Journal of Water Resource and Protection, 2019, 11, 311-332
http://www.scirp.org/journal/jwarp
ISSN Online: 1945-3108
ISSN Print: 1945-3094

Statistical and Geospatial Assessment of Groundwater Quality in the Megacity of Karachi

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How to cite this paper: Khan, M.K., Ayoub, W., Saied, S., Hussain, M.M., Masood, S.S., Siddique, A. and Khwaja, H.A. (2019) Statistical and Geospatial Assessment of Groundwater Quality in the Megacity of Karachi. *Journal of Water Resource and Protection*, **11**, 311-332.
https://doi.org/10.4236/jwarp.2019.113018

Received: August 10, 2018
Accepted: March 15, 2019
Published: March 18, 2019

Abstract

Inserting Groundwater quality variability and sources potentially contributing to aquifer recharge was evaluated in metropolitan Karachi. Selected sampling sites were characterized by large waste dumping sites, industrial zones, and the presence of open streams receiving heavy loads of industrial and domestic wastes. Levels of pH, electrical conductivity (EC), fluoride (F^-), chloride (Cl^-), bromide (Br^-), nitrate-N (NO_3^--N), sulfate (SO_4^{2-}), sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and ammonium (NH_4^+) were determined and compared with the WHO permissible limits. Concentrations of the measured ions were in the order of $Cl^- > Na^+ > SO_4^{2-} > Mg^{2+} > Ca^{2+} > NO_3^-\text{-N} > K^+ > F^- > Br^-$. EC values were above the WHO guidelines, representing the presence of high ionic concentration in the groundwater. The health risk index (HRI) for NO_3^--N indicated that inhabitants of Karachi are at risk of high NO_3^--N exposure. Ingestion of high concentrations of NO_3^--N in water can cause methemoglobinemia and birth defects. Results of multivariate statistical analysis, principal component analysis (PCA), cluster analysis (CA), and geographic information system (GIS) map analysis revealed that human activities are leading to adverse effects on the existing groundwater quality in Karachi.

Keywords

Groundwater, Karachi, Water Quality, Multivariate Analysis, Geospatial, Health Risk Index

1. Introduction

Groundwater is the most accessible alternate source of water wherever surface water (e.g. lakes, streams) is scarce. The urban centers of the world, particularly those in developing countries, face an acute shortage of water. These shortages are due to rapid urbanization and substandard economic conditions, problem that are compounded by the lack of appropriate arrangements by government bodies. Natural and anthropogenic activities pose a potent threat to groundwater quality by altering constituent levels [1]. It is worthwhile to monitor the composition of natural water to identify the level of hazard posed by human activities, especially in megacities where water sources are more vulnerable [2].

Natural waters are exposed to pollutants in many ways, including anthropogenic and geogenic activities [3]. High concentrations of major ions and trace elements have been reported by many researchers, along with biological and chemical oxygen, total dissolved solids (TDS) and other ions [4] [5] [6]. Instead of existing in a free state, elements in different aquifers occur in dissolved forms such as ions, complexes, suspended particles and colloid ions, whereas in sediments, they exist as solids. Various factors greatly affect the concentrations of these ions, including pH, ion strengths, redox potentials, and both organic and inorganic ligand activities. Scavenging and biological processes also contribute to changes in the amount of such species in aquatic systems [7].

Several parameters affect the configuration of groundwater, including the mineral composition of watersheds and aquifers, precipitation, geology of the underground beds, and geochemical processes occurring naturally or anthropogenically [8]. Seasonal and spatial changes observed in groundwater chemistry are the cause of reactions occurring in aquifer minerals and other redox reactions [9]. Both natural processes and human activities are responsible for maintaining groundwater chemistry. The influence of minerals on the chemical reactions occurring in water beds heavily impacts the quality of groundwater, affecting its use for drinking, industrial and agricultural purposes.

To manage groundwater resources effectively, it is important to understand the geochemical evolution of groundwater in dry or desiccated areas, as this information can improve the knowledge of hydrochemical systems [10] [11] [12]. Many cities or small towns situated along the seashore are mainly dependent on groundwater to fulfill their domestic and commercial requirements, including agriculture and industries, but continuous infiltration of seawater has led to declining groundwater quality, which has become a major concern.

Due to the increase in population and the scarcity of water, it is of utmost importance to identify the relationship between groundwater and saline water in coastal cities, as this information can be employed to summarize the presence and processes of chemicals occurring in aquifers, with a view towards assessing and classifying groundwater reservoirs for specific uses [9]-[21].

The coastal megacity of Karachi, Pakistan is confronting several serious environmental threats. The water supply in Karachi is currently threatened by water scarcity, as well as groundwater contamination due to growing municipal and industrial pollution. The present study was aimed at evaluating the pollution status of groundwater in Karachi. Multivariate techniques were used to assess the similarities and dissimilarities at different sampling sites, and to determine the pollution sources affecting the groundwater quality.

2. Materials and Methods

2.1. Study Area

Karachi is the biggest industrial hub of Pakistan. It has five major industrial zones, including Korangi, Landhi, Sindh Industrial Trading Estate (SITE), Federal B (FB) Area, and North Karachi. It is situated at the northern coastal area of Arabian Sea at an elevation of 22 m with longitude and latitude values of 25˚N, 67˚E. As an important port, Karachi has become a central point of trade, with two airports, five railway stations and a huge system of transport for goods as well as for people. This has caused a rapid industrialization of the city with the growth of oil refineries, textile, pharmaceutical, polymer, plastic, cement, cotton, heavy chemicals, petrochemicals, edible oil, leather and various other cottage industries.

The city has two distinct seasons, winter and summer, while spring and autumn are almost indistinguishable, due to nearly identical temperatures. The average temperature range throughout the year is from 10˚C to 40˚C, while the annual average rainfall is 150 - 200 mm.

Karachi lies within the Hub River Basin and the Malir River Basin. The Hub Dam, and the Malir and Lyari rivers contribute to the recharge systems of the aquifers of Karachi through seepage. Large quantities of domestic and industrial wastes are dumped into the Malir and Lyari rivers. These are then drained into Arabian Sea at Cape Mount Beach within an area of 336 km. Since 1980, the Hub Dam, situated north-west of Karachi city, has catered to the domestic and irrigation requirements of the residents. Currently, the three major water supply systems fulfilling citizens' water requirements are: the Indus River, the Hub Dam, and boring wells. In order to satisfy domestic requirements like drinking, irrigation, and poultry husbandry, various bore wells are dug. Hence, it is important to scrutinize the quality of groundwater on a regular basis, and to investigate artificial methods to recharge Malir River Basin through seepage.

