Journal of Civil Engineering
The Institution of Engineers, Bangladesh
Vol. CE 29. No. 2, 2001

GROUNDWATER CONTAMINATION IN DHAKA CITY FROM TANNERY WASTE

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ABSTRACT: The Tannery industries located at Hazaribagh are one of the major polluting industries in Dhaka. Chromium-rich wastewater from the tannery industries is discharged through open drains into a wastewater pond/lagoon, which finally flows into the Buriganga River. The stagnant pond area serves to retain the tannery wastewater for prolonged periods of time and poses a threat to groundwater contamination. Groundwater samples were collected from 21 deep tubewell stations from six water supply zones of Dhaka, including all seven stations located in Zone 2 covering Hazaribagh area, and analyzed for a wide range of parameters. Chromium concentrations [present primarily as Cr(III)] in the groundwater from Zone 2 were found to be significantly higher than those from other zones. Out of the 14 groundwater samples from Zone 2, two exceeded the Bangladesh drinking water standard of 0.05 mg/l. Average chromium concentration in Zone 2 (0.036 mg/l) was about ten times higher than the average in other five zones. In the absence of any natural source of chromium and the presence of a large number of tanneries, it appears that chromium from tannery wastewater is already contaminating the groundwater in and around Hazaribagh area. Concentration of sulfide was also found to be higher in the groundwater samples from Zone 2, which also appears to suggest groundwater contamination by the tannery wastewater. Apart from chromium, alarmingly high concentrations of lead, varying from 0.001 to 0.14 mg/l, were detected in many of the groundwater samples. Among the 21 samples analyzed, 17 exceeded the WHO guideline value (for drinking water) of 0.01 mg/l and two exceeded the Bangladesh drinking water standard of 0.05 mg/l. Very high accumulation of chromium (reaching close to 15,000 mg/kg of sediment) was detected in the top layer of sediment. The accumulation of chromium appears to be restricted primarily to the first 10 feet of soil. This is probably due to the fact that most of the chromium in the tannery wastewater is present in Cr(III) form and Cr(III) generally is not transported to great distance by groundwater because of its low solubility. However, groundwater with low levels of Cr(III), leached from the heavily contaminated sediments, can still move downward and slowly contaminate the aquifer below.

KEY WORDS: Groundwater contamination, chromium concentration, tannery effluent.

INTRODUCTION

The important industries in Bangladesh include leather tanning, textile, paper and pulp, fertilizer, sugar, steel, oil refining, chemical, pharmaceutical and other small scale agro-based and agro-allied industries. In terms of waste load generation, the principal polluting

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industries are paper and pulp, textile (dyeing and printing) and the tanneries. In Dhaka, environmental pollution from tannery industries is a particular concern. Majority of the tannery industries is located in the Hazaribagh area in Dhaka near the Buriganga River. About 200 tanneries are processing leather in these industries, which account for most of the processed leather in Bangladesh. The tanning process requires a huge amount of chromium especially in blue green section of the industry. A significant fraction of this chromium is discharged along with the effluent from the industry. An estimated 15,800 m^3/day of wastewater with a BOD load of 17600 kg/day and high chromium concentration is discharged from the tannery industries at Hazaribagh (BKH, 1995). Wastewater from tannery industry typically contains chromium, dissolved lime, hydrogen sulfide, dyes, oils, organic matter, and suspended solids. Chromium is a toxic heavy metal and its presence in tannery waste is cause of great concern. Very high chromium concentrations, reaching close to 4000 mg/l, have been detected in tannery wastewater.

After the devastating flood of 1988, a dike was constructed in the flood plain between the Buriganga River and Hazaribagh area. At present wastewater from the tannery industries is discharged through open drains into the stagnant pond that now exists between the dike and Hazaribagh area and finally into the Buriganga River through three outfalls. The stagnant pond area serves to retain the tannery wastewater for prolonged periods of time, allowing dissolved constituents (e.g., chromium) from the wastewater to percolate into the subsurface. Depending on the subsurface geology, hydrogeology and geochemistry, dissolved contaminants such as chromium may eventually reach the aquifer, contaminating the precious groundwater resource. Wastewater containing chromium that is eventually discharged into the Buriganga River pollutes the river water as well and the pollutants may in turn find their way into the aquifer as a result of recharge.

