-1}$ with a mean value of 355 $\mu\text{g.L}^{-1}$. Similarly, the

range for Zn was found to be 385 to 1672 $\mu\text{g.L}^{-1}$ with 694 $\mu\text{g.L}^{-1}$ as a mean value. Contents of Cu, Pb, Cr, and Ni in $\mu\text{g.L}^{-1}$ were estimated in the range of 1 to 141, 7 to 33, 4 to 46, and 2 to 13, respectively. Their mean values were 39, 13, 9 and 6 $\mu\text{g.L}^{-1}$, respectively. A critical study of Tables 1- 2 and Fig. 2 revealed that nine and five groundwater samples have higher concentrations set by WHO and NEQS for Fe (300 $\mu\text{g.L}^{-1}$) and Pb (10 $\mu\text{g.L}^{-1}$), respectively.

Table 1. Heavy metal concentration in groundwater of Korangi industrial estate, Karachi.

Samples No.	Fe	Zn	Cu	Pb	Cr	Ni
	$\mu\text{g.L}^{-1}$					
GW ₁	199	492	73	09	09	07
GW ₂	320	628	19	10	11	05
GW ₃	187	407	16	26	11	07
GW ₄	196	495	21	08	15	08
GW ₅	562	392	131	33	46	11
GW ₆	631	1285	01	08	11	13
GW ₇	246	399	15	08	08	07
GW ₈	770	1023	141	26	07	06
GW ₉	165	473	19	08	04	06
GW ₁₀	253	561	18	27	06	07
GW ₁₁	209	396	35	08	04	06
GW ₁₂	286	1672	37	09	06	04
GW ₁₃	253	1617	23	15	07	08
GW ₁₄	358	385	32	07	04	02
GW ₁₅	361	583	38	08	05	04
GW ₁₆	433	506	31	07	04	03
GW ₁₇	308	638	43	08	06	03
GW ₁₈	647	546	13	07	07	04
MAC ¹	300	3000	2000	10	50	20

Table 2. Descriptive statistics of heavy metals in groundwater of Korangi industrial estate, Karachi.

Metal	N	Minimum	Maximum	Mean	Std. Error	Std. Deviation
					$\mu\text{g.L}^{-1}$	
Fe	18	165	770	354.67	42.73	181.30
Zn	18	385	1672	694.33	97.93	415.50
Cu	18	01	141	39.20	9.08	38.54
Pb	18	07	33	12.90	2.03	8.62
Cr	18	04	46	9.50	2.26	9.60
Ni	18	02	13	6.17	0.66	2.80

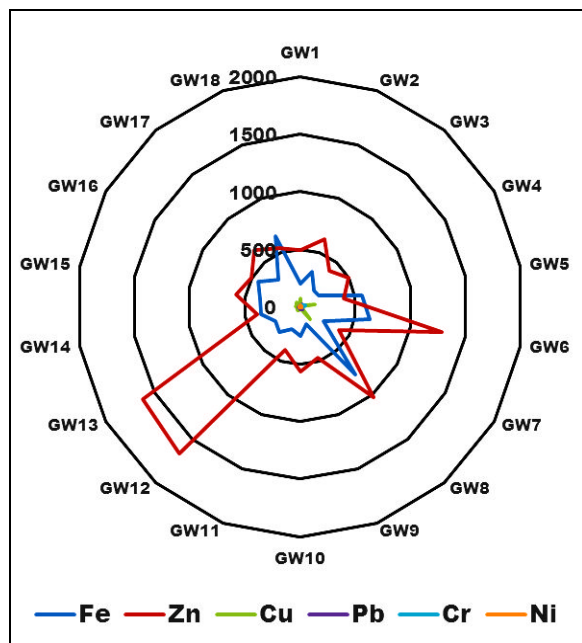


Figure 2. Heavy metals concentration in different sampling points of Korangi industrial estate, Karachi

Table 3 shows the correlation analysis between heavy metals in the groundwater of the study area. Fe and Cu showed a strong correlation with Ni ($p < 0.5$) whereas Zn had significant correlation with Cr ($p < 0.05$), Cu and Pb ($p < 0.01$). In the study area, a higher correlation between parameters indicates that these elements are moving together in groundwater from industrial sources [21]. This is possible because of the adsorption characteristic and redox condition between these variables [22].

