Distribution of Heavy Metals in the Ground Water of Taluka Daur, District Nawabshah, Sindh, Pakistan, and its Impacts on Human Health

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Summary: Ground water samples (38) collected from Taluka Daur, District Nawabshah were analyzed for their heavy metal concentration. The concentration of heavy metals were found in the ranges Cd 2-17 μg/L, Pb 6-53 μg/L, Zn 0-228 μg/L, Cu 0-99 μg/L, Ni 13-90 μg/L, Fe 75-1355 μg/L, Co 5-48 μg/L and Mn 1-517 μg/L. Eleven water samples out of 38 were found as safe for drinking purpose based on total dissolved salts (500 mg/L), but only two water samples were suitable for human consumption with respect to their metal concentrations. The water samples were found contaminated with toxic metals Pb and Cd. Among these metals Pb-Co, Fe-Zn, Mn-Cd, Cu-Zn and Ni-Cd showed a similarity index. Contamination index (C_d) for the metal ions examined was calculated at each sampling station. The results indicated 4 samples low ($C_d < 1$), 4 samples medium ($C_d < 3$) and 28 samples high ($C_d > 3$) contaminated.

Introduction

Toxic metals such as Cd and Pb may be present in ground water. These metals have been of a great concern due to their health implications. They are non essential metals with no physical benefits to human beings and wild life. Sources of these metals are generally from weathering of minerals and soils [1]. According to World Health Organization (WHO) declaration, access to potable water is a basic right to all. However, in developing and also developed countries so many masses rely on ground water and surface water for drinking purpose, being unaware of its quality. The water contains organic as well as inorganic pollutants, which, if present in above concentration than some fixed levels, cause health problems to users.

It is necessary to check the quality of water, especially the concentration of heavy toxic metals like Cd and Pb, before it is used for drinking purpose.

Taluka Daur formerly a part of Taluka Nawabshah, District Nawabshah is located at northern edge of District Nawabshah. The soil of the Taluka is saline; however, some of its parts are fertile and well cultivated. The climate is mostly dry, hot in summer and cold in winter.

About 80 % of the people reside in villages and use ground water for drinking and other domestic purposes. Two water supply schemes are working in the Daur and Jam Sahab towns, but rest of the taluka rely on ground water.

A number of workers reported quality of surface and ground water of different parts of Pakistan [2-8], but not any work has been reported on the quality of ground water of Taluka Daur. Hence the need was felt to analyze the ground water of this part of the country. Present work examines the quality of ground water and surface water (only two samples) with respect to its heavy metals (Cd, Pb, Zn, Cu, Ni, Fe, Co and Mn).

Results and Discussion

The map of district Nawabshah with sampling numbers is shown in Fig. 1. Total dissolved solids of the water samples studied were found between 188-26752 mg/L. Eleven water samples indicated their TDS contents within the safe guidelines of 500 mg/L prescribed by World Health Organization (WHO) for drinking water. The maximum level of TDS (26752 mg/L) was observed in sample J2 collected from Jam Sahab town. All the ground water collected from this town showed very high levels of TDS, may be due to saline soil with high salts deposits.

pH

pH of water samples varied between 6.64-8.18 within the range set by WHO for drinking water (6.5-8.5). Two water samples (D10 and J2) indicated pH below 7 (6.87 and 6.64) while three samples (D2, J3 and J4) showed pH values above 8 (8.18, 8.05 and

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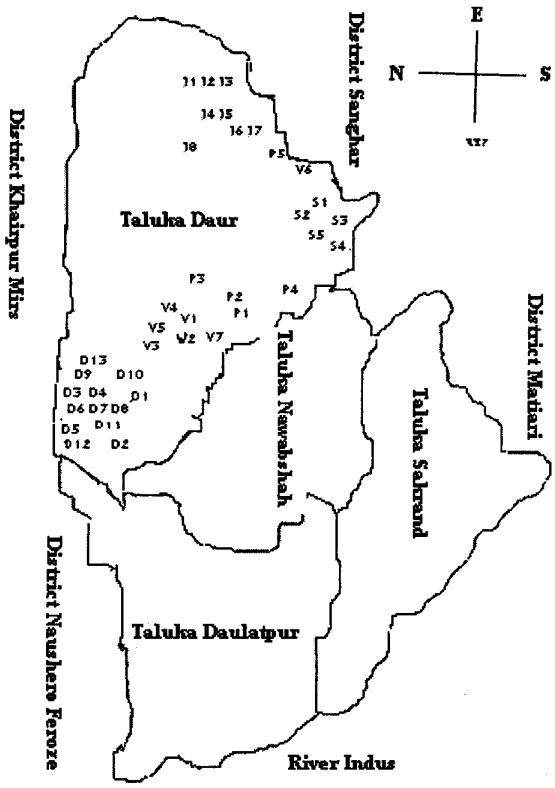

