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CONTAMINATION OF SOIL AND PLANT BY THE HAZARIBAGH TANNERY INDUSTRIES

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Abstract

An investigation was made at Hazaribagh Tannery area, comprising about 145 industries in Dhaka Metropolitan area. The analyses of soil and plant samples showed that heavy metals contribute significantly towards environmental contamssination resulting from industrial activities. Concentration of heavy metals (Cr, Zn, Pb, Cd, Mn, Fe and Ni) in soil and plant samples cross the MAC (Maximum allowable concentration) in both wet and dry season. In case of soil sample the highest concentration of Cr (172792 ppm) was found at main disposal point. Chromium, Zn, Pb, Cd, Mn, Fe and Ni concentrations at Hazaribagh plant samples respectively ranged from 171-1348, 247-777, 45-96, 1.66-2.17, 72-231, 354-787, and 18-38 ppm respectively in dry season and 75-1142, 209-691, 29-84, 1.02-2.00, 66-124, 331-664, 11-37 ppm respectively in wet season. Concentration went down gradually with increasing distance from the main disposal point (spot 1). But again high concentration (150708 ppm of Cr) was noted in spot 6. Similar results were found for plant samples. High concentrations of heavy metals were found in plant samples which consequently affect food chain, which may be a major environmental concern.

Key words: Chromium, Copper, Lead, Cadmium, Zinc, Tannery wastes, Effluents, Heavy metal

Introduction

Soil and environment are under tremendous pressure due to industrial expansion and increased use of agricultural chemicals. Very few are aware of this globally important issue. The third world countries, especially Bangladesh are now in a vulnerable position. Bangladesh has now more than 30,000 industrial units (DOE 1991). With the advent of industrialization, wastes and effluent are being discharged into the natural ecosystems without treatment, creating pollution especially of heavy metals (Cr, Zn, Pb, Cd, Fe, Mn, Ni etc.).

Tannery industries of Hazaribagh situated in a heavily populated residential area discharge some 21,600 square meters of liquid wastes and 150 metric tons of solid waste everyday. These harmful wastes, including chromium, lead, sulphur, ammonium, salt and other materials, are severely polluting the capital city and the river Buriganga (Elahi *et al.* 2010). About 59% of the total wastage comes from processing of hides and skin and accumulates in the swamp-sludge. A recent research revealed that out of 270 tanneries in the country, except for two BATA and Dhaka Leather Complex-none of the tanneries has a treatment plant as required by the law (ImmamulHuq 1998).

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Rice and wheat which were grown in a pot experiment in soils from the tannery area showed delayed maturity and stunting growth while rice showed late flowering and maturity with dark green colour (Chamon *et al.* 2005). In another experiment it was observed that application of tannery effluents to soils of differing textures resulted in reduction of rice yield and the adverse effect was more pronounced in light soils than in heavy soils (Elahi *et al.* 2010). The effluent was also found to negatively affect performance (Elahi *et al.* 2010). Similar results were also reported by Chamon *et al.* (2005). Reduction of rice yield production (43.6%) due to heavy metal toxicity with hazaribagh soil was observed before by Chamon *et al.* (2005). Extreme concentration of Cr (27,000 ppm) around the vicinity and 1335 ppm Cr in 4 km down from the main disposal point were also reported by Nuruzzaman *et al.* (1995). Heavy matals concentration at hazaribagh area increased day by day. According to Ullah *et al.* (1999) at hazaribagh soil, Cr concentration increased to 25014 ppm.

Heavy metals, even in trace amounts, destroy enzymes and interfere with or inactivate enzymes of living cells (Rahman 1992) and hence their discharge into the environment must be carefully controlled and minimized.

Tannery industry is one of the most important and largest industrial businesses in Bangladesh. The 50 years old tannery complex comprising about 194 units are discharging their solid wastes and effluents to the channels, farmer's fields, in low lying areas, along road sides and water bodies without treatment and thereby causing environmental pollution especially due to heavy metals and organic toxins. The specific objectives of the research are to study the effects of wastes and effluents on the intensity of pollution to the soils by the heavy metals and to investigate the concentration of heavy metals in the plant samples causing contamination of the food chain.

Materials and Methods

Location of Hazaribagh tannery area: The Hazaribagh tannery complex situated in Dhaka municipality area (WSW) of the city are located inside the greater Dhaka flood protection embankment. The embankment was built in the year 1989 (Chowdhury *et al*. 1996). There are about 145 tannery factories in Hazaribagh residential area. Of the 270 tannery units, 90% are located on 25 hectares of land in Hazaribagh. Liquid waste makes its way on the other side of the embankment round the clock. This liquid waste ultimately goes into the water of the Buriganga river and causes immense harm to the fish and other aquatic organisms. Toxic materials in liquid waste seep into the surrounding cropland and underground water levels. Eventually, the tannery waste poisons the soil, water, plant and air round the clock. Tannery wastes also poison the health, houses and utensils of those situated around (Iwegbue *et al*. 2006).