In Dhaka, groundwater is the principal source of water supply. Groundwater is extracted through a network of about 300 deep tubewells (DTWs) and distributed to the city dwellers through a distribution system. Any contamination of groundwater would endanger the entire water supply system in Dhaka. Chromium is a toxic heavy metal and it has significant adverse health effects. This paper presents as assessment of possible groundwater contamination in Dhaka City from tannery wastes. Twenty-one groundwater samples collected from DWASA deep tubewell pump stations (including all seven stations located in the Hazaribagh area) and three wastewater samples collected from Hazaribagh area have been analyzed. Accumulation and downward migration of chromium in the sediments at the tannery effluent discharge area at Hazaribagh were evaluated through collection and analysis of borehole sediment samples, as well as groundwater samples from the boreholes.

MATERIALS AND METHODS

Collection and Analysis of Groundwater and Wastewater Samples

Groundwater samples were collected from 21 deep tubewell pump (DTW) stations located in six DWASA zones. The Hazaribagh area belongs to Zone 2 of DWASA and water samples were collected from all

Table 1. Sampling locations (DWASA water pumps)

Zone	Well No.	Location	Date of Sampling
1	1	Baldha garden pump, Narinda Dhaka.	03-06-2000
	2	Kaptan Bazar Pump, Kaptan Bazar, Dhaka.	03-06-2000
	3	Bangabhaban Park Pump, Bangabhaban, Dhaka.	03-06-2000
2	4	Hazaribagh Park Pump, Hazaribagh, Dhaka.	15-03-2000 06-06-2001
	5	Badda Nagar Pump, Hazaribagh, Dhaka.	15-03-2000 06-06-2001
	6	College of Leather Technology, Hazaribagh, Dhaka.	15-03-2000 06-06-2001
	7	Tannery Area Pump, Hazaribagh, Dhaka.	15-03-2000 06-06-2001
	8	BDR Gate-1 Pump, Pilkhana, Dhaka.	15-03-2000 06-06-2001
	9	Nawabgong Pump, Nawabgong, Dhaka.	15-03-2000 06-06-2001
	10	Azimpur Shishupark Pump, Azimpur, Dhaka.	15-03-2000 06-06-2001
3	11	Bashbari Water Pump, Mohammadpur, Dhaka.	23-05-2000
	12	Road No.- 8 ,Dhamondi , Dhaka.	02-05-2000
4	13	Dawan Para Pump. Mirpur, Dhaka	20-05-2000
	14	Block-C, Mirpur-10, Dhaka	20-05-2000
	15	Pallabi Water Pump, Mirpur, Dhaka.	03-06-2000
5	16	Tejkunipara Water Pump, Tejkunipara, Firmgate, Dhaka.	30-05-2000
	17	Mohakhali Lab. Pump, Mohakhali, Dhaka.	03-06-2000
	18	Tibbet Water Pump, Tejgaon, Dhaka	03-06-2000
6	19	Banasree Housing Ltd. Rampura, Dhaka.	23-05-2000
	20	Osmani Uddan Pump, Osmani Uddan, Dhaka	03-06-2000
	21	High Court Water Pump, High Court, Dhaka.	06-06-2000

seven DTW stations located in this zone. Table 1 lists the DTW stations from which samples were collected along with sampling dates. For each DTW station, water samples were collected in two pre-washed plastic containers. One container was acidified in the field with concentrated HCl acid for analysis of metal ions. Wastewater samples were collected from three different locations: Hazaribagh Bazar outfall, Gazmahal shikaritala, and Bengal Leather Complex.

Groundwater and wastewater samples were analyzed for a wide range of parameters including chromium, iron, lead, manganese, cadmium, copper, pH, color, turbidity, carbon-di-oxide, alkalinity, chloride, sulfide, sulfate, ammonia, nitrate, nitrite, phosphate, BOD_5, COD, total solids, total dissolved solids and total suspended solids. Chromium, lead and cadmium concentrations were measured with an AAS (flame) (Shimadzu, Model 680). To analyze for heavy metals, wastewater samples were digested in order to convert all the metallic forms into dissolved ionic state. In order to determine speciation of chromium, concentration of Cr^{6+} was measured (in groundwater samples from Zone 2) following the 1,5-Diphenylcarbohydrazide Method using a spectrophotometer (HACH, DR4000U). Lead concentration was also measured with the atomic absorption spectrophotometer. Manganese concentration was measured using the PAN method with a spectrophotometer (HACH, DR4000U), and iron concentration was measured using the thiocyanate colorimetric method. Arsenic concentration was determined using the Silver-diethyl-dithiocarbamate method (AWWA, 1985); absorbance was measured using a spectrophotometer (HACH, DR/EL4).

