



Hydrochemical Analysis and Evaluation of Groundwater Quality and Agriculture Soil of Khairpur Taluka, Sindh, Pakistan

Tajnees Pirzada^{1*}, Mir Munsif Ali Talpur¹, Aziza Aftab²,
Maria Kaleem³ and Bushra Shahab³

¹Institute of Chemistry, Shah Abdul Latif University, Khairpur, Sindh, Pakistan.

²Department of Chemical Engineering, Mehran University of Engineering and Technology, Jamshoro, Pakistan.

³Department of Geology, University of Karachi, Karachi 75270, Pakistan.

*Corresponding Author Email: tajnees@yahoo.com

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Abstract

The inhabitants of Khairpur Taluka mostly consume groundwater for drinking and agriculture purposes. The present study was conducted to monitor the essential quality parameters of groundwater and soil. Both groundwater and soil samples of the area were classified as alkaline. All the major ions except Na and SO₄ were found within the permissible limits, while the concentrations of Zn, Fe, Co, Pb, Ni and Mn in studied groundwater samples were found above the specified limit of WHO. However, soil samples were found rich in major and trace elements except Cd, which was low in comparison to world average of agriculture soil. Irrigation character of water samples on Sodium Adsorption Ratio (SAR) vs. Na% plot display fair type with few exceptions. The piper diagram implied mixed water composition with Na-Ca-Mg and HCO₃-SO₄+Cl as dominant ions. Diverse shapes of Stiff polygons also support the mixed nature of groundwater in the study area.

Keywords: Groundwater; Agriculture soil; Physical parameters; Chemical contaminants; Trace elements

Introduction

The availability of good quality of water and soil for irrigation are the key factors of lucrative agriculture. The inhabitants of Taluka Khairpur mostly consume groundwater for drinking and agriculture purposes. Therefore, the quality of water may influence their healthiness and agricultural lands. Mostly the local people of the region are agriculturist by profession. Ali et al. [1] and others [2] emphasized for the availability of clean water to the humanity. Since the groundwater is lying below the soil surface hence considered to be more-safe and free from all contaminations. In European countries about 65% people are consuming groundwater for drinking purpose and

it is not possible to chlorinate bulk water supply, especially in the rural areas [3].

In agriculture lands, tube wells are the main source of water, the steadily increase of soil pollution is due to use of treated wastewater and animal manure [4]. Increase in use of fertilizers and pesticides on agriculture lands is also a cause of soil contamination [5]. Rainfall is the major cause of mobilization of metal ions in soil [6]. Unprocessed sewage generally possesses high level of pH, total dissolved solids, electrical conductivity, hardness, alkalinity, cations and trace metals. The mobilization of heavy metals and metalloids make up the natural complex and

complicated biochemical processes among the soil, water and plants and exaggerated by natural as well as anthropogenic activities [7]. These contaminants when crop up in water becomes dangerous for the human health, fertility of soil and growth of plants [8].

The reason of present study is to appraise abundance and distribution of major and trace elements of groundwater and soils of Taluka Khairpur. It is also aimed to evaluate their impact on human life and agricultural crops of the area. The current study will also assist water supply agencies and farmer for better utilization of groundwater in the area.

Materials and Methods

Seven groundwater and soil samples from Hussainabad, Khairpur, Shadi Shaheed, Therhi, Garhi Mori, Faizwah and Piryalo areas of Khairpur Taluka were collected. The soil and water samples collected in polyethene bags and pre-cleaned polypropylene bottles. The physicochemical parameters temperature, pH and electrical conductivity were determined on spot before taking them to the laboratory and acidified to pH <5 by using HNO₃ to prevent precipitation and absorption on walls of container. By applying American Public Health Association (APHA) [9] standard methods chloride, hardness, alkalinity, sulfate, total dissolved solids were analysed. Metal ions concentration was estimated with reference to standard solution of each element by using Atomic Absorption Spectrophotometer. The measured parameters were compared with the data presented elsewhere in the literature and guidelines suggested by [9-11].

Results and Discussion

The results of the major and trace elements of groundwater and associated soil along with important irrigation quality parameters are given in Table 1. Variation in physical parameters and distribution of major ions are illustrated in Fig. 1 and 2, respectively.

Table 1. Physical, chemical parameters and ionic ratios of groundwater samples of study area.

