Speciation Analysis of Nickel in the Soils of Tejgaon Industrial Area of Bangladesh

A. S. Chamon,* M. N. Mondol, B. Faiz, M. H. Rahman and S. F. Elahi

Department of Soil, Water and Environment, University of Dhaka, Dhaka-1000, Bangladesh

Abstract

The main focus of the study is Tejgaon industrial area which is located within the Dhaka City Corporation and about 5 km north of the city centre. The industries around the study area like battery, chemical manufacturing, electrical and electronic, metal finishing, mining, paint and dye, textiles, pharmaceuticals, pesticides, etc, discharge heavy metals like Ni with their effluents and wastes. At Tejgaon soil the minimum pH value was 5.3 and the maximum 7.6 (at 26^OC). High buffering capacity resulting from high soil organic matter content (4.87-11.55%) probably influenced soil pH. Electrical conductivity (EC) (25-551 µS/cm) and organic matter (OM) (4.87-11.55%) contents were also influenced by the industrial wastes and effluents of the factories. In the wet season, the average Ni concentration in different soil fractions was 1.69, 4.16, 13.21 and 93.12 mg kg^{-1} in water-soluble, NH_4OAC extractable, DTPA extractable and total fractions respectively. Comparing wet season and dry season sampling data, total Ni concentrations in different locations were higher in the dry season and the mean concentration of total Ni was 223.89 mg kg^{-1}, which was more than 4 times higher than the tolerable limit. Concentrations of total Ni in different locations during wet season were found above the natural background level with few exceptions. Ni concentration in the group of tolerable level was 21% (>022-$\leq$50 mg kg^{-1}) and 75% ($\geq$50 mg kg^{-1}) soil samples were found in the group of in excess of tolerable level during wet season. During dry season, 11% of Ni ($\leq$50 mg kg^{-1}) samples were in the normal range and 89% (>50 mg kg^{-1}) soil samples were found in the group of in excess of tolerable level. Ni concentration during dry season samples in different extraction i.e in NH_4OAC extractable, DTPA extractable and in total fraction was found to decrease with distance away from the disposal point source due to dilution of the effluent and water. The decreasing tendency with distance indicates the accumulation of metals by the industrial operations.

Key words: Speciation, Tejgaon soil, Industrial area, Nickel.

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* Corresponding author.

Introduction

Industrial wastes and effluents are being discharged randomly on soils, into canals, rivers, along the road sides or in the vicinity of the industrial operations without any treatment in Bangladesh. They pollute productive soils, natural water systems as well as ground water. The important heavy metals discharged from Tejgaon industries in Bangladesh are cadmium, lead, chromium, mercury, zinc, arsenic and in few cases copper and manganese. The industries around the study area like battery, chemical manufacturing, electrical and electronic, metal