In this study, pH was measured using a pH meter (HACH), conductivity was measured using a conductivity meter, and turbidity was measured using a standard turbidity meter. Hardness was measured using EDTA titrimetric method and chloride was measured using $AgNO_3$ titrimetric method. Color, ammonium, nitrate, fluoride, sulfate, sulfide, and phosphate concentrations were determined with a spectrophotometer (HACH, DR4000U). Ammonium was determined using Nessler method, nitrate by the cadmium reduction method, and phosphate by the molybdenum blue method. Alkalinity, carbon-di-oxide, and total and dissolved solids were determined by volumetric methods following Standard Methods (AWWA, 2000). Other parameters were measured following Standard Methods (AWWA, 2000).

Collection and Analysis of Borehole Sediment Samples

At Hazaribagh effluent discharge area, two boreholes were constructed using wash boring method. Both boreholes were constructed up to a depth of 100 feet and sediment samples were collected at 5 feet intervals. After collection, the sediment samples were immediately sealed in plastic bags and transported to laboratory for analysis. Sediment samples were also collected from a 100-feet borehole constructed in an uncontaminated area at Shar-E-Bangla Nagar, Dhaka. Sediment samples collected from the three boreholes were analyzed for pH, total chromium, and lead. The pH values were measured using the pH indicator paper (Universal Indicator pH 1-10, MERCK). Total chromium and lead concentrations of the sediment samples were determined by extracting these metals from the sediments (using aqua-regia) and then analyzing the extractants for chromium and lead using an AAS (Shimadzu Model No. AA 680).

RESULTS AND DISCUSSION

Chromium in Groundwater

Chromium concentration in the groundwater samples varied from 0.002 mg/l to 0.12 mg/l (Table 2). It is clear that chromium concentrations in water samples from Zone 2 are significantly higher than those from the other DWASA zones. Out of seven water samples from Zone 2, two exceeded the Bangladesh drinking water standard and WHO guideline value of 0.05 mg/l (GOB, 1997). It should be noted that water samples from the seven DTW stations in Zone 2 were collected on two different occasions and there are significant variations in chromium concentrations in these two samples. Except for one DTW station (Well No. 4), chromium concentration in all water samples collected in June 2001 were lower than those in water samples collected in March 2000. This may be due to the fact that the second sampling operation was carried during early monsoon (in June) and possible higher recharge during this time may be responsible for lowering of chromium concentration due to dilution. This suggests that regular monitoring of chromium concentration in the water samples from these DTW stations is needed to ascertain the level as well as variation in chromium concentration.

Chromium concentrations in none of the water samples from the 14 DTW stations from other zones exceeded the Bangladesh standard. Average chromium concentration in 14 water samples from the seven tubewells of Zone 2 is about 0.036 mg/l; while average chromium concentration in water samples from the 14 tubewells from 5 other zones is about 0.004 mg/l, about ten times less than that for Zone 2. In the absence of any natural source of chromium and the presence of a large number of tanneries in the Hazaribagh area, it appears that tannery wastes are responsible for the higher chromium concentrations in DTW water samples from Zone 2.

Table 3 shows speciation of chromium in groundwater samples from Zone 2. It shows that very little chromium is present in the more toxic Cr^{6+} form. In fact, most of the values are below the detection limit of 0.006 mg/l. Thus, majority of dissolved chromium in groundwater is present in less toxic Cr^{3+} form.

Table 2. Chromium in groundwater samples

Zone	Well No.	Total Cr (mg/l)	Zone	Well No.	Total Cr (mg/l)
1	1	0.003	3	11	0.003
	2	0.003		12	0.003
	3	0.003	4	13	0.004
2	4	0.0020[a] 0.0205[b]		14	0.004
	5	0.0300[a] 0.0147[b]		15	0.003
	6	0.1100[a] 0.0142[b]	5	16	0.011
	7	0.1200[a] 0.0169[b]		17	0.004
	8	0.0300[a] 0.0088[b]		18	0.005
	9	0.0400[a] 0.0120[b]	6	19	0.006
	10	0.0500[a] 0.0327[b]		20	0.002
	-	-		21	0.004