Parameter	Min	Max	Mean
<i>Groundwater</i>			
TDS (mg/L)	305	906	584
Temperature °C	22.5	25.0	23.6
EC (mS)/cm	0.258	1.342	0.741
pH	7.25	7.88	7.47
TH (mg/L)	164	480	290
Na ⁺ (mg/L)	144.82	280.37	208.66
K ⁺ (mg/L)	3.91	9.00	7.52
Ca ²⁺ (mg/L)	83.30	131.12	119.71
Mg ²⁺ (mg/L)	18.71	39.02	32.21
SO ₄ ²⁻ (mg/L)	125.40	834.70	367.94
Cl ⁻ (mg/L)	20.20	197.34	96.80
HCO ₃ ⁻ (mg/L)	140.00	580.00	385.71
Zn (mg/L)	1.21	5.37	3.12
Fe (mg/L)	12.10	13.15	12.63
Co (mg/L)	0.08	1.57	0.89
Pb (mg/L)	1.73	2.84	2.19
Ni (mg/L)	0.20	0.38	0.29
Mn (mg/L)	0.57	3.15	1.31
Na%	49.8	68.4	59.98
SAR	2.96	5.65	4.58
<i>Soil</i>			
Na (mg/kg)	452.42	736.55	614.60
K (mg/kg)	17.83	28.64	21.08
Ca (mg/kg)	269.90	414.29	360.39
Mg (mg/kg)	74.41	79.36	77.27
Cu (mg/L)	2.50	9.70	5.75
Zn (mg/L)	3.40	38.00	21.74
Fe (mg/L)	14.20	28.20	19.73
Co (mg/L)	5.20	8.00	6.58
Cd (mg/L)	2.50	8.20	6.20
Pb (mg/L)	4.50	15.70	9.01
Cr (mg/L)	2.00	7.50	3.88
Ni (mg/L)	8.70	19.20	15.35
Mn (mg/L)	9.80	21.40	14.21
Na%	48.98	61.93	54.24
SAR	5.45	10.23	7.69

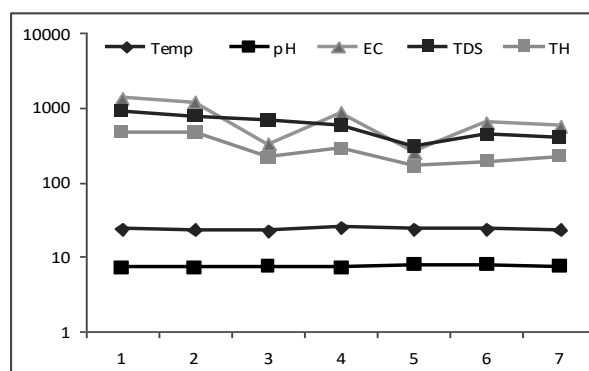


Figure 1. Physical parameters of ground water of Khairpur area

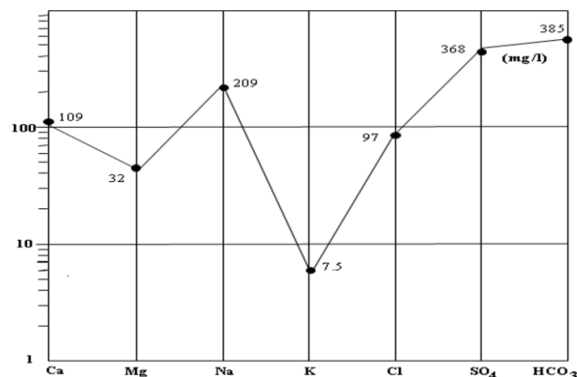


Figure 2. Schoeller diagram showing average composition (mg/L) of major ions of ground water of Khairpur area

Physical parameters

Practically the measurement of quantity of odor is not possible but it guides to gross contamination of water [12]. Results show that almost all samples were odorless which indicates the presence of very less quantity of chemicals especially organic matter in the water or soil [13] and also indicative of decreased biological or industrial activity [14].

Color of the water is mainly due to influence of iron and manganese, vegetation and particles of soil [14]. No health based guidelines are given for color in water [11]. All water samples appeared colorless, while slight brown color is observed in soil samples. The measurement of temperature largely affects the physical and chemical properties of groundwater [15]. The temperatures of ground water samples varied from 23-25°C (Table 1) which suggested that all water samples are suitable for plant growth because at temperature more than 30°C delay and decay the plant growth [16], however, the rate of biological as well as chemical activities increases, almost doubles with every 10°C rise in temperature [17].