Fig. 1: The map of Nawabshah District showing the sampling locations.

8.08). The pH of the water samples of study area were near to neutrality.

Iron and Manganese (Fe and Mn)

Iron is an essential element without any significant health effect, but develops a yellowish color and a peculiar taste when present in high concentration in water bodies. The highest concentration of iron (1355 μg/L) was found in sample D3 collected from Daur town may be due to geological reasons and the lowest concentration (75 μg/L) was observed in D6. In general, the water samples of the study area contained higher contents of iron (Table-1), which indicates that the local mineral deposits in the catchment area studied may have high levels of iron. The WHO threshold for iron in drinking water is 300 μg/L. Iron concentration of 18 samples was observed above and 20 samples within the permissible limits [9].

Manganese concentration of water of the study area ranged between 1-517 μg/L. 17 samples showed within and 21 samples showed above the limits of (100 μg/L) of Mn set by WHO for drinking water (Table-1) [10]. Iron and manganese can affect the flavor and the color of food and water; they may react with the tannins in tea, coffee and some alcoholic beverages to produce a black sludge, which affect both the taste and appearance. Iron and manganese produce bacteria (iron manganese bacteria) which do not pose a health threat; however, they do produce a red-brown (iron) or black-brown (manganese) slime in toilet tanks and can clog water system [11].

Zinc (Zn)

Zinc has been found to have low toxicity to human beings; prolonged consumption of large doses can however, result in health complications such as fatigue, dizziness and neutropenia [1]. The analyzed water samples showed their zinc concentration in the range of 0-268 μg/L in agreement with other workers [12]. The maximum concentration (268 μg/L) was observed at location S1 (S1 sample was collected from 60th MILE town) and minimum concentration (BDL) was found in samples S3 and P1 (Table-1). The WHO guidelines of zinc for drinking water are 500 μg/L. All the samples indicated their Zn contents within the safe limits.

Copper (Cu)

All the water samples studied (except D6 and D8) indicated the presence of copper (Table-1). The location J1 was found as highly contaminated with copper having concentration of 99 μg/L. The WHO acceptable limit of Cu is 30 μg/L. 27 water samples indicated the Cu contents within and 11 samples above the limits. The over doses of Cu may lead to neurological complications, hypertension, liver and kidney dysfunction [12, 14, 15].

Nickel (Ni)

Sources of nickel in water include contamination from municipal sewage sludge, waste water from sewage treatment plants and ground water near landfill sites [13]. The nickel concentration of the water samples of the study area was found from 13 μg/L to 92 μg/L (Table-1). Sample D2 indicated highest concentration (92 μg/L) and D13 indicated

Table-1: Sampling sources, TDS, pH and Heavy metal (Fe, Zn, Cu, Mn, Co, Pb, Ni and Cd) contents of water samples and WHO standards.