[a] Sample collected on 15-03-2000; [b] Sample collected on 06-06-2001

Table 3. Speciation of chromium of groundwater samples from Zone 2

Zone	Well No.	Total Cr (mg/l)[a]	Chromium(VI) Cr^{6+} (mg/l)[a]
2	4	0.0205	0.006
	5	0.0147	0.006
	6	0.0142	0.001
	7	0.0169	0.003
	8	0.0088	0.000
	9	0.0120	0.000
	10	0.0327	0.006

[a] Sample collected on 06-06-2001

Iron, Lead, Manganese and Arsenic in Groundwater

Iron concentrations in the groundwater samples were found to vary from negligible to 1.5 mg/l (Table 4). Only one sample from Zone 6 exceeded the Bangladesh drinking water standard of 1.0 mg/l. The calculated average concentrations of iron in the six zones are 0.07, 0.21, 0.06, 0.08, 0.01, and 0.52 mg/l, respectively. Very high concentration of iron (1.5 mg/l) in one tubewell is responsible for the high average of Zone 6. Among the other five zones, iron concentration in Zone 2 (which includes the Hazaribagh area) is the highest. In fact, average iron concentration for this zone is 3 to 20 times higher than the average value in the other four zones.

Lead concentrations in the groundwater samples varied from 0.001 to 0.14 mg/l (Table 4). Among the 21 samples, 17 exceeded the WHO guideline value (for drinking water) of 0.01 mg/l and two exceeded the Bangladesh drinking water standard of 0.05 mg/l. Of the two DTWs exceeding the Bangladesh standard, one is located in Zone 5 and the other in Zone 6. However, no clear zone-wise trend of lead concentration could be observed.

Table 4. Iron, lead, manganese and arsenic in groundwater

Zone	Well No.	Iron (mg/l)	Lead (mg/l)	Manganese (mg/l)	Arsenic (μg/L)
1	1	0.02	0.02	0.031	< 5
	2	0.04	0.01	0.037	< 5
	3	0.15	0.04	0.070	< 5
2	4	0.35	0.001	0.095	10
	5	0.10	0.008	0.078	< 5
	6	0.50	0.015	0.140	< 5
	7	0.08	0.012	0.058	< 5
	8	0.05	0.021	0.031	< 5
	9	0.20	0.023	0.107	< 5
	10	0.20	0.01	0.098	< 5
3	11	0.1	0.03	0.002	< 5
	12	< 0.02	0.02	0.027	< 5
4	13	< 0.02	0.026	0.023	12
	14	0.15	0.018	0.046	< 5
	15	0.08	0.012	0.036	< 5
5	16	< 0.02	0.14	0.032	< 5
	17	< 0.02	0.02	0.039	< 5
	18	< 0.02	0.04	0.036	< 5
6	19	1.5	0.08	0.001	< 5
	20	< 0.02	0.02	0.057	< 5
	21	0.05	0.03	0.057	< 5

Manganese concentrations were found to vary from 0.001 to 0.14 mg/l (Table 4). Among the 21 samples, two exceeded the Bangladesh drinking water standard of 0.1 mg/l; and none exceeded the WHO guideline value of 0.5 mg/l. The calculated average concentrations of manganese in the six zones are 0.046, 0.087, 0.015, 0.035, 0.036, and 0.038 mg/l, respectively. Thus, manganese concentrations in water samples from Zone 2 appear to be significantly higher than those from the other zones, although most samples satisfy the Bangladesh drinking water standard for manganese. Except for two samples, arsenic concentrations of all the water samples were below the detection limit of

5 μg/L (Table 4). Only two samples showed arsenic concentration above the detection limit; but even in these samples arsenic concentrations were very low (10 and 12 μg/L).

Other Water Quality Parameters

The pH values in the groundwater samples varied within a narrow range, from 5.8 to 6.6. Carbon-di-oxide concentrations varied from 22 mg/l to 118 mg/l; higher carbon-di-oxide values in general could be associated with lower pH values (Saha, 2001). Chloride concentrations varied from 18 mg/l to 110 mg/l, all satisfying the Bangladesh standard (Saha, 2001). Since tannery wastes contain high concentrations of chloride and since chloride is a conservative solute, higher concentration of chloride was expected in water samples from Zone 2. However, water samples from Zone 1 were found to contain the highest concentrations of chloride. Total dissolved solids (TDS) concentrations of groundwater samples varied from 194 to 502 mg/l, and conductivity varied from 114 μs/cm to 328μs/cm. Chloride, TDS and conductivity values followed similar trend (Saha, 2001). Color concentrations were found to be low, varying from 0 to 8 Pt.-Co. unit. No clear zone-wise trend for color concentration could be observed. Turbidity values of water samples were low, varying from 0.14 NTU to 3.7 NTU. Alkalinity (as $CaCO_3$) varied from 98 to 211 mg/l. Hardness (as $CaCO_3$) of water samples was relatively low, varying from 40 mg/l to 206 mg/l (Saha, 2001). Fluoride concentrations varied from 0 mg/l to 0.30 mg/l, and nitrate (NO_3) concentration in water samples varied from 0.1 mg/l to 4.6 mg/l, all satisfying the Bangladesh standard for drinking water.