2.2. Lithology of Karachi

The megacity Karachi and its enclosed neighborhoods are situated on bare stone composed of lime and sand on an area comprising the rearmost part of the Nari formation, which is of the Oligocene age. The characteristics of the Nari formation include siltstone, limestone, and shale interlayers in soft stones of sand. The Shab and sandstones are the subsidiaries of limestone in the Gaj formation. The major portion of the Gaj formation consists of dolomitic gypsum in the underline beds, covered by an alkaline soil. The Mianchar formation is fully covered by conglomerate, mainly dumped as a Quaternary deposit. The most important anticlines in the topography of Karachi include Pir Mangho, Landhi-Korangi, and Drig Road, which are used by the non-perennial Lyari and Malir rivers to unload their recurring water and effluvium into the Arabian Sea. Karachi is situated in the Hab River Basin and Malir River Basin. Both rivers are responsible for draining the Malir River Basin. Hence, the coastal aquifer of the mega city is principally revitalized by seepage from Hab River, Hab Dam as well as the Malir and the Lyari Rivers. Hab River flows along the boundary of Karachi and Lasbela 30 km away from the city to the west. After completion of 336 km long drainage course, it sets into the Arabian Sea in the neighborhood of Cape Monze. Saruna, Samotri and Wira Hab are its foremost tributaries. Hab River progressively broadens and, for about 80 km ahead from its mouth, is enclosed by fine pasture land. Water from rivers is used for domestic and irrigation functions once the Hab Dam was built in 1980 [22].

2.3. Sampling and Analysis

To account for the range of anthropogenic activities occurring in various areas of Karachi, as well as the additional expected contribution of natural processes, sampling sites were selected covering nearly the whole city. The selected sites were attributed to industrial and commercial activities along with heavy traffic density and sea water intrusion. In total, 19 samples of groundwater were collected from different areas of the metropolitan city, while 10 samples of ice water were also taken from major markets situated in thickly populated areas (**Figure 1**). The depth of these production bores ranges from 175 to 250 ft, depending upon the activities occurring in the areas they supply [23]. Global Positioning System (GPS) locations were also measured at the sampling sites using a Garmin Vista™ GPS device to interpret results using geo-spatial mapping through Inverse Distance Weightage (IDW) with the help of software ArcGIS 10.1®.

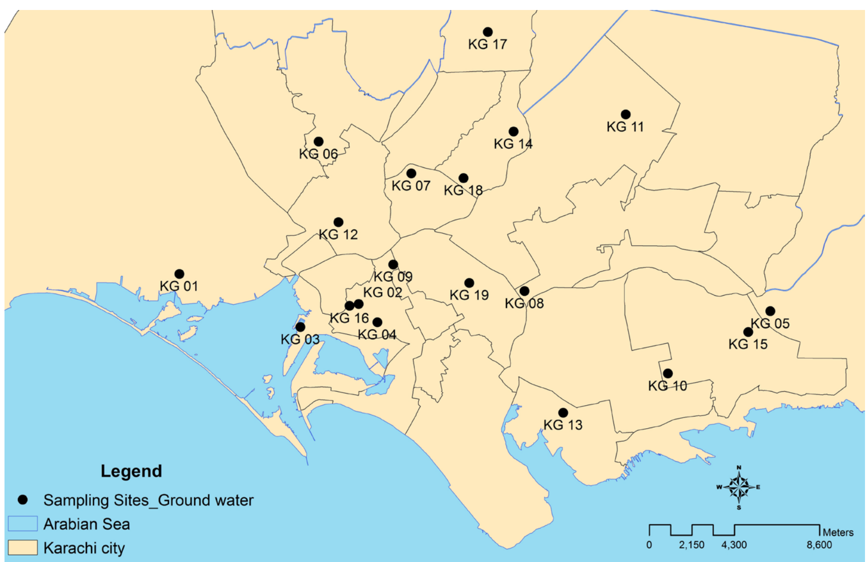

Figure 1. Map of Karachi showing sampling sites.

Samples were collected during December 2012 and January 2013 in polypropylene bottles, which were acidified with concentrated nitric acid (HNO_3), washed twice by double deionized water and dried. Samples were stored at 4˚C at the time of collection as well as in the laboratory. pH and EC were measured using a Jenway™ pH meter Model 3310 calibrated by buffer solution of pH 4.0 and pH 10 and a Jenco™ Conductivity meter Model No: 3010 (μS/cm) calibrated by a standard solution of potassium chloride (KCl). Replicates of each sample were collected to ensure quality assurance, and each sample was divided in equal halves for anion and cation analysis. Determinations of ions were conducted by Dionex ion chromatograph coupled with an auto sampler.

Stringent quality control and quality assurance procedures were adopted through standardization, blank measurements, duplicate and spiked samples. The accuracy of calibration curves was evaluated by analyzing quality control standards containing the analyte at a concentration in the low-and high-calibration range. The percent standard deviation of measurements, evaluated on duplicate samples was found to be better than ±10%, while spike recoveries ranged between 90% - 104%.

3. Results and Discussion

3.1. Chemical Composition

To account for the demography and land use of the industrial hub, groundwater samples were collected and measured for different physicochemical parameters including pH, EC, anions (F^-, Cl^-, Br^-, NO_2^--N, NO_3^--N, SO_4^{2-}), and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+). As evident from Table 1, the abundance of measured ions in groundwater was found in the following order: Cl^- > Na^+ > SO_4^{2-} > Mg^{2+} > Ca^{2+} > NO_3^--N > K^+ > F^-. pH in groundwater samples varied

Table 1. Range, mean and relative standard deviation of physicochemical parameters of ground water and ice water in Karachi.

	Ground Water			Ice Water		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean
pH	4.90	7.50	6.34 ± 0.09	4.5	6.8	5.52 ± 0.16
EC	727	3448	1887 ± 0.56	131	999	503 ± 0.56
F^-	0.32	2.85	0.84 ± 0.78	0.21	1.41	0.41 ± 0.38
Cl^-	79.5	22165	2254 ± 2.50	6.0	152	61.0 ± 0.76
NO_3^--N	0.01	344	25.8 ± 3.10	0.07	23.4	7.34 ± 1.30
SO_4^{2-}	92.1	6115	610 ± 2.28	5.4	130	59.8 ± 0.72
Na^+	141	7567	1537 ± 1.22	33.5	2333	492 ± 1.45
K^+	5.5	80	18.3 ± 1.15	1.3	24.6	8.26 ± 0.89
Mg^{2+}	12.6	147	50.8 ± 0.94	0.2	21.3	4.76 ± 1.36
Ca^{2+}	2.4	133	30.8 ± 0.96	4.9	69.0	30.9 ± 0.61

*EC in μS/cm and all other concentrations are in mg/L except pH.

from 4.90 to 7.50 (6.34 ± 0.09), indicating a slightly acidic nature. These levels were within the pH range defined by World Health Organization (WHO) guidelines (6.5 - 8.5), except a few samples with pH values less than the lower limit. This might be because of leaching phenomena, as the site is situated where various open seasonal nullahs receive high loads of domestic and industrial wastes [24].

Electrical conductivity is one of the indicators of dissolved salts depending upon their ionic strength and mobility [25]. Its value ranged from 727 to 3448 µS/cm with a mean value of 1887 µS/cm. High EC values represent the high mineral content. In our study, all the samples except seven had higher EC than the WHO permissible limit of 1500 µS/cm. The seven sites with samples below this limit included Quaidabad (KG 05), Falcon Complex (KG 08), Suparco (KG 11), Haroonabad (KG 12), FB. Area Block-16 (KG 12), North Karachi 11-A (KG 17), and PECHS (KG 19) (**Figure 1**).

