

Physicochemical and Spectroscopic Elemental Analysis of Ground Water in Thickly Populated and Industrial Area of Quetta Valley Pakistan

Hayatullah Khan ¹, Attiq-ur-Rehman Kakar ^{2*}, Samiullah Khan ², Naqeebullah Khan ², Irshad Ali ² and Abdul Baqi Achakzai ¹

¹Colleges, Higher and Technical Education Department, Balochistan, Quetta 87300-Pakistan.

²Department of Chemistry, University of Balochistan, Quetta 87300-Pakistan.

* Corresponding author: arkakar10@gmail.com

Abstract

Quetta valley the capital of Balochistan Province, has faced twice the rush of immigrants i.e; Afghan refugees after Saur Revolution and people from interior Balochistan due to drought in Balochistan from the last two decades. Additionally a number of industries at various areas has been established. This abrupt increase in the population and discharge from the industries have affected the drinking water quality in the valley. To assess these affects, nine ground water samples taken from densely populated and industrial areas were analyzed for their physicochemical (taste, order, color, temperature, conductivity, turbidity, alkalinity, pH, total hardness and total dissolved salts) and concentrations of cations (Na, K, Fe, Mn, Co, Ni, Cu, Cd and Pb) by Flame Photometer and Atomic Absorption Spectrometer. The results obtained were compared with both Pakistan National Standards (PNS) for drinking water Quality (2010) and World Health Organization (WHO), standards for drinking water. All the results were in the limits of the standards except cobalt (0.095 – 0.12 mg/L) and cadmium (0.0348 – 0.041 mg/L) which were found to be in high concentrations that are attributed to the anthropogenic activities.

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Introduction

The main source for drinking water is the groundwater that contains more than 90% of fresh water is a vital source of drinking water for human beings and other living organisms [1]. Clean water vouchsafes good health of people and a key indicator for the development of a country. It has been estimated that in the next four decades [2] the urban population of the developing countries will increase by 3 billion. Due to anthropogenic activities, the average temperature of the earth is being raised which is a key factor for changing the climatic pattern to an extreme level. Consequently, the precipitation pattern is being changed while turning some regions of the world wetter while the other drier [3]. Meanwhile, besides diminishing level of groundwater in most regions of the world, it has been contaminated by natural and most apparently by anthropogenic activities, agriculture and industrialization [4]. In the present time the ubiquity of heavy elements and trace elements and the change in the physical properties of water cannot be denied.

The water contaminated with heavy metals are altogether dangerous for health [5], though the trace elements are needed in very small amount for the metabolic activities of the organisms but their high doses can be lethal [6]. According to a study; contaminated water causes 2-12 million deaths per year throughout the world [7].

Physical parameters of water mainly involve taste, color, odor, turbidity, alkalinity, hardness, total dissolved solids and conductivity. The level of these parameters are disturbed by natural and anthropogenic activities [8,9]. Whereas, color, odor and turbidity which directly interfere with the aesthetic value of water, can also be the cause or sign of increased microbial activities in any water body [10]. Alkalinity and hardness are interdependent parameters [11]. Hardness of water is mainly caused by Ca and Mg ions. Hard water is the main cause of hair loss, lathering of the soap, cardiovascular diseases, reproductive failure and growth retardation [12,13]. Total dissolved salts (TDS) which is directly related to conductivity, causes a

reduction in performance and health while in higher doses, it can be lethal [14,15].

Heavy and trace elements such as Na, K, Fe, Mn, Se, Co, Ni, Cu, Cd, Zn, As and Pb are generally present in groundwater in very small quantity; but sometimes the optimum value of these elements exceeds in drinking water. The main sources of heavy elements in groundwater may be natural or most apparently anthropogenic sources including industrial, agricultural and municipal wastes [16]. They are the main cause of kidney impairment, respiratory tract diseases, an increased rate of Osteoporosis nervous disorders, gonadal dysfunction in man, disturbed calcium metabolism, mitochondrial injury, interference in the enzyme activities, abdominal cramps, sleeplessness, irritability, headache and joint pain [17,18]. Trace elements are required in a minute quantity to perform metabolic activities, impulses and transport inside the cell. But their excessive amount can be lethal for human beings causing a number of toxicities such as clastogenic effects in human cells causes necrosis [19], changes in appetite level nausea [20], diarrhea, gastrointestinal disturbances, headache, shortness of breath and fatigue, carcinogenesis, mutagenesis etc [21,22].