The pH is hydrogen ion activity and is defined as the reciprocal of the hydrogen ion activity at a given temperature. The pH is measured in scales of 0 to 14 [15]. In all the water samples of study area pH is fluctuated between 7.25-7.88 which is suitable for drinking purpose [16] and within WHO limit (6.5-8.5). The pH of

soil samples ranges from 8.5-9.0. Both the ground water and soil samples indicate alkaline nature which may be due to fertilizers commonly used to increase the fertility of soil containing sulfate or pesticides/ insecticides [18, 19].

Water capability to transmit electric current is known as electrical conductivity (EC) [20]. Water is able to conduct electric current when the conductivity is proportional to the amount of dissolved ions in water. It is a helpful to appraise water purity [21]. The correlation matrix between EC and SO₄ and Cl is 0.97 and 0.92 respectively (Table 2). The standard value for irrigation water suggested by [19] is less than 2 mS/cm considered excellent for irrigation and production whereas; 4.0 mS/cm, shows drastic effects on water and physiological drought to crops [22]. According to [11] normal range of electrical conductivity for water is 400-600µS/cm [23]. The value of EC in all water samples exceeded the safe limits of WHO (2006), and thus cannot be suitable for drinking purpose, it's probably due to the presence of dissolved salts like NaCl, poor irrigation management domestic discharges and elements from water runoff [24].

The quantity of total dissolved solids in water determines the quality of drinking water. The amount of different types of water soluble minerals and organic matters define total dissolved solid [25]. Normal range of TDS for drinking water is 50-250mg/ml [21]. The TDS of water samples found between 305-906mg/l, in samples 1, 2 & 3 TDS are 600-900 mg/l considered fair, samples 4, 5, 6 and 7 are of good quality with 300-600mg/l TDS values (Fig. 1). None of the samples possess values higher than 1000mg/l the WHO recommended guidelines, also saline or brine nature was not observed in any sample. Umadevi et al [26, 27] worked previously in the area and reported that TDS less than 1000 is 'fresh water' and secure to be utilized for drinking and irrigation purposes.

Chemical parameters

Sodium (Na) is significantly contributed from the rocks weathering or by the of sodium salt

deposition in the soil [28]. It may cause increased pH ≥ 8 and TDS content in water [22] which makes water hazardous for drinking and irrigation. In a base-exchange reaction in water Ca and Mg cations are replaced by sodium ions makes the soil more alkaline leads to the direct effects on the fertility rate of agriculture soil. Sodium concentration in groundwater varies from 144-280mg/L (Table 1), minimum at Shadi Shaheed and maximum at Hussainabad. Only samples 3, 4 and 7 are within the recommended guidelines values of 200mg/L [11]. Present finding is compatible with the work of Majidano et al. [29], which may be due to the saline water imposition or industrial and domestic discharges on the ground [26]. High concentration of Na ion in drinking water may cause high systolic blood pressure, risk of hyper tension and cardio vascular disease [30].

In all the soil samples Na ranging between 452-736mg/kg. High pH of soil shows the presence of Na salts which makes it hard, dry and inclined to crust leads to less intake of water in the soil, poor plant growth and germination [31]. The major role of higher Na concentration in water may increase the water logging and salinity in soil. Water-soil relationship is important to evaluate the degree of leaching and other climatic factors. In the study area, the ratio of Na in water and soil ranges between 0.22-0.54 with a mean of 0.34 (Fig. 3).

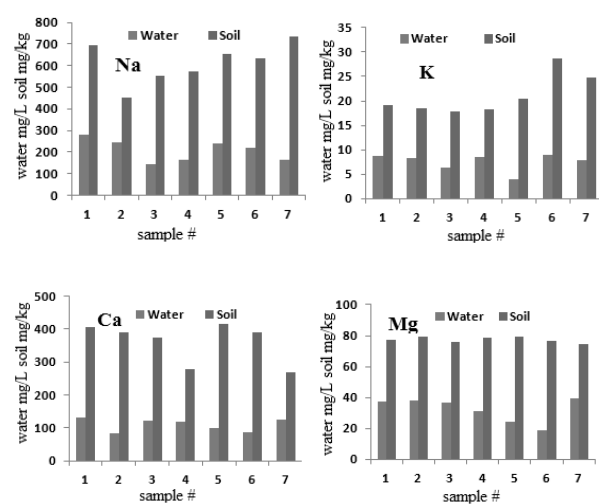


Figure 3. Average ratios of Na, K, Ca and Mg in ground water and soils of Khairpur area

