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An Investigation of Quality of Groundwater of Taluka Nawabshah

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ABSTRACT
Sixty five water samples (four surface water and sixty one groundwater) were collected from taluka Nawabshah and were analyzed for physico-chemical parameters; pH, electrical conductivity (EC), total dissolved salts (TDS) and heavy metals, Fe, Zn, Cu, Mn, Co, Pb, Ni and Cd. The results were obtained in the ranges; pH 6.95-8.87, EC 239-13170 µS/cm and TDS 153-8429. The concentration of heavy metals was observed in the ranges; Fe 46-1070 µg/L, Zn 0-460 µg/L, Cu 3-311 µg/L, Mn 4-418 µg/L, Co 0-33 µg/L, Pb 6-50 µg/L, Ni 0-37µg/L and Cd 0-18µg/L. The results were compared with world health organization (WHO) and local standards set for drinking water. Contamination index of groundwater was observed within 0.2-20.7. Only two water samples (both surface water) were observed suitable for drinking purpose, but all the remaining samples were highly contaminated with toxic heavy metals. An elevated level of toxic heavy metals in the groundwater of the area is of great concern.

1. INTRODUCTION
The importance of clean and pure drinking water is well known. The water we drink should meet some national and international standards. Chemical composition of surface and groundwater is one of the major factors to which the suitability of water for industrial, domestic and agricultural purpose depends. The groundwater is only 0.6% of the total fresh water available on our earth[1]. Groundwater is not only the source of drinking water, but is also used as irrigation water in Pakistan. The use of groundwater for irrigation purpose has increased from 3.34 MAF in 1959 to 48 MAF in 1996-1997[2] and is increasing day by day. This situation decreases the groundwater deposits and may result in the poor quality due to increase in the concentration of a number of polluting agents. The pollution of groundwater results from all the processes and reactions which the water faces from the moment it condensed in the atmosphere to the time it is discharged by a well or hand pump and varies from place to place with depth[3]. Major portion of the rural population depends upon the groundwater due to unavailability of water treatment and supply of potable water. 40% of the deaths in Pakistan are caused by water borne diseases directly or indirectly[4]. A number of factors cause pollution of surface as well groundwater including urbanization and industrialization. The quality of groundwater in Pakistan is deteriorating day by day[2]. Pollution of water resources with heavy metals, especially Pb and Cd is a health-associated problem in many parts of Asia and rest of the world. It focused the attention of the environmental scientists to study the polluted sites in detail and suggest the measures for their remediation. Heavy metals like Zn and Cu in drinking water are necessary in low concentration, however the majority of the heavy metals present in the drinking water may be toxic and harmful for the health.

Heavy metals are the elements with molecular weight greater than 53, density greater than 6 gm/cm^3 and atomic number greater than 20 [5]. Natural sources of the heavy metals are weathering of minerals and soils. Few heavy metals like, Fe, Mn, Mo, Cu and Zn are necessary in low concentrations for all living organisms, while most of them present toxicity hazards at high concentrations, on the other hand As, Hg, Cd and Pb have no any biological importance and are highly toxic to health[6-7]. A number of attempts have been made to examine water quality of surface and groundwater from different parts of the country including Sindh province[8-12]. The studies are also carried out to determine the metal contents in the water bodies[13-19]. We earlier reported the arsenic concentration in groundwater of Khairpur and Matiari districts of Sindh province and quality of groundwater with respect to heavy metals and physico-chemical parameters of some parts of the district Nawabshah[20-22].