Soils in Hazaribagh Area: The soil series around Hazaribagh belonging to Khaler Char (Soil Survey Staff 1975) remains seasonally flooded, up to 120-150 cm deep for more than 6 months and they are poorly to very poorly drained soils, developed in mainly medium textured Brahmaputra alluvium in permanently wet channels or depression on the old and young Brahmaputra, Meghna and Jamuna floodplains. Their profiles show little sign of development. General soil type is non-calcarious alluvium and Fluvaquent. The area inside the embankment is just organic wastes, on Jamuna alluvium, permanently wet by the effluents of the tannery factories.

Sampling: A total of 6 sampling points was chosen based on assumption of pollution intensity and types of samples. Spots are located inside and outside the embankment respectively. Spot 1 is considered the main disposal point and the increasing numbers of the spots indicate increasing distance from the main point. Soil and existing plant samples (with 3 replications) were collected twice (wet and dry seasons) on the basis of the local environmental conditions. The sampling spots were kept fixed throughout the whole sampling periods. Contaminated soil samples (with 3 replications) were collected from 0-15 cm depths of a profile with the help of spade. Out of six, 3 soil samples were collected from inside the embankment and 3 soil samples were collected outside of the embankment. The sampling points were geo referenced with GPS (Geographical Positioning System) and marked on the map. GPS locations of sampling point are presented in Table 1.

Table 1. GPS location of sampling points (both in wet and dry seasons).

No of Sampling Site	Latitudes	Longitude	Soil	Plant
1	$23^0$44.013'N	$90^0$21.807'E	√	×
2	$23^0$41.156'N	$90^0$21742'E	√	√
3	$23^0$44.552'N	$90^0$21.604' E	√	√
4	$23^0$44.673'N	$90^0$21.549' E	√	×
5	$23^0$44.600'N	$90^0$21.279' E	√	√
6	$23^0$44.501'N	$90^0$21.109' E	√	√

Soil samples collection and preservation: The soil samples collected were air dried, ground and screened to pass through 2 mm sieve and then mixed thoroughly to make it a composite sample. Dry root, grasses and other substances were discarded from the sample. Each soil sample was further ground and screened to pass through 1.0 mm and 2.0 mm sieve and was used for physical and chemical analyses.

Plant Samples collection and preservation: At main disposal point i.e. sampling point 1, all heavy metals concentration in soil was so high that no plants sample was found on that spot. The plants samples collected from other different spots are presented in Table 2.

Table 2. List of collected plant samples.

Spot No	Type of plants samples	Scientific Name
Spot 2	Grass	*Cynodon dactylon*
Spot 3	Kalmi	*Ipomoea aquatica*
Spot 4	Kalmi	*Ipomoea aquatica*
Spot 5	Grass	*Cynodon dactylon*
Spot 6	Water hyacinth	*Eichhornia crassipes*

Plant samples were collected fresh from the polluted area in required amounts, wrapped in polyethylene bags and transported to laboratory and preserved at $+4^0$C for processing on the next day. All plant samples were air dried and placed in oven for drying at 70^0C and then ground to powder for passing through a 2-mm sieve for chemical analysis. All plant samples were kept in plastic containers for chemical analyses.

Determination of physical soil properties

Soil Texture: The particle size distribution of the soils was measured by the hydrometer method (ÖNORM 1991). The textural class was determined from the Marshalls triangular co-ordinates as described by the United States Department of Agriculture (USDA 1975).

Moisture content of soil: The percent of moisture content of the soil was determined by known amount of soil in an electric oven at 105^0C for 25 hours until constant weight was obtained and moisture percentage was calculated from the sample as described by Black (1965).

Determination of chemical and physicochemical properties of Soil

Soil pH: The pH of the soil was measured electrochemically using a corning glass electrode pH meter as suggested by Jackson and Alloways (1962). The ratio of soil to water was 1:2.5.

Electrical conductivity: The electrical conductivity of the soil was measured at a soil: water ratio of 1:2 by an EC meter.

Organic Carbon and organic matter: Organic carbon was determined by wet oxidation method of Walkley and Black (1934) as describe by Piper (1950) and Jackson and Alloways (1962). The organic matter content of the soils was determined by multiplying the percentage of organic carbon with the conventional “Van-Bemmelen’s Factor” of 1.72 (Piper 1950).