Phosphate (PO_4) concentration in water samples varied from 0.416 mg/l to 0.783 mg/l and sulfate concentrations varied from trace quantity to 48.9 mg/l (Table 5), all satisfying the Bangladesh standard for drinking water. Sulfate concentrations in water samples from Zone 1 and Zone 2 were the highest, averaging about 44 and 21 mg/l, respectively. Ammonia (NH_4^+-NH_3) concentrations in water samples varied from 0.021 mg/l to 0.795 mg/l (Table 5). Ammonia concentrations were relatively higher in water samples from Zones 1, 3 and 6. In fact, two water samples from Zone 3 and one from Zone 6 exceeded the Bangladesh standard for drinking water. Sulfide concentrations in water samples varied from 0 to 3 g/l (Table 5). It is interesting to note that sulfide was detected in all the seven wells located in Zone 2. Among the other samples, only those from Zone 4 showed presence of sulfide. Thus, none of the water samples from Zones 2 and 4 satisfy the Bangladesh drinking water standard of 0 g/l for sulfide. Since tannery wastewater contains significant concentration of sulfide, its presence in well waters from Zone 2 may result from discharge and subsequent leaching of tannery waste in the subsurface.

Table 5. Phosphate, sulfate, sulfide and ammonia in groundwater

Zone	Well No.	PO_4 (mg/l)	SO_4 (mg/l)	Sulfide (µg/L)	NH_3-N (mg/l)
1	1	0.588	43.4	Nil	0.137
	2	0.586	47.8	Nil	0.320
	3	0.601	41.7	Nil	0.331
2	4	0.416	21.8	3	0.188
	5	0.547	29.0	3	0.187
	6	0.431	17.7	2	0.073
	7	0.428	13.4	3	0.021
	8	0.387	22.2	3	0.475
	9	0.419	18.5	1	0.250
	10	0.483	27.0	2	0.195
3	11	0.728	1.0	Nil	0.795
	12	0.625	22.8	Nil	0.610
4	13	0.425	2.7	2	0.102
	14	0.620	0.8	1	0.212
	15	0.552	2.6	1	0.107
5	16	0.668	Nil	Nil	0.207
	17	0.506	6.4	Nil	0.125
	18	0.521	3.4	Nil	0.141
6	19	0.783	0.8	Nil	0.658
	20	0.584	48.9	Nil	0.238
	21	0.519	44.3	Nil	0.301

Characteristics of Tannery Effluent and its Pollution Potential

Table 6 shows characteristics of tannery wastewater samples collected from three different sampling locations. Variation in wastewater characteristics probably represents the variation in sampling locations. Wastewater Sample-1 collected from the Hazaribagh Bazar outfall represents the mixture of wastewater (from tannery industries and other industrial/commercial activities) flow that falls into the low-lying area. Wastewater Sample-2 collected from Gazmahal Shikaritala represents mainly wastewater coming from Chowdhury Leather Complex and partly coming from different industrial and commercial activities; while Wastewater Sample-3 primarily represents wastewater coming from the Bengal Leather Complex.

With a few exceptions (e.g., chloride, sulfide, TDS, ammonia, lead and phosphate), concentrations of most of the parameters in Sample-1 are lower compared to those in the other two-wastewater samples. This is probably due to the fact that Sample-1 represents the combined wastewater flow while the other two represent primarily those coming out from two tannery industries. Very high chromium concentration was detected in the wastewater samples, varying from 11.2 to 74.2

mg/l. It should be noted that chromium concentrations reported by Rahman (1997) appears to be significantly higher (reaching as high as 4043 mg/l for one industry) compared to those found in this study. This is primarily due to the fact that data reported by Rahman (1997) represent characteristics of wastewater collected directly from tannery industries, whereas in this study wastewater samples were collected from open drains carrying the combined flow of tannery effluent and water/wastewater from a variety of other sources. The same is also true for chloride; data reported by Rahman (1997) show significantly higher chloride concentration compared to those found in this study. The differences are not as dramatic for other parameters. This probably suggests that these other constituents are also contributed by other industrial and commercial activities in the area; whereas the tanneries primarily contribute chromium and chloride. Speciation of chromium in limited wastewater samples showed that most of the chromium in the wastewater samples are present in Cr(III) form.