The Nawabshah district is located at the center of the Sindh province and Nawabshah city is the exact center of the Sindh province and is the administrative head quarter of the district as well as taluka. The Nawabshah city is situated at a distance of 298 kilo meters in the north east of provincial capital Karachi. The taluka was established in 1907 and the Nawabshah city was established in November 1912. Total population of the Nawabshah district and Nawabshah city is 1071533 and 229590 respectively (Census 1998). The projected population of the city will reach to about 418843 people by the year 2020. Most of the soil of the district is fertile growing different crops, besides; there are some saline and uncultivated pieces of soil also. Rohri canal is the major source to provide water for drinking and irrigation purpose in the district. The people in the villages mostly use groundwater for drinking purpose, but in Nawabshah city, the groundwater and surface water thorough water supply scheme is used for drinking purpose. The climate of the area is hot and dry but falls to -4^{0}C in December to February. Water supply schemes are available in the different parts of the Nawabshah city but groundwater is also being used as a source of drinking water. As the population of the city is growing rapidly which increases the basic needs of the peoples including clean drinking water. The industries, like Habib Sugar Mills and Chemi Visco Fiber are throwing the effluent into the Canal (Gajra wah) running along the city, damaging the quality of the surface as well as groundwater badly. Present work is one of the steps made to analyze the heavy metals contamination of groundwater of the study area.

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2. RESULTS AND DISCUSSION

Fig-1 indicates the map of Nawabshah district pointing at the taluka Nawabshah (Sampling area). pH of water samples ranged between 6.59 and 8.87 (Table-1). Eleven sites (V2, V3, V8, V23, V24, V25, P4, P5, P8, P11 and N11) were found basic with maximum pH (7.53-8.87). Five sites (V6, V7, V15, V17 and N21) were slightly acidic with pH (6.59-6.88). The pH of rest of the sites was around 7. Total dissolved salts (TDS) of the water samples were found in the range of 153-8429mg/L. Thirteen sites (N2, N3, N7, N8, N11, N12, V3, V5, V11, P5, P13, P16 and P18) were observed as suitable for drinking purpose on basis of TDS (TDS within 500 mg/L). Out of these thirteen sites, four are surface waters and are studied as reference samples and rest of the nine samples are groundwater samples. 36 groundwater samples are being used for drinking purpose but the TDS of only 9 of the samples (groundwater) was within the safe limits of WHO set for drinking water. Most of these sites indicated their TDS values below 2000 mg/L. The water samples with TDS 2000 or above are not being used for drinking purpose but are being used for cattle/ live stock and cleaning of house hold utensils. Minimum and maximum contents of TDS (153 and 8429 mg/L) were found at sites N17 and P12 respectively. Sample No P12 was collected from Nawabshah city (Unar Petrol Pump), the soil around, was saline and no any cultivation was there. The higher level of TDS may be due to high deposits of salts in the soil there. Water at 18 sites (including 4 surface waters) may be classified as fresh water with TDS below 1000 mg/L and rest of the 47 sites are brackish with TDS 1000-10000 mg/L[23].

