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Assessment of the Quality of Drinking water of Thari Mirwah Town and Surrounding villages, District Khairpur, Sindh, Pakistan

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Abstract

The ground water of Thari Mirwah town, Sindh, Pakistan and its surrounding villages was studied to check the chemical and physical suitability for drinking purpose. We measured several physico-chemical parameters; such as total dissolved salts (TDS), electrical conductivity (EC), chlorides, sulfate, phosphorus, nitrate-nitrogen, total hardness, alkalinity and total organic matter. The obtained results were in the range of: pH 6.9-8.1, temperature 25-30 ^{0}C, electrical conductivity 540-3140 μS/cm, total dissolved solids 362-2104 mg/L, chlorides 14.8-1657 mg/L, sulfate 69-308 mg/L, phosphate-phosphorus 0.003-0.56 mg/L, nitrate-nitrogen 0.00-9.9 mg/L, total hardness 58-760 mg/L, alkalinity 383-950 mg/L and total organic matter 0.022-0.89 mg/L. All these samples were analyzed using the standard methods of American Public Health Association (APHA) by atomic absorption spectrometer (AAS). The concentration of analyzed metals was found in the range of: sodium (Na) 2.57-1066.74 mg/L, calcium (Ca) 8.35-329.33 mg/L, manganese (Mn) 0.003-0.401 mg/L, nickel (Ni) 0.006-0.154 mg/L, zinc (Zn) 0.002-0.533 mg/L, copper (Cu) 0.004-0.169 mg/L, cobalt (Co) 0.00-0.040 mg/L, chromium (Cr) 0.0054-0.0322 mg/L, iron (Fe) 0.002-0.499 mg/L and cadmium (Cd) 0.00-0.014 mg/L. Study reveals that above parameters are not within safe limits of WHO/EPA/EU guidelines and all ground water samples were not fit for drinking and irrigation purposes.

Keywords: Ground water; Physico-chemical Parameters; Atomic Absorption Spectroscopy; Thari Mirwah.

Introduction

Water is the most important common resource, vital for the existence of life and is essential for mankind [1-4]. Some heavy metals found in water are toxic above definite concentration, while at lower concentrations some act as micronutrients [5, 6]. Water is vital constituent of metabolic processes and serves as solvent for many bodily solutes. The ongoing research reveals that the contaminated drinking water causes more than 50,000 deaths per day [7-10]. Water exists on earth as saline and fresh water [11-14]. Water pollution changes the taste, smell, color and odor of the water [15]. Water is contaminated by two types of substances, naturally occurring and fashioned by men's activities [16]. People of the most of rural areas of Pakistan are suffering from shortage of safe drinking water [17]. Iron and copper are biologically crucial elements but are highly toxic in excess [18, 19]. Due to contamination level and toxicity of heavy metals, it is very important to find out their amount in drinking water. Recently, numerous analytical methods are developed to assess the quality of drinking water [20-22].

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Metals like nickel, cadmium and arsenic are very harmful if present in excessive amounts in water. Nickel is a particularly, toxic metal because it can cause fatal diseases such as oral and intestinal cancer, heart failure, hemorrhages, kidney dysfunction, low blood pressure, paralysis and other physiological disorders. Cadmium is also a lethal metal and many pathological symptoms are associated with it [23-25].

Therefore, the analysis of water is essential for comparing the levels of essential and toxic metals to the desired and permissible level as given in the guidelines of WHO, EPA, EU, and FAO. This study can provide awareness to the people of the affected areas so that safety measure can be taken to solve this problem. To analyze these essential and toxic elements from drinking water, we have used the sensitive and latest techniques such as; flame atomic absorption spectrometer (FAAS) and other related techniques for determination of ultra-trace quantities of these metals. This study also provides useful information related to water pollution and other environmental studies [26-29].

The metals concentration in drinking water is being analyzed by using the many analytical techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission (ICP-OE), inductively coupled plasma-mass spectrometry (ICP-MS), UV-visible spectrometry etc. Atomic absorption spectrophotometer is widely used instrument for the determination of trace and heavy metal ions in drinking water [30-32].

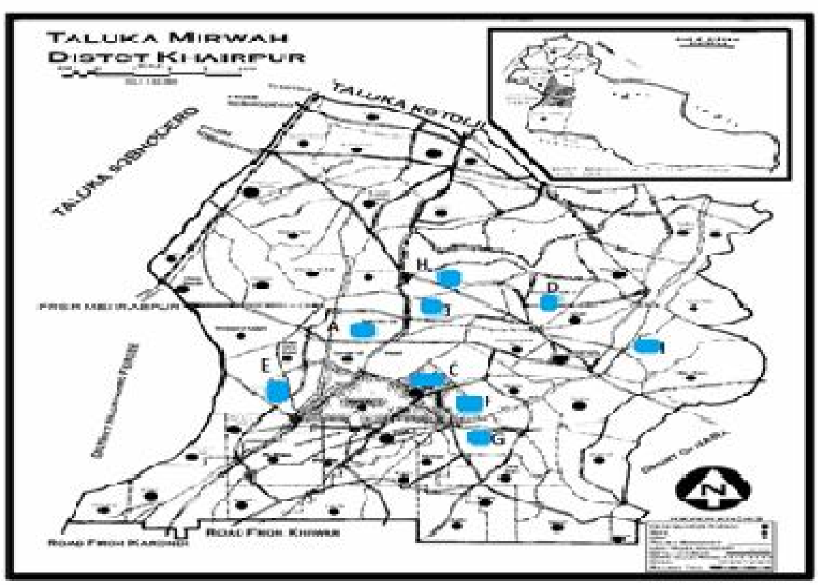
Materials and Methods

Materials

All the chemicals used for the purpose of analysis were ultrapure, taken from BDH, Merck, and Fluka. Perkin Elmer pure atomic spectroscopy standards of respective metals were also used to calibrate the equipment and to compare the correlation coefficient of standards.

Sample collection

Sixty eight samples of drinking water were collected from nine different villages of Taluka Thari Mirwah, District Khairpur. These villages include:Village Malak Chaudaghi, Village Bhutta Bachrah, Village Nawab Khan Rind, Village Tando Mir Ali, Village Allah Dino Khan Aamur, Village Haji Nangar Soomro, Village Rahim Bux Hajano, Village Habib ji Wandh and Village Mandan (Fig. 1). Sample codes and sample numbers are given in the (Table 1).



KEY
A Malak Chaudaghi
B Butta Bachrah
C Nawab Khan Rind
D Tardo Mir Ali
E A.D. Khan Aamur
F Haji Nangar Soomro
G Rahim Bux Hajano
H Habib ji Wandh
I Mandan

Figure 1. **Map of Sampling Sites.**

Table 1. **Sample Codes for Villages of Thari Mirwah (TM) Tehsil of District Khairpur, Sindh, Pakistan.**

S. No	Village Name	Sample Code	No: of samples
1	Malak Chaudaghi	TM-265 to TM-267, 272	=04
2	Bhutta Bachrah	TM-268 to TM-271	=04
3	Nawab Khan Rind	TM-273 to TM-274	=02
4	Tando Mir Ali	TM-275 to TM-286	=12
5	Allah Dino Khan Aamur	TM-287 to TM-291	=05
6	Haji Nangar Soomro	TM-292 to TM-296	=05
7	Rahim Bux Hajano	TM-297 to TM-302	=06
8	Habib ji Wandh	TM-303 to TM-305	=03
9	Mandan	TM-69 to TM-95	=27
		Total No: of Samples	*=68*

Triplicate samples were collected from each location. Sampling was done from the month of April to June. The water samples were stored in polyethylene bottles, washed with detergent, nitric acid and three times with same sample. Global Positioning System (GPS), pH, electrical conductance (EC) and temperature (^{0}C) were measured on the spot. Drinking water samples were transported to the chemistry research laboratory, Shah Abdul Latif University, Khairpur for analysis of further parameters, on the same day.

Physicochemical analysis of drinking water

pH was measured by using pH meter model (HANNA Instruments pH 210 woon socket –RI-USA Made in Romania) at sampling spot. The instrument was calibrated with buffers of pH 4 and 9. According to WHO/Pakistan guidelines the pH of drinking water should range from 6.5-8.5. Extreme pH values (<4 and >9) may badly affect human health [33]. Temperature was recorded with alcoholic thermometer; electrical conductance was checked with conductivity meter (HANNA Instruments, HI 9033 Multi-range EC portable meter). TDS, chlorides, sulphate, phosphorus, nitrate-nitrogen, TH, alkalinity and organic matter were analyzed by standard methods [34].

Sample preparation

Samples of drinking water were brought to the laboratory of chemistry. The pre-treatment and pre-concentration were performed by taking 250 mL of the sample into 500 mL beaker. Water was evaporated on controlled electric hot plate and the temperature was maintained at about 70-80 ^{0}C below its boiling point. After evaporating the sample; it was transferred to 25 mL volumetric flask and 1 mL of concentrated nitric acid was added to make the sample clear. De-ionized water was added to make up the volume up to the mark. Samples were filtered through Whatmann # 42 filter paper and were taken for heavy metals analysis [35].

Preparation of standards

Standard solutions of metals under study were prepared from their metal salts. A 1000 mg/L solution of each metal was prepared and solutions of various concentrations were prepared by diluting the prepared standards of 1000 mg/L. Double distilled and de-ionized water were used throughout research work and samples were stored in glass containers.

Analysis

Analysis of heavy metals was performed with the Atomic Absorption Spectrophotometer (Analyst AAS-100), made up of Perkin Elmer Company. To analyze the amount of elements under study, the respective hollow cathode lamps (Perkin Elmer LUMINA ™ Shelton, CT 06484-4794 USA) were used and the mixture of air/acetylene was used as fuel.