Drinking water should be free from all sorts of contamination. Due to the absence of proper monitoring and management; water contamination is rampant throughout most areas of the world especially Pakistan due to population increase, urbanization, heavy usage of agrochemicals, industrialization, natural and other anthropogenic activities. Groundwater is the only source in Quetta valley which is used for domestic and agricultural purpose. But its depletion has been taking place by leaps and bounds. Moreover, the improper drainage of huge municipal wastes from the Valley may have a greater contribution to the contamination of drinking water. The discharge of several hospitals and different industries make complex the common municipal waste.

This research study aimed to quantify the various physicochemical and elemental levels in the ground water of the Quetta valley and to compare these results with standards for the drinking water established by Pakistan and

World health organization. Through this study a water quality index for the city of Quetta could be established that will increase the awareness in the society as well as help the Government for future planning of drinking water.

Experimental

Geography and geological survey of the area

The Quetta valley is the capital city of Balochistan Province, Pakistan. The typical area is confined by longitude $66^{\circ} 50'$ to $67^{\circ} 20'$ E and latitude $29^{\circ} 39'$ to $30^{\circ} 26'$ N whereas altitude varies 550-3580 meter above mean sea level [23]. The valley has typical subtropical continental high land environment having average temperature in summer of 33° C and winter of 2° C [24]. On the basis of geography, the valley has been divided in to three major areas [25]; the mountain area consists in Murdar, Chiltan, Zarghoon and Takatu. These areas have some reserves of groundwater at higher depth. The Piedmont plain which exists between highland slopes and the main valley where the water table is at a relatively lower depth. The central valley; where the water table is comparatively shallow.

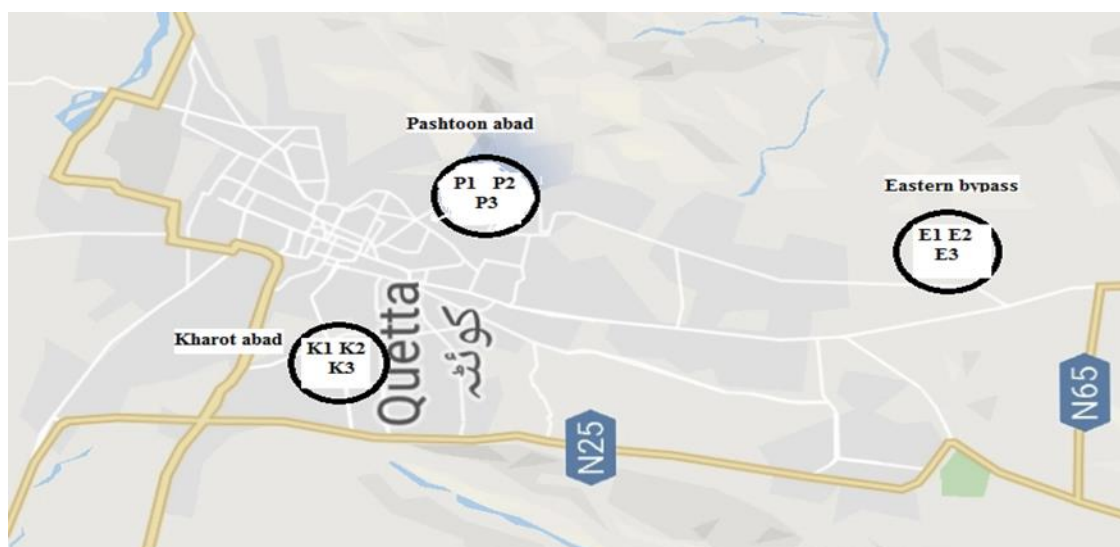


Figure: Map of the Quetta City and circles indicate the sampling areas i.e., E1, E2, E3 for Eastern Bypass, K1, K2, K3 for Kharot abad and P1, P2, P3 for Pashtoon abad. [Google Maps].

Geologically, the valley consists of several faults and folds filled with alluvial deposits. The aquifer system of the valley can be divided into four categories [25-27]. The alluvial fan consists of gravel, pebble and sand. It includes all slopes of the valley which has high hydraulic conductivity and has a good aquifer system. The alluvium which consists of clay, silt and sand. It includes the stream channels and flood plains which have intermediate hydraulic conductivity. Bostan which consist of clay, silt and sand. It includes streambed and flood plains which has low hydraulic conductivity. The Chiltan and murder range which are entirely made of limestone which has high hydraulic conductivity; thus, making it a good aquifer system. The valley has two drainage systems i.e. Northern basin and Southern basin. The Northern basin which is the main source of drinking water for Quetta city consists of Sariab Lora and Baleli river system. Whereas, the Southern basin which obtains water by flood from the mountains of Dagari and Kumbelan.