Available and total Nitrogen: Available and total nitrogen of the soil were determined by “Micro Kjeldhal”s distillation method as described by Black (1965).

Total Phosphorus, Potassium, Calcium, Magnesium and Sulfur: The total P, K, Ca and Mg were extracted by digesting the soil with aqua regia (Vdlufa 1975). The total phosphorous content of the soil was determined colorimetrically at 470 nm using a spectrophotometer (UV-1200) after developing the yellow colour with vanadomolybdate as described by Jackson and Alloways (1962). Total Ca and Mg were measured titrimetrimetrically by EDTA compleximetry method (Jackson and Alloways 1962). Total and exchangeable Na and K were measured by flame photometer.

Total heavy metals in soil and plant samples

Digestion of soil samples with aqua regia (HCl: HNO_3): Soil samples were digested with $HCl+HNO_3$ (3:1) mixture under closed system (Blum *et al.* 1996). Aqua regia decomposes nearly almost all complex forming soil particles (clay minerals, organic substances, oxides, etc.) through which most of the ions go into solution and can be measured quantitatively.

Digestion of plant samples with HNO_3-$HClO_4$: 0.2g of finely ground plant sample was weighed and digested with 20 ml conc. HNO_3 and 10 ml conc. $HClO_4$ (Blum *et al*. 1996).

Measurements of Total heavy metals: All the trace elements were measured in the extracts with the help of an Atomic Absorption Spectrophotometer (AAS), model no AA421.

Results and Discussion

Physical, Chemical and Physicochemical properties of soils

Moisture content: Soil characteristics of Hazaribagh tannery area are presented in Table 3. The moisture content (%) of the soil at various sampling points ranged from 18 to 28 and 22 to 36% in dry season and wet season, respectively (Table 3).

pH: Soil pH did not vary appreciably between sampling points and ranged from 7.06 to 8.32 and 6.95 to 8.47 in dry and wet seasons, respectively (Table 3). Nuruzzaman *et al.* (1998) and Immamul Huq (1998) reported that pH of the top soil at Hazaribagh tannery area were 7.3 and 7.2. A wide range of pH from 7.2 to 12.0 and 7.3 to 9.9 was observed by Nuruzzaman *et al.* (1998) in tannery effluents and waste water, respectively,which did not affect soil pH (7.3). This might be due to buffering capacity of these soils containing high amounts of organic matter. Various tanning and coloring materials are mainly responsible for wide range of pH variation.

Particle size: The soil of Hazaribagh belongs to Khaler Char soil series and there was no noticeable difference in particle size fraction as well as sand, silt and clay percentage between the wet and dry season soil samples (Table 3).

Eh: Eh values of the soil samples ranged from -233 to -350 and -274 to -350 (mV) in dry and wet seasons, respectively (Table 3). Eh values with minus sign at different spots indicate highly reduced condition and under reduced condition almost all heavy metal remain available to aquatic flora and fauna.

Organic matter: The organic matter content (%) in various sampling points was found to range from 4.9 to 12.6 and 3.8 to 16.2, in dry season and wet season, respectively (Table 3). In dry season maximum accumulation was observed at sampling point 1 (12.6 %) and gradually decreasing values were observed from source point 1 to downstream and outside the embankment. Same findings were also observed in wet season where the highest value of organic matter was observed at the source point i.e at the sampling point 1 (16.2%). Nuruzzaman *et al.* (1998) reported a value of organic matter (%) of 10.3% at source point. Deposition and decomposition of huge quantities of tannery effluents and solid wastes are mainly responsible for the organic matter content of the soil.

EC (Electrical Conductivity): Higher EC means higher amounts of soluble Na, Caand Mg. EC greater than 4 dS/m is harmful for plant growth (Ponnamperuma 1985). The EC (dS/m) in various sampling point ranged from 3.5 to 5.9 and 3.7 to 7.1 dS/m in dry season and wet season,respectively (Table 3). Higher values of EC at Hazaribagh tannery area were also reported before (Ullal *et al.* 1999 and Elahi *et al.* 2010).

Table 3. Physical, Chemical and physicochemical properties of soils.