Results and Discussion
Physicochemical analyses

The different parameters of the drinking water showed signs of significant discrepancy from sample to sample. All the measurements were carried out at room temperature. Experiments were carried out to find out the contamination levels of drinking water. Results of present study are given in (Tables 2).

Table 2(a). **physico-chemical parameters of ground water of nine different villages of Tehsil Thari Mirwah, District Khairpur, Sindh Pakistan.**

Sample ID	pH	Temp: (^{0}C)	Cond. (µS/cm)	TDS (mg/L	Chlorides
	WHO LIMIT 6.5-8.5	***WHO LIMIT =NS***	***WHO LIMIT 1000 (µS/cm)***	***WHO LIMIT 1000 mg/L***	***WHO LIMIT 250 mg/L***
TM-265	7.51±0.01	29.2±0.300	1720±0.13	1152.4±1.386	1299.83±0.153
TM-266	7.25±0.01	28.5±0.200	3140±0.10	2103.8±0.058	649.92±0.000
TM-267	7.18±0.01	28.3±0.200	2090±0.06	1400.3±0.115	239.29±0.058
TM-272	7.25±0.01	27.8±0.351	1310±0.06	877.7±0.112	82.72±0.000
TM-268	7.68±0.01	28.1±0.153	1030±0.12	690.1±0.135	682.41±0.115
TM-269	7.48±0.01	27.4±0.208	2080±0.06	1393.6±0.127	1128.49±0.153
TM-270	7.23±0.01	27.7±0.100	2450±0.13	1641.5±0.055	555.38±0.058
TM-271	7.43±0.01	26.6±0.153	2110±0.18	1413.7±0.066	206.79±0.153
TM-273	7.11±0.01	26.9±0.208	1190±0.11	797.3±0.075	623.33±0.173
TM-274	7.10±0.01	28.2±0.153	1750±0.06	1172.5±1.455	983.74±0.000
TM-275	7.15±0.006	29.3±0.200	2040±0.11	1366.8±2.236	79.76±0.058
TM-276	7.06±0.02	29.4±0.153	900±0.06	603±0.458	809.44±0.100
TM-277	6.96±0.02	28.6±0.153	1040±0.18	696.8±0.430	1657.29±0.058
TM-278	7.22±0.01	26.4±0.153	2980±0.06	1996.6±1.408	82.72±0.058
TM-279	7.41±0.03	26.3±0.153	850±0.12	569.5±1.876	188.34±0.058
TM-280	7.07±0.01	25.7±0.100	1190±0.10	797.3±1.876	215.65±0.115
TM-281	7.25±0.02	25.9±0.208	1100±0.07	737±0.439	153.62±0.000
TM-282	7.84±0.04	27.2±0.153	1010±0.06	676.7±0.282	174.3±0.000
TM-283	7.24±0.03	28.7±0.100	1340±0.12	897.8±0.292	239.29±0.058
TM-284	7.29±0.02	28.9±0.208	1230±0.06	824.1±0.488	223.15±0.058
TM-285	7.33±0.04	27.8±0.153	1170±0.07	783.9±0.373	212.7±0.000
TM-286	7.28±0.03	26.5±0.153	1090±0.06	730.3±0.586	156.57±0.000
TM-287	7.44±0.04	27.4±0.153	1090±0.20	730.3±0.478	180.2±0.115
TM-288	7.19±0.01	27.9±0.208	1220±0.25	817.4±2.347	186.11±0.058
TM-289	7.23±0.01	29.4±0.100	810±0.45	542.7±3.125	168.39±0.058
TM-290	7.36±0.02	25.8±0.100	1100±0.10	737±1.028	200.88±0.058
TM-291	7.26±0.02	25.9±0.153	1100±0.21	737±1.804	180.2±0.000
TM-292	7.09±0.01	26.3±0.153	1310±0.02	877.7±0.000	342.68±0.100
TM-293	7.21±0.015	26.5±0.153	1120±0.06	750.4±3.350	144.75±0.000
TM-294	6.98±0.018	26.7±0.100	1550±0.10	1038.5±4.130	283.6±0.000
TM-295	6.87±0.012	27±0.208	2500±0.10	1675±1.050	1205.3±0.173
TM-296	7.13±0.011	26.1±0.100	820±0.02	549.4±3.800	70.9±0.153
TM-297	7.18±0.013	25.7±0.100	1230±0.02	824.1±1.350	283.6±0.058
TM-298	7.25±0.013	25.4±0.100	1050±0.06	703.5±3.350	194.98±0.115

Table 2(b). **physico-chemical parameters of ground water of nine different villages of Tehsil Thari Mirwah, District Khairpur, Sindh Pakistan.**

Sample ID	pH	Temp: (^{0}C)	Cond. (µS/cm)	TDS (mg/L)	Chlorides (mg/L)
	WHO LIMIT 6.5-8.5	***WHO LIMIT =NS***	***WHO LIMIT 1000 (µS/cm)***	***WHO LIMIT 1000 mg/L***	***WHO LIMIT 250 mg/L***
TM-299	7.26±0.099	26.3±0.411	1170±0.10	783.9±4.130	262.92±0.058
TM-300	7.35±0.078	26.9±0.311	1030±0.02	690.1±1.050	162.48±0.058
TM-301	7.38±0.011	28.4±0.215	1080±0.04	723.6±3.800	209.75±0.058
TM-302	8.11±0.011	28.8±0.462	1800±0.02	1206±1.350	121.12±0.115
TM-303	8.02±0.016	29.7±0.264	2010±0.06	1346.7±1.540	251.1±0.058
TM-304	8.13±0.020	29.9±0.319	1780±0.10	1192.6±3.350	138.85±0.058
TM-305	7.98±0.023	30.2±0.211	2070±0.01	1386.9±4.130	203.84±0.200
TM-69	7.85±0.027	25.3±0.265	700±0.01	469±1.050	82.72±0.058
TM-70	7.75±0.012	25.7±0.319	540±0.05	361.8±1.350	14.77±0.058
TM-71	7.32±0.013	26.1±0.264	770±0.02	515.9±3.800	41.36±0.100
TM-72	7.65±0.017	26.4±0.262	1090±0.06	730.3±1.350	135.89±0.058
TM-73	7.18±0.015	26.6±0.264	930±0.08	623.1±2.450	70.9±0.115
TM-74	7.63±0.011	27.2±0.264	690±0.01	462.3±3.130	67.95±0.058
TM-75	7.51±0.011	27.3±0.211	1080±0.04	723.6±2.360	159.53±0.153
TM-76	7.62±0.012	27.1±0.319	770±0.03	515.9±3.160	91.58±0.058
TM-77	7.63±0.017	25±0.264	770±0.06	515.9±2.950	79.76±0.058
TM-78	7.58±0.016	25.5±0.211	670±0.02	448.9±1.880	129.98±0.058
TM-79	7.62±0.010	25.4±0.319	960±0.02	643.2±3.350	109.3±0.000
TM-80	7.4±0.009	25.8±0.264	870±0.06	582.9±4.130	118.17±0.153
TM-81	7.39±0.010	26.5±0.264	1470±0.10	984.9±1.050	254.06±0.058
TM-82	7.77±0.012	26±0.264	1050±0.09	703.5±1.360	118.17±0.000
TM-83	7.29±0.014	26.7±0.319	1080±0.08	723.6±2.580	127.03±0.058
TM-84	7.63±0.015	27±0.211	1200±0.09	804±4.760	203.84±0.100
TM-85	6.98±0.018	25.9±0.211	1050±0.01	703.5±3.500	153.62±0.000
TM-86	7.22±0.011	26.6±0.263	1280±0.01	857.6±2.450	233.38±0.000
TM-87	7.61±0.010	26.3±0.264	1090±0.03	730.3±3.060	183.16±0.058
TM-88	7.49±0.018	26.7±0.264	940±0.07	629.8±1.120	79.76±0.115
TM-89	7.61±0.011	27.4±0.211	980±0.02	656.6±2.210	121.12±0.100
TM-90	8.08±0.016	25.9±0.319	750±0.05	502.5±1.450	62.04±0.200
TM-91	7.81±0.009	25.3±0.211	810±0.08	542.7±2.950	62.04±0.0173
TM-92	7.57±0.099	26.1±0.211	710±0.04	475.7±1.150	62.04±0.0115
TM-93	7.59±0.010	25.8±0.211	760±0.05	509.2±1.260	73.85±0.0112
TM-94	7.65±0.019	25.7±0.319	1180±0.08	790.6±2.185	165.43±0.058
TM-95	7.62±0.020	28.1±0.264	930±0.09	623.1±1.760	115.21±0.0200

Table: 2(c). **physico-chemical parameters of ground water of nine different villages of Tehsil Thari Mirwah, District Khairpur, Sindh Pakistan.**