Table 6. Characteristics of tannery wastewater

Parameters	**Unit**	**Sample-1**[a]	**Sample-2**[b]	**Sample-3**[c]	**Discharge Criteria (ECR, 97)**
BOD$_5$	mg/l	1080	22400	10400	50
COD	mg/l	1560	24800	15800	200
Chloride	mg/l	1300	1620	960	600
Total Chromium	mg/l	11.195	74.157	18.981	0.5
Sulfide	mg/l	180	46	5040	1
Total Solids	mg/l	6013	11374	7721	-
TSS	mg/l	1078	23.06	5010	150
TDS	mg/l	4935	9068	2711	2100
NO$_2$-N	mg/l	0.182	0.384	0.36	-
NO$_3$-N	mg/l	10	15	20	10
NH$_3$-N	mg/l	86.2	170.7	1003.2	50
Sulfate	mg/l	770	1142	4648	
pH	mg/l	7.6	8.6	5.4	6.9
Alkalinity as CaCO$_3$	mg/l	754	1358	820	-
Cadmium	mg/l	0.0119	0.022	0.0152	0.05
Lead (Pb)	mg/l	0.1091	0.1529	0.1051	0.1
Iron (Fe)	mg/l	1.9708	2.3235	8.4914	2
Copper (Cu)	mg/l	0.1829	0.2265	0.2177	0.5
Manganese	mg/l	0.07	0.08	0.08	5
CO$_2$	mg/l	Nil	Nil	Nil	-
Phosphate	mg/l	2.28	2.01	1.79	8.0
Color	Pt.-Co.	800	1120	792	-
Turbidity	NTU	26.8	28.6	792	-

a: Hazaribagh bazar outfall, b: Gazmahal-Shikaritala, c: Bengal leather complex.

As shown in Table 6, with a few exceptions (e.g., chloride, nitrate, iron), concentrations of most of the parameters in all three wastewater samples exceed the criteria set by Bangladesh Environment Conservation Regulation (ECR) 1997 for discharge into surface water bodies. This is particularly true for BOD_5, COD, Chromium and Sulfide.

Chromium in Sediments at the Discharge Site

Figure 1 shows very high accumulation of chromium in the top sediment at the wastewater discharge site at Hazaribagh (Fig. 1a, 1b). Here chromium levels are almost two orders of magnitude higher than that in an uncontaminated area (Fig. 1c). The sediment samples from borehole-1 located near Hazaribagh Bazar outfall showed significantly higher levels of chromium (Fig. 1a) compared to the samples from borehole-2 (Fig. 1b). This is probably due to the fact that borehole-1 is located very close to the point where wastewater first fall (from the open drains that carry tannery wastewater) in the low-lying area; while borehole-2 is located about a kilometer away from this site. At borehole-1, the first 10 feet appears to be most contaminated, with chromium in the sediment reaching close to 15,000 mg/kg of sediment. There appears to be a sharp drop of chromium concentration in the sediment below 10 feet depth. At borehole-2, the top ten feet also appears to be the most contaminated, although the chromium levels here are significantly lower that those at borehole-1.

At borehole-1, sediment samples from surface to a depth of about 4 feet were basically accumulated sludge; while at borehole-2 the top two to three feet represented accumulated sludge. Thus it appears that chromium from accumulated sludge and wastewater has penetrated into the soil below, but restricted primarily to the top 10 feet of soil. This is not surprising because, as discussed earlier, most of the chromium in the tannery wastewater is present in Cr(III) form and Cr(III) generally is not transported to great distances by groundwater because of its low solubility. The low solubility of the Cr(III) solid phases [e.g., $Cr_2O_3(s)$] is the major reason why Cr(III) rarely occurs at concentrations above the drinking water standard of 0.05 mg/l (Hem, 1977). In addition, Cr(III) is also bound by a variety of ligands (e.g., soil organic matter) that render it insoluble, immobile, and un-reactive. Cr(III), as well as Cr(VI), can also be rendered immobile by adsorption on iron oxy-hydroxides in the sediment. However, groundwater with low levels of Cr(III), leached from chromium contaminated top sediments, can still move downward and slowly contaminate the aquifer below.