Spot No	% Moisture	pH	% sand	% silt	% clay	Eh (mV)	OM%	EC (dS/m)	CEC (Meq/100g)
Dry season									
1	19.2	8.04	35.3	46	18.7	-333	12.6	5.9	38.2
2	25.12	7.70	31.6	45.8	22.6	-320	10.8	4.3	31.9
3	22.5	8.32	40	42.9	17.1	-338	10.1	4.5	29.6
4	18.12	7.72	36.9	42.6	20.5	-350	9.63	4.8	29.9
5	27.5	7.21	30.6	49.8	19.6	-235	6.9	3.9	20.6
6	24.42	7.06	40.5	42.8	16.7	-233	4.9	3.5	20.3
Wet season									
Spot No	% Moisture	pH	% sand	% silt	% clay	Eh (mV)	OM%	EC (dS/m)	CEC (Meq/100g)
1	32.2	7.23	35	46.9	18.1	-300	16.2	6.2	32.3
2	35.12	8.47	31.3	45.7	23	-350	11.3	6.8	34.4
3	36.2	7.56	40.9	42.9	16.2	-348	11.2	7.1	30.5
4	28.9	7.87	32.2	47.3	20.5	-348	9.1	4.2	29.1
5	29.6	6.95	30.6	39.8	29.6	-274	6.25	3.7	22.3
6	21.6	7.25	40.5	44.5	15	-296	3.8	4.2	26.7

CEC (cation exchange capacity): CEC (Meq/100g of the soil) at various sampling points of Hazaribagh tannery area were found to range from 20.3 to 38.2 and 22.3 to 34.5 (Meq/100g) for dry season and wet season in soil respectively (Table 3). The high CEC was related to their high organic matter content as reported by Nuruzzanman *et al.* (1995).

Total N and Available N: High concentrations of total N as well as available N were observed in the surface soil (0 to 15 cm) at Hazaribagh tannery area in both wet and dry season (Table 4). Tannery wastes increased the total N concentration of surface soils (Nuruzzanman *et al*. 1995 and Chamon *et al.* 2005*)*.The higher accumulation was observed in dry season (Table 4) (January) and lower in wet season (August).

Table 4. Physical, Chemical and physicochemical properties of soils.

Spot No	Total N	Available N	Total P	Available P	Total K	Available K	Total S	Ca	Mg	K	Na
Dry season											
								Exchangeable			
					ppm						
1	2478	960	3690	6.9	1854	148	1587	6.8	2.8	0.4	40.9
2	2158	821	3244	5.8	1485	125	1481	6.3	2.3	0.2	35
3	1965	185	2963	7.2	1250	98	1125	5.1	1.8	0.3	32.2
4	1258	89	2717	7.6	1145	89	1025	5.6	1.2	0.4	31.3
5	1325	93	2561	5.2	1006	75	658	6.4	1.9	0.4	30.6
6	1357	96	1583	2.4	654	28	745	7.2	3.6	0.5	40.5
Wet season											
Spot No	Total N	Available N	Total P	Available P	Total K	Available K	Total S	Ca	Mg	K	Na
								Exchangeable			
					ppm						
1	2145	652	3602	6.1	1569	245	1365	5.2	2.9	0.3	26.2
2	2123	478	3230	5.5	1405	124	1145	5.7	2.1	0.6	21.5
3	1658	143	2978	6.3	1236	87	1258	5.1	1.9	0.2	12.3
4	1332	92	2689	7.2	1128	98	1198	5.8	2.1	0.2	3.2
5	1258	84	2798	4.9	984	114	695	6.8	2.8	0.6	1.3
6	1378	92	1545	3.6	965	16	845	6.3	2.5	0.1	5.3

Total P and Available P: High concentrations of total P and available P were observed in the soil at Hazaribagh tannery area in both dry and wet seasons. This observed higher concentration might be due to use of higher amounts of various phosphate salts, which are used in various steps in tanning process. Compared to dry season, a lower value of total P and available P was observed in wet season ranging from 1545 to 2978 ppm and 2.4 to 7.2 ppm for total P and available P, respectively (Table 4).

Total K and Available K: The concentrations of total K at various sampling points of Hazaribagh tannery area ranged from 654 to 1854 ppm and 965 to 1569 ppm for dry and wet seasons in soil, respectively (Table 4).

Total S: The concentrations of total S in soil at various sampling points of study area were found to range from 658 to 1587 ppm and 695 to 1365 ppm in dry and wet seasons, respectively (Table 4). Higher value of total S (1587 ppm) was observed at sampling point 1 which gradually decreased with increasing distance and the lowest value (654 ppm) of total S was observed at sampling point 6. Similar results were observed in case of wet season. Observation of lower value of total S in wet season might be due to dilution by rain water.