The range of F^- across all the sampling sites was 0.32 - 2.85 mg/L (0.84 ± 0.78 mg/L). Concentrations of F^- at some sites were found to be higher than the maximum tolerance limit (1.5 mg/L) recommended by WHO. The sites with elevated F^- concentrations were Bismillah Colony (KG 06), Nazimabad Block-7 (KG 07), Saddar (KG 16), and Hussainabad (KG 18) (**Figure 1**), all of which are characterized by cottage industries with high coal combustion and vehicular emissions. In addition to this, industrial, agricultural and domestic waste water and untreated effluents pass into nearby open streams that contribute to the recharge of the aquifers [26]. Ingestion of water with F^- concentration above 1.5 mg/L causes fluorosis [27], with other possible negative effects ranging from stiffness and rheumatism to a permanently crippling skeletal rigidity.

Extremely high Cl^- concentrations of the groundwater were also observed, ranging from 79.5 - 22,165 mg/L with a mean value of 2254 ± 2.50 mg/L. The upper limit of this range is much higher than the WHO recommended limit of Cl^- (250 mg/L). In our study, only 50% of the samples complied with this standard. High Cl^- concentrations may be considered a health hazard, as well as contributing an unpleasant taste to the water. Elevated levels of Cl^- can indicate infiltration from dumpsites and open tributaries passing nearby [24].

Only five of the samples (at the KG 09, KG 06, KG 19, KG 13, and KG 03 sites) had Br^- concentrations above the detection limit. The maximum Br^- value was found at sampling site KG 03 as 171 mg/L, while the minimum value was recorded as 8.0 mg/L at the Garden site (KG 09). Extremely high concentrations were measured at the Fisheries site (KG 03), which is closer to the sea shore indicating a possible effect of seawater intrusion [28]. Compared to other sites, PECHS (KG 19) and Bhittai Colony (KG13) also yielded higher concentrations of Br^- (23 and 41 mg/L, respectively), possibly due to the greater use of fertilizers because of high vegetation [29].

Nitrate in groundwater originates primarily from run-off of fertilizer, septic systems, feedlots, and manure from barnyards or spreading operations. Concentration of NO_3^--N was found to be in the range of 0.01 to 344 mg/L (25.8 ± 3.10

mg/L) with elevated values at the Bhittai Colony site (KG 13), possibly due to the high level of industrialization around it. Bismillah Colony (KG 06, 10.4 mg/L), Nazimabad Block 7 (KG 07, 13.2 mg/L), Fisheries (KG 03, 15.4 mg/L), Saddar (KG 16, 16.6 mg/L), Landhi (KG 15, 23.3 mg/L), and Bhittai Colony (KG13, 344 mg/L) sites showed NO_3^--N levels exceeding the United States Environmental Protection Agency (USEPA) and WHO permissible limits of 10 mg/L measured as NO_3^--N (**Figure 2**). These sites are characterized by dense populations, open streams receiving heavy loads of untreated domestic and industrial waste water, and large fields used for cattle farms producing heavy quantity of manure and animal wastes, all of which could be considered as major causes of increasing concentrations of NO_3^- [30] [31] [32]. Excess levels of NO_3^- can cause methemoglobinemia, or "blue baby" disease, as well as birth defects.

High concentrations of SO_4^{2-} were found, ranging from 92.1 to 6115 mg/L with a mean value of 610 ± 2.28 mg/L. Concentrations of SO_4^{2-} at five locations, specifically Nazimabad Block 7 (KG 07), Garden (KG 09), PECHS (KG 19), Fisheries (KG 03), and Bhittai Colony (KG 13) were 1.1 - 24 fold higher than the WHO permissible limit of 250 mg/L. The highest concentration of SO_4^{2-} (6115 mg/L) was found in the Bhittai Colony site. This site is a residential area situated very close to industrial zones, with large dumping sites and heaps of industrial and domestic wastes ejected into the seasonal river crossing through it. Its location is likely the explanation of the elevated concentrations of SO_4^{2-} [33].

Sodium ions were observed as the most dominant cation with a range of 141 to 7567 mg/L (1537 ± 1.22 mg/L). Groundwater was found to be contaminated with Na^+ above the WHO permissible limit of 200 mg/L. Almost all samples showed high concentrations of Na^+ and were drawn from sites characterized by seawater intrusion and leaching from the dumping sites [24] [34]. A high Na^+

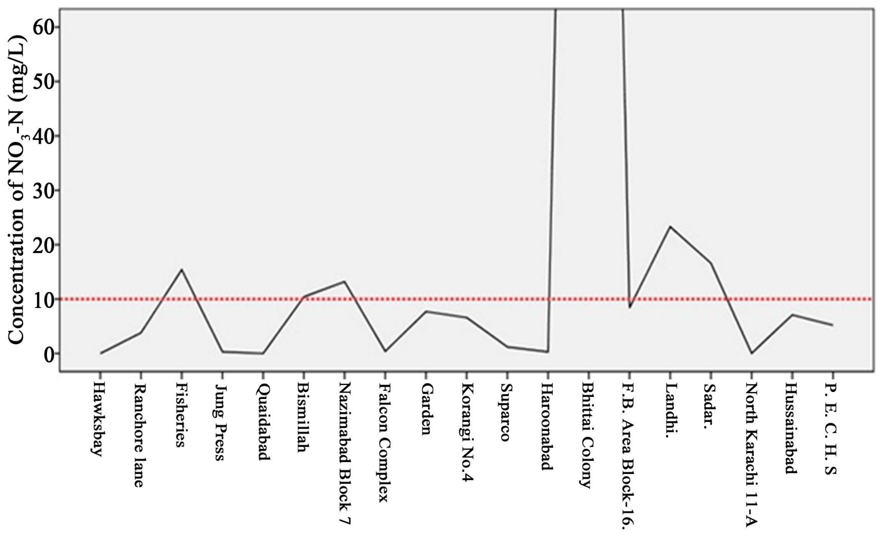

Figure 2. Concentrations of NO_3^--N in ground water at sampling sites.

concentration in the groundwater may be a serious health concern to people with medical conditions such as hypertension, heart, kidney or liver diseases, or other conditions requiring a low Na^+ diet.

Concentrations of K^+ ranged from 5.5 to 80 mg/L with a mean value of (18.3 ± 1.15 mg/L), which is higher than the WHO recommended value of 12 mg/L. The sampling sites included areas with large dumping sites, cattle raising activities, and nearby open streams containing high loads of industrial and domestic wastes (including large quantities of manure and fertilizers), all of which generally show elevated concentrations of K^+ [31] [32] [33] [34].

The range of Mg^{2+} in groundwater was 12.6 - 147 mg/L (50.8 ± 0.94 mg/L). Generally, ferro-magnesium minerals are the main cause of Mg^{2+} concentrations (Farooq *et al.*, 2010), and the main reason for its presence was undoubtedly the lithology of the study area. The presence of Mg^{2+} is an essential part of nutrition. However, in combination with SO_4^{2-}, Mg^{2+} produces a laxative effect, and hence is considered unfit for drinking purposes [34]. In all locations except one (PECHS-KG 19), the concentration of Ca^{2+} was found to be within the safe zone of WHO permissible limit of 100 mg/L (2.4 - 133 mg/L).