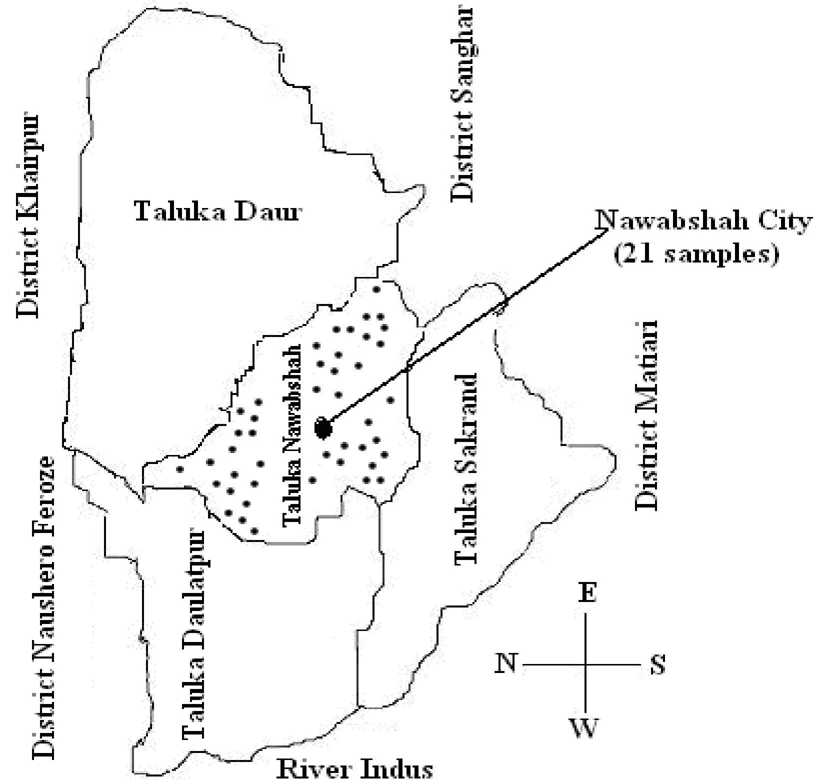

Fig-1: Map of Nawabshah District (dots shows the sampling locations).

The concentration of heavy metals is presented in Table-1. Iron (Fe) is one of the most abundant metals in the earth's crust and is an essential element in human nutrition. Fe concentration of water samples ranged between 46 and 1070 µg/L. Twenty three sites were unsuitable for drinking purpose with their Fe contents above 300 µg/L and rest of the forty two sites were within the limits of WHO for drinking water **(**Fig-2**).** Higher concentration of Fe at these sites may be due to geochemical reasons. Elevated levels of iron in drinking water may impose bad taste to water and cause vomiting. The concentration of zinc (Zn) in the water samples was found in the range of 0-460 µg/L. None of the sites indicated Zn contents above the WHO threshold (3000 µg/L). Water of all the sites was suitable for drinking purpose, with respect to Zn contents. Concentration of copper (Cu) ranged as 3-311 µg/L. Cu is essential for life but may cause health problems if present in high concentrations in the drinking water. Concentration of copper (Cu) at all sites was within the limits of WHO (1000 µg/L). Manganese (Mn) is an essential nutrient and plays a key role in bone mineralization, protein and energy metabolism. Mn contents of water samples were found between 4 and 418 µg/L. Excess amount of Mn may cause damage to liver, kidneys and brain[7]. All the sites indicated their Mn concentration within the threshold set by WHO (500 µg/L) for drinking water. The cobalt is of relatively low abundance in the Earth's crust and in natural waters. The cobalt is used to treat anaemia with pregnant women, because it stimulates the production of red blood cells. The Co is an essential metal and is part of vitamin B12 with no any health hazards. Cobalt concentration of water samples was found between 0 and 33 µg/L. Eleven sites (V5, V6, V7, V8, V11, P12, P13, N1, N18, N19 and N20) indicated a little higher concentration of cobalt ranging between 26 and 33 µg/L (n=11),

Table-1: Concentration of Heavy Metals at different sampling sites.

