Trace Metals Contamination in Ground Waters of SITE Area Karachi

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(Received 29th June, 2004, revised 27th December, 2005)

Summary: Levels of trace metals in SITE (Sind Industrial Trading Estate), and its adjoining residential area have been determined. Altogether 39 samples were collected from different industries and residential colonies around SITE area. The elevated levels of trace metals found in these samples, determined by AAS, are due to indiscriminate disposal of industrial effluents. The average and ranges (given in parentheses) of these metals, in the area were found to be, Fe 0.766 (0.012 – 10.85) ppm, Mn 0.028 (0.002 - .165) ppm, Zn 0.564 (0.016 – 4.206) ppm, Cu 21.25 (1.3 – 61.6) ppb, Pb 23.24 (0.72 – 199.25) ppb, Cr 21.20 (3.2 – 173.5) ppb, Ni 9.65 ppb (below detection limit in a single sample to be as high as 38 ppb) and Cd 0.19 ppb (below detection limits in nine samples and maximum concentration was found to be 0.64 ppb). Moreover, some significant correlations (values given in parentheses) were also estimated for Mn & Cd (0.7206) , Zn & Ni (0.5722), Cu and Pb (0.5621) for the industrial area and Fe & Mn (0.6176), Cu & Cr (0.7715) for the adjoining residential area. Some other important correlations were also obtained for Mn & NO_2 (0.568), Cu & NO_3 (0.5305), Ni & Cl (0.6537) Ni & SO_4 (0.5818), and Cd & NO_3 (0.5146) for groundwaters of SITE area. The chemical quality of these waters shows a highly dissolved salt content and the percentage composition of mineral contents is almost same as that of sea water, which indicates that there might be sea water intrusion in this particular area and which may be due to excessive water pumping and low rain fall.

Introduction

Sind Industrial Trading Estate (SITE) is the most important industrial area of Karachi metropolis, which covers an area of about 16 km^2 having approximately 500 major industrial units. Among them most are textile mills and others are of diverse type, dealing with beverages, food products, chemicals, detergents, vegetable oil, paints etc. [1]. Due to acute shortage of water supply, most of the industries meet their water requirements through groundwater resources. In addition to industrial use, these resources are also been utilized for domestic household & drinking purpose in adjoining residential colonies.

Groundwater is generally considered a good source of drinking water, due to the inherent purification properties of the soil. However it is also prone to be polluted through leaching from dump sites, poor sanitation, and industrial activities etc. [2].

Heavy metals are supposed to be one of the major contaminant and a good pollution indicator from industrial activities. Several authors have reported an interrelation between ground water pollution by heavy metals and industrial activities [3-12]. Ground water samples from shallow aquifers around bicycle industry were analyzed and found to have anomalously higher concentration of Cr, Cu, Fe & Ni [3], whereas quite higher chromium concentration in some groundwaters of Uttar Pradesh and its adjoining areas was reported as ($\leq$ 31000 g/L), which was also associated to industrial waste/effluent disposal [4]. Ground water around tanning areas in Palar River Basin of India was found to be severely polluted due to waste water discharge by tanning industry [5]. A study of surface and groundwater in the area of Legnica Copper works, Poland showed that they were contaminated due to infiltration of acid solution from industrial installation and by the elution of pollutants from dumps and metallurgical wastes and polluted soil [6]. An excessive Pb burden in groundwater samples was reported to be a major cause of infiltration through contaminated soil & sediments from a battery reclamation site [7]. Trace metal levels in ground waters of Tehran, collected from industrial sectors, were found to be at elevated levels as compared to those collected from residential and agricultural areas [8]. Several other studies from India have also reported higher levels of trace elements in well water samples located in industrial sectors of Visakapatnam, Andhra Pradesh, Hyderabad and Calcutta [9-12]. An identical earlier study of groundwater contamination of Korangi Industrial Area (KIA), Karachi has also reported their

contamination with various trace metals, due to percolation of industrial waste water into the aquifer of the area [1].