ID	Sulphate (mg/L)	Phosphorus (mg/L)	Nitrate-N (mg/L)	TH (mg/L)	Alkalinity (mg/L)	Org: Matter (mg/L)
	WHO LIMIT 250 mg/L	***WHO LIMIT =NS***	***WHO LIMIT 10 mg/L***	***WHO LIMIT 300 mg/L***	***WHO LIMIT 500 mg/L***	***WHO LIMIT = NS***
TM-265	235.08±0.282	0.021±0.001	3.68±0.074	366.67±0.047	716.67±0.058	0.373±0.010
TM-266	228.42±2.525	0.03±0.001	0.11±0.011	835±0.058	583.33±0.058	0.095±0.010
TM-267	108.93±0.959	0.01±0.001	0.13±0.009	231.67±0.058	500±0.000	0.253±0.010
TM-272	223.54±1.016	0.018±0.001	0.13±0.012	140±0.058	450±0.000	0.044±0.010
TM-268	168.7±2.151	0.02±0.000	0.94±0.084	373.33±0.058	583.33±0.058	0.3±0.0200
TM-269	211.52±0.430	0.064±0.001	0.48±0.011	620±0.115	500±0.000	0.398±0.0312
TM-270	261.28±1.016	0.011±0.001	0.02±0.00	288.33±0.058	350±0.000	0.437±0.010
TM-271	270.58±0.282	0.018±0.001	0.4±0.016	160±0.047	583.33±0.058	0.636±0.010
TM-273	306.73±2.666	0.014±0.001	1.41±0.016	463.33±0.110	416.67±0.058	0.812±0.010
TM-274	257.24±1.876	0.018±0.001	1.02±0.016	660±0.118	433.33±0.058	0.502±0.058
TM-275	115.37±2.236	0.016±0.000	0.39±0.016	260±0.000	566.67±0.058	0.166±0.020
TM-276	268.14±0.430	0.02±0.001	2.43±0.026	418.33±0.058	500±0.000	0.044±0.020
TM-277	214.9±0.430	0.021±0.001	4.6±0.018	760±0.058	450±0.000	0.215±0.012
TM-278	94.52±1.408	0.019±0.000	0.8±0.016	208.33±0.047	550±0.000	0.104±0.021
TM-279	239.4±1.876	0.021±0.001	0.02±0.00	115±0.000	500±0.000	0.792±0.045
TM-280	194.05±0.430	0.023±0.001	0.6±0.014	313.33±0.058	533.33±0.058	0.892±0.056
TM-281	168.61±0.282	0.014±0.001	1.87±0.014	206.67±0.058	533.33±0.058	0.171±0.011
TM-282	249.17±0.282	0.021±0.000	0.06±0.009	220±0.058	450±0.000	0.074±0.000
TM-283	233.39±0.488	0.003±0.000	0.9±0.013	243.33±0.047	733.33±0.058	0.051±0.000
TM-284	180.28±1.386	0.003±0.000	0.02±0.000	255.45±0.100	756.45±0.000	0.123±0.010
TM-285	114.52±0.373	0.003±0.000	0.17±0.035	283.33±0.115	616.67±0.048	0.099±0.001
TM-286	275.46±0.586	0.003±0.000	0.02±0.000	115±0.100	616.67±0.058	0.07±0.000
TM-287	136.87±1.147	0.003±0.000	0.06±0.009	186.67±0.047	416.67±0.000	0.06±0.000
TM-288	202.13±4.150	0.003±0.000	0.44±0.013	115±0.058	566.67±0.000	0.095±0.010
TM-289	170.3±1.016	0.01±0.001	2.3±0.016	258.33±0.085	450±0.000	0.101±0.009
TM-290	131.14±1.408	0.019±0.001	0.02±0.000	216.67±0.076	483.33±0.100	0.107±0.011
TM-291	299.45±0.000	0.018±0.001	4.53±0.063	251.67±0.065	450±0.000	0.634±0.008
TM-292	205.04±0.430	0.028±0.000	1.71±0.014	343.33±0.058	600±0.058	0.051±0.005
TM-293	206.26±0.430	0.018±0.001	1.53±0.041	251.67±0.058	550±0.000	0.057±0.006
TM-294	238.61±1.842	0.015±0.000	1.17±0.016	335±0.047	550±0.058	0.096±0.008
TM-295	160.81±0.163	0.01±0.000	7.74±0.177	585±0.100	466.67±0.058	0.161±0.011
TM-296	166.45±0.163	0.011±0.001	2.81±0.021	218.33±0.047	616.67±0.058	0.055±0.004
TM-297	151.89±0.325	0.558±0.002	0.13±0.011	290±0.058	450±0.058	0.068±0.005
TM-298	151.89±0.325	0.005±0.000	4.79±0.015	215±0.010	483.33±	0.055±0.004

Table: 2(d). **physico-chemical parameters of ground water of nine different villages of Tehsil Thari Mirwah, District Khairpur, Sindh Pakistan.**

Sample ID	Sulphate (mg/L)	Phosphorus (mg/L)	Nitrate-N (mg/L)	TH (mg/L)	Alkalinity (mg/L)	Org:Matter (mg/L)
	WHO LIMIT 250 mg/L	***WHO LIMIT = NS***	***WHOLIMIT 10 mg/L***	***WHOLIMIT 300 mg/L***	***WHOLIMIT 500 mg/L***	***WHO LIMIT = NS***
TM-299	258.46±0.563	0.011±0.001	2.08±0.018	258.33±0.058	433.33±0.058	0.085±0.002
TM-300	230.48±0.215	0.012±0.001	1.23±0.009	243.33±0.100	416.67±0.058	0.126±0.010
TM-301	105.37±0.976	0.015±0.001	3.66±0.118	216.67±0.047	433.33±0.058	0.042±0.004
TM-302	106.68±0.508	0.048±0.002	0.00±0.000	63.33±0.058	933.33±0.416	0.081±0.009
TM-303	190.86±0.906	0.018±0.002	0.00±0.000	83.33±0.100	850±0.115	0.126±0.011
TM-304	248.18±0.000	0.071±0.002	0.00±0.000	33.33±0.058	950±0.416	0.186±0.012
TM-305	194.62±0.000	0.083±0.002	0.00±0.000	58.33±0.100	900±0.100	0.028±0.004
TM-69	130.86±0.430	0.06±0.001	2.88±0.005	115±0.058	350±0.000	0.063±0.007
TM-70	83.68±0.163	0.015±0.001	1.62±0.004	120±0.1000	416.6±70.058	0.076±0.008
TM-71	151.52±0.000	0.018±0.001	1.50±0.007	216.67±0.082	550±0.058	0.126±0.010
TM-72	61.75±0.000	0.079±0.002	3.60±0.070	115±0.058	550±0.058	0.545±0.012
TM-73	164.54±0.275	0.01±0.001	0.00±0.000	188.33±0.100	633.33±0.115	0.111±0.011
TM-74	206.35±0.282	0.004±0.000	3.3±0.018	116.67±0.047	366.67±0.000	0.022±0.000
TM-75	197.62±0.282	0.021±0.001	9.25±0.021	230±0.058	466.67±0.058	0.052±0.004
TM-76	183.82±0.282	0.076±0.001	5.72±0.013	115±0.047	433.33±0.058	0.047±0.005
TM-77	142.41±0.709	0.003±0.000	0.15±0.009	153.33±0.058	433.33±0.047	0.082±0.007
TM-78	157.06±0.163	0.016±0.001	1.02±0.009	115±0.058	383.33±0.000	0.066±0.005
TM-79	210.67±0.488	0.046±0.001	6.96±0.025	301.67±0.100	433.33±0.058	0.044±0.004
TM-80	188.7±0.282	0.016±0.001	3.29±0.016	176.67±0.115	500±0.058	0.177±0.012
TM-81	149.17±1.446	0.029±0.001	8.43±0.011	238.33±0.100	666.67±0.100	0.119±0.012
TM-82	178.46±0.430	0.054±0.002	4.97±0.014	128.33±0.115	500±0.058	0.139±0.013
TM-83	165.13±1.923	0.012±0.001	0.00±0.000	341.67±0.000	566.67±0.058	0.249±0.020
TM-84	220.34±0.906	0.019±0.001	7.40±0.025	241.67±0.047	466.67±0.047	0.035±0.003
TM-85	109.59±1.228	0.034±0.001	0.32±0.011	226.67±0.058	583.33±0.100	0.066±0.005
TM-86	120.2±0.325	0.021±0.001	9.89±0.013	115±0.058	516.67±0.058	0.053±0.005
TM-87	198.84±0.081	0.046±0.001	8.54±0.016	201.67±0.058	433.33±0.078	0.067±0.007
TM-88	123.54±0.586	0.068±0.002	2.95±0.067	111.67±0.058	533.33±0.074	0.748±0.018
TM-89	188.23±0.906	0.036±0.001	5.40±0.074	196.67±0.094	416.67±0.058	0.054±0.005
TM-90	84.57±0.325	0.029±0.001	0.00±0.000	58.33±0.058	450±0.058	0.253±0.012
TM-91	124.76±2.151	0.043±0.001	0.35±0.014	113.33±0.100	500±0.058	0.185±0.015
TM-92	126.26±2.151	0.044±0.002	0.47±0.013	151.67±0.100	433.33±0.000	0.054±0.005
TM-93	158.09±0.709	0.078±0.002	0.92±0.012	115±0.115	466.67±0.046	0.044±0.004
TM-94	121.75±0.467	0.044±0.001	4.84±0.013	196.67±0.100	566.67±0.058	0.130±0.012
TM-95	133.86±0.154	0.020±0.000	1.58±0.025	188.33±0.058	433.33±0.000	0.051±0.005

pH

The pH is a measure of hydrogen ion concentration of water. It is measured on a logarithmic scale from 0 to 14, and is described as the negative log of the hydrogen ion concentration (-log $[H^+]$).The pH of all samples was found within safe WHO limit. When the pH is about 6.0 to 7.0, the biodiversity within the ecosystem is wide. As the pH decreases and the acidity increases, fewer organisms can survive [36].

Temperature

The range of temperature detected was found acceptable in all ground water samples under study; used for drinking purposes. The maximum and minimum average temperatures of 30.2 ^{0}C and 25 ^{0}C were measured in samples TM-305 and TM-77 respectively.

Electrical conductivity

The conductivity (or specific conductance) of an electrolyte solution is a measure of its ability to conduct electricity. The SI unit of conductivity is Siemens per meter (S/m). Out of 68 samples; 34 samples were higher in conductance (>1000 µS/cm) [37]. The highest as well as the lowest conductivity of 3140 µS/cm & 670 µS/cm was shown by the samples TM-266 and TM-78, respectively.