If irrigation water has a high sodium adsorption ratio (SAR), the Na^+ in water can displace Ca^{2+} and Mg^{2+} in the soil, reducing the soil ability to form stable aggregates and resulting in the loss of soil structure and tilt. The SAR was calculated to evaluate the suitability of the sampled groundwater for use in agricultural irrigation by using the equation:

$$\text{SAR} = \left[\text{Na}^{+}\right] \Big/ \left\{1/2\left(\left[\text{Ca}^{2+}\right] + \left[\text{Mg}^{2+}\right]\right)\right\}^{1/2}$$

where Na^+, Ca^{2+}, and Mg^{2+} concentrations are in meq/L. Generally, good quality irrigational water should have a SAR value of <10 [35]. Results revealed that 72% of the groundwater samples had SAR values much higher than 10 (range = 4.7 - 109), indicating that the water quality was generally unsuitable for irrigation.

Commercially available water from ice marketed for common use was also analyzed for the physicochemical parameters (**Table 1**). Due to the scarcity of water resources, groundwater is commonly used to make ice on a commercial scale. In general, pH, EC and major ions in the ice water were lower than their concentrations in groundwater. Except for pH, NO_3^--N, and Na^+, the concentrations of the measured analytes in ice water fell within the WHO standard for drinking water, suggesting that the ice factories in Karachi are using groundwater mixed with other water sources for ice making. However, at three locations, including Bhittai Colony (KG 13, 10.5 mg/L), Saddar (KG 16, 23.4 mg/L), and Haroonabad (KG 12, 22.7 mg/L), the concentration of NO_3^--N in ice water was still found to be above the WHO permissible limit of 10 mg/L (**Figure 3**).

Certain parameters are measurable through concentration ratios in meq/L, indicating the possible sources of contaminants in water. These concentration ratios can shed light on the details of the bed rocks, the extent to which groundwater is replaced, the effects of seawater and changes in the host aquifer [36].

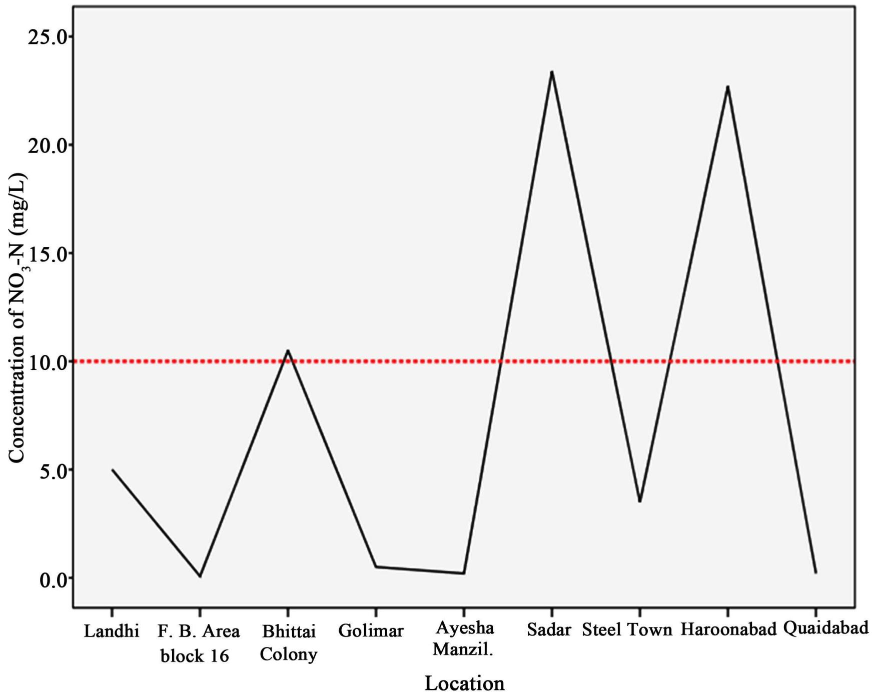

Figure 3. Concentration of NO_3^--N in ice water.

Na^+/K^+ ratios indicate whether the groundwater is affected by seawater intrusion or influenced by the recharge phenomena occurring in the specific area. Ratios of $Na^+/K^+ = 50 - 70$ in this study suggested that the cause of depletion of the aquifer was the adsorption of Na. Jung Press, Landhi, and Suparco sites had Na^+/K^+ ratios of 43.7, 22.8, and 55.2, respectively. These areas are in a part of the old city and therefore have older groundwater. A $Na^+/K^+ < 10$, indicating of the effects of rain water was observed in Fisheries, which showed a ratio of 0.509.

Cl^-/SO_4^{2-} ratios correspond to the high salinity and the presence of surplus salts in the aquifers. A $Cl^-/SO_4^{2-} = 1 - 10$ indicates the presence of high Cl^- concentration. All the sites except the FB Area exhibited Cl^-/SO_4^{2-} ratios that were greater than 1, with the Garden site displaying the largest ratio (5.8).

Mg^{2+}/Ca^{2+} ratios indicate the presence of lithologies incorporating limestone or underground beds rich in magnesium. A ratio of $Mg^{2+}/Ca^{2+} > 0.9$ corresponds to the rocks silicate and magnesium. Higher Mg^{2+}/Ca^{2+} ratios were observed at Ranchore Lane (1.7), Quaidabad (4.4), Bismillah (7.1), Falcon Complex (273), Garden (7.3), Korangi (1.3), Suparco (1.2), Haroonabad (2.2), Bhittai Colony (9.3), FB. Area (5.5), Landhi (79.7), Saddar (27.5), North Karachi 11-A (1.3), Hussainabad (1.5), and P. E. C. H. S (1.7). Lower ranges of Mg^{2+}/Ca^{2+} ratios (0.7 - 0.9 and 0.5 - 0.7) signify the existence of aquifers in dolomitic rocks and limestone lithologies, respectively. Ratios of 0.965 and 0.455 were observed at Nazimabad and Jung Press sites, respectively.

Na^+/Cl^- ratios are related to the seawater intrusion and the level of salinity. They are also associated with marine salts or groundwater interacting with evaporitic salt-bearing underground beds. A ratio of $Na^+/Cl^- > 1$ indicate infiltration of water through flysch or the aquifers in contact with the flysch in the presence of metamorphic rocks or a similar alkaline medium, with the ion exchange process of Na^+ with alkaline ions contributing. All the sites except Fisheries had Na^+/Cl^- ratios > 1. Ratios of $Na^+/Cl^- < 0.78$ reflect seawater invasion and the residual salts that suspend due to the formation of sedimentation. In this study, FB. Area and Fisheries sites fell into this category, with respective ratios of 0.424 and 5.22×10^{-5}. The $Na^+/(Na^+ + Cl^-)$ ratio is indicative of the interaction between groundwater and evaporitic minerals in sediment formation. A ratio of $Na^+/(Na^+ + Cl^-) = 0.5$ suggests that groundwater obtained its salinity through dissolution of halite within sedimentary aquifer. The ratios in this study were all in the range 0.297 - 0.98, indicating the effect of halite minerals [37].