The present study has been aimed to observe the level of trace metal contamination in ground water samples collected from another well developed industrial sector of Karachi city i.e. SITE Industrial Area, and to provide a database on the trace metal levels as well as groundwater quality in industrial and as well its adjoining residential areas and also to determine correlation (if any) between different pollutants.

Results and Discussion

Altogether thirty nine samples were collected from both industrial as well as its adjoining residential areas and the samples were collected from dug as well as bore wells. The depth of the wells was ranging between 30 – 250 feet and out of 39 samples; twenty one samples were collected from industrial area of SITE, whereas 18 samples were collected from its adjoining residential areas.

The chemical quality of the sample is determined in terms of its major cation and anions. 37 out of 39 samples both from industrial and residential sectors were analyzed for their chemical quality and the results are shown in Tables 1 and 2 respectively.

A review of the data shows, that there is no significant difference in the chemical quality of groundwater of the two sectors. pH ranges between 7.1 – 8.7 for industrial areas and 7.2 – 8.8 for adjoining residential area, suggesting that these water samples are weakly alkaline. Five out of thirty seven samples were found to have pH higher than World Health Organization (WHO) recommended value of 8.5 [13]. However, the average pH value for ground water samples of SITE area is 7.88.

A further review of the data presented in Tables-1 and 2 also shows, that these samples contain high concentrations of both major cations and anions and may safely be characterized as saline water because sodium as well as chloride contents were found to be more than 50% of the total dissolved salt contents, whereas the magnesium hardness in majority of water samples was more than the calcium hardness. Similarly sulfate contents were also particularly on the higher side in these water samples. A typical composition of seawater shows that its dissolved salt content on the average contains about 1-2% Ca, 3-4% Mg, 25-35% Na,1-2% K, 45-55% Cl, and 7-8% SO_4. A review of the analytical data of these water samples shows an average percentage composition of total dissolved salts content, quite close to that of seawater. It may therefore be suggested, that the groundwater samples are under direct influence of seawater and their might be sea

Table-1:Chemical Quality of groundwater of SITE Industrial Area

Sample I.D.	pH	Ca ppm	Mg ppm	Na ppm	K ppm	Cl ppm	SO_4 ppm	NO_3 ppm	NO_2 ppm	HCO_3 ppm	TDS ppm	Alkalinity as $CaCO_3$ ppm	Hardness as $CaCO_3$ ppm
S. 1	7.99	83	23	255	4.5	337	235	3.3	BDL	171	1110	140	304
S. 2	7.82	345	331	4203	21.5	6887	1652	2.05	BDL	342	13800	280	2220
S. 3	8.54	120	151	2000	27	2938	1623	11.05	3.26	538	7400	441	920
S. 4	8	120	148	1150	11.5	1552	1075	4.62	BDL	346	4410	284	910
S. 5	7.8	131	75	460	9	779	466	2	BDL	192	2120	157	636
S. 6	8.68	46	32	510	5.5	660	358	5.342	BDL	500	2126	410	248
S. 7	8.72	26	9	320	4	192	111	9.2	BDL	448	1116	367	104
S. 8	8.59	29	28	255	4.5	205	111	7.9	BDL	397	1036	325	188
S. 9	8.49	34	20	390	3.5	363	189	2.7	BDL	391	1398	321	168
S. 10	8.66	34	30	430	8.5	403	222	7.8	BDL	474	1606	389	208
S. 11	7.96	35	70	600	10.5	627	148	1.2	BDL	665	2160	545	374
S. 12	7.68	48	102	825	10.5	1155	366	0.05	0.106	356	2870	291	540
S. 13	7.8	36	75	370	8.5	363	170	1.51	0.009	585	1616	479	400
S. 15	7.78	16	29	410	8.25	277	197	2.29	0.956	598	1540	490	160
S. 16	7.228	28	100	825	10	924	374	5.21	0.011	588	2856	482	500
S. 17	7.56	40	97	912	11.5	990	310	4.72	0.026	715	3088	586	190
S. 18	7.66	36	24	360	12.75	396	197	2.15	0.062	369	1400	302	510
S. 19	7.31	80	75	1050	10	1254	407	1.41	0.006	717	3600	588	330
S. 20	7.64	24	66	600	8.5	594	239	5.24	0.006	688	2230	564	410
S. 21	7.15	24	85	435	9.5	495	193	8.18	0.136	619	1866	507	480
Average	7.95	67	79	818	9.97	1070	432	4.40	0.229	485	2968	397.56	490
Std. Dev	0.50	74.32	72.19	896.95	5.64	1508.2	461.86	3.07	0.74	163.37	2943	133.88	467.22