Total dissolved solids

Many dissolved materials are objectionable in water. Dissolved minerals, gases and organic constituents may produce aesthetically offensive color, taste and odor. Some dissolved organic chemicals may reduce the dissolved oxygen in the receiving waters [38]. The higher levels of total dissolved solids were determined in the fourteen samples, while the highest and the lowest levels of 2103.8 mg/L and 448.9 mg/L were determined in the samples TM-266 and TM-78, respectively.

Chlorides

Chloride is one of the most important inorganic anion in water. In clean water, the saline taste is produced due to chloride concentrations. There is no documented confirmation about the human health hazards caused by chlorides. For this reason, chlorides are generally limited to 250 mg/L in water for drinking purposes. According to Annoh (1997) [39], excess chloride content in water can impact bad taste and cause corrosion in intestinal system when consumed. It is noted that the removal method of chloride concentration is expensive. Most of the drinking water samples were found within the safe range of WHO maximum contaminant level (MCL) for chlorides, whereas the maximum concentration of 1657.29 mg/L of chlorides was analyzed in the sample TM-277.

Sulfate

The occurrence of high levels of sulfate in water may deliver to the corrosion of distribution system. Besides this, it may contribute to the drinking water a bad taste; it can also act as a purgative in humans [40]. Maximum and minimum contents of 306.73 mg/L and 61.75 mg/L of sulfate were shown by the samples TM-273 and TM-72, respectively.

Phosphate-phosphorus

Phosphorous may occur in water as result of household sewage, detergents, agricultural effluents with fertilizers and industrial waste water. High concentration of phosphorous, therefore, is indicative of pollution [41]. For phosphate-phosphorus, there was no specific guideline mentioned, however, the maximum level of 0.558 mg/L was found in sample TM-297.

Nitrate-nitrogen

WHO maximum permissible limit of nitrate-nitrogen is 10 mg/L. All the samples were free from nitrate-nitrogen contamination. Nitrate-nitrogen in excess of 10 mg/L in drinking water causes methenoglobinemia in infants, a disease characterized by blood changes. Although it’s content is apparently tolerated by most adults [42]. Maximum nitrate-nitrogen concentration of 9.89 mg/L was present in the sample TM-86, which is very close to the WHO maximum permissible limit.

Total hardness

Hardness of water is caused by the presence of multivalent metallic cations and is largely due to calcium (Ca^{2+}), and magnesium (Mg^{2+}) ions. Hardness is reported in terms of $CaCO_3$ amount. Hardness is the measure of capacity of water to react with soap; hard water necessitates noticeably more soap to create lather. It is not caused by distinct material but by a variety of dissolved polyvalent metallic ions, mainly calcium and magnesium cations. Maximum permissible value of total hardness as set by WHO is 300 mg /L [43]. Thirteen samples indicated the alarming levels of total hardness.

Alkalinity

Highly alkaline waters are usually unpleasant. Excess alkalinity in water is harmful for irrigation which harms the soil and decreases crop yields. Alkalinity is buffering power of a water body and is defined as capacity of water to neutralize acids present in the water. Its maximum contamination level (MCL) as set by WHO is 500 mg/L [44]. Most of the samples were found with higher than the MCL of alkalinity which is an alarming condition.

Total organic matter

Organic matter is matter composed of organic compounds that are produced from the remains of organisms such as plants and animals and their waste products in the environment [45]. MCL for organic matter is not specified by WHO guidelines [46]. However; maximum value of 0.892 mg/L of organic matter was analyzed in the sample: TM-280.

Heavy metals analyses

Results of heavy metals including sodium and calcium are given in the Table 3.

Sodium (Na)

The sodium ion is always present in water. Sodium (Na^+) is significant to people on a low-sodium diet. It has permissible content in water of 200 mg/L [47]. The content beyond 200 mg/L will be hazardous to human health. Box plot 2 (a) shows the distribution of sodium content in ground water of studied areas which was determined in 75% samples within 200 mg/L of WHO recommended value. High sodium and potassium intake have adverse effects which might result into cardiac, renal or circulation problems which are related to some form of hypertension [48]. Scatter plot given in figure 3 (a) demonstrates that moderate positive correlation was shown by sodium.

Calcium (Ca)

Calcium has the MCL value of 200 mg/L in drinking water. Calcium is a major constituent of various types of rocks. It is one of the most common ingredients present in natural waters ranging from zero to several hundred milligrams per liter depending on the source and treatment of the water. It is frequently present in the form of carbonates, bicarbonates, sulfates, chlorides and nitrates. Calcium is a source for hardness in water and incrustation in boilers. Out of 68 samples, only four samples declared calcium level above WHO guidelines [49]. Maximum and minimum calcium amount of 329.33 mg/L and 8.35 mg/L was present in samples; TM-266 and TM-304, respectively. Negative strong correlation was announced in calcium, although calcium was also found below 200 mg/L in most of the samples as indicated by the box plot figure 2 (b).

Manganese (Mn)

The highest value of 0.401 mg/L was analyzed in the sample TM-296. According to Standard Organization of Nigeria, (2007), manganese (Mn^{2+}) is a nuisance chemical that causes neurological disorder in human and causes troublesome stains and deposits on light colored clothes and plumbing fixtures. Excessive amounts cause dark discoloration in some food and beverages with unpleasant taste. Only a maximum of 0.2 mg/L of Mn is allowed in drinking water and amount beyond is dangerous to the health [50]. The most of the samples indicated that manganese content was within safe levels, however it exhibit weak correlation. Fig. 2 (c) and 3 (c) show box and scatter plots, respectively.

Table 3(a). **Concentration of heavy metals of ground water of nine different villages of Tehsil Thari Mirwah, District Khairpur, Sindh Pakistan.**

ID	Na (mg/L) WHO LIMIT =200 mg/L	Ca (mg/L) WHO LIMIT = 200	Mn (mg/L) WHO LIMIT =0.1 mg/L	Ni (mg/L) WHO LIMIT =0.02 mg/L	Zn (mg/L) WHO LIMIT =3.0 mg/L
TM-265	835.14±3.880	141.81±0.068	0.111±0.006	0.075±0.0023	0.02±0.008
TM-266	414.07±0.899	329.33±0.100	0.088±0.011	0.038±0.0013	0.032±0.011
TM-267	148.03±0.548	87.76±0.049	0.151±0.005	0.018±0.0013	0.223±0.007
TM-272	126.98±2.342	51.06±0.079	0.01±0.003	0.010±0.0013	0.217±0.035
TM-268	46.59±0.124	144.48±0.066	0.006±0.002	0.023±0.0023	0.026±0.008
TM-269	435.12±2.767	243.25±0.100	0.011±0.002	0.051±0.0013	0.07±0.006
TM-270	724.13±1.988	110.45±0.043	0.153±0.003	0.020±0.0023	0.006±0.004
TM-271	352.82±0.877	59.06±0.100	0.1±0.005	0.026±0.0013	0.011±0.001
TM-273	396.85±1.880	180.52±0.057	0.01±0.003	0.041±0.0013	0.276±0.005
TM-274	630.35±0.988	259.26±0.100	0.025±0.002	0.032±0.0013	0.199±0.021
TM-275	44.68±2.564	99.1±0.082	0.276±0.003	0.013±0.0013	0.171±0.036
TM-276	517.43±3.009	162.5±0.068	0.012±0.004	0.027±0.0013	0.274±0.058
TM-277	1066.74±3.787	299.3±0.100	0.142±0.004	0.081±0.0013	0.100±0.009
TM-278	46.59±0.213	78.42±0.047	0.173±0.006	0.027±0.0013	0.047±0.009
TM-279	99.76±1.467	41.05±0.058	0.039±0.005	0.018±0.0013	0.075±0.009
TM-280	132.72±0.898	120.46±0.047	0.021±0.004	0.022±0.0013	0.076±0.007
TM-281	92.53±0.343	77.75±0.058	0.042±0.002	0.023±0.0023	0.191±0.014
TM-282	105.93±0.216	83.09±0.100	0.08±0.003	0.027±0.0013	0.206±0.052
TM-283	148.03±0.788	92.43±0.115	0.026±0.004	0.02±0.0013	0.27±0.009
TM-284	139.8±0.413	88.43±0.118	0.255±0.002	0.03±0.0013	0.127±0.009
TM-285	130.81±0.988	108.45±0.117	0.254±0.003	0.034±0.0013	0.12±0.010
TM-286	94.44±0.877	41.05±0.048	0.011±0.002	0.031±0.0013	0.014±0.007
TM-287	109.75±1.655	69.74±0.047	0.006±0.003	0.041±0.0013	0.088±0.009
TM-288	113.58±0.654	41.05±0.055	0.007±0.000	0.044±0.0013	0.09±0.009
TM-289	102.1±0.877	98.44±0.048	0.003±0.002	0.02±0.0013	0.468±0.009
TM-290	123.15±0.565	81.75±0.058	0.051±0.012	0.023±0.0013	0.055±0.009
TM-291	109.75±0.787	95.77±0.058	0.006±0.003	0.025±0.0013	0.179±0.009
TM-292	215.02±0.999	132.47±0.094	0.035±0.004	0.034±0.0013	0.07±0.009
TM-293	86.78±0.356	95.77±0.058	0.096±0.012	0.041±0.0013	0.067±0.009
TM-294	176.74±0.766	129.13±0.100	0.113±0.003	0.039±0.0013	0.081±0.009
TM-295	773.9±0.876	229.23±0.100	0.396±0.009	0.057±0.0013	0.065±0.009
TM-296	38.94±0.129	82.42±0.115	0.401±0.012	0.027±0.0013	0.094±0.009
TM-297	176.74±1.770	111.12±0.100	0.175±0.009	0.02±0.0013	0.210±0.014
TM-298	119.33±0.875	81.09±0.100	0.069±0.003	0.02±0.0013	0.099±0.009