	pH	EC	TDS	Fe	Zn	Mn	Cu	Co	Ni	Pb	Cd
N1	7.29	5040	2326	113	25	227	8	28	20	22	5
N2	7.71	314	201	300	49	27	27	7	0	10	0
N3	7.77	257	164	250	44	14	90	3	0	9	1
N4	7.53	2350	1504	105	44	52	6	6	15	32	2
N5	7.24	3280	2099	273	116	159	38	1	26	35	4
N6	7.16	6540	4186	485	288	208	41	4	20	32	5
N7	7.99	327	209	350	24	24	10	2	11	10	3
N8	7.13	633	405	159	31	8	57	8	18	25	11
N9	7.10	2150	1376	46	199	116	103	11	21	6	12
N10	7.09	3650	2336	173	87	52	12	0.2	22	20	13
N11	8.63	239	153	290	28	216	32	3	24	25	11
N12	7.61	696	445	192	43	11	76	8	18	31	18
N13	7.53	1223	783	217	67	41	100	7	19	27	15
N14	7.63	1856	1188	517	259	80	10	10	27	24	10
N15	7.57	2860	1930	119	294	199	31	7	31	28	11
N16	8.23	900	576	131	294	23	8	5	19	27	10
N17	7.76	7170	4589	146	313	153	34	7	32	11	17
N18	7.07	6840	4377	90	169	214	12	29	26	34	7
N19	7.05	6500	4160	59	140	201	16	33	24	26	6
N20	7.09	6740	4314	71	210	196	3	32	21	26	6
N21	6.95	1634	1046	1000	240	55	51	6	16	40	4
V1	7.39	2890	1850	326	50	36	30	27	32	31	4
V2	7.55	3780	2419	318	67	39	24	14	24	36	6
V3	7.94	370	237	90	47	35	101	0	22	20	2
V4	7.10	1008	645	107	70	40	51	0	36	38	5
V5	7.02	746	477	26	129	20	70	32	25	30	4
V6	6.86	1362	872	230	70	115	24	31	32	40	5
V7	6.88	1106	708	260	108	60	20	32	26	25	4
V8	7.83	3120	1997	17	36	21	21	27	31	40	5
V9	7.03	1784	1142	70	33	63	21	11	29	38	4
V10	7.02	1703	1090	620	122	91	21	13	29	22	5
V11	6.96	757	484	1070	68	15	19	26	24	19	4
V12	6.93	2050	1312	180	63	83	41	0	25	27	4
V13	6.99	2160	1382	890	350	163	26	3	30	35	4
V14	7.05	4260	2726	580	240	87	38	4	37	45	4
V15	6.64	3170	2029	210	141	229	42	12	20	50	4
V16	7.19	2550	1632	380	180	180	37	13	24	40	3
V17	6.76	2140	1370	37	215	190	194	5	35	42	4
V18	6.98	4810	3078	15	24	410	19	3	23	49	4
V19	6.93	2800	1792	60	185	259	112	11	30	46	4
V20	7.07	2020	1293	460	330	224	42	4	21	20	3
V21	7.45	1160	742	600	64	24	137	11	31	21	5
V22	7.28	3590	2298	278	47	141	52	12	26	22	6
V23	7.56	3290	2106	344	0	128	159	16	28	39	7
V24	7.53	3670	2349	327	330	233	44	14	24	34	7
V25	7.76	1345	861	272	56	24	76	10	25	17	4
P1	7.42	4290	2746	450	25	9	12	8	33	49	8
P2	7.29	1386	887	352	177	82	18	5	28	30	7
P3	7.28	1703	1090	358	68	4	47	7	29	32	6
P4	8.37	1780	1139	475	294	24	140	3	20	41	5
P5	8.87	319	204	548	82	16	11	5	22	47	7
P6	7.32	3160	2022	600	460	140	73	26	28	33	6
P7	7.26	1835	1174	625	390	52	199	4	33	42	4
P8	7.88	2750	1760	660	51	84	19	5	33	44	4
P9	7.16	893	572	383	21	70	58	0	36	30	4
P10	7.13	946	605	162	21	100	14	9	36	33	3
P11	7.58	4750	3040	139	0	32	12	17	29	31	6
P12	7.99	13170	8429	70	39	47	18	33	25	43	7
P13	7.52	440	282	270	240	63	20	30	23	22	4

P14	7.00	2180	1395	180	200	418	311	9	36	32	5
P15	7.14	1146	733	120	350	10	184	13	31	31	5
P16	7.12	619	396	320	44	42	24	0	24	42	3
P17	7.02	2920	1869	530	310	254	29	10	31	20	4
P18	7.71	394	252	170	141	6	151	1	13	29	3
P19	7.61	2170	1389	223	74	54	91	10	30	20	5

N = Nawabshah city, V = Villages, P = Common public places.