Excess use of potash fertilizers in irrigation and weathering of potash silicate minerals are the main sources of K in soil and water [32]. In general, K is less abundant in water due to the low abundance of K-bearing rocks and minerals. The average concentration of K in the groundwater samples found 7.5 mg/L (Fig. 2), which is within the permissible limits of WHO (12 mg/L). K plays vital role in the physical fluid system and supports nerve functions of human body [33]. In plants K is an essential macronutrient which helps in growth by increasing absorption capacity of the roots in the production of agronomic yields [34]. Deficiency of K stunts the plant growth and reduces the yields [35]. K is also released from dead plants and animal excrements and it strongly attached to clay particles and remained there to be reabsorbed by the roots of other plants [36]. It is important to note that the average ratio of K (0.36) in the water and soil is nearly similar to Na (Fig. 3), representing close association between the two members of alkali metals.

In the groundwater samples Ca concentration ranges between 83-131mg/L, slightly higher than the WHO limits 75mg/L at Hussainabad. Calcium in higher quantities is responsible for hardness in water. Hard water is not only unsuitable for washing and bathing but also results in gastrointestinal diseases and high Ca contents form kidney stones, but at the same time hard water helps in strengthening bones and teeth [26].

Calcium is one among the most abundant element of the soil and plays a pivotal role in the plants as macronutrient [37]. Ca concentration in all the soil samples is 269.9-414.3mg/kg due to passage of water through deposits of limestone. It is very mobile in soil and easily neutralizes the acidity of soil as nutrient lime CaCO_3 [38].

The level of Mg in all water samples ranges between 18.71-39.02 mg/l (Fig. 2) within the permissible limits of WHO 30-50 mg/l. Magnesium is the fourth most abundant mineral in the human body and also an essential electrolyte, it

is consumed regularly with variable daily allowance [39]. Being the most abundant cation in cells of all living organisms, numerous physiological processes in plant depend on it [40]. In all soil samples Mg found higher which may be attributed the occurrence of soil minerals, particularly dolomitic limestone. The idea get supports from the very high correlation matrix (0.92) among Mg and HCO_3 ions in the groundwater and negative with pH (Table 2). Magnesium serves as a nutrient in the soil and as MgCO_3 to neutralize soil acidity [41]. Mg contents found highest in the groundwater and in the soil is highest (0.41) as compared to Na, K and even Ca (Fig. 3), probably the high leaching of Mg from dolomitic limestone is due to smaller atomic size.

The level of chlorides in the entire water samples is less than the WHO (2006) permissible limit of 250 mg/L (Table 1). Such lower values are also reported in previous literature [19, 42, 43]. The mutual relation among Cl and SO_4 is $r = 0.90$ (Table 2). The chloride level decreases due to natural inputs and increases which gradually increase with the degree of eutrophication [44]. In drinking water, the salty taste is due to the chloride concentrations [25]. The concentration of Cl found less than 70 mg/L in all water samples suggesting the water is considered to be safe for the growth of all plants [45].

Sulfate ions concentration lies between 125-835mg/L (Table 1). It is found that samples from Hussainabad, Khairpur and Theri have higher sulfate values than WHO limit of 250mg/L which is comparable and in agreement with the literature

[18, 29]. Sulfate ion increases the salinity in irrigation water hence its becomes toxic and cause difficulties in uptake of nutrients into the plants but at the same time presence of boron sulfate in irrigation water is favorable for fertility and results in maximum crops yield [19]. Higher values of sulfates are indicative of the brackish water [46]. In soil, sulphide is oxidized to sulphate by biochemical reaction, amount of this depends on how much quantity of sulphides are present in soil [47].

Total hardness refers the presence of bicarbonates and sulphates of calcium and magnesium [25]. It is important to note that the correlation among TH and SO_4 and Cl is excellent (Table 2). The obtained values were well within permissible limits, ranges between 172-256mg/l, attributed to Ca and Mg salts presence in water. The health hazards of hardness of water are not reported but its higher values more than 250mg/L affects the taste of water [26].