Table 3(b). **Concentration of heavy metals of ground water of nine different villages of Tehsil Thari Mirwah, District Khairpur, Sindh Pakistan.**

ID	Na (mg/L)	Ca (mg/L)	Mn (mg/L)	Ni (mg/L)	Zn (mg/L)
	WHO LIMIT =200 mg/L	WHO LIMIT = 200	WHO LIMIT =0.5 mg/L	WHO LIMIT =0.02 mg/L	WHO LIMIT =3.0 mg/L
TM-299	163.34±0.909	98.44±0.058	0.009±0.003	0.034±0.0013	0.054±0.009
TM-300	98.27±1.765	79.62±0.077	0.061±0.003	0.07±0.0023	0.306±0.009
TM-301	128.89±0.878	81.75±0.060	0.076±0.003	0.066±0.0013	0.221±0.014
TM-302	71.47±0.565	20.36±0.058	0.036±0.003	0.044±0.0013	0.067±0.009
TM-303	155.68±0.787	28.37±0.078	0.025±0.003	0.052±0.0013	0.533±0.009
TM-304	82.96±0.880	8.35±0.058	0.035±0.009	0.096±0.0023	0.186±0.009
TM-305	125.07±0.564	18.36±0.088	0.014±0.005	0.044±0.0013	0.147±0.009
TM-69	46.59±0.787	41.05±0.058	0.012±0.002	0.093±0.0023	0.005±0.001
TM-70	2.57±0.880	43.05±0.100	0.055±0.002	0.07±0.0023	0.017±0.001
TM-71	19.8±0.564	81.75±0.058	0.017±0.002	0.089±0.0023	0.007±0.000
TM-72	81.04±1.019	41.05±0.100	0.01±0.002	0.033±0.0023	0.002±0.000
TM-73	38.94±1.475	70.41±0.047	0.01±0.002	0.061±0.0023	0.002±0.003
TM-74	37.02±0.598	41.71±0.058	0.015±0.002	0.023±0.0023	0.075±0.001
TM-75	96.36±2.287	87.09±0.100	0.181±0.002	0.075±0.0023	0.09±0.003
TM-76	52.33±2.927	41.05±0.058	0.011±0.002	0.056±0.0023	0.032±0.002
TM-77	44.68±0.576	56.39±0.058	0.009±0.002	0.006±0.0013	0.049±0.001
TM-78	77.21±0.885	41.05±0.058	0.004±0.001	0.015±0.0013	0.009±0.001
TM-79	63.81±0.240	115.79±0.058	0.008±0.002	0.047±0.0023	0.009±0.002
TM-80	69.56±0.891	65.74±0.058	0.285±0.002	0.021±0.0023	0.191±0.001
TM-81	157.6±1.987	90.43±0.047	0.058±0.003	0.077±0.0023	0.006±0.001
TM-82	69.56±1.243	46.38±0.047	0.07±0.001	0.054±0.0023	0.005±0.002
TM-83	75.3±2.311	131.8±0.058	0.345±0.002	0.068±0.0023	0.045±0.002
TM-84	125.07±1.455	91.76±0.058	0.127±0.002	0.11±0.0023	0.051±0.005
TM-85	92.53±1.653	85.76±0.100	0.101±0.002	0.086±0.0023	0.051±0.005
TM-86	144.2±0.119	41.05±0.058	0.329±0.002	0.133±0.0023	0.272±0.001
TM-87	111.67±0.177	75.75±0.115	0.063±0.002	0.1±0.0023	0.009±0.003
TM-88	44.68±0.290	39.71±0.058	0.218±0.003	0.154±0.0023	0.035±0.003
TM-89	71.47±2.625	73.75±0.047	0.087±0.003	0.1±0.0023	0.036±0.001
TM-90	33.19±2.988	18.36±0.058	0.057±0.003	0.117±0.0023	0.006±0.001
TM-91	33.19±0.625	40.38±0.058	0.057±0.003	0.121±0.0023	0.006±0.001
TM-92	33.19±2.736	55.73±0.058	0.063±0.005	0.098±0.0023	0.009±0.002
TM-93	40.85±1.983	41.05±0.058	0.056±0.003	0.084±0.0023	0.006±0.002
TM-94	100.18±1.284	73.75±0.047	0.206±0.005	0.091±0.0023	0.029±0.001
TM-95	67.64±2.286	70.41±0.115	0.053±0.003	0.112±0.0023	0.007±0.001

Table 3(c). **Concentration of heavy metals of ground water of nine different villages of Tehsil Thari Mirwah, District Khairpur, Sindh Pakistan.**

ID	Cu (mg/L)	Co (mg/L)	Cr (mg/L)	Fe (mg/L)	Cd (mg/L)
	WHO LIMIT =2 mg/L	***WHO LIMIT = 0.1 mg/L***	***WHO LIMIT =0.05 mg/L***	***WHO LIMIT =0.3 mg/L***	***WHO LIMIT =0.003 mg/L***
TM-265	0.169±0.040	0.029±0.004	0.0187±0.0046	0.132±0.002	0.003±0.0002
TM-266	0.014±0.040	0.04±0.004	0.0184±0.0046	0.057±0.002	0.006±0.0002
TM-267	0.004±0.000	0.03±0.004	0.017±0.0062	0.058±0.002	0.006±0.0001
TM-272	0.004±0.000	0.022±0.004	0.0193±0.0046	0.024±0.002	0.011±0.0002
TM-268	0.004±0.000	0.022±0.004	0.016±0.0046	0.062±0.015	0.007±0.0002
TM-269	0.004±0.000	0.016±0.004	0.0221±0.0062	0.032±0.002	0.009±0.0002
TM-270	0.004±0.000	0.022±0.004	0.0222±0.0060	0.045±0.002	0.011±0.0002
TM-271	0.004±0.000	0.025±0.004	0.02±0.0046	0.083±0.002	0.013±0.0002
TM-273	0.004±0.000	0.013±0.004	0.0229±0.0046	0.037±0.002	0.014±0.0002
TM-274	0.004±0.000	0.023±0.004	0.0258±0.0046	0.138±0.002	0.012±0.0002
TM-275	0.004±0.000	0.025±0.004	0.0322±0.0062	0.042±0.002	0.012±0.0002
TM-276	0.004±0.000	0.011±0.004	0.0187±0.0046	0.068±0.002	0.01±0.0002
TM-277	0.01±0.004	0.022±0.004	0.0236±0.0046	0.057±0.002	0.012±0.001
TM-278	0.008±0.001	0.035±0.004	0.0164±0.0046	0.022±0.002	0.01±0.0002
TM-279	0.009±0.004	0±0.000	0.0133±0.0046	0.011±0.002	0.013±0.0002
TM-280	0.009±0.001	0.011±0.004	0.0152±0.0046	0.029±0.002	0.013±0.0002
TM-281	0.018±0.004	0.011±0.004	0.0172±0.0046	0.075±0.002	0.011±0.0002
TM-282	0.016±0.004	0.016±0.004	0.0202±0.0046	0.062±0.002	0.012±0.0002
TM-283	0.014±0.004	0.015±0.004	0.0185±0.0046	0.041±0.002	0.009±0.0001
TM-284	0.021±0.004	0±0.000	0.0165±0.0030	0.033±0.002	0.009±0.0002
TM-285	0.034±0.006	0.015±0.004	0.0205±0.0046	0.046±0.002	0.009±0.0002
TM-286	0.021±0.004	0.017±0.004	0.0184±0.0046	0.077±0.002	0.01±0.002
TM-287	0.012±0.004	0.015±0.004	0.0205±0.0062	0.03±0.002	0.007±0.0002
TM-288	0.021±0.004	0.015±0.004	0.0207±0.0060	0.045±0.002	0.006±0.001
TM-289	0.011±0.004	0.016±0.004	0.0198±0.0030	0.052±0.002	0.003±0.0002
TM-290	0.015±0.004	0.015±0.004	0.0194±0.0046	0.027±0.004	0.004±0.0004
TM-291	0.035±0.006	0.02±0.004	0.0189±0.0030	0.092±0.002	0.003±0.0003
TM-292	0.012±0.004	0.016±0.004	0.0185±0.0046	0.015±0.002	0.006±0.0004
TM-293	0.012±0.004	0.015±0.004	0.019±0.0046	0.016±0.002	0.004±0.0004
TM-294	0.012±0.004	0.016±0.004	0.0176±0.0046	0.036±0.002	0.005±0.0004
TM-295	0.021±0.006	0.021±0.007	0.0217±0.0046	0.124±0.002	0.006±0.0004
TM-296	0.013±0.004	0.023±0.004	0.0169±0.0046	0.036±0.002	0.001±0.000
TM-297	0.012±0.004	0.021±0.004	0.014±0.0062	0.053±0.002	0.004±0.0004
TM-298	0.012±0.004	0.026±0.004	0.0157±0.0046	0.052±0.002	0.005±0.0005

Table 3(d). **Concentration of heavy metals of ground water of nine different villages of Tehsil Thari Mirwah, District Khairpur, Sindh Pakistan.**