Exchangeable Na, K, Ca and Mg: Higher amounts of exchangeable Na, K, Ca and Mg in soil were recorded at different sampling points at Hazaribagh tannery area (Table 4). The high concentration of EC in different spots within the embankment were attribute to the increase in soluble salts particularly Na, K, Ca and Mg from the tannery effluent, values exceeding 4dS/m which is the harmful limit for rice seedling establishment (Nuruzzanman *et al.* 1995).

Heavy metals in Soil at Hazaribagh tannery area

Chromium in soil in dry and wet seasons: Chromium concentration at Hazaribagh sampling area ranged from 42792 to 172792 and 26654 to 148446 ppm in dry and wet season, respectively (Table 5). Highest Cr concentration was observed in main disposal point i.e. at spot 1 and decreasing value was observed with increasing distance from the discharge point. Significant differences were found among different sampling spots.

High Cr concentration (150708 ppm) observed at spot 6 was significantly different from other spots except spot 1, during dry season. Similar results were also observed in wet season (Table 5).Ullah *et al.* (1999) reported 25014 ppm Cr concentration at Hazaribagh area. Previously similar findings were also reported at Hazaribagh area (Chamon *et al.* 2005 and Elahi *et al.* 2010). Chromium concentration of 59333 ppm in soil was reported by Elahi *et al.* (2010). Relatively lower value of Cr was observed at the same sampling point in wet season. This might be due to dilution of Cr in soil by rain water in wet season. High Cr concentration may occur due to use of higher amount chromium sulphate ($[Cr\ (H_2O)_6]_2(SO_4)_3$), regarded as one of the most efficient and effective tanning agent, during liming, pickling and curing stage.

Cr concentration at 6 sampling points (both in dry and wet season) cross the MAC (Maximum allowable concentration) for soil (100 mg/kg) (Kloke 1980). It is evident that very high level of Cr (Table 5) along with other heavy metals were found in spot 1 which serves as a settling basin and gradually concentration went down with increasing distance of spots from spot 1. But again high concentration was noted in spot 6 (Table 5). This spot may be previously contaminated before 1989, when there was no embankment to protect this area from the tannery waste and effluents. The result indicates that the soil is extremely polluted with Cr, even outside the embankment (Nuruzzanman *et al.* 1998).

As stated earlier, the tannery discharges the effluents and wastes into the river system. Consequently, there is a large area of sludge alongside the flood protection embankment and the liquid wastes are dumped into the river through a flood control regulator-cum-sluice near Hazaribagh. During monsoon months, the flood protection embankment protect Dhaka from heavy flooding while making it difficult to flash out the waste water, thereby creating a great environmental hazards in the neighborhood of the tanneries. On the other hand, during the dry season the waste water is flushed out into the river, causing pollution of the river water (spot 6) and ultimately affecting the aquatic flora and fauna. Likewise the dumping of the solid wastes is seriously affecting the soil and plants, besides vitiating the air, ground water and human health (Immamul Huq 1998).

Zinc (Zn) concentration in soil indry and wet seasons: Total zinc concentration at Hazaribagh sampling area ranged from 1000 to 1950 ppm and 1264 to 1896 ppm in dry and wet seasons respectively (Table 5). Highest Zn concentration was observed in main disposal point i.e. at spot 1 and decreasing value were observed with increasing distance from the discharge point. Ullah *et al.* (1999) reported 365 ppm of Zn concentration at Hazaribagh area soil. Similar findings (290 ppm) were also reported by Nuruzzaman *et al.* (1998). Elahi *et al.* (2010) found 3000 ppm Zn concentration at Hazaribagh area bulk soil (Table 5). Zn concentration at 6 sampling points (both dry and wet season) cross the MAC (Maximum allowable concentration) for soil (300 mg/kg) (Kloke 1980).

Lead (Pb) in soil in dry and wet seasons: Lead concentration at Hazaribagh sampling area was found to range from 80.5 to 157 and 24.17 to 144.57 ppm in dry and wet seasons, respectively (Table. 5). Highest Pb concentration was observed in main disposal point i.e. at spot 1 and decreasing value was observed with increasing distance. Significant differences were found among different sampling spots. 131.0 ppm of Pb concentrationwas observed at spot 6 outside of the embankment, which was significantly different from other spots except spot 1 and 2, during dry season. The value was different in case of wet season. Significant differences were observed among sampling point (Table 5). The tests of significance of differences at of different sampling points were calculated by DMRT at 5% level. 44.2 and 68.1 ppm of Pb concentration was reported by Ullah *et al.* (1999) and Nuruzzanman *et al*. (1998), respectively.

Relatively higher Pb concentrations were found at spot 6 in dry and wet seasons (131.0 and 114.57 ppm), respectively. That spot may be previously contaminated before 1989 when there was no embankment to protect this area from tannery waste or huge amounts of waste water and effluents are now continuously being added from other different industries (Ullah *et al.* 1999).