may be due to geological reasons. Lead (Pb) is considered as highly toxic and is pollution indicator. It is toxic to nervous system inducing sub-oncephalopathic neurological and behavioral effect. 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 originate also due to industrial activities[24]. Pb concentration of the water samples was observed in the range of 6-50 µg/L. The upper limit of Pb in drinking water is 10 µg/L. Average concentration of Pb at all the sites was 31 µg/L (n=65). Only four sampling sites from surface water indicated their Pb concentration within the regulations set by WHO. All the rest groundwater samples were found contaminated with Pb and were unsuitable for drinking purpose. Main source of Pb in groundwater of these sites may be geological and industrial waste of the battery workshops. The lead from these batteries may be entering in the groundwater. The higher concentration of lead may be a threat to the masses using the water of these sites for drinking purpose because it has no any physiological benefits but causes several health hazards. The United States of America Environmental Protection Agency (USA EPA) has classified Pb to be hazardous and toxic. Nickel (Ni) is known to be a carcinogen to humans. It is more hazardous when taken in empty stomach through drinking water than taken with food[7]. Sources of nickel in groundwater, apart form geological, include contamination from municipal sewage sludge, waste water from sewage treatment plants and groundwater near landfill sites [25]. The concentration of Ni in the water samples of the study area ranged as 0-37 µg/L. Fifty one sites indicated the levels of Ni above the limits set by WHO (20 µg/L) for drinking water. Cadmium (Cd) is one of the heavy metals with no any health benefits but is very toxic, its sources are natural as well as human made, like, wastes from Cd made batteries, industries, run offs from agricultural soils. It accumulates into liver and kidney and leads to kidney dysfunction. Cd also has been implicated in renal problems in humans and has been found to induce cell injury and death by interfering with calcium regulation in biological systems[24]. Cadmium (Cd) contents of the water samples of study area were observed in the range of 0-18 µg/L. Cd concentration at only eight sites (V3, P10, P16, P18, N2, N3, N4 and N7) was within the WHO threshold. The concentration of Cd in drinking water set by WHO is 3 µg/L. Fifty seven sites were contaminated with Cd (Fig-3). The industries, tractor workshops and battery workshops present in the city may be responsible for Cd contamination at these sites.

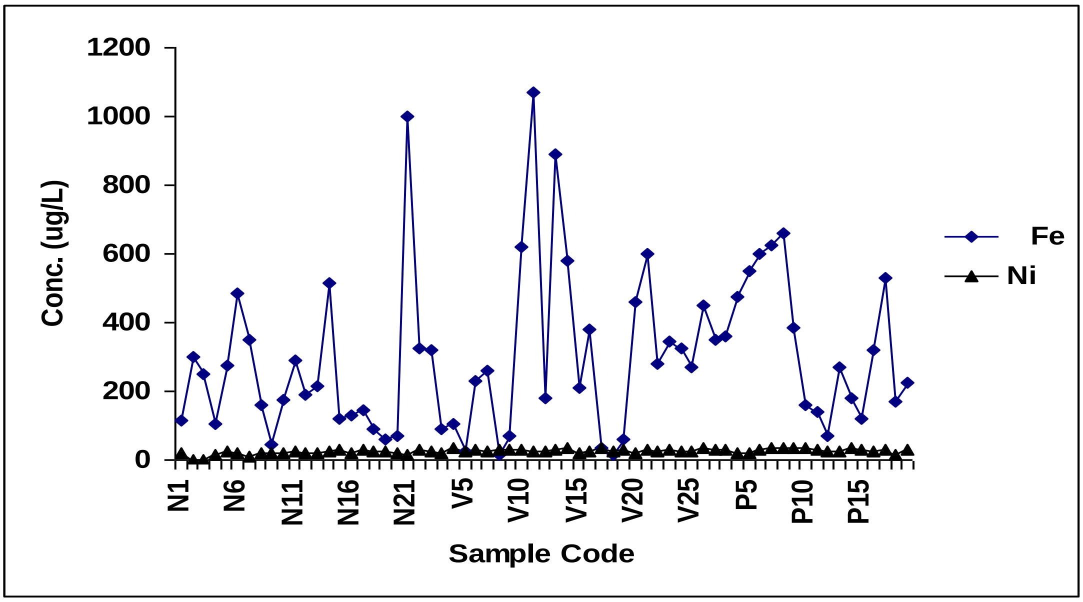

Fig-2: Comparison among the concentration of Fe and Ni.