ID	Cu (mg/L)	Co (mg/L)	Cr (mg/L)	Fe (mg/L)	Cd (mg/L)
	WHO LIMIT =2 mg/L	***WHO LIMIT = 0.1 mg/L***	***WHO LIMIT =0.05 mg/L***	***WHO LIMIT =0.3 mg/L***	***WHO LIMIT =0.003 mg/L***
TM-299	0.011±0.004	0.010±0.004	0.0162±0.0030	0.032±0.002	0.004±0.0004
TM-300	0.014±0.004	0.013±0.004	0.0142±0.0046	0.098±0.002	0.006±0.0004
TM-301	0.012±0.004	0.007±0.003	0.0151±0.0046	0.071±0.002	0.004±0.0003
TM-302	0.015±0.004	0.009±0.003	0.0136±0.0046	0.041±0.002	0.004±0.0003
TM-303	0.032±0.004	0.007±0.003	0.0152±0.0046	0.089±0.002	0.005±0.0003
TM-304	0.011±0.006	0.011±0.003	0.0176±0.0046	0.499±0.002	0.006±0.0002
TM-305	0.012±0.004	0.011±0.003	0.0142±0.0046	0.19±0.002	0.007±0.0002
TM-69	0.005±0.002	0.006±0.003	0.0054±0.0000	0.035±0.000	0.003±0.0000
TM-70	0.015±0.004	0.007±0.003	0.0054±0.0000	0.219±0.004	0.002±0.000
TM-71	0.007±0.002	0.006±0.003	0.0076±0.0017	0.003±0.000	0.001±0.000
TM-72	0.007±0.002	0.006±0.003	0.0054±0.0000	0.006±0.002	0.007±0.000
TM-73	0.007±0.004	0.005±0.003	0.0067±0.0017	0.003±0.000	0.002±0.0002
TM-74	0.02±0.004	0.006±0.003	0.0073±0.0017	0.002±0.000	0.001±0.0002
TM-75	0.031±0.004	0.008±0.003	0.0093±0.0060	0.006±0.002	0.001±0.0001
TM-76	0.02±0.004	0.006±0.003	0.0064±0.0017	0.005±0.002	0.002±0.0002
TM-77	0.095±0.004	0.005±0.003	0.0079±0.0017	0.013±0.002	0.001±0.0002
TM-78	0.006±0.001	0.006±0.003	0.0054±0.0000	0.008±0.002	0.001±0.0002
TM-79	0.016±0.002	0.007±0.003	0.0073±0.0017	0.002±0.000	0.001±0.0001
TM-80	0.014±0.004	0.010±0.004	0.0079±0.0017	0.034±0.002	0.001±0.0002
TM-81	0.01±0.002	0.009±0.003	0.0083±0.0035	0.003±0.000	0.001±0.002
TM-82	0.008±0.004	0.008±0.003	0.0079±0.0017	0.003±0.000	0.000±0.0000
TM-83	0.017±0.004	0.010±0.004	0.007±0.0017	0.039±0.002	0.000±0.000
TM-84	0.067±0.004	0.007±0.003	0.0067±0.0017	0.038±0.004	0.000±0.000
TM-85	0.025±0.004	0.008±0.003	0.0083±0.0035	0.048±0.002	0.000±0.000
TM-86	0.014±0.002	0.013±0.007	0.0107±0.0046	0.092±0.004	0.000±0.000
TM-87	0.007±0.001	0.010±0.004	0.0054±0.0000	0.122±0.004	0.000±0.000
TM-88	0.01±0.004	0.006±0.003	0.0054±0.0000	0.089±0.002	0.001±0.0001
TM-89	0.012±0.004	0.008±0.003	0.0112±0.0046	0.128±0.002	0.001±0.0001
TM-90	0.011±0.002	0.006±0.003	0.0079±0.0017	0.239±0.004	0.002±0.0002
TM-91	0.007±0.002	0.010±0.007	0.0054±0.0000	0.003±0.000	0.002±0.0002
TM-92	0.007±0.002	0.000±0.000	0.0054±0.0000	0.005±0.002	0.002±0.0002
TM-93	0.02±0.002	0.000±0.000	0.0073±0.0017	0.004±0.002	0.002±0.0002
TM-94	0.008±0.002	0.000±0.000	0.0054±0.0000	0.006±0.002	0.002±0.0002
TM-95	0.026±0.004	0.020±0.009	0.0131±0.0046	0.002±0.000	0.002±0.0002

Nickel (Ni)

Ni is called the "depression and suicide" mineral, as it is associated with these feelings and symptoms [51]. As it is clear from the Tables 3(a) and 3(b) that the most of samples were contaminated with Ni, because its level was above MCL. Maximum amount of 0.154 mg/L of nickel was analyzed in the sample TM-88. Moderate positive correlation was shown by nickel as shown in scatter plot mentioned in figure: 3 (d), whereas box plot given in figure 2 (d) shows that broad distribution of nickel in mentioned study area.

Copper (Cu)

The WHO guidelines for copper recommend 2.0 mg/L of it in drinking water; whereas the concentration of copper in all samples was found below than prescribed level. The analysis for copper is important because of dissolved copper salts even in low concentrations are toxic to some biota. Copper is found mostly as a sulphide, oxide, or carbonate in the natural resources. Copper enters the water system through mineral dissolution, industrial effluents, because of its use as algaecide and insecticide and through corrosion of copper alloy in water distribution pipes. It may occur in simple ionic form or in one of many complexes with groups, such as cyanides, chlorides, ammonia or organic ligands [52]. The copper showed the lowest median in the mentioned localities as is given in the box plots figure 2 (e), whereas zero correlation was declared by copper as mentioned in the figure 3 (e).The highest copper content of 0.169 mg/L was detected in the sample TM-265.

Zinc (Zn)

Zinc is an essential and valuable element in body growth. The levels of zinc measured in all the samples were below the WHO limit of 3.0 mg/L. Very high concentrations may cause a pungent taste and opalescence in alkaline water. Zinc generally goes into the domestic supply from corrosion of galvanized iron and dezincification of brass. Zinc in water may also come from anthropogenic water pollution [53]. The box plot of zinc given in figure 2 (f) shows that most of samples fall in the range of 0.3 mg/L, while WHO upper limit of zinc is 3.0 mg/L, while scatter plot (figure 3 f) shows the weak positive correlation. The highest zinc content of 0.533 mg/L was analyzed in the sample TM-303.

Cobalt (Co)

Cobalt is beneficial for humans because it is a part of vitamin B_{12}, which is essential for human health. Cobalt is used to treat anemia in pregnant women, because it stimulates the production of red blood cells. However, very high concentrations of cobalt may damage human health. It may cause asthma and pneumonia, vision problems, nausea, heart problems and thyroid damage [54]. Box plot of cobalt as given in the figure 2 (g) displays that maximum number of samples show the concentration of cobalt below 0.04 mg/L, while scatter plot of cobalt in figure 3 (g) determines weak positive correlation. Maximum value of 0.029 mg/L of cobalt was determined in water sample no: TM-265, although maximum contaminant level of cobalt is not specified by WHO drinking water standards. According to United States Environmental Protection Agency (USEPA) guidelines the permissible limit of cobalt is 0.1 mg/L.

Chromium (Cr)

Chromium is carcinogenic metal. Its highest concentration was found as 0.0322 mg/L which was within the safe limit prescribed by WHO guidelines (0.05 mg/L). The MCL for total chromium (USEPA 2004) is 0.1 mg/L. The absorption of chromium after oral exposure is relatively low and depends on the speciation. Cr(VI) is more readily absorbed from the gastrointestinal tract than Cr(III) and is able to penetrate cellular membranes. In general, food appears to be the major source of intake [55]. The highest median was shown by the chromium which is illustrated in the figure 2 (h), while moderate positive correlation was determined in the scatter plot of chromium given in figure 3 (h).

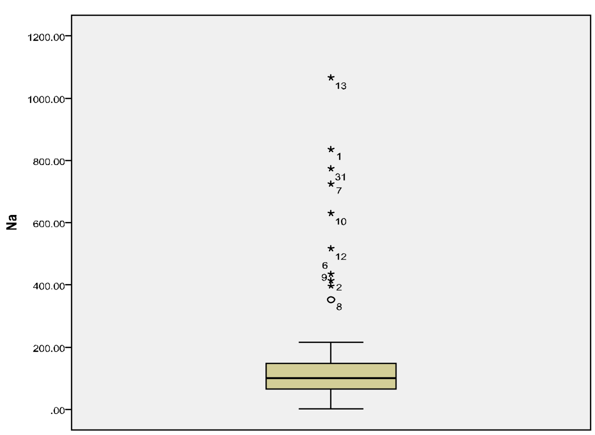
Iron (Fe)

Iron is an essential element of human diet. Approximation of the minimum daily requirement for iron depends on age, physiological status, sex and iron bio-availability. It ranges from about 10 to 50 mg/day. Long time utilization of drinking water with a high concentration of iron can lead to liver diseases (hemosiderosis). Iron also promotes the growth of iron-bacteria. This gives rusty appearance to the waters. It is clear from the box plot of iron set in figure 2 (i) that amount of iron in most of the samples was lower than 0.2 mg/L; however zero correlation was detected in declared localities as shown in figure 3 (i). Only one sample TM-304 displayed the highest concentration of 0.499 mg/L of iron (Fe) which is above WHO maximum guidelines (0.30 mg/L) [56, 57]. Iron concentrations in the rest of the samples were within safe limits of WHO guidelines.

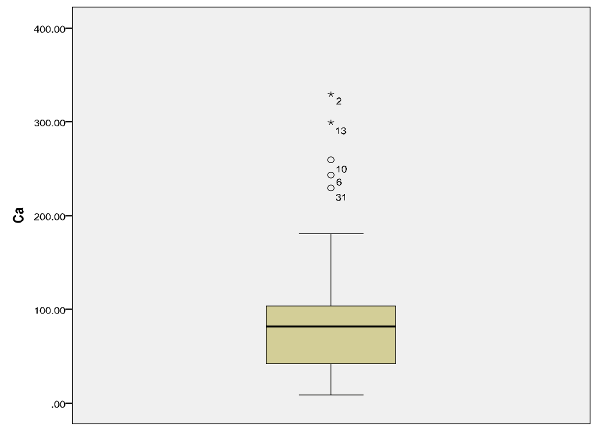
Cadmium (Cd)

Cadmium is called the “pseudo-macho” or the “violent” element. Unfortunately, it is also a fatal metal associated with heart disease, cancers of all kind, kidney disease, diabetes and other health problems [58]. Scatter plot illustrates that strong positive correlation was given by the cadmium given in the figure 3 (j); whereas box plot in figure 2(j) displays that the concentration of cadmium in most of the samples was found higher than 0.01 mg/L. Among 68 samples; 38 samples displayed higher cadmium concentrations which were greater than WHO maximum limits.