Sample Code	Source	TDS mg/L	pH	Fe μg/L	Zn μg/L	Cu μg/L	Mn μg/L	Co μg/L	Pb μg/L	Ni μg/L	Cd μg/L
D1	G W (HP)	5139	7.03	1005	80	92	428	19	26	82	12
D2	G W (HP)	22912	8.18	536	237	47	248	32	27	92	17
D3	G W (HP)	919	7.24	1355	212	9	179	9	31	46	12
D4	G W (HP)	3277	7.22	132	96	1	197	14	12	48	14
D5	G W (HP)	2266	7.28	242	91	4	93	14	30	36	13
D6	G W (HP)	1030	7.41	75	87	BDL	20	7	47	37	12
D7	GW (EM)	474	7.34	91	29	3	15	6	34	34	12
D8	G W (HP)	2490	7.93	859	41	BDL	153	12	25	45	12
D9	GW (EM)	5754	7.38	165	30	6	397	19	29	48	12
D10	GW (EM)	8806	6.87	101	14	2	517	27	27	42	14
D11	GW (EM)	7354	7.46	112	13	2	464	25	39	23	11
D12	GW (EM)	1754	7.13	379	115	2	173	11	47	15	5
D13	GW (EM)	3443	7.17	374	131	1	331	15	36	13	7
S1	G W (HP)	409	7.88	769	268	15	18	7	12	23	3
S2	G W (HP)	487	7.87	223	24	17	3	6	9	31	3
S3	G W (HP)	338	7.12	128	BDL	32	127	5	12	21	3
S4	G W (HP)	257	7.71	128	31	25	17	6	11	14	2
S5	G W (HP)	361	7.52	341	18	13	32	6	6	27	3
J1	GW(HP)	472	7.13	280	217	188	38	29	30	27	4
J2	GW(HP)	26752	6.64	180	86	17	294	46	53	54	6
J3	WS	192	8.05	620	47	17	28	32	45	24	4
J4	WS	188	8.08	730	125	22	65	46	28	26	3
J5	GW(HP)	24640	7.15	210	49	15	150	50	45	38	5
J6	GW(HP)	2448	7.07	98	44	12	140	37	35	47	6
J7	GW(HP)	25472	7.01	115	37	13	212	26	32	50	6
J8	GW(HP)	25280	7.10	103	50	19	197	48	50	31	4
V1	GW(HP)	4058	7.47	383	191	42	6	20	30	80	10
V2	GW(HP)	1466	7.51	404	128	58	27	11	42	63	6
V3	GW(EM)	1984	7.06	163	130	48	344	13	44	88	7
V4	GW(EM)	1683	7.19	310	69	65	106	13	38	64	7
V5	GW(EM)	1053	7.11	320	33	20	213	11	30	52	6
V6	GW(HP)	1453	7.21	370	70	21	153	11	33	58	7
V7	GW(HP)	934	7.68	86	30	8	55	8	25	15	3
P1	GW(HP)	301	7.73	317	BDL	43	10	6	29	35	4
P2	GW(HP)	202	7.70	285	45	16	3	6	21	22	4
P3	GW(TW)	19968	7.14	370	27	29	58	45	44	90	16
P4	GW(HP)	1299	7.77	602	98	38	1	10	30	50	6
P5	GW(HP)	2029	7.13	212	56	34	269	13	29	87	6
WHO Standards	---------	500	6.5-8.5	300	5000	----	100	-----	10	1300	3

G W (HP) = Ground water (Hand Pump), G W (EM) = Ground water (Electric Motor).
G W (TW) = Ground water (Tube Well), WS = water supply, D = Daur town, S = 60th Mile town,
J = Jam Sahib town, V = Village, P = Public place, BDL = below detection limit

lowest concentration (13 μg/L) of nickel. The normal threshold prescribed by WHO is 1300 μg/L. All the samples were found within the limits. The most common adverse effects of nickel are skin allergies and dermatitis. The lung is the target organ for nickel toxicity in humans [13].

Cobalt (Co)

The cobalt is of relatively low abundance in the earth's crust and in natural waters. The cobalt is used to treat anaemia in pregnant women, because it stimulates the production of red blood cells. The concentration of Co in the water samples of the study area varied widely (Table-1). Some samples showed relatively low concentrations and others high. The highest concentration (48 μg/L) was found at location J8 and the lowest (5 μg/L) at location S3 (Fig. 2). The locations D3, D6, D7, S1, S2, S4, S5, V7, P1 and P2 showed their Co contents below 10 μg/L. The Co is an essential metal and is part of vitamin B12 without any health hazards.