Sampling

Sample collection was done during October-November (2018) from nine sites (tube well/bores) i.e.; three are in Pashtoon abad (P1, P2, P3), three in Kharot abad (K1, K2, K3) and three in industrial zone, Eastern bypass (E1, E2, E3) at Quetta city (as shown

in figure). The method of sampling was similar to that listed [27, 28] by the American Public Health Association (APHA). The pre-cleaned plastic containers were used for samples collection. In order to ensure purity, the sampling bottles were flushed with plenty of the sampled water several times at a sampling site. Each sample container was labeled, taken to the lab with great care to avoid contamination, filtered through Whatman filter paper No. 4 and refrigerated at 4 °C in dark.

Materials and methods

All the glassware used during the study were per-cleaned with 20 % HCL for 24 h, rinsed thoroughly with ultra-high purity (UHP) deionized water (Elga, Purelab Option UK) and stored in plastic-zip bags before use to prevent contamination. All the reagents and salts used for the study were of analytical grade (BDH, Merck) unless not stated, solution and stocks were made in UHP deionized water from these salts and commercially available Atomic Absorption standards (1000 ppm) for metals were used. All of these solutions were diluted with UHP water before use.

Instrumentation and Procedure

The physical and chemical parameters of the collected water samples were analyzed by the methods of the American Public Health Association (APHA) for water analysis [29].

At the moment when samples were being collected, the physical parameters such as conductivity, pH and temperature of all water samples were determined by conductivity meter (HI-8033, HANNA Instruments, UK), pH meter (Model-3305, Jenway, UK) and thermometer respectively, while the other physical parameters were determined in the laboratory. Total alkalinity was determined by electrometric titration [30] while Phenolphthalein and mixed indicator (Methyl Orange + Bromocresol) and the end points were noted for concordant values. TDS were determined by evaporating dish method. Each sample was filtered and evaporated at 110 °C. After evaporation, the dish was cooled and weighed [31] as final which was computed with the initial weight and the readings were noted. Determination of total hardness was carried out by complexometric EDTA titration that uses Erichrome black T (EBT) as an indicator. In order to maintain pH of the solution between 9-10, $\text{NH}_4\text{Cl}+\text{NH}_4\text{OH}$ was used as a buffer and the readings were noted for concordant values [32]. Turbidity was determined by using turbidimeter. The standard solution was prepared by mixing 5ml of each hydrazine sulphate and hexamethylenetetramine (4000 NTU) which was diluted to 200 NTU. This concentration was used for the calibration of the instrument. Each sample was run through the instrument and the readings were noted.

Elemental analysis was done by using Flame Photometer (Jenway, Model PFP7, UK) and Atomic Absorption Spectrophotometer (Thermo- Electron Corporation, S4 AA System, Ser No, GE711544, China). The concentration of Na^+ and K^+ were determined with the help of Flame Photometer after calibrating with standards. The quantity of Cu^{+2} , Co^{+2} , Fe^{+2} , Mn^{+2} , Ni^{+2} , Cd^{+2} and Pb^{+2} were determined by Atomic Absorption Spectrometer after obtaining a calibration curve with five standards for each element. The AAS instrument was allowed for 30 minute to stabilize before use.

Results and Discussion

The results of various physicochemical properties and levels of different cations of water samples acquired are given in Tables (1

and 2). All the results obtained are compared with Provisional Guidelines of Drinking Water, World Health Organization [19] and Pakistan National Standards [33] for drinking Water Quality-2010. The levels of these parameters in ground water depend upon many factors including the depth of water table (more distance decreases the chance of contamination by reacting with soil/filtration) and the quantity of precipitation (less rainfall will result in less contaminants entering the ground water during recharge) [34]. The water table of Quetta valley is more than 300 m and soon the city will face a water crisis in the near future [35].

Physical Parameters

Different physical parameters of the water samples were analyzed and the results are shown in Table (1). The taste, order and color of all the water samples were not detected. The results obtained for temperature (noted at the time of sampling that ranges from 21 to 23°C), conductivity (0.4 to 0.82 $\mu\text{S}/\text{cm}$), turbidity (0.6 to 1.3 NTU), alkalinity caused by CO_3^{-2} , HCO_3^{-1} and OH^{-1} [10] (133 to 186 mg/L), pH (7.1 to 7.9), total hardness (55 to 73 mg/L) and total dissolved salts is mainly due to sulfates, chlorides, carbonates and bicarbonates (143.4 to 262.6 mg/L). All of these results are within the limits of PNS and WHO standards values.

Table (1)
Result obtained for physicochemical parameters of water samples.