Table 2: Chemical Quality of Groundwater of adjoining residential areas of SITE Industrial Area

Sample I.D.	pH	Ca ppm	Mg ppm	Na ppm	K ppm	Cl ppm	SO_4 ppm	NO_3 ppm	NO_2 ppm	HCO_3 ppm	TDS ppm	Alkalinity as $CaCO_3$ ppm	Hardness as $CaCO_3$ ppm
R. 1	7.33	565	379	3250	28	5084	2233	23.5	BDL	281	11828	230	2970
R. 2	8.01	256	160	1000	28	1519	853	10.7	BDL	390	4210	320	1300
R. 3	8.03	345	267	3000	20	4622	1001	5.25	BDL	293	9550	240	1960
R. 4	7.73	1094	951	8750	38	17201	3469	11.9	BDL	154	31680	126	6640
R. 5	8.25	144	124	1400	11.5	1882	836	8.2	BDL	589	4990	484	870
R. 6	8.18	103	52	240	10	284	251	8.75	BDL	397	1340	325	468
R. 7	8.75	44	34	830	6.5	835	350	12.2	BDL	615	2720	504	248
R. 8	8.12	149	115	1075	10	1631	334	24.57	BDL	436	3760	357	844
R. 9	7.95	23	62	710	12.5	728	225	5.14	0.11	631	2400	517	312
R. 10	8.13	6	46	690	13.5	568	234	2.19	0.813	608	2188	498	202
R. 11	7.38	34	34	540	8	426	234	1.28	0.015	482	1770	395	228
R. 13	7.49	56	46	410	10	444	253	2.22	0.956	413	1640	338	332
R. 14	7.73	48	33	155	8	177	181	1.17	BDL	367	980	301	256
R. 15	7.48	150	154	825	21	1029	786	0.05	0.009	470	3440	385	1008
R. 16	7.61	145	256	1650	22.5	2378	1111	0.07	0.011	493	6060	404	1416
R. 17	8.07	79	77	730	32	674	732	1.15	0.211	459	2790	376	512
R. 18	7.24	327	193	1200	15	1455	1601	1.25	0.113	505	5300	414	1608
Average	7.85	210	175	1556	17.3	2408	863.8	7.03	0.132	446	5686	366	1246
Std. Dev	0.40	270.6	223.2	2041.1	9.5	4064.6	875.7	7.6	0.38	128.9	7301.6	105.8	1582.2

water intrusion in the groundwater of SITE industrial area and its adjoining residential areas.

The mean concentration and ranges (in parenthesis) in ppm, for major cations and anions in SITE industrial area are Ca 66.9 (16 – 344.7), Mg 78.6 (9.2 – 330.7), Na 818 (255 – 4203), K 9.97 (4 – 21.5), Cl 1069.7 (191.5 – 6887), SO_4 432 (111.2 – 1652.1), and HCO_3^- 484.9 (171 – 688). Total dissolved salts content was also found to be quite high in ground waters of SITE industrial area and out of twenty analyzed samples, TDS in all of the samples was found to be more than 1000 ppm, which is the maximum threshold limit, recommended by WHO [13]. The case is not very different for groundwater samples of its adjoining residential area. Out of seventeen samples analyzed, none had TDS level below 1000 ppm, whereas the mean levels of the major cations and anions and their ranges (given in parenthesis) in ppm, were Ca 209.9 (5.6– 1094.2), Mg 175.5 (33.1 – 950.9), Na1556.2 (155 – 8750), K 17.3 (6.5 – 38), Cl 2408 (177.5 – 17201), SO_4 863.8 (181 – 3469), and HCO_3 446 (154 – 631).