Lead (Pb)

Lead is considered as highly toxic and is a pollution indicator. It is toxic to nervous system inducing sub-oncephalopathic neurological and behavioral effects. It can accumulate in the skeleton. The infants/children up to six years of age and pregnant women are more susceptible to its adverse health effects. Pb enters in water bodies from natural sources, but it originates largely due to industrial activities [12]. The WHO permissible guidelines for

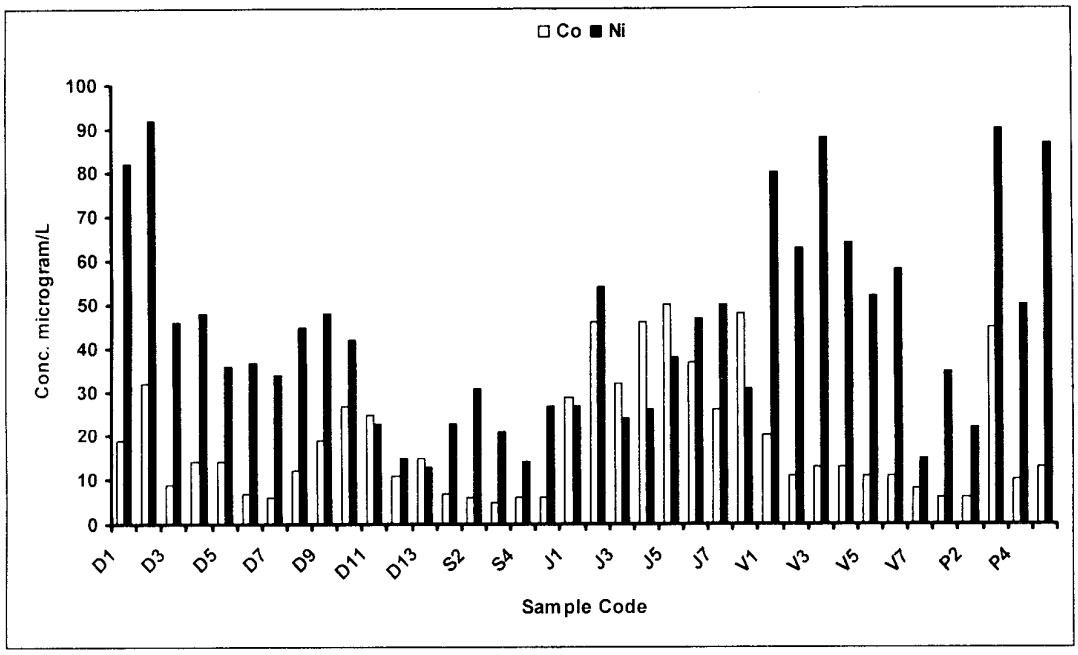

Fig. 2: Graphical representation of Co and Ni contents of water samples.