The measure of the acid buffering capacity of water is known as alkalinity [16] and contributed to bicarbonate and carbonate ions which act as proton acceptors to determine total alkalinity of water [48,49].The WHO limit for alkalinity of water is 200mg/l and the permissible limit is 600 mg/L, beyond this, the taste of water becomes unpleasant. Among all water samples HCO_3 found higher than the regulations set by WHO (250mg/l) except sample 4 and 5 and water having 10meq/L is not suitable for irrigation, therefore samples 4 and 5 can be safely utilized for long-term irrigation [22].

Table 2. Correlation matrix of physicochemical parameters of groundwater samples of study area.

	pH	EC	TH	Cl ⁻	TDS	SO_4	HCO_3	Ca	Mg	Na
pH										
EC	-0.67									
TH	-0.73	0.58								
Cl ⁻	-0.69	0.92	0.92							
TDS	-0.77	0.78	0.88	0.83						
SO_4	-0.67	0.97	0.92	0.90	0.83					
HCO_3	-0.85	0.38	0.59	0.45	0.74	0.42				
Ca	-0.48	0.04	0.05	-0.13	0.24	0.14	0.42			
Mg	-0.84	0.40	0.58	0.35	0.60	0.43	0.92	0.54		
Na	0.11	0.56	0.58	0.47	0.33	0.63	-0.18	-0.34	-0.14	
K	-0.48	0.70	0.49	0.60	0.48	0.56	0.19	0.07	0.16	0.04

Water type and facies

The stiff diagram is visual method for the comparing directly the relativity of dissolved ions concentration [50]. The areal distribution of stiff diagram constructed for the groundwater samples showed chemical composition and ionic balance. Stiff patterns can be a relatively distinctive method which reveals the analogies, dissimilarities and different types of waters. Major ionic composition of all studied samples is displayed in Fig. 4. All of them show different patterns due to unbalance ionic composition. The polygons exhibits high Ca and SO_4 and low Mg, probably the use of gypsum as fertilizer is responsible for this unbalancing, furthermore, the use of fertilizer containing K, Ca, Mg is also disturbed the ionic balance.

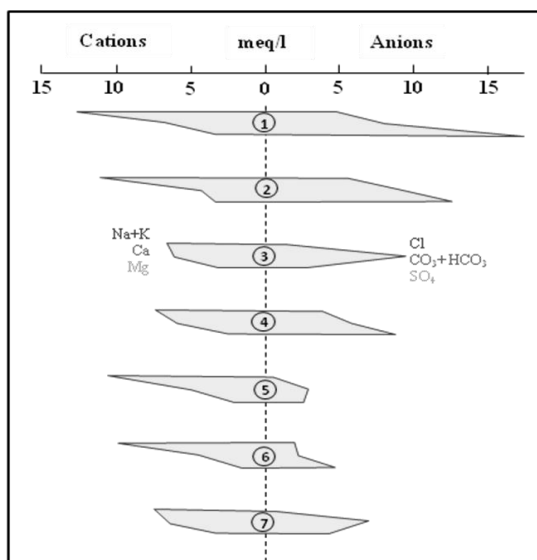


Figure 4. Major ionic composition of ground water of Khairpur area on Stiff diagram

The concept of hydrochemical facies was developed to identify and classify the water composition [51, 52]. Plots of groundwater composition of Khairpur area is illustrated in the trilinear piper diagram (Fig. 5). In general, (Na+K) dominates the cation composition of water, whereas, the anion composition is dominated by HCO_3 and SO_4 . According to these plots the samples 1, 2, 4, 6 are (Na+K)- (SO_4+Cl)- HCO_3 type. In the cation triangle 1, 2, 5, 6 are in the region assigned to (Na+K) while 3, 5, 7 are

inclined towards Ca. In anion triangle sample 1 is in the area of SO_4 , 3, 7 in HCO_3 and 2, 4, 5, 6 found in the center but moving towards SO_4 . This distribution of water is probably mixed type in which Na-Ca-Mg are dominating cations and HCO_3 - SO_4 as common anions, as reported in literature [2]; The ground water collected from different locations has been characterized by sodium-bicarbonate-type waters, as noticed by other investigators [53] with mixed cations and same dominant anion. The similarity in most water samples suggests that same geochemical processes may be controlling major-ion chemistry and that the waters had similar origins.