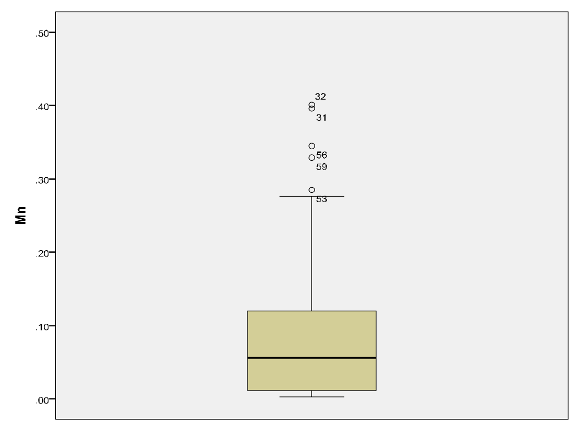
(a) Na



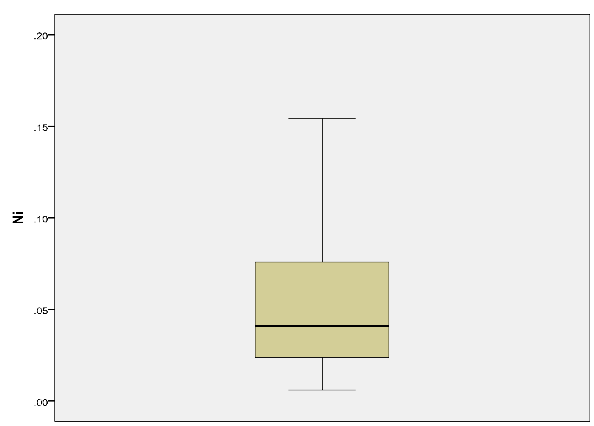
(b) Ca



(c) Mn



(d) Ni



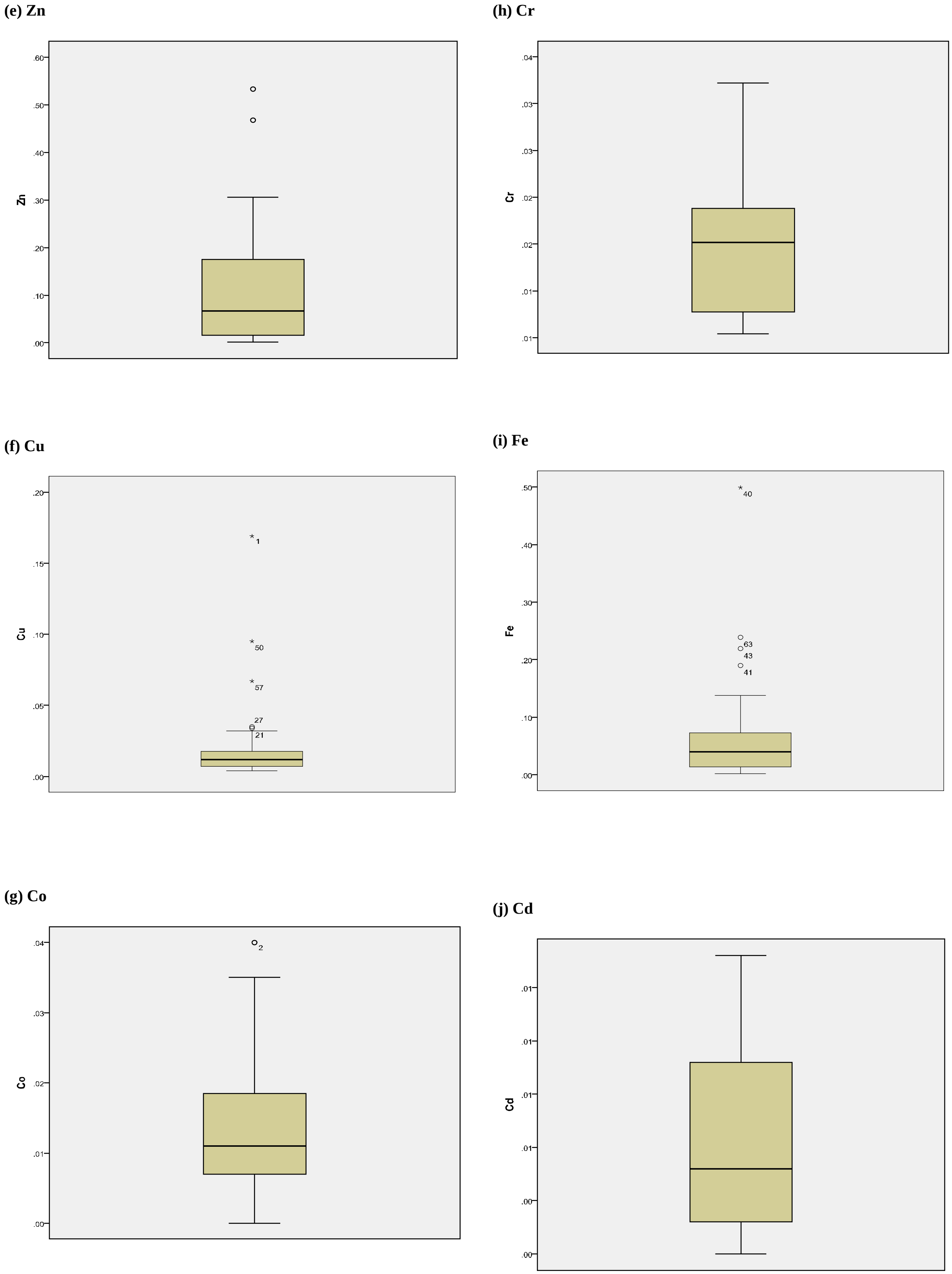
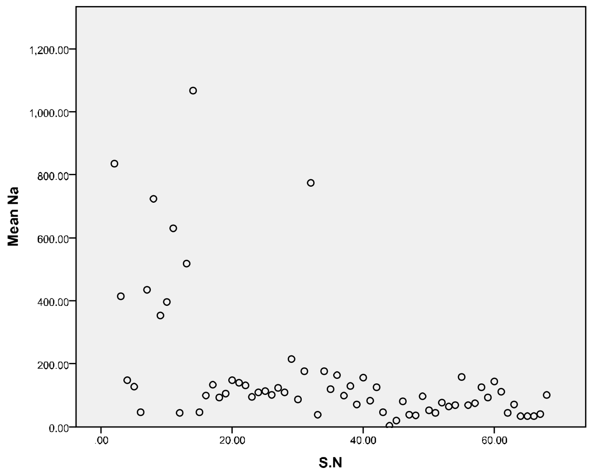
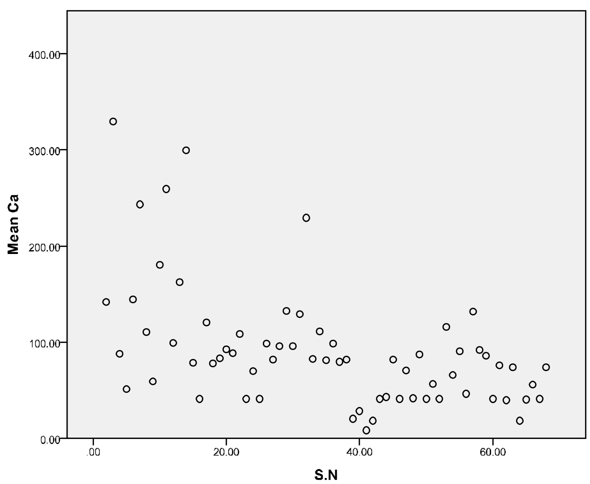