3.2. Statistical Analysis

A multivariate analysis of the groundwater quality data set was performed using Pearson's correlation, cluster analysis (CA), and principal components analysis (PCA) [38]. As shown in **Table 2**, statistically significant correlations were found between EC and other ions *i.e.* Na^+ (r = 0.688), K^+ (r = 0.604), Mg^{2+} (r = 0.574), Cl^- (r = 0.574), and SO_4^{2-} (r = 0.524). Magnesium is more strongly correlated with EC as compared to Ca^{2+} (r = 0.388) probably because its smaller size increases its affinity towards water. Fluoride did not appear to be dependent on other water-soluble components. The significant correlation found between SO_4^{2-} and Cl^- (r = 0.657) corresponded to anthropogenic activities, while weak correlations between SO_4^{2-} and Na^+ and K^+ suggested a low-probability of their presence via natural sources [6]. A significant positive relationship between Na^+ and K^+ (r = 0.870) was indicative of their common source, which is usually seawater intrusion [39]. The association of Br^- and Cl^- (r = 0.724) suggests that the Br^- comes from the seawater.

Table 2. Correlation coefficient matrix for physicochemical parameters in ground water in Karachi.

	pH	EC	F^-	Cl^-	Br^-	NO_3^--N	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
pH	1.00										
EC	0.110	1.00									
F^-	0.277	0.133	1.000								
Cl^-	−0.184	**0.574**	−0.288	1.00							
Br^-	−0.034	0.047	−0.197	**0.724**	1.00						
NO_3^--N	**−0.549**	0.398	−0.110	**0.479**	−0.055	1.00					
SO_4^{2-}	**−0.463**	**0.524**	−0.208	**0.657**	0.094	**0.960**	1.00				
Na^+	0.251	**0.688**	0.160	0.085	**−0.441**	0.296	0.393	1.00			
K^+	0.069	**0.604**	−0.052	0.196	−0.356	**0.570**	**0.634**	**0.870**	1.00		
Mg^{2+}	0.115	**0.575**	0.093	0.059	**−0.519**	**0.428**	**0.427**	**0.731**	**0.785**	1.00	
Ca^{2+}	0.399	0.388	−0.032	0.117	−0.100	−0.063	0.115	**0.697**	**0.559**	0.339	1.00

*Bold values indicate statistically significant correlations at the level of $p < 0.5$.

3.3. Principal Component Analysis (PCA)

PCA was applied to examine the contribution of each variable in the data set [40] (Marengo *et al.*, 2008). Four factors explaining 89.1% of the total variance were retained. The first component accounted for 37.1% of the total variance in the data set of groundwater, with high positive loadings that clearly showed the strong relationships between EC, Na^+, K^+, Mg^{2+}, and Ca^{2+} (**Table 3** and **Figure 4**). The variables involved in this component are mainly associated with natural

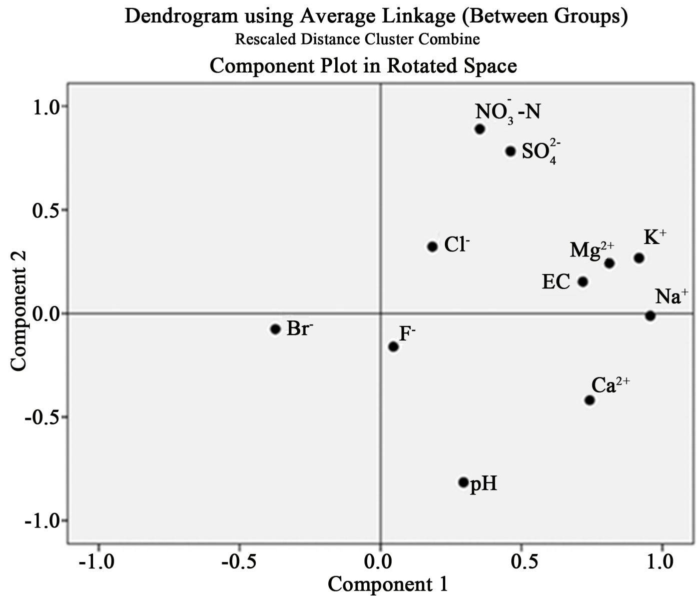

Figure 4. Loading plot of PCA.

Table 3. Rotated component matrix with %variance for the ground water of Karachi.

	Component				Extraction
	1	2	3	4	
pH	0.295	**−0.815**	0.043	0.205	0.795
EC	**0.718**	0.153	**0.460**	0.279	0.828
F^-	0.046	−0.161	−0.132	**0.937**	0.924
Cl^-	0.184	0.322	**0.910**	−0.114	0.978
Br^-	−0.373	−0.076	**0.894**	−0.107	0.957
NO_3^--N	0.352	**0.890**	0.157	0.013	0.941
SO_4^{2-}	**0.461**	**0.783**	0.350	−0.092	0.957
Na^+	**0.957**	−0.012	−0.077	0.095	0.931
K^+	**0.917**	0.267	−0.050	−0.077	0.921
Mg^{2+}	**0.812**	0.242	−0.220	0.141	0.785
Ca^{2+}	**0.742**	**−0.419**	0.122	−0.243	0.800
% Variance	37.1	23.0	18.8	10.2	

*Bold values indicate statistically significant correlations at the level of $p < 0.5$.

sources, including seawater intrusion and geothermal fluids attributed to lithologic effects. The second component, explaining 23% of the total variance, had high loadings for NO_3^--N and SO_4^{2-}, which may be explained by anthropogenic sources including agricultural activities, livestock and seepage from the open streams with heavy loads of the domestic and industrial wastes. The third component of the PCA accounted for 18.8% of the total variance with high positive loadings on Cl^- and Br^-, possibly due to intrusion of sea water in lower layers. The fourth component, explaining 10.2% of the total variance, had a strong positive loading for F^-.

3.4. Cluster Analysis (CA)

CA was performed to distinguish spatial similarity for grouping of sampling sites (spatial variability) [26] [40]. The output dendrogram (tree diagram; **Figure 5**) was clustered into five groups, with the first showing significant relationships between F^-, Br^-, NO_3^--N, K^+, Ca^{2+} and Mg^{2+}, and the pH. This may be due to the non-point sources, *i.e.* fertilizers, large dumping sites, leakage from the sewage water and to some extent rock-water interaction. Cl^- and SO_4^{2-} did not have a significant relationship, likely due to the difference of their sources, namely, seawater intrusion for Cl^- versus anthropogenic sources like dumping sites, industrial and household wastes for SO_4^{2-}. EC is mainly related to Na^+ ions, which have very high solubility in water and penetration through the ion exchange method.