Many researchers around the world have carried out groundwater quality in terms of heavy metals (Table 4). The current study shows that heavy metal in the groundwater of the study area follows the order $Zn > Fe > Pb$. The concentrations of heavy metals in groundwater are extremely variable and dependent on many factors. Land use and soil geochemistry are important factors for metal pollution in groundwater. The trace metals are not easily degradable as other organic pollutants [23]; thus, they persist longer, can infiltrate groundwater, tend to accumulate,

involved in absorption, chemical combination, and complex formation [24].

Table 3. Correlation among tested heavy metals in groundwater of Korangi industrial estate, Karachi.

	Fe	Zn	Cu	Pb	Cr	Ni
Fe	1					
Zn	0.413	1				
Cu	0.051	0.929**	1			
Pb	0.341	0.918**	0.013	1		
Cr	0.300	0.534*	0.026	0.011	1	
Ni	0.524*	0.449	0.655*	0.092	0.012	1

*Correlation is significant at the 0.05 level **Correlation is significant at the 0.01 level

Table 4. Comparison of current investigation with past studies

Metals	Current study	Lofti	Bekhiri	Singh	WHO
		[25]	[26]	[27]	
$\mu\text{g.L}^{-1}$					
Fe	355	120	-	250	300
Zn	694	770	148	10000	3000
Cu	39	630	241	300	2000
Pb	13	01	87	00	10
Cr	10	04	-	00	50
Ni	06	00	-	30	20

Chemical Indices

The NPI results revealed that only a few sampling points showed moderate to severe pollution problems, and their NPI values are greater than one (Table 5) [28]. It is used to measure the severity and variation of pollution in the groundwater. Results indicated that the metals' contamination factor (CF) such as Zn, Cu, Cr, and Ni in the study area is less than one. Whereas CF values of Fe and Pb are higher than one, it indicates that groundwater of the study area is contaminated concerning these metal ions, perhaps due to the influence of industrial activity and anthropogenic sources [29, 30]. The PLI values of all the sampling locations of the study area were found to be generally low (< 1). The chemical indices results show the difference in insensitivity towards the groundwater pollutant. These values

confirmed that the groundwater of the study area is facing environmental pollution for Fe and Pb. These can be due to the increased release rate of untreated industrial effluent to ground and surface water [31].

The degree of pollution is measured quantitatively by I_{geo} in groundwater [32]. The results of I_{geo} showed that groundwater in the study area was uncontaminated to moderately contaminate regarding Fe and Pb in a few sampling points. I_{geo} value in the case of Zn, Cu, Cr, and Ni is less than one, revealing no contamination for these metals' ions in the groundwater of KIE (Table 6).

The concentrations of Fe and Pb were found higher in a few groundwater samples in Korangi industrial estate, exceeding WHO and NEQS guidelines. The higher concentration of Fe in KITE may be due to geological origin as well as the number of factors such as; steel industry, rusting of iron scrapes and corrosion of Fe containing metals are responsible for the same [33, 34]. The higher value of Pb may be attributed to fuel additives and also present in coal which is used as fuel in many industries [35, 36]. It is inferred from the results obtained from different chemical indices applied to evaluate the groundwater quality in the study area closely in agreement with each other.

Table 5. NPI and PLI values of groundwater samples of KIE.