Lead concentration at 6 sampling points (both dry and wet seasons) crossed the MAC for soil (100 mg/kg) (Kloke 1980).

Table 5. Chromium (Cr), Zinc (Zn) and Lead (Pb) concentration (ppm) in soil at various sampling points of Hazaribagh area in dry and wet seasons.

Spot No	Cr (ppm)		Zn (ppm)		Pb (ppm)	
	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Spot 1	172792 a	148446 a	1950 a	1896 a	157 a	145 a
Spot 2	71542 b	71238 b	1878 a	1765 a	130 ab	142 a
Spot 3	87375 b	52488bc	1778 b	1065 b	104 b	43 b
Spot 4	42792 b	26654 d	1780 b	299 b	81 c	32 b
Spot 5	59875 b	40821 cd	1586 b	200 c	75 c	24 b
Spot 6	150708 a	56238 bc	1264 c	1150 b	131 ab	115 a
Mean	97514	63411	1706	1062	113	83

Means followed by same letter in a column do not differ significantly from each other at 5% level by DMRT.

Cadmium (Cd) in soil in dry and wet seasons: Cadmium concentration at Hazaribagh sampling area ranged from 2.33 to 1.5 ppm and 0.75 to 2.10 ppm in dry and wet season, respectively (Table 6). The highest Cd concentration was observed in main disposal point i.e. at spot 1 and decreasing value was observed with increasing distance from discharge point. Significant differences were found among different sampling spots except spot no 1, 3 and 4. 1.50 ppm of Cd concentration was observed at spot 6 which were not significantly different from other spots (Spot no 3 and 4) during dry season. The value was different in case of wet season. Significant difference was observed among sampling points (Table 6). The tests of significance of different sampling point were calculated by DMRT at 5% level.

Lower value of Cd concentration observed in wet season might be due to dilution of Cd of soil by rain water. Cadmium concentration may be higher due to use of cadmium sulphate during curing and finishing stage. Huge amount of cadmium sulphate and cadmium phosphate are used to polish the hide and skin. Cadmium concentration at 6 sampling points (both in dry and wet season) did not cross the MAC for soil (3.00 mg/kg) (Kloke1980).

Manganese (Mn) in soil in dry and wet seasons: Manganese concentration at Hazaribagh sampling area ranged from 333 to 733 and 183 to 601ppm in dry and wet seasons, respectively (Table 6). The highest Mn concentration was observed in main disposal point i.e. at spot 1 and decreasing value was observed with increasing distance. Significant differences were found among different sampling spots. Manganese (Mn) concentration of 561 ppm was observed at spot 6 which was significantly, different from other spots, during dry season. The value was different in case of wet season. No significant differences were observed among sampling point 1, 2, 3, 6 and 4, 5 (Table 6). The tests of significance of different sampling point were calculated by DMRT at 5% level. Ullah *et al.* (1999) had reported 263 ppm Mn concentration at Hazaribagh area and 425 ppm of Mn concentration in soil was reported by Nuruzzaman *et al.*(1998). Manganese concentration at 6 sampling points (both in dry and wet season) did not cross the MAC for soil (1000 mg/Kg) (Kloke 1980).

Iron (Fe) in soil in dry and wet seasons: Iron concentration at Hazaribagh sampling area ranged from 21081 to 55914 ppm and 21498 to 50991 ppm in dry and wet seasons, respectively (Table 6). Fe concentration at spot 1 (both dry and wet season) crossed the MAC for soil (50,000 mg/kg) (Chiroma *et al.* 2012)

Table 6. Cadmium, Mn and Fe concentration (ppm) in soil at various sampling points of Hazaribag area in dry and wet seasons.

Spot No	Cd Concentration (ppm)		Mn Concentration (ppm)		Fe Concentration (ppm)	
	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Spot 1	2.33 a	2.10 a	733 a	601 a	55914 a	50991 a
Spot 2	1.5 b	2.0 a	641 a	562 a	45787 a	47914 a
Spot 3	1.75 ab	1.250 b	633 a	521 a	37412 a	28414 b
Spot 4	1.79 ab	1.83 ab	366b	374 b	35437 b	23414 b
Spot 5	1.25 c	0.58 c	333 b	183 b	21081 b	21497 b
Spot 6	1.50 b	0.75 c	560 ab	448ab	25416 b	24247 b
Mean	1.68	1.40	566	454	36841	32746

Means followed by same letter in a column do not differ significantly from each other at 5% level by DMRT.