Nitrate is an important pollutant and as well as good pollution indicator. It is supposed to be causative agent of methaemoglobinaema (blue baby syndrome), in infants up to 6 months of age [14] and its contamination in ground water originates mainly through extensive use of nitrogenous fertilizer or leaching from open disposal of agricultural, animal and human wastes [15]. Nitrate has been detected in all of the ground water samples of SITE industrial and its adjoining residential areas and its mean concentration in the two areas was 4.4 ppm and 7.03 ppm respectively. Out of thirty seven samples analyzed, six samples have been found to contain higher nitrate concentration than the WHO maximum permissible limit of 10 ppm [13].

Trace metals content of groundwater samples of industrial and residential areas of SITE are given in Tables 3 & 4 respectively, and it is quite evident that ground water of SITE is generally heavily polluted and laden with these metals. The instance of comparatively higher concentration of most of these metals was found in ground water samples of SITE industrial area, than its adjoining residential area.

Iron was the most abundant trace metal found both in industrial and adjoining residential areas of SITE, with mean concentration and ranges (in parentheses) in ppm 0.962 (0.029 – 10.85) and 0.494 (0.012 – 3.44) respectively. The maximum iron concentration was found in Sample No 5 of SITE industrial area which was collected from a spinning and weaving mill at Manghopir road. Iron is generally found in natural waters within the range of 0.5-50 ppm, whereas no health based guideline value for iron in drinking water is proposed by WHO [13].

Manganese usually occurs together with iron in ground water, and the mean concentration of manganese in ground water samples of SITE industrial area was 0.023 ppm with range of 0.002-0.165 ppm. The maximum manganese concentration

Table-3:Levels of trace metals in SITE Industrial Area

Sample I.D.	Fe (ppm)	Mn (ppm)	Zn (ppm)	Cu (ppb)	Pb (ppb)	Cr (ppb)	Ni (ppb)	Cd (ppb)
S. 1	0.081	0.006	0.089	9.22	3.29	9.25	1.75	0.07
S. 2	0.302	0.049	0.776	17.8	4.74	12.32	7	0.07
S. 3	0.809	0.165	1.89	21.83	4.26	14.42	12	0.64
S. 4	0.118	0.008	0.433	31.52	1.19	8.15	9	0.46
S. 5	10.85	0.079	1.24	16.15	22.2	12.87	3.6	0.42
S. 6	0.071	0.005	0.284	14.27	1.92	9.57	4	0.26
S. 7	0.045	0.002	0.027	16.16	1.45	72.56	2.3	0.07
S. 8	0.073	0.004	0.03	8.53	1.41	173.5	2.65	0.07
S. 9	0.029	0.004	0.044	1.3	0.72	15.18	2.7	0.11
S. 10	0.053	0.004	0.074	7.58	3.76	161.71	3.6	0.12
S. 11	0.265	0.007	1.994	18.201	30.67	57.4	8.315	0.028
S. 12	0.184	0.0112	0.041	7.115	17.65	14.7	6.077	BDL
S. 13	0.282	0.006	0.481	30.55	48.04	12.9	12.577	0.187
S. 14	3.94	0.039	1.175	40.05	199.25	7.8	6.147	0.3
S. 15	1.6	0.026	0.074	20.01	78.22	7.1	6.707	0.062
S. 16	0.26	0.022	0.158	27.93	40.4	16.6	6.217	0.134
S. 17	0.165	0.019	4.206	37.1	27.8	7.1	7.477	0.114
S. 18	0.315	0.007	0.059	18.44	30.21	7.4	8.732	0.192
S. 19	0.312	0.003	0.083	13.81	13.55	8.4	6.847	BDL
S. 20	0.124	0.008	0.915	34.24	22.22	5.5	8.732	BDL
S. 21	0.315	0.016	3.23	16.23	24.21	4.2	26.55	BDL
Average	0.962	0.023	0.824	19.43	27.48	30.41	7.28	0.157
Std Dev	2.43	0.037	1.15	10.59	43.96	48.67	5.34	0.171

BDL = Below Detection Limit

Table 4 Trace Metal Levels in adjoining residential area of SITE Industrial Area.