Figure 2. **Box Plots of ten Metals.**

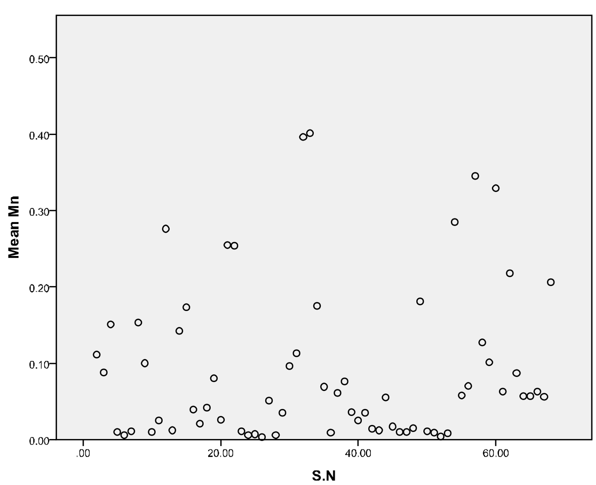
(a) Na
R^2=0.45



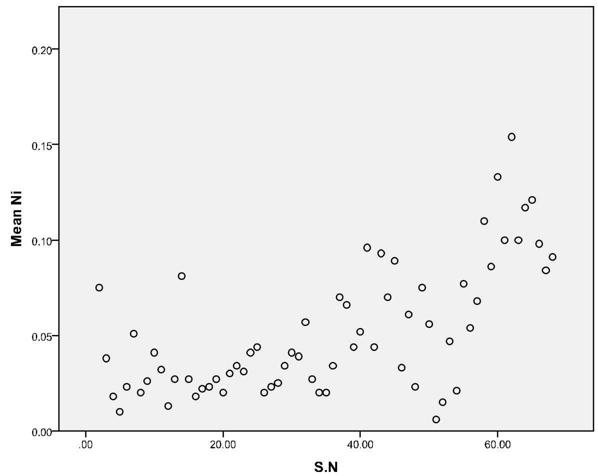
(b) Ca
R^2 = -1.08



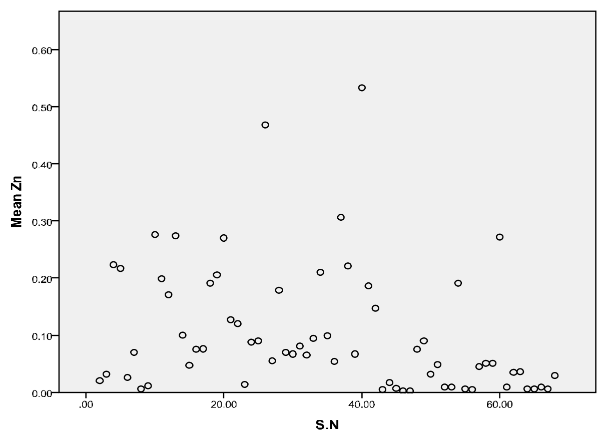
(c) Mn
R^2 = 0.005



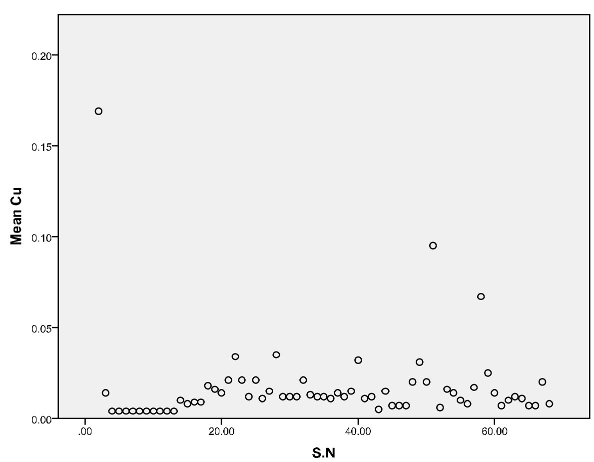
(d) Ni
R^2 = 0.438



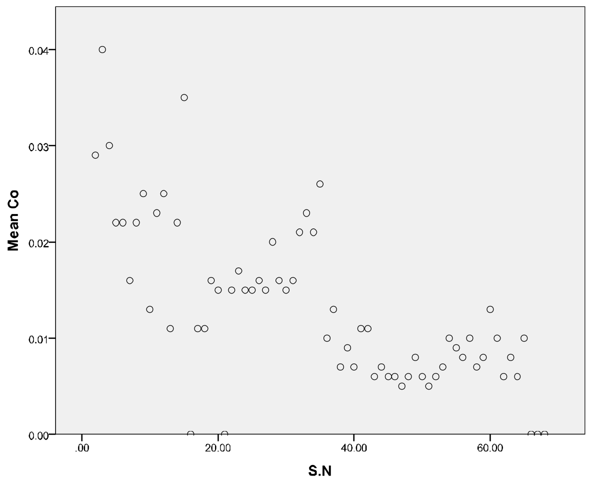
(e) Zn
R^2 = 0.090



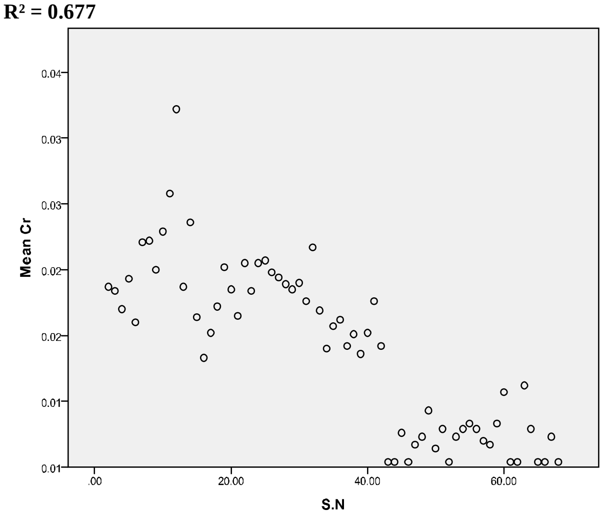
(f) Cu
R^2 = 0.000



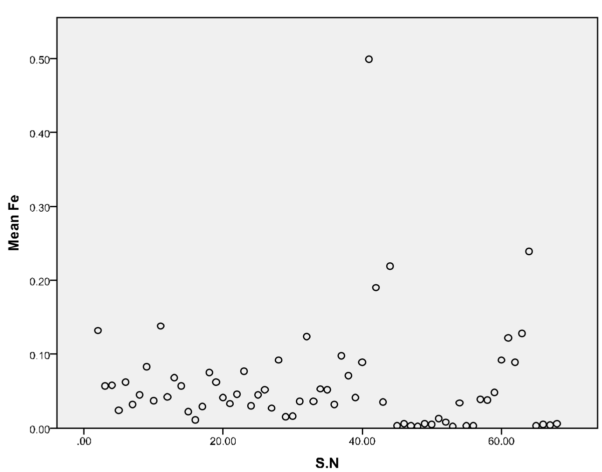
(g) Co
R^2 = 0.438



(h) Cr
R^2 = 0.677



(i) Fe
R^2 = 0.000



(j) Cd
R^2 = 0.646

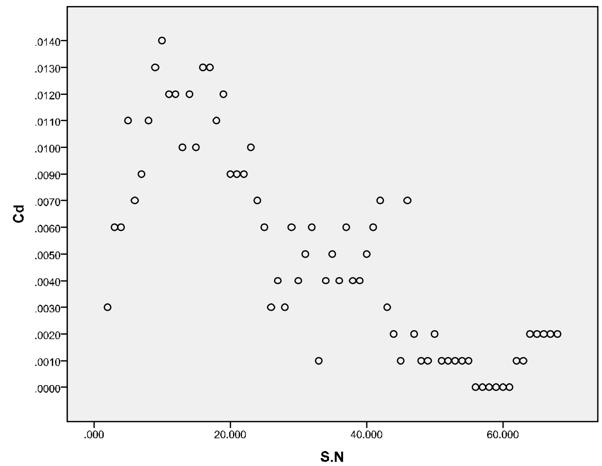


Figure 3. **Scatter Plots of ten Metals.**

Analysis of variance (ANOVA)

The statistical tool analysis of variance (ANOVA) was used to test the hypothesis and analyze the distribution of metals and the results are summarized in Table 4. The total metal contents of drinking water were correlated with themselves and between various pairs of elemental constituents to find out their behavior and source. Sodium exhibited positive relationship with calcium, this may suggest that sodium and calcium may have common mineral source in the ground water. Positive correlation of manganese was also observed with nickel, zinc, copper, cobalt and chromium; which illustrates that there may be similar mineral source. The positive correlation was also observed between zinc and chromium (0.414), zinc and cadmium (0.278), cobalt & chromium (0.659), cobalt & cadmium (0.390) and chromium and cadmium (0.743). Significant correlation was also determined in the metals; sodium & calcium, whereas manganese did not indicate positive as well as negative significant correlation. Positive significant correlation was observed in zinc & cadmium, while cobalt & chromium displayed positive correlation at 0.01 significant level (Table 4).

Table 4. **Correlation coefficient between metals.**

	Na	Ca	Mn	Ni	Zn	Cu	Co	Cr	Fe	Cd
Na	1.00	.732**	0.14	-0.08	0.07	.230*	.442**	.519**	0.11	.416**
Ca		1.00	0.15	-0.17	0.05	0.01	.515**	.499**	-0.09	.342**
Mn			1.00	0.14	0.01	0.04	0.19	0.08	-0.01	-0.12
Ni				1.00	-.260*	0.07	-.356**	-.510**	.245*	-.522**
Zn					1.00	-0.07	0.13	.414**	0.18	.278*
Cu						1.00	0.07	-0.03	0.06	-.222*
Co							1.00	.659**	0.09	.390**
Cr								1.00	0.14	.743**
Fe									1.00	0.06
Cd										1.00

**. Correlation is significant at the 0.01 level (1-tailed).
*. Correlation is significant at the 0.05 level (1-tailed)

Conclusion

The hand pump water samples from nine villages; Malak Chaudaghi, Bhutta Bachrah, Nawab Khan Rind, Tando Mir Ali, Allah Dino Khan Aamur, Haji Nangar Soomro, Rahim Bux Hajano, Habib-ji-Wandh and Mandan were taken to examine their quality in terms of their physico-chemical properties and heavy metals contamination levels. The results exposed that drinking water of villages surrounding Tehsil Thari Mirwah were highly contaminated. All the villages have pH values and nitrate-nitrogen amount within safe range of WHO maximum permissible levels. Analyses indicated that drinking water of village Malak Chaudaghi was highly contaminated and was not potable. Drinking water of village Bhutta Bachrah had shown higher levels of conductance, TDS, chlorides and TH. It may be due to number of brick chimneys surrounding that village; pollute their ground water. Na, Ca, Ni, Mn and Cd were also in higher concentration in the village Bhutta Bachrah. In Village Nawab Khan Rind unacceptable levels of EC, TDS, Cl^{-1}, SO_4^{-2} and TH were analyzed. Ca, Mn, Zn, Cu, Co and Fe were within harmless range of WHO permissible levels in drinking water of this village. Almost all the pollutants/ contaminants less or more were present in samples under study. Finally we can conclude that these sampling locations cannot be used for drinking purposes before they are exposed to technological processes for treatment of drinking waters.

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