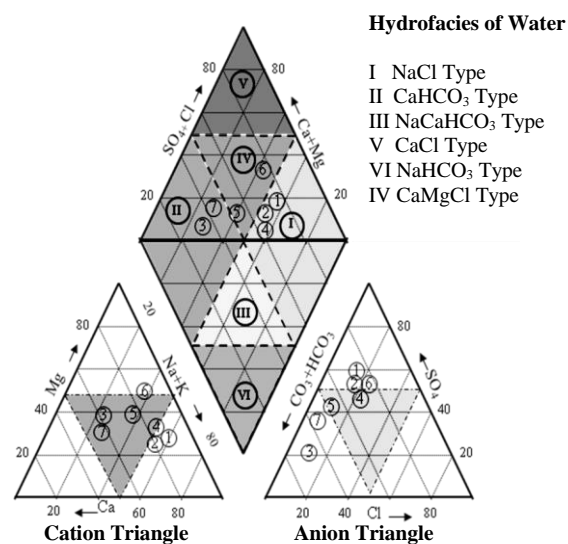


Figure 5. Piper diagram of ground water chemistry in the study area

This study also generates the idea that these water samples are belonging to the same “geochemical facies” and only subtle differences in water chemistry are noticed, which indicates that most of the major ions are natural in origin i.e. groundwater dissolves only small quantities of mineral matters because of the relative insolubility of the rock composition.

Level of Na in soil is often stated as SAR, which influences the infiltration rate of water. Low SAR value is desirable both for human beings and crops, in addition to EC and pH [54]. Sample with SAR value ≤ 6 and EC ≤ 1.5 dS/cm considered being suitable for irrigation purposes. All studied water and soil sample are suitable for agriculture

purposes with reference to SAR values (Table 1). In addition to Na%, EC is also valuable to infer suitability for crops (Fig. 6). According to this classification, groundwater with EC <0.5dS/cm is excellent, good up to 1.5dS/cm, 3dS/cm is fair and above 3dS/cm is harmful. Among collected samples, majority of the samples are plotted in the fair domain, sample number 3 is good and samples 1 and 2 are poor with respect to irrigation water quality (Fig. 6).

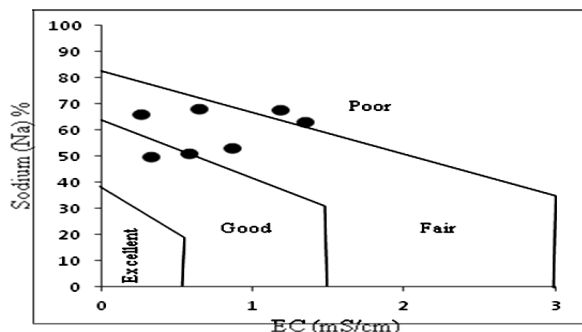


Figure 6. Na% vs EC plots of the groundwater samples of the study area and its suitability for irrigation

Trace elements

Trace elements has dual role in the human body, some of the trace elements are required for certain physiological functions and their excess or deficiency can cause health problem [55]. On the contrary, Pb, Cd, Hg and As are injurious to health [56]. The assessment of trace elements is essential with respect to environmental problem, both in the drinking water and agriculture soil. Heavy metals contamination is serious environmental and health problem because of their persistence and non-biodegradability [57, 58]. The amount of Zn, Fe, Co, Pb, Ni and Mn in all studied samples was found above the specified limit of WHO [59] for drinking purposes (Table 3). The high content of

trace elements in the groundwater of Khairpur poses environmental threat in the inhabitants of the area. In the absence of any rock exposure in the vicinity of the study area, possibly it is related to the soil of the area. A comparative study of trace elements showed relatively high content of trace element in the soil as compare to corresponding groundwater (Fig. 7). The slight alkaline pH of groundwater (av. 7.47) may reduce the concentration of trace elements. Possibly the trace elements are derived from the leaching of soil, as indicated by [60]. Additionally fertilizers, pesticides and insecticides, domestic and industrial discharges also release trace elements in the aquifer. Similarly the concentration of Zn, Fe, Co, Ni and Mn was also higher than the permissible limit of WHO [11] for irrigation purpose (Table 3).