Samples	CF ¹						PLI ²	NPI ³
	Fe	Zn	Cu	Pb	Cr	Ni		
GW ₁	0.663	0.164	0.037	0.9	0.18	0.35	0.25	0.382
GW ₂	1.067	0.209	0.009	1.0	0.22	0.25	0.22	0.459
GW ₃	0.623	0.136	0.008	2.6	0.22	0.35	0.23	0.656
GW ₄	0.653	0.165	0.01	0.8	0.3	0.4	0.22	0.388
GW ₅	1.873	0.131	0.066	3.3	0.92	0.55	0.55	1.14
GW ₆	2.103	0.428	0.0003	0.8	0.22	0.65	0.26	0.7
GW ₇	0.82	0.133	0.007	0.8	0.16	0.35	0.18	0.378
GW ₈	2.567	0.341	0.007	2.6	0.14	0.3	0.29	0.992
GW ₉	0.55	0.158	0.009	0.8	0.08	0.3	0.16	0.316
GW ₁₀	0.843	0.187	0.009	2.7	0.12	0.35	0.23	0.7
GW ₁₁	0.697	0.132	0.018	0.8	0.08	0.3	0.18	0.338
GW ₁₂	0.953	0.557	0.018	0.9	0.12	0.2	0.24	0.458
GW ₁₃	0.843	0.539	0.011	1.5	0.14	0.4	0.28	0.572
GW ₁₄	1.193	0.128	0.016	0.7	0.08	0.1	0.16	0.369
GW ₁₅	1.203	0.194	0.019	0.8	0.1	0.2	0.20	0.419
GW ₁₆	1.443	0.169	0.016	0.7	0.08	0.15	0.18	0.426
GW ₁₇	1.027	0.213	0.022	0.8	0.12	0.15	0.20	0.388
GW ₁₈	2.157	0.182	0.006	0.7	0.14	0.2	0.19	0.564

¹Contamination factor, ²Pollution load index, ³Nemerow's pollution index.

Table 6. I_{geo} values of groundwater samples of KIE.

Samples	Fe	Zn	Cu	Pb	Cr	Ni
GW ₁	-1.181	-3.204	-5.379	-0.739	-3.069	-2.107
GW ₂	-0.493	-2.850	-7.328	-0.587	-2.778	-2.594
GW ₃	-1.271	-3.478	-7.577	0.796	-2.778	-2.107
GW ₄	-1.203	-3.195	-7.183	-0.91	-2.329	-1.913
GW ₅	0.322	-3.533	-4.533	1.141	-0.707	-1.452
GW ₆	0.489	-1.814	-12.329	-0.91	-2.778	-1.210
GW ₇	-0.874	-3.507	-7.67	-0.91	-3.239	-2.107
GW ₈	0.777	-2.144	-4.426	0.796	-3.433	-2.329
GW ₉	-1.452	-3.261	-7.328	-0.91	-4.243	-2.329
GW ₁₀	-0.834	-3.014	-7.406	0.851	-3.656	-2.107
GW ₁₁	-1.11	-3.518	-6.443	-0.91	-4.243	-2.329
GW ₁₂	-0.656	-1.433	-6.363	-0.739	-3.656	-2.917
GW ₁₃	-0.834	-1.482	-7.051	0.0	-3.433	-1.913
GW ₁₄	-0.331	-3.559	-6.573	-1.103	-4.243	-3.920
GW ₁₅	-0.319	-2.958	-6.324	-0.91	-3.920	-2.917
GW ₁₆	-0.055	-3.163	-6.619	-1.103	-4.243	-3.333
GW ₁₇	-0.549	-2.827	-6.145	-0.91	-3.656	-3.333
GW ₁₈	0.526	-3.053	-7.877	-1.103	-3.433	-2.917

Conclusion

In the current study, the impact of anthropogenic activities on heavy metal concentration in groundwater was evaluated using the chemical indices approaches. Overall results showed that groundwater quality in the study area had deteriorated mainly due to the contamination of Fe and Pb. In a few samples, the concentrations of Fe and Pb are higher than WHO and NEQS guidelines. It is concluded that to minimize the risk to human health and the extent of heavy metal pollution, sincere efforts must be made, followed by an action plan to reduce Fe and Pb concentrations in groundwater. Consistent monitoring of groundwater around the study areas is also necessary.

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Conflict of interest

The authors declare that there is no conflict of interest.

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