Sample I.D.	Fe (ppm)	Mn (ppm)	Zn (ppm)	Cu (ppb)	Pb (ppb)	Cr (ppb)	Ni (ppb)	Cd (ppb)
R. 1	0.012	0.007	0.243	34.12	4.28	7.35	13.5	0.35
R. 2	0.192	0.011	0.217	23.42	2.51	6.52	4.95	0.43
R. 3	0.278	0.146	0.675	10.21	5.23	17.45	26	0.6
R. 4	2.276	0.061	0.194	9.72	7.98	4.85	38	0.48
R. 5	0.078	0.041	0.259	32.25	2.48	10.57	28.75	0.43
R. 6	0.045	0.027	0.051	32.05	3.63	3.2	4.82	0.38
R. 7	0.08	0.005	0.154	61.6	2.03	42.67	BDL	0.45
R. 8	0.066	0.004	0.201	58.54	2.22	28.47	6	0.35
R. 9	0.23	0.008	0.051	16.99	23.25	7.2	9.782	0.103
R. 10	0.19	0.009	0.329	23.18	16.31	4.9	12.017	0.14
R. 11	0.156	0.008	0.314	16.5	35.36	7.1	9.292	0.202
R. 12	3.44	0.143	0.066	19.57	45.65	6.4	9.782	0.107
R. 13	0.632	0.018	0.622	9.59	30.58	9.9	9.292	BDL
R. 14	0.19	0.014	0.073	14.06	36.75	5.2	8.525	BDL
R. 15	0.196	0.008	0.063	10.5	23.28	5.5	9.642	BDL
R. 16	0.26	0.075	0.016	7.86	21.52	5.2	10.062	BDL
R. 17	0.265	0.038	0.948	17.59	40.42	6.1	11.667	BDL
R. 18	0.312	0.007	0.223	22.84	25.7	9.6	11.387	BDL
Average	0.494	0.035	0.261	23.37	18.29	10.45	12.42	0.233
Std. Dev	0.893	0.045	0.250	15.62	15.05	9.97	9.07	0.208

BDL = Below Detection Limit

was found in a sample collected from a textile industry. All of the samples, collected either from industrial or residential areas, contain average manganese concentration within permissible WHO limits of 0.5 ppm for drinking water [13]. Levels of manganese in adjoining residential area were within the range of .004 – 0.146 ppm, with a mean value of 0.035 ppm (Table 4).

Zinc is normally found in all groundwater samples but usually its concentration does not exceed 0.05 ppm [12]. However in this study, zinc was detected in almost all of the samples, and its level in term of mean and ranges were 0.824 ppm (0.027-4.206 ppm) and 0.261 (0.016-0.948 ppm) for industrial and adjoining residential areas respectively. Like iron, no WHO guideline value is available for zinc. However zinc concentration of more than 3.00 ppm is not acceptable to consumer due to taste. Concentration > 3 ppm was found only in Sample # 17, collected from a hydrant located near a fan manufacturing factory.

Concentration of copper in all of the groundwater samples was found below the WHO guideline value of 2 ppm. Average concentration of copper found in industrial area was 19.4 ppb with a range of 1.3-40.05 ppb which was comparatively lower than that found in the adjoining residential area (23.37 ppb and range of 7.86-61.6 ppb).