It should be noted that chromium (III) has been shown to form highly soluble organic complexes in the laboratory, particularly under acidic conditions (Bartlett and Kimble, 1976a; James and Bartlett, 1983a). Thus, in a complexed form, Cr(III) may exist at much higher concentrations in groundwater. However, the existence of Cr(III) complexes has not been documented under field conditions. The small amount of Cr(VI) present in tannery wastewater is also likely to be quickly reduced to Cr(III) after discharge. Cr(VI) transported by groundwater is transformed to and precipitated as Cr(III) if the groundwater enters a low redox zone. Laboratory studies have shown that Cr(VI) can be reduced readily to Cr(III) in the presence of organic matter, especially at low pH (Bartlett and Kimble, 1976b; Bloommfield and pruden, 1980). Schroeder and Lee (1975) found that Cr(VI) could also be reduced by Fe(II) and dissolved sulfides. High concentration of organic matter in tannery wastewater (as shown by the levels of BOD and COD) and presence of dissolved iron [Fe(II)] and sulfide suggest that Cr(VI) present in groundwater would be quickly be reduced to Cr(III).

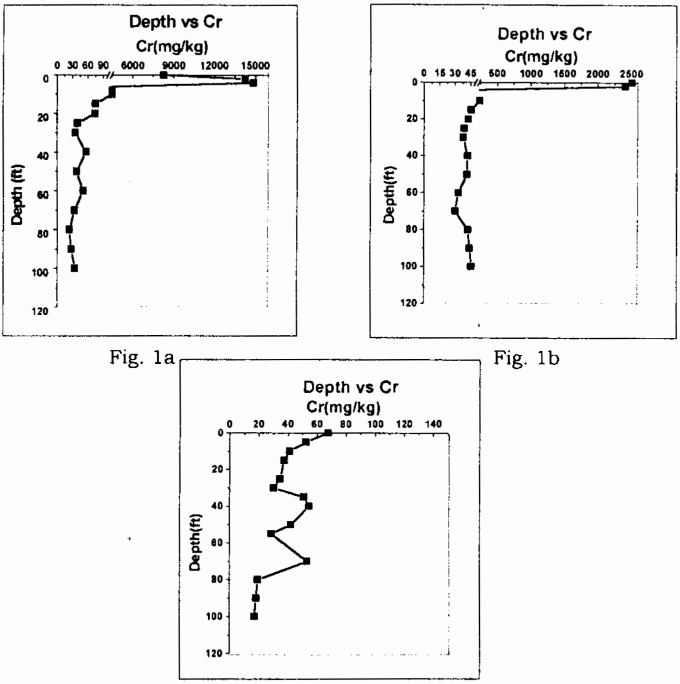

Fig. 1a

Fig. 1b

Fig. 1c

Fig. 1. Chromium in borehole sediment samples

It is possible for Cr(III) to be converted to the more soluble Cr(VI) if the redox state at a particular region in the subsurface becomes oxidizing. Cr(III) has been found to be oxidized by manganese under natural conditions (Bartlett and James, 1979; Schroeder and Lee, 1975). However, there is no evidence that such oxidation is taking place in the subsurface at Hazaribagh site.

Lead in Sediments at the Discharge Site

Very high concentration of lead was found in the top sediments at borehole-1 (Fig. 2a). As was the case for chromium, high concentration of lead was restricted to the first ten feet of sediment. Unlike borehole-1, sediment samples from borehole-2 did not show presence of higher levels of lead (Fig. 2b). In fact, lead concentrations in sediments from borehole-2 were comparable to those found in the uncontaminated sediments from borehole-3 (Fig. 2c). The lower level of lead in borehole-2 is probably due to the fact that it is located far away from the point where wastewater first fall in the discharge area (from the open drains), about a kilometer away from borehole-1. It appears that majority of the lead is either adsorbed or precipitated before reaching the location around borehole-2.