Nickel (Ni) in soil in dry and wet seasons: Nickel concentration at Hazaribagh sampling area ranged from 37 to 355 and 31 to 256 ppm in dry and wet seasons respectively, (Fig.1). The highest Ni concentration was observed in main disposal point (i.e. at spot 1) which crossed the MAC for soil (50 mg/Kg) (Kloke 1980) and decreasing value was observed with increasing distance. Significant differences were found among different sampling spots. At spot 6 (outside of the embankment), 142 ppm of nickel (Ni) was observed which were significantly different from other spots, during dry season. Spot 6 may be previously contaminated before 1989 when there was no embankment to protect this area from tannery waste or huge amounts of waste water and effluents are now continuously added from other different industries (Ullah *et al.* 1999).

The concentration was different in case of wet season. There were no significant differences observed at various sampling points. The tests of significance of different sampling point were calculated by DMRT at 5% level.

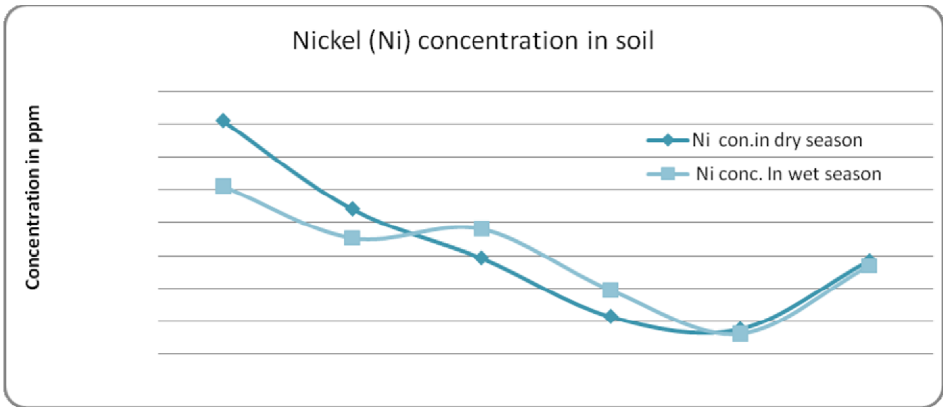

Fig.1. Ni concentration (ppm) in Soil at various sampling points of Hazaribagh area in dry and wet season.

Heavy metal concentrations in plant samples at Hazaribagh tannery area

Chromium (Cr) in plant samples in dry and wet seasons: Chromium concentrations in plant samples at Hazaribagh sampling area ranged from 171 to 1348 and 75 to 1142ppm in dry and wet seasons, respectively (Table 7). Chromium concentrations in dry season were 684, 564, 243, 171 and 1348 ppm in sampling point 2 (grass), 3 (kalmi), 4 (kalmi), 5 (grass) and 6 (water hyacinth), respectively (Table 7). Higher Cr concentration (1348 ppm) was observed in water hyacinth (spot 6) which was significantly different from other spots. Significant differences were found among other different sampling spots expect sampling point 2 and 3 i.e grass and kalmi. Similar results were also observed in wet season (Table 7). The tests of significance of different sampling point were calculated by DMRT at 5% level. Water hyacinth might be contaminated by various chromium salt that were used in tannery industries or huge amounts of waste water and effluents which are now continuously being added from other different industries. Due to variation of plant species uptake of heavy metals by plants also varies differently as reported by Chamon *et al.* (2005).

Relatively lower value of Cr was observed in all type of plant samples at the same sampling point in wet season. The lowest (75 ppm) and the highest (1142 ppm) concentrations of Cr was found at sampling point 5 and 6 i.e in grass and water hyacinth. Significant differences were found among different sampling spots. Chromium concentration observed at wet season might be due to dilution of available Cr for plant by rainfall. Elahi *et al.* (2010) reported 6591 ppm Cr in the root of water hyacinth and 756 ppm Cr in the shoot of water hyacinth at Hazaribagh area. Similar findings were also reported by Nuruzzaman *et al.* (1998). Similar findings were reported by Mark *et al.*(1995) for the uptake of heavy metals by water hyacinth in Lake Chivers which is fed by the two rivers being considered here. As long as the rate of absorption by the root is higher than the rate of translocation to the stem and leaves, the metal concentration will be higher in the root than the tops (Mark *et al.* 1995). Chromium concentration at 6 sampling points (both dry and wet seasons) crossed MAC for plant (1-2 mg/kg) (Lake *et al*. 1984).

Zinc (Zn) in plants in dry and wet seasons: Zinc concentrations in plant samples at Hazaribagh sampling area ranged from 247 to 777 and 209 to 691 ppm in dry and wet seasons, respectively (Table 7).