Trace metals like lead, nickel, chromium and cadmium are considered as highly toxic and are also major pollution indicators. Lead is toxic to nervous system inducing sub-oncephalopathic neurological and behavioral effect. It can accumulate in the skeleton and infants/children up to six year of age and pregnant women are more susceptible to its adverse health effects. There are evidences, that cadmium, haxavalent chromium and nickel are carcinogenic and cadmium is also responsible for kidney damage [13]. All of the four metals have natural sources, but they originate largely due to industrial activities like lead and cadmium compounds are widely used in battery manufacturing whereas lead is also used in the production of solders and alloys. The organo-lead compounds, tetraethyl and tetramethyl lead have also been used extensively as anti knocking and lubricating agent in petrol. Nickel is mostly released from nickel taps and fittings, while source of chromium is mainly tanning industries [13].

The permissible WHO guidelines value for lead, chromium, nickel, and cadmium in drinking water are 10, 50, 20 & 3 ppb respectively [13]. Lead level in groundwater samples of industrial areas were found to be quite higher than that of adjoining residential areas and the level was as high as 199.25 ppb in sample # 14 collected from industrial area located nearby a metal industry. In twelve samples collected from industrial area, lead level was found to be exceeding WHO permissible limits. The mean and ranges of lead concentration in water samples of industrial and its adjoining residential area were 27.48 (0.72-199.25) ppb and 18.29 (2.03-45.65) ppb respectively.

Level of chromium was also found to be higher in groundwater samples of industrial area and was as high as 161.7 ppb and 173.5 ppb in two samples, collected from SITE water pumping station and a textile based industry. The level of chromium found in water samples of adjoining residential areas were comparatively lower and within permissible WHO limits. The mean and ranges of Cr found in this case were 30.4 (4.2-173.5) ppb and 10.45 (3.2-42.7) ppb, for industrial and adjoining residential areas respectively.

The scenario is a bit different for nickel and cadmium, as these are found in quite higher concentration in residential areas of SITE, as compared to that of industrial area, but there was no significant difference in mean and ranges of the two areas which were 12.4(BDL-28.75) ppb and 7.3(1.75-26.55) ppb for nickel and 0.233(BDL-0.6) ppb and 0.16 (BDL-0.64) ppb for cadmium, in residential and industrial areas respectively.

In order to find out common sources of pollution, linear correlation coefficient was calculated for the two areas independently and data is represented in Tables 5 & 6 respectively. Significant co-relation was found for manganese & cadmium, zinc & nickel and copper & lead, for industrial area, whereas iron & manganese, copper & chromium were found to have good correlation with each other in adjoining residential areas, indicating same source of pollution for these metals in this area. A negative correlation may also be seen from Tables 5&6 for lead & chromium and lead & cadmium in adjoining residential areas. Table 7 depicts the correlation coefficient between certain anions and trace metals in all the groundwater samples of SITE Area Karachi, and is showing a good correlation between Mn and NO_2 (0.568), Cu and NO_3 (0.5305), Ni and Cl (0.6537), Ni and SO_4 (0.5818), and Cd and NO_3 (0.5146). These correlations are quite significant in identifying the sources of pollution in the area.

The data generated through this study for groundwater samples collected from SITE industrial area shows quite higher accumulation of metals in these samples, making it unsafe for human consumption as well as for industrial purpose. It may be due to uncontrolled disposal of untreated industrial effluents. This horrible situation makes it quite essential to evolve necessary rules and regulations to

Table-5: Correlation Coefficients between trace metal contents in groundwater of SITE Industrial Area.

	Fe	Mn	Zn	Cu	Pb	Cr	Ni	Cd
Fe	1							
Mn	0.4143	1						
Zn	0.1076	0.2993	1					
Cu	0.0984	0.1510	0.4319	1				
Pb	0.3121	0.0611	0.1141	0.5621	1			
Cr	-0.1505	-0.2015	-0.2358	-0.3934	-0.2324	1		
Ni	-0.1357	0.1621	0.5722	0.2789	0.0798	-0.3283	1	
Cd	0.4167	0.7206	0.0945	0.2855	0.0819	-0.1716	0.0096	1