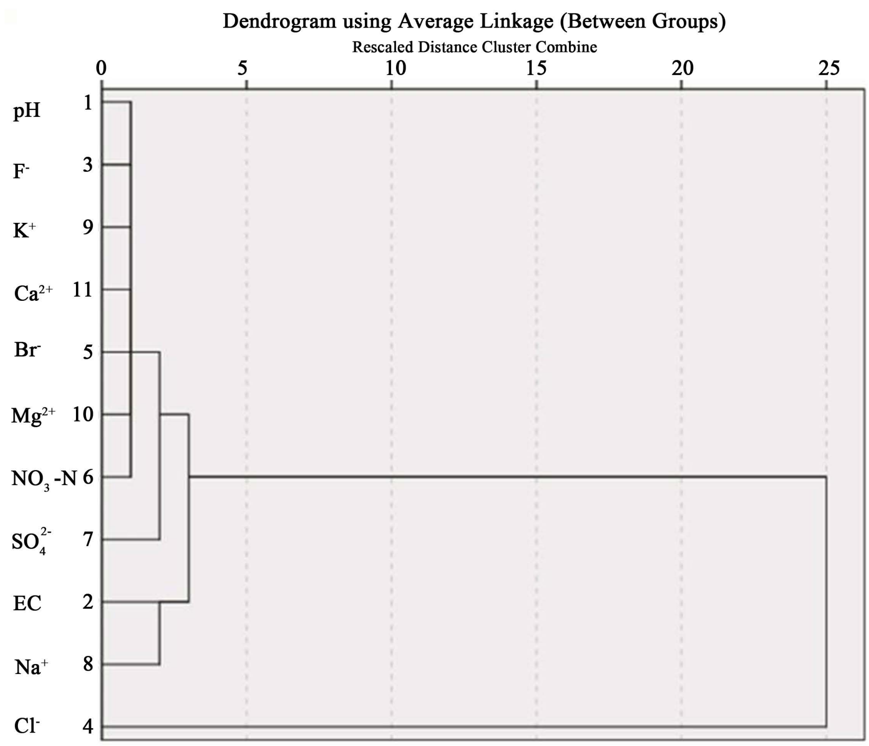

Figure 5. Dendogram of ground water samples.

3.5. Risk Assessment

Nitrate level is a key source of information for assessing groundwater contamination through leakage and seepage from sewage systems [41] and industrial fertilizers, along with some redox reactions of nitrogen containing compounds [32]. High concentrations of NO_3^--N may cause blue baby syndrome in infants and pregnant women [42], which may lead to gastrointestinal carcinoma and thyroid disorders [43]. Therefore, it is very important to closely monitor the NO_3^--N levels in groundwater. A health risk index (HRI) was calculated by using the equation:

$$\text{HRI} = \text{CDI}/\text{RfD}$$

where CDI is the chronic daily intake and RfD is the reference dose (mg/kg/day). The CDI was determined by using the equation:

$$\text{CDI} = \text{C} \times \text{DI}/\text{BW}$$

where C is the concentration of NO_3^--N (μg/L), DI is the daily average intake of water (L/day), and BW is the average body weight (kg). The RfD, DI, and BW used in the calculations were 1.6 mg/kg/day, 2 L/day for adult and 1 L/day for children, and 72 kg for adult and 32 kg for children, respectively [44].

A hazard index of >1 is indicative of increased health risk from NO_3^--N exposure. In the present study, HRI values for all the groundwater samples were <1 for adults as well as children, indicating that contamination of NO_3^--N is within the safety limit, and therefore no adverse effect is expected, apart from Bhittai Colony site (KG 13). High values of HRI (5.97 for adults and 7.72 for children) at the Bhittai Colony site suggest a significant increase in risk to the population consuming this water. The site is characterized by the large dumping sites, open streams receiving very high loads of industrial and domestic wastes, cattle farming producing large quantity of nitrogenous wastes, and use of fertilizers in the nearby agricultural area.

3.6. Geospatial Analysis

Using the localized data points, GIS interpolation tools were used to create a continuous surface in order to explain the similarities and differences between the measured and neighboring sites and describe the level of spatial reliance and inter correlation [32] [45] [46]. For this purpose, measurement data for all ions were interpreted using the geo-spatial tool IDW through ArcGIS 10.1® on a Karachi map. **Figures 6-16** present information on the spatial variations in the pH, EC, and concentrations of measured ions in groundwater. The highest pH level found in the PECHS site (**Figure 6**), may be due to high concentrations of alkalis and alkalines (**Figure 14** and **Figure 15**). This supposition is also supported by a high EC value (**Figure 7**). Sites characterized by large dumping sites and seawater intrusion (**Figure 17**) show elevated values of Na^+ with low concentrations of Ca^{2+} due to ion exchange process (**Figure 13** and **Figure 16**). Bhittai Colony site showed highest concentration of SO_4^{2-} (**Figure 12**). The Fisheries site yielded

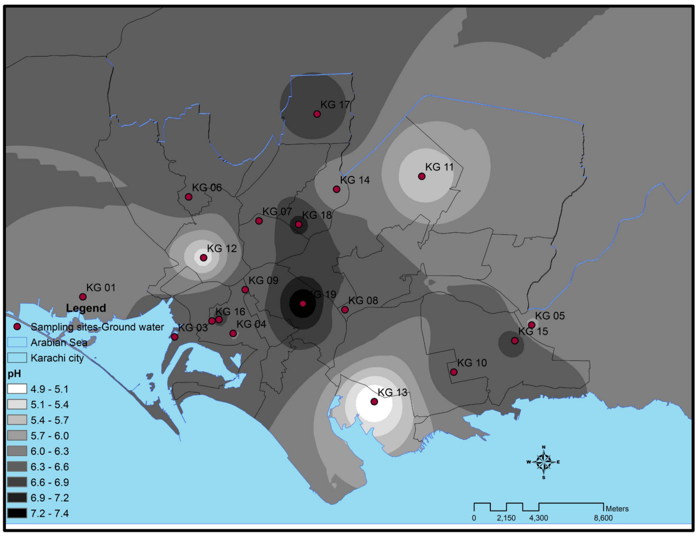

Figure 6. Spatial distribution of pH.

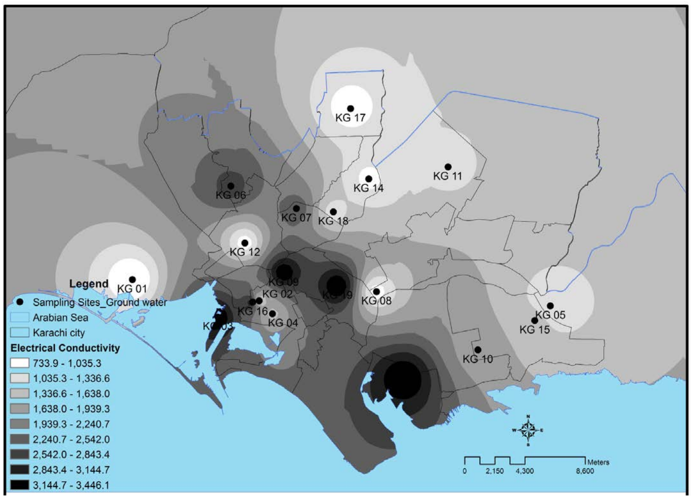

Figure 7. Spatial distribution of EC.