The results revealed that sites of present study were contaminated with heavy metals, which may cause several health complications to the inhibitors of the area. Only two sites (N2 and N3) indicated all the parameters within the safe limits set by WHO and may be used for drinking purpose. Both these samples were surface waters (water supply and filter plant respectively). Rest of the sixty three sites were unsuitable for drinking purpose. It is clear from the results obtained during this study that presence of excess of heavy metals like, Cd, Ni, and Pb in groundwater is an environmental problem and removal of these metals from environment (specially from water) is challenge for the current era. The hazardous health effects caused by heavy metals are in most cases not immediately apparent but manifest by disrupting enzymatic and metabolic activities resulting in nutritional, developmental and immunological problems[7].

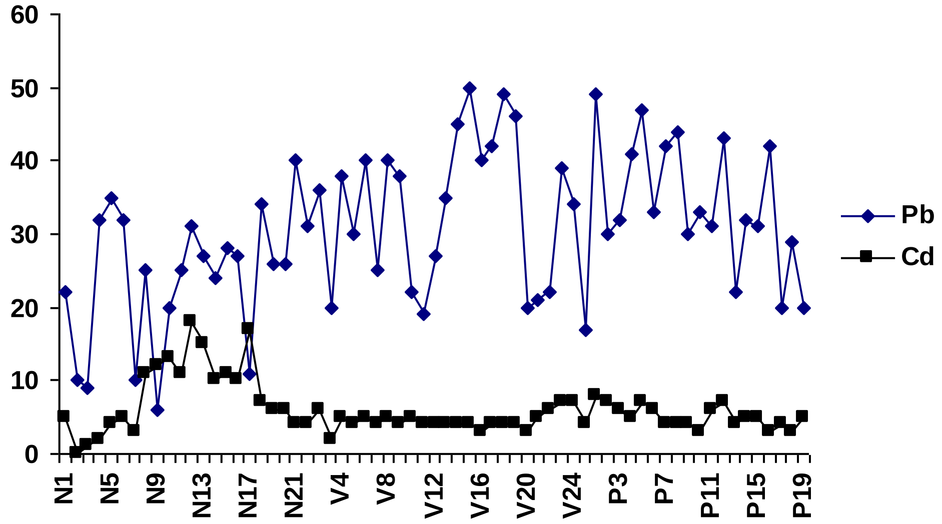

Fig-3: Comparison between the concentration of Pb and Cd.

2.1 *Coefficient of determination (r^2)*

The coefficient of determination (r^2) is calculated to note the similarities in occurrence of the heavy metals analyzed. A coefficient of determination was noted between all the pairs of elements. The r^2 of zinc with iron, copper and manganese was 0.0769, 0.0543 and 0.0866 respectively and maximum value of r^2 (0.1667) was observed between Pb and Ni. All the other elements indicated smaller values of coefficient of determination, thus may be of different origin.

2.2 *The contamination index C_d*

Contamination index (C_d) is the degree of contamination on an individual site as a whole including all parameters which exceed the standards. Calculation of C_d gives a clear idea that to how much level an individual site is polluted.

Table-2: Contamination index (C_d) of the sites investigated.

S. No	C_d	S. No	C_d	S. No	C_d	S. No	C_d	S. No	C_d
N1	10.2	N14	8.6	V6	6.7	V19	10.6	P7	8.9
N2	0	N15	11.6	V7	3.9	V20	5.8	P8	11.6
N3	0	N16	5.4	V8	10.9	V21	5.3	P9	4.7
N4	7.3	N17	22.7	V9	7.5	V22	10.7	P10	4.5
N5	10.5	N18	20.6	V10	6.8	V23	12.2	P11	14.7
N6	19.3	N19	18.4	V11	4.0	V24	12.4	P12	37.6
N7	0.2	N20	18.9	V12	6.5	V25	3.7	P13	1.7
N8	4.2	N21	8.9	V13	9.9	P1	16.7	P14	8.3
N9	7.6	V1	9.8	V14	15.6	P2	6.5	P15	5.3
N10	12.8	V2	12.5	V15	11.5	P3	7.2	P16	3.5
N11	4.4	V3	1.1	V16	9.0	P4	7.9	P17	9.1
N12	7.1	V4	5.9	V17	8.7	P5	6.0	P18	1.9
N13	7.9	V5	2.6	V18	15.7	P6	15.1	P19	6.7