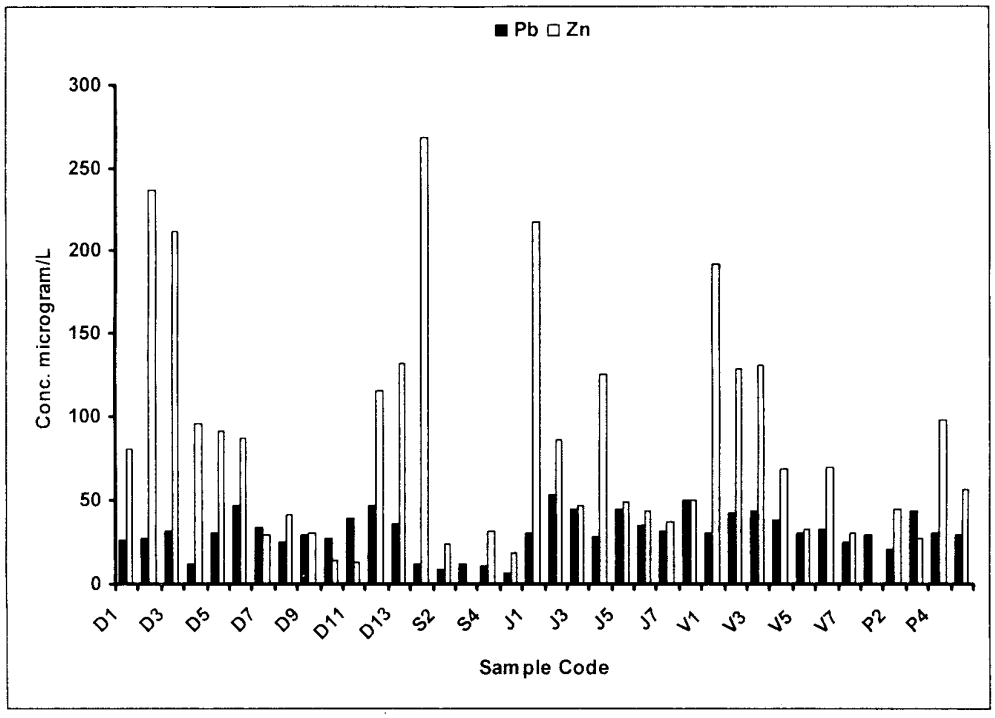

Fig. 3: Graphical representation of Pb and Zn contents of water samples.

Pb in drinking water are 10 μg/L. The concentration of lead in the water samples of the study area (Table-1) varied between 6 μg/L and 53 μg/L. Only two samples S2 and S4 indicated Pb contents within the limits. The highest concentration of Pb (53 μg/L) was found in sample J2 (Fig. 3) collected from Jam Sahab town, may be due to some geological and environmental effects.

Cadmium (Cd)

Like lead, Cd is also toxic metal; it can impair kidney and testicular tissue, and may damage red blood cells [16, 17] and filtering mechanism. Cd is extremely toxic to aquatic biota even at low concentrations [17]. The WHO safe guidelines of Cd in drinking water is 10 μg/L. 25 water samples of the study area indicated Cd contents within the limits, while remaining 13 samples indicated above the limits. The maximum concentration (17 μg/L) was found at location D2. The sample was collected from Daur town near Tractor workshops, and minimum concentration (2 μg/L) was found at location S4.

Coefficient of Determinations among Metal Contents of Ground Water

The metal contents of 38 samples collected from different sampling sites of study area were correlated within themselves and between various pairs of elemental constituents to find their behavior and possible source. The results of coefficient of determinations (r^2) between various pairs of elemental constituents (Table-2) indicate positive correlations which may be indicative of common source. The minimum correlation (r^2) was observed for Cu-Pb = 0.00002 and maximum between Pb-Co = 0.276 (Fig. 4). A significant similarity index (positive relations) was observed for Fe with Zn (r^2 = 0.2464), Mn with Cd (r^2 = 0.1713), Cu with Zn (r^2 = 0.1327), Ni with Cd (r^2 = 0.2714) and Pb with Co (r^2 = 0.276). The elements may be having common source in the minerals and common mechanism of transport of the elements from minerals to ground water.

The Contamination Index C_d

The contamination index (C_d) developed by Backman *et al.* [18] examines the quality of water by calculating the degree of contamination. The C_d is calculated separately for the each sample analyzed and is based on the sum of the factors obtained from the parameters exceeding the upper permissible level.

Table-2: Coefficient of determinations among metal constituents of ground water.

	Fe	Mn	Cu	Zn	Ni	Pb	Co	Cd
Fe	1.00	0.0027	0.0172	0.2464	0.0231	0.0102	0.0036	0.019
Mn		1.00	0.0112	0.0096	0.0675	0.0439	0.0612	0.1713
Cu			1.00	0.1327	0.0722	0.00002	0.0079	0.0184
Zn				1.00	0.0412	0.0011	0.0012	0.0162
Ni					1.00	0.051	0.0352	0.2714
Pb						1.00	0.276	0.0251
Co							1.00	0.0119
Cd								1.00

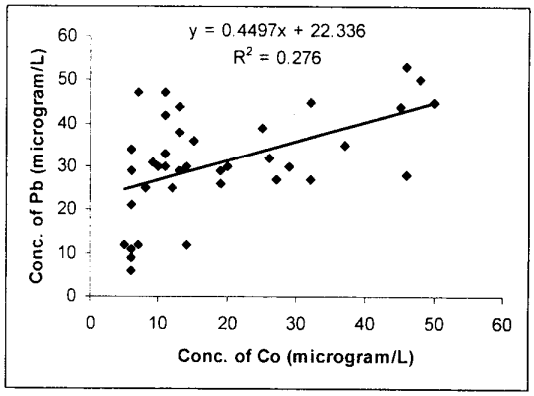

Fig. 4: Correlation between Co-Pb.