The average trace element content of soil of the studied sample exhibit Zn>Fe>Ni>Mn>Pb>Co>Cd>Cu>Cr distribution pattern (Table 1). Samples collected from study area have low amount of trace elements, except Fe and Zn (Fig. 7). The trend of occurrence of Ni and Co is quite similar in all the seven localities, reflection close geochemical association among them. The average abundance of majority of the trace elements in the soil is low in contrast to world average of agriculture soil [61]. The exception is Cd, whose concentration in the soil of the study area is 6.2mg/kg in contrast to world average 1.1mg/kg. Lead (Pb), Co and Cd are toxic to crops, therefore, it is of great importance to protect agricultural soils and ensure its sustainability [8]. Contamination of toxic elements in the groundwater and soil is very serious concern and detrimental to health of the people [58].

Table 3. Average concentration of trace elements in the groundwater and soils of the study area and its comparison with drinking and irrigation water quality (WHO, 2006); and average in the world soil (Alloway, 2005).

	Zn	Fe	Co	Pb	Ni	Mn	Cu	Cd	Cr
	Groundwater (mg/l)								
Present study	3.12	12.63	0.89	2.19	0.29	1.31	BDL	BDL	BDL
Drinking water*	3.0	1.0	0.04	0.01	0.02	0.05	--	--	--
Irrigation water*	2.0	5.0	0.05	5.0	0.2	0.2	--	--	--
	Soil (mg/kg)								
Present study	21.74	19.72	6.58	9.01	15.35	14.21	5.75	6.2	3.88
Irrigation soil (Av.)†	64	5000	7.9	32	20		20	1.1	54

*(WHO, 2006); †(Alloway, 2005); BDL: Below detection limit

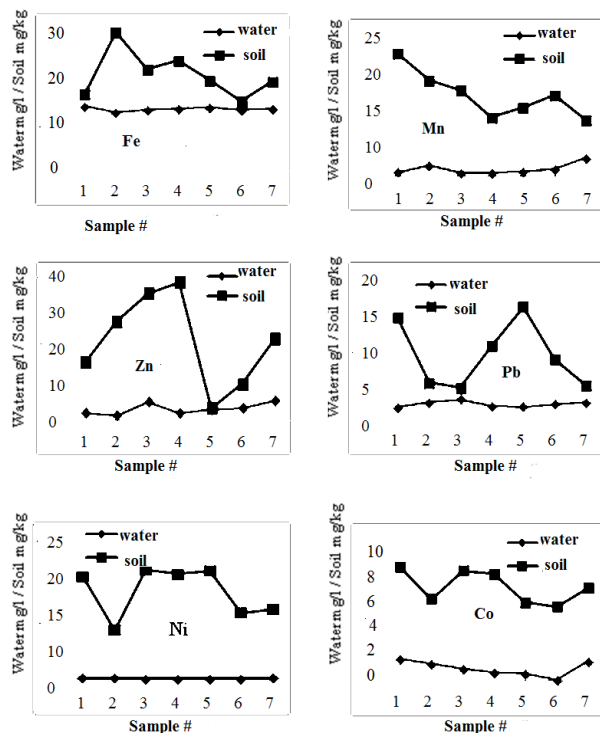


Figure 7. Concentration of trace elements in ground water and soils of Khairpur

Conclusion

The range of pH in the studied water sample is suitable for drinking purpose, while the pH of soil samples ranges from 8.5-9.0. Sample 1, 2 and 3 had relatively high amount of TDS, while the rest are in safe limit. Sodium concentration in groundwater found higher while potassium is within the permissible limit of WHO and the ratio of both Na and K in water and soil is nearly same (0.36). Ca and Mg are found suitable for drinking purpose. All anions are within the specified limit for drinking and irrigation water, except SO_4 in some of the samples. Stiff polygon reveal unbalance ionic composition of studied samples due to the use of different fertilizers, particularly gypsum. Plots of samples on Piper diagram exhibits mixed type in which Na-Ca-Mg are dominating cations and $\text{HCO}_3\text{-SO}_4\text{+Cl}$ as common anions. Irrigation character of samples on SAR vs. Na% plot display fair type with few exceptions.

The amount of trace elements in all studied groundwater samples are found above the specified limit of WHO, set for drinking purposes, while soil

samples exhibit $\text{Zn}>\text{Fe}>\text{Ni}>\text{Mn}>\text{Pb}>\text{Co}>\text{Cd}>\text{Cu}>\text{Cr}$ distribution pattern. Except Cd, majority of the trace elements in the soil are found low in contrast to world average of agriculture soil.

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