Parameters	Sample ID			Sample ID			Sample ID			*PNS	†WHO
	Pashtoon abad			Kharot abad			Eastern bypass				
	P1	P2	P3	K1	K2	K3	E1	E2	E3		
Taste	**ND	ND	ND	ND	ND	ND	ND	ND	ND	None	None
Odor	ND	ND	ND	ND	ND	ND	ND	ND	ND	None	None
Color	ND	ND	ND	ND	ND	ND	ND	ND	ND	≤15 TCU	≤15 TCU
Temperature (°C)	22	22	23	22	23	23	22	21	23	***NA	NA
Conductivity (μS/cm)	0.50	0.48	0.40	0.53	0.82	0.74	0.60	0.53	0.51	NA	250
Turbidity (NTU)	0.8	0.8	0.9	1.1	0.9	1.3	0.8	0.6	0.9	<5	<5
Alkalinity (mg/L)	171	162	176	133	143	137	175	172	186	NA	<200
pH	7.3	7.1	7.3	7.3	7.4	7.4	7.8	7.8	7.9	6.5-8.5	6.5-8.5
Total hardness (mg/L)	55	58	57	61	59	62	71	73	71	<500	<200
TDS (mg/L)	224.6	233.6	250.6	168.8	173.6	143.4	248.2	262.6	248.8	<1000	<1000

† World Health Organization, standards for drinking water.

* Pakistan National Standards for drinking water Quality (2010)

** Not detected

*** Not available

Chemical Parameters

Chemical parameters were analyzed and the results are given in Table (2), which show that, sodium, potassium, iron and manganese are in the range of both WHO and PNS standards, nickel, copper and lead are below our detection limits and cobalt and cadmium are above the prescribed standards. The sources of cobalt include wind-blown dust, seawater spray, volcanoes, forest fires, and continental and marine biogenic emissions, burning of fossil fuels, sewage sludge, phosphate fertilizers, mining and smelting of cobalt ores, processing of cobalt alloys, and industries that use or process cobalt compounds etc [36] and cadmium include pigments in plastics, electric batteries, electronic components, anticorrosive, electroplated onto steel and phosphate fertilizers. The surrounding of Quetta valley is mostly agricultural area that uses different fertilizer and the number of automobiles is also increasing day by day which uses fossil fuel and storage batteries. The storage batteries are not only used by automobiles, but homes are diverting from main power supplies to the solar energy systems which use storage batteries. So the elevated concentrations of cobalt and cadmium could be attributed to these anthropogenic activities.

Table (2)
Result of chemical parameters of water samples.

Parameters	Sample ID			Sample ID			Sample ID			*PNS	†WHO
	Pashtoon abad			Kharot abad			Eastern bypass				
	P1	P2	P3	K1	K2	K3	E1	E2	E3		
Na (mg/L)	8.2	8.3	7.9	10.1	7.9	9.2	10.2	9.8	8.8	NA	200
K (mg/L)	1.2	1.2	1.0	1.4	1.4	1.3	1.2	0.9	1.3	NA	<50
Fe (mg/L)	0.2469	0.0597	0.0669	0.1051	0.1326	0.1493	0.099	0.0841	0.0899	NA	0.5-50
Mn (mg/L)	0.0672	0.1105	0.0843	0.1041	0.1138	0.1313	0.097	0.0873	0.1009	≤0.5	≤0.5
Co (mg/L)	0.102	0.106	0.112	0.120	0.119	0.095	0.110	0.099	0.095	NA	0.001-0.01
Ni (mg/L)	**BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	≤0.02	0.02
Cu (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	2	2
Cd (mg/L)	0.0407	0.0345	0.0363	0.0348	0.0363	0.0349	0.038	0.0364	0.0338	0.01	0.003
Pb (mg/L)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	≤0.05	0.01

† World Health Organization, standards for drinking water.

* Pakistan National Standards for drinking water Quality (2010).

** Below Detection Limit.

*** Not available.

Conclusion

Both the physical and chemical contamination makes water hazardous to health and aesthetically bad for consumers. Though groundwater is not highly vulnerable to the sources of contamination but sometimes the natural and anthropogenic activities are directly and indirectly involved in its contamination. In the present study, three different thickly populated areas of Quetta valley were selected for their physicochemical and elemental analysis to evaluate the effects of population on it. Most of the physical and chemical parameters analyzed were compared with both Pakistan National Standards for drinking water Quality (2010) and World Health Organization standards for drinking water. These results were found to be within the limits of both standards except cobalt and cadmium which were present in elevated levels. The reasons for their high levels are mostly anthropogenic activities such as the use of phosphate fertilizers and storage batteries by automobiles and in houses.

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