Fig. 4: Correlation between Co-Pb.

The factors which were within permissible level were not used in calculation of C_d. The upper permissible levels used for the calculation of C_d were recommended levels of World Health Organization (WHO) (Table-1). The C_d combines different quality parameters considered harmful to household water.

The results of C_d are summarized in Table-3. The samples may be classified in three categories based on the observed values of C_d [18]. Four samples indicated low contamination with $C_d < 1$, five samples medium contamination with $C_d < 3$ and 28 samples high contamination with $C_d > 3$. The samples with high contamination indicated the C_d values in the range 3.2-59.7. Six samples (D2, J2, J5, J7, J8 and P3) collected from Jam Sahab town with high C_d values (within 46.9-59.7) may indicate regionally contaminated zone.

Experimental

Study Area

The samples were collected from towns and villages of Taluka Daur, District Nawabshah. Daur town, the Taluka head quarter is situated about 26 km in the north of Nawabshah city.

Table-3: Values of contamination index (C_d) of ground water samples.

Sample Code	C_d	Sample Code	C_d
D1	19.51	J2	59.74
D2	53.46	J3	5.1
D3	10.24	J4	3.23
D4	10.39	J5	52.95
D5	8.87	J6	7.8
D6	7.76	J7	54.26
D7	5.4	J8	54.86
D8	10.87	V1	11.73
D9	18.38	V2	6.48
D10	26.15	V3	10.14
D11	22.91	V4	6.53
D12	4.17	V5	5.3
D13	12.38	V6	6.4
S1	1.76	V7	2.37
S2	0	P1	2.29
S3	0.47	P2	1.43
S4	0.1	P3	46.9
S5	0.14	P4	5.6
J1	2.33	P5	7.65

Sampling Strategy and Pre-treatment

Water samples (38) were collected (36 ground water and 02 surface water), comprising Daur Town 13, Jam Sahab 08, 60th MILE town 05, different villages 07 and common public places 05. The water samples were collected from 09 electrical motors, 01 water supply pipe, 01 water supply pond, 01 tube well and 26 from hand pumps. The samples were collected randomly from residential houses of the area into clean 1.5 L plastic bottle washed twice with sample at the sampling point and preserved with 5 mL conc. HNO_3.

Reagents

All the reagents used were of analytical grade and all the glassware used was washed properly with double distilled water before use. The metal standard solutions were prepared by dilution from 1000 ppm stock solution of each metal.

Instrumentation

The total dissolved salts (TDS) were evaluated with Orion 115 conductivity meter and the pH was measured with "Orion 420A" pH meter (Orion, Boston, USA).

The concentrations of metals were determined using VARIAN Spectr AA-20 Atomic absorption spectrometer with standard burner head and air acetylene flame at conditions recommended by the manufacturer.

The analysis was carried out in triplicate with integration time 3 sec and delay time 3 sec. Sample (250 mL) containing nitric acid (1 mL) was heated gently at 90-95 °C and was concentrated to about 15-20 mL. Then final volume was adjusted to 25 mL.

The Contamination Index C_d

The contamination index C_d [18] is calculated for each sample, which is the sum of contamination factors of every parameter of a single sample exceeding the World Health Organization (WHO) limits set for drinking water, using following formula:

$$C_d = \sum_{i=1}^{n} C_{fi}$$

where

C_{fi} = $[(C_{Ai} / CN_i)]$
C_{fi} = contamination factor for the i-th component
C_{Ai} = analytical value for the i-th component
CN_i = upper permissible concentration for the i-th component

Conclusion

The analysis of the ground water of Taluka Daur, District Nawabshah was carried out for TDS, pH and eight elements Fe, Mn, Cu, Ni, Pb, Co, Zn and Cd. The results revealed that the concentrations of toxic metals in majority of the ground water samples of the study area were high. The Pb contents of 36 samples and Cd of 13 samples crossed the WHO threshold. Two samples S1 and S5 indicated their Pb as well as Cd within the limits and may be used for drinking purpose. The possible sources of Pb and Cd pollution are geological. The ground water of the study area (except two samples S1 and S5) was found contaminated with toxic metals and may cause several health problems to consumers. The higher concentrations of the metals in ground water may be a concern for human health of Daur Taluka.

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