Lead (Pb) in plant samples in dry and wet seasons: Lead concentrations in plant samples at Hazaribagh sampling area ranged from 44.55 to 95.6 and 28.83 to 84.17 ppm respectively, in dry and wet seasons (Table 7).

Cadmium (Cd) in plant samples in dry and wet seasons: Cadmium concentrations in plant samples at Hazaribagh sampling area ranged from 1.66 to 2.17 and 1.02 to 2.00 ppm in dry and wet season, respectively (Table 7).

Cadmium concentration at 6 sampling points (both dry and wet seasons) crossed the MAC for plant (5-10mg/kg) (Lake *et al.* 1984 and Sauerbeck 1982).

Manganese (Mn) in plant samples in dry and wet seasons: Manganese concentrations in plant samples at Hazaribagh sampling area ranged from 72 to 231 and 66 to 124 ppm in dry and wet season, respectively (Table 8).

Iron (Fe) in plants in dry and wet seasons: Iron concentrations in plant samples at Hazaribagh sampling area found to range from 354 to787 and 331 to 664 ppm in dry and wet season, respectively (Table 8).

Nickel (Ni) in plants in dry and wet seasons: Nickel concentrations in plant samples at Hazaribagh sampling area were found to range from 18 to 38 and 11 to 37 ppm in dry and wet seasons, respectively (Fig. 2).

Table 7. Chromium, Zn and Pbconcentrations (ppm) in plants at various sampling point of Hazaribagh area both in dry and wet seasons.

Spot No	Type of plants samples	Cr Concentration (ppm)		Zn Concentration (ppm)		Pb Concentration (ppm)	
		Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Spot 2	Grass	684 b	475 a	498 b	472 b	96 a	84 a
Spot 3	Kalmi	564 b	410 a	384 b	312 b	76 a	65 b
Spot 4	Kalmi	243 a	375 c	247 c	209 c	70 b	58 b
Spot 5	Grass	171 c	75 c	318 b	331 b	45 b	29 c
Spot 6	Water hyacinth	1348 a	1142 a	777 a	691 a	80 a	25 c
Mean		602	495	445	403	73	52

Means followed by same letter in a column do not differ significantly from each other at 5% level by DMRT.

Table 8. Cd, Mn and Fe concentration (ppm) in plants at various sampling point of Hazaribagh area both in dry and wet seasons.

Spot No	Type of plants samples	Cd (ppm)		Mn (ppm)		Fe (ppm)	
		Dry season	Wet season	Dry season	Wet season	Dry season	Wet season
Spot 2	Grass	2.17 a	2.01 a	231 a	124 a	787 a	472 a
Spot 3	Kalmi	2.08 a	2.0 a	196 ab	116 a	637 a	534 a
Spot 4	Kalmi	1.75 a	1.5a	102ab	108 a	354 a	331 a
Spot 5	Grass	1.66 a	1.02 a	72 b	66 a	683 a	664 a
Spot 6	Water hyacinth	2.17 a	2.00 a	167 ab	74 a	381 a	239 a
Mean		1.97	1.704	153	98	568	448

Means followed by same letter in a column do not differ significantly from each other at 5% level by DMRT.

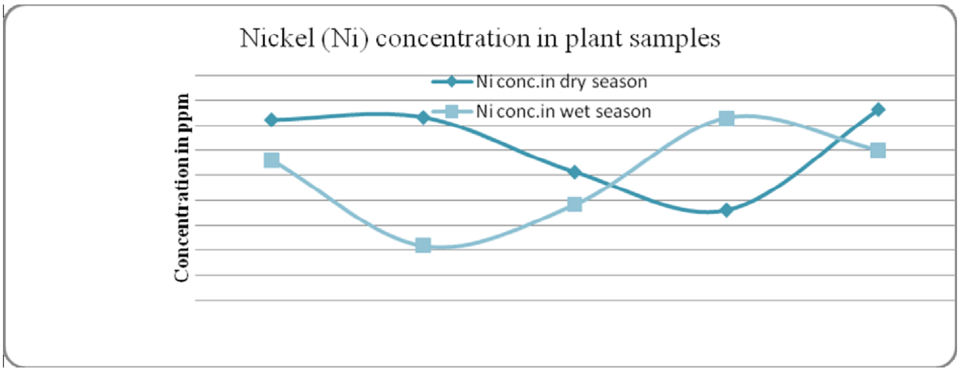

Fig. 2. Ni concentration (ppm) in plants at various sampling point of Hazaribagh area both in dry and wet seasons.

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