Only two surface water samples (N2 and N3) were found to have zero value of C_d (Table-2) with all the parameters within the safe limits of WHO for drinking water and water of these sites may be used for drinking purpose. The C_d of rest of the sites ranged between 0.2 and 20.7. Minimum C_d was observed for site N7 which was also the water supply scheme, but the water was taken from another part of the city. Thirty nine sites indicated their C_d5 or above and are considered as highly polluted sites. The water can be classified into three classes on the bases of C_d, (I) low contaminated ($C_d < 1$), (II) medium contaminated ($C_d < 3$) and (III) highly contaminated ($C_d > 3$). None of the groundwater can be placed in class (I), however three surface water samples can be placed in this categories, four water samples may be classified as (II) and rest of 58 groundwater samples are placed in class (III). The calculation of C_d reveals that the study area is highly contaminated zone with toxic heavy metals. The groundwater of the area is not suitable to be used for drinking purpose and may cause a number of health problems to the habitants.

3. EXPERIMENTAL

3.1 *Study Area*

The samples were collected from Nawabshah city and different villages of taluka Nawabshah, District Nawabshah.

3.2 *Sampling strategy and pre-treatment*

Water samples (65) were collected (61 groundwater and 04 surface water), comprising; 02 from water schemes of the city, 01 from filter plant, 01 from canal running through the city and 61 groundwater samples from different parts of the taluka; 17 from Nawabshah city, 25 from different villages and 19 from some common public places like schools, bus stops and other government institutions. The groundwater samples were collected from 12 electrical motors and 49 from hand pumps. Out of the 61 groundwater samples, about 36 samples in different villages were being used for drinking purpose due to unavailability of potable water. The samples were collected randomly from the study area into clean 1.5L plastic bottle washed twice with sample at the sampling point and preserved with 5ml conc. HNO_3.

3.3 *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 mg/L stock solution of each metal.

3.4 *Instrumentation*

The electrical conductivity (EC) and 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 the conditions recommended by the manufacturer.

The analysis was carried out in triplicate with integration time 3 sec and delay time 3 sec. Sample (250ml) containing nitric acid (1ml) was heated gently at 90-95^{0}C and was concentrated to about 15-20ml. Then final volume was thus adjusted to 25ml.

3.5 *The contamination index C_d*

The contamination index C_d[26] 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

$$C_{fi} = [(C_{Ai} / CN_i)-1]$$

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

4. CONCLUSION

Sixty five sites were sampled and analyzed for their heavy metal contents. The results revealed that only surface water was observed as suitable for drinking purpose with all the parameters within the respective limits set by WHO. Majority of the sites (all ground waters) were highly contaminated with toxic heavy metals, especially with Pb and Cd. The industrial waste and geological reasons were the main pollutants. The groundwater pollution of the area is of main concern.

Table-3: Coefficient of correlation among the Heavy Metals

	Fe	Zn	Cu	Mn	Co	Pb	Ni	Cd
Fe	1	0.0769	0.0036	0.022	0.0251	0.0038	0.003	0.0298
Zn		1	0.0543	0.0866	0.0002	0.0002	0.0212	0.0065
Cu			1	0.0159	0.0411	0.0022	0.0243	0.0024
Mn				1	0.0028	0.0248	0.0391	0.0007
Co					1	$5x10^{-5}$	0.0101	0.001
Pb						1	0.1667	0.0224
Ni							1	0.0052
Cd								1

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