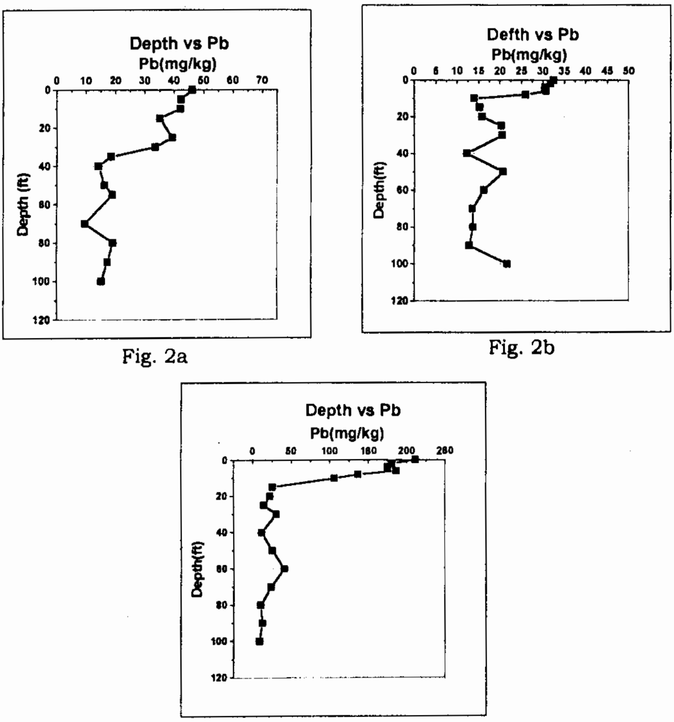

Fig. 2a

Fig. 2b

Fig. 2c

Fig. 2. Lead in borehole sediment samples

In the Hazaribagh area, two paint industries (Roxy paint and Pailac paint), one glue industry (Brothers Chemical Ltd.) and about 70 manually operated glue factories were identified. These industries are likely to contribute to the pollution problem at Hazaribagh. For example, the paint industries may be responsible for higher lead in wastewater, sediment and groundwater in the area.

CONCLUSION

In order to assess possible contamination of groundwater by tannery wastewater, water samples from 21 deep tubewell pump stations in six DWASA Zones, including the seven stations located in Hazaribagh area (Zone 2), were collected and analyzed for detailed characterization. High levels of chromium [mostly present as Cr(III)] were detected in groundwater samples from Zone 2. Out of 14 water samples from Zone 2, two exceeded the Bangladesh drinking water standard and WHO guideline value of 0.05 mg/l. Average chromium concentration in groundwater of Zone 2 is 0.036 mg/l, about ten times higher than the average chromium concentration of 0.004 mg/l in water samples from other five zones. In the absence of any natural source of chromium and the presence of a large number of tanneries in the Hazaribagh area, it appears that chromium from tannery wastewater is contaminating the groundwater in and around Hazaribagh area. Sulfide was detected in all the seven groundwater samples collected from Zone 2. Since tannery wastewater contains very high concentration of sulfide, presence of sulfide also appears to suggest contamination of groundwater in Hazaribagh area from tannery wastewater.

Apart from chromium, alarmingly high lead concentrations were also detected in many of the DWASA groundwater samples. Among the 21 samples, 17 exceeded the WHO guideline value (for drinking water) of 0.01 mg/l and two exceeded the Bangladesh drinking water standard of 0.05 mg/l. Thus, groundwater samples of DWASA should be regularly monitored for chromium and lead and appropriate measures should be taken to protect public health and safety.

Analysis of tannery wastewater samples showed very high levels of chromium [mostly present as Cr(III)], varying from 11.2 to 74.2 mg/l. Besides chromium, the wastewater samples contained very high concentrations of BOD_5, COD, Sulfide, TS, TSS and Ammonia. Concentrations of most of the parameters in all three wastewater samples exceeded the national criteria for discharge into surface water bodies. Results from this study as well as previous studies clearly suggest that the tannery effluents have high pollution potential and must be treated before disposal.

Analysis of borehole sediment samples collected from the wastewater discharge site at Hazaribagh showed very high accumulation of chromium (reaching close to 15,000 mg/kg of sediment) in the top layers of sediment. The accumulation of chromium appears to be restricted primarily to the first 10 feet of soil. This is probably due to the fact that most of the chromium in the tannery wastewater is present as Cr(III) and movement of Cr(III) is usually restricted by its low solubility. However, water with low levels of Cr(III) can leach from chromium-rich top sediments and can contaminate the aquifer below. Detection of higher levels of chromium in groundwater samples (from DTWs) located in the Hazaribagh area probably suggests that such a process is actually taking place. Besides chromium, very high concentration of lead was found in the top sediment samples from the borehole located close to the first point of discharge. This lead may come from the tannery effluents as well as from other industrial and commercial activities in the Hazaribagh area.

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