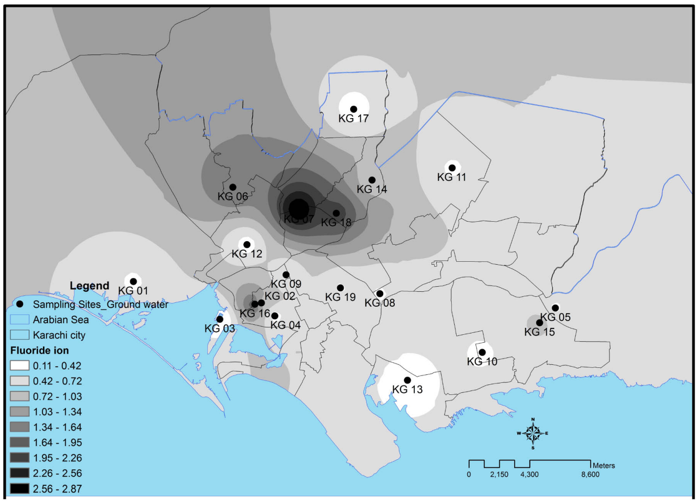

Figure 8. Spatial distribution of F^{-}.

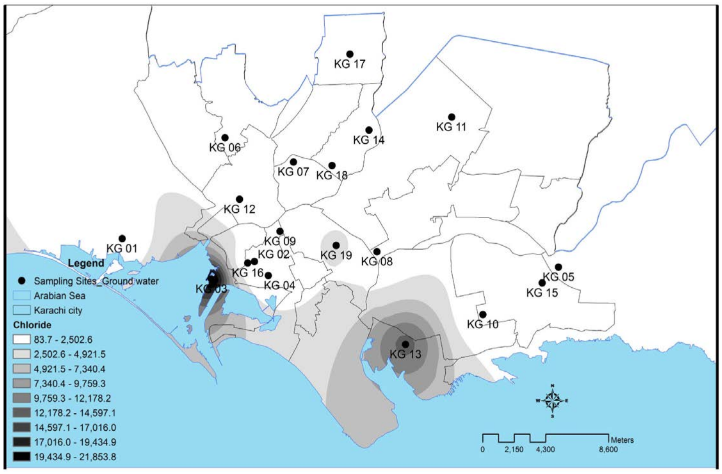

Figure 9. Spatial distribution of Cl^-.

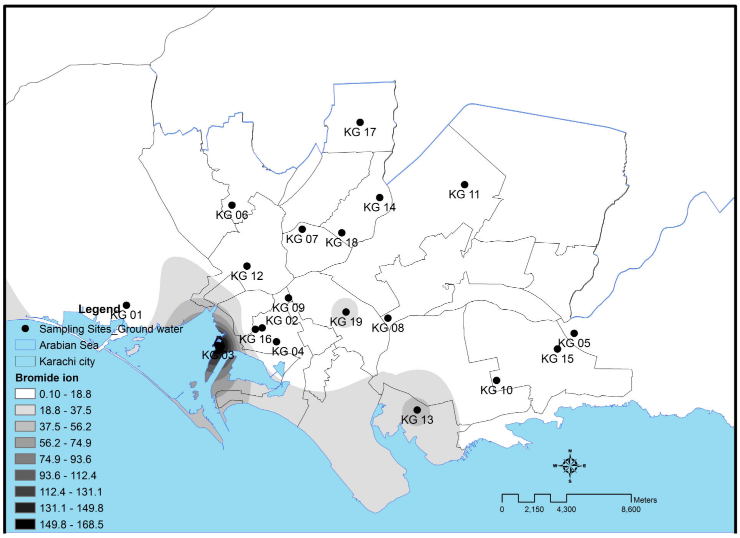

Figure 10. Spatial distribution of Br.

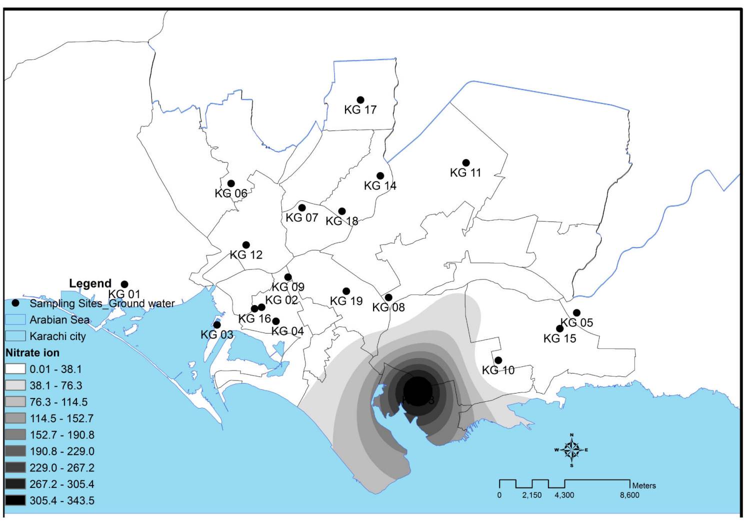

Figure 11. Spatial distribution NO_3^--N .

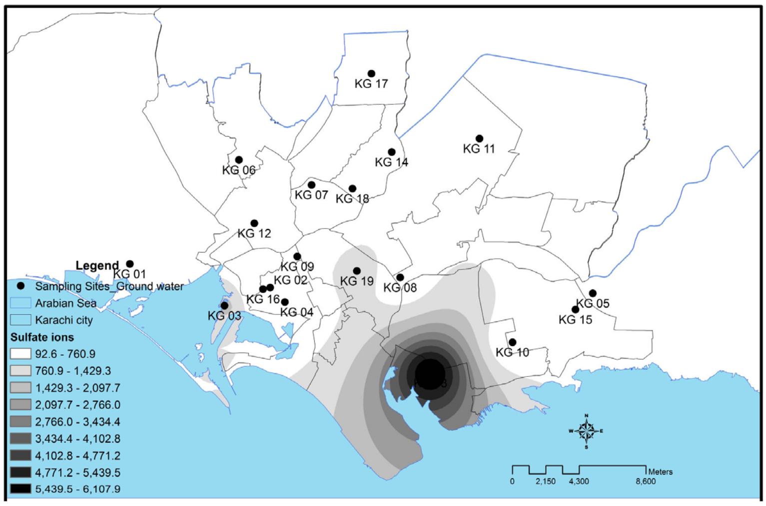

Figure 12. Spatial distribution of SO_4^{2-}.

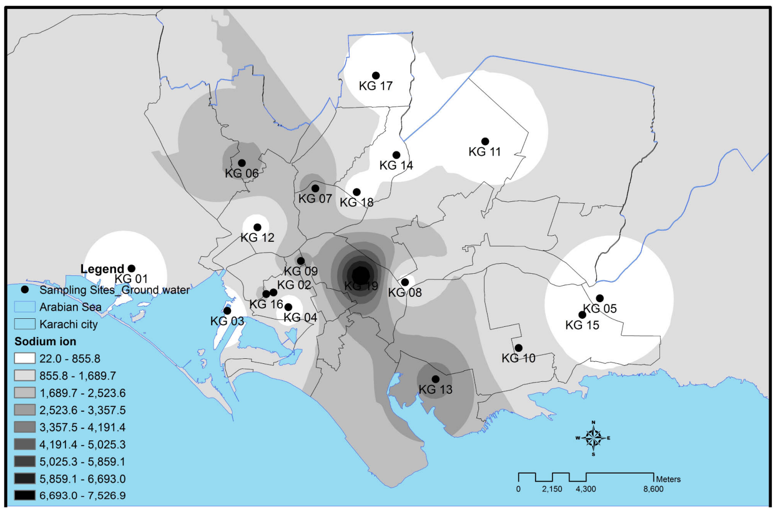

Figure 13. Spatial distribution of Na.

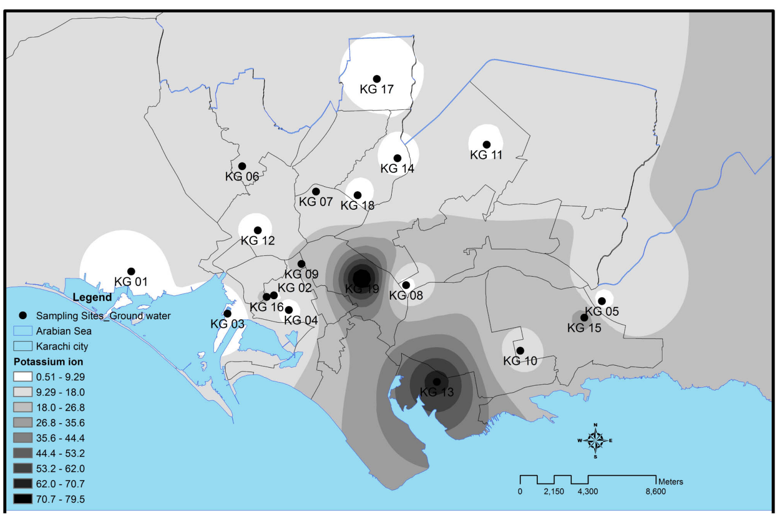

Figure 14. Spatial distribution of K.

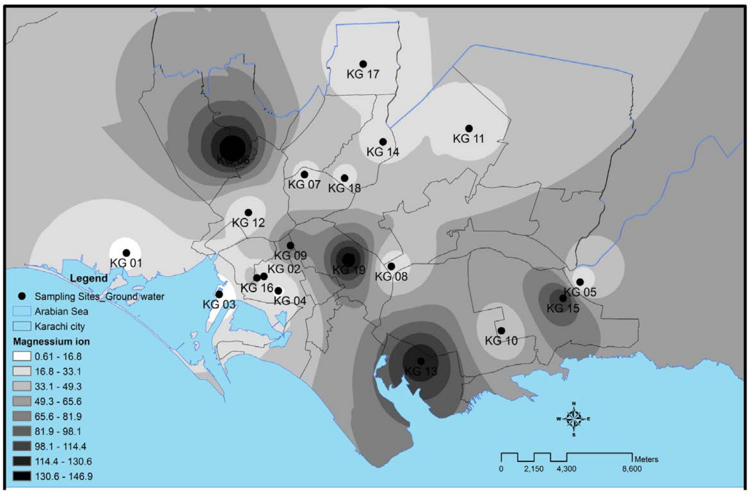

Figure 15. Spatial distribution of Mg.

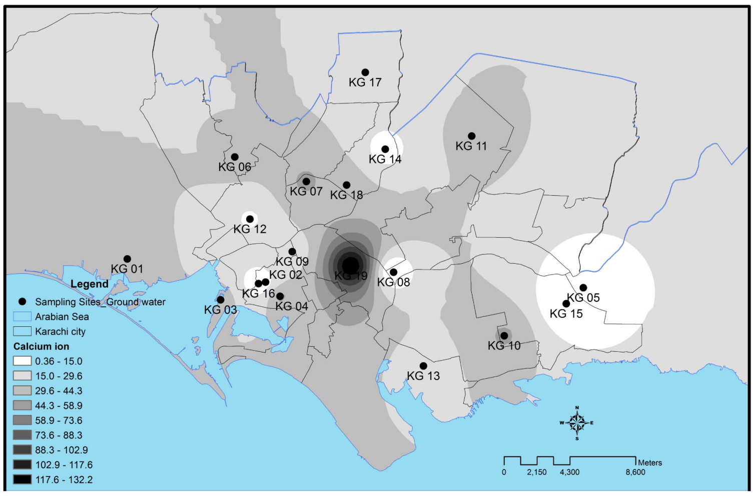

Figure 16. Spatial distribution of Ca.

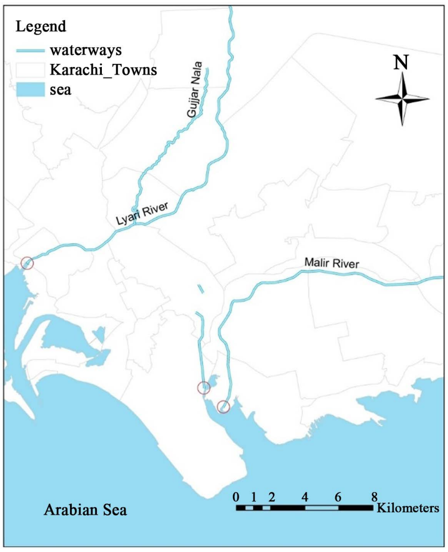

Figure 17. Sea water intrusion points for Karachi City.

extremely high concentrations of Cl^- because of dumping of large quantities of industrial and domestic wastes (**Figure 9** and **Figure 12**). High concentrations of Cl^- were observed at Fisheries and PECHS sites (**Figure 9**) due to causes identical to Na^+. Elevated NO_3^--N concentrations were observed at Bhittai Colony site (**Figure 11**). This site is characterized by open streams and large dumping sites containing heavy loads of contaminants. **Figure 10** shows high concentrations of Br^- at sites, which have cattle activities, high use of fertilizers, and open streams receiving large quantity of domestic and industrial wastes. High F^- concentrations were seen in the Nazimabad Block 7 site (**Figure 8**), which may be due to vehicular and industrial emissions.

4. Conclusions

The present study highlighted the fact that the physicochemical parameters measured were the functions of both the geology of the area and human activities (dumping of heavy quantity of industrial and domestic wastes, use of fertilizers, etc.). With only a few exceptions, most of the water quality parameters showed elevated concentrations that exceeded the WHO guidelines, which may be taken as an indicator of the declining quality of the groundwater. The SAR index suggested that 72% of the groundwater samples were unsuitable for irrigation purposes. High concentrations of NO_3^--N in groundwater were found, which may pose a significant threat to human health in Karachi city.

It is of utmost importance to monitor the concentrations of NO_3^--N in groundwater and its possible sources so that the health risks posed by dangerous contaminants can be minimized. To understand and interpret the results graphically, Arc GIS 10.1® was used to show the spatial distribution of the measured parameters. The spatial distribution of water quality parameters revealed that the groundwater quality of Karachi city faces a serious threat from the untreated wastes, which are the byproduct of industries and households. It is strongly recommended that the authorities take major steps to control and monitor the invasion of these and other contaminants.

Acknowledgements

We express our appreciation to Wadsworth Center, New York State Department of Health for the support. We extend our thanks to Dr. Kim McClive-Reed for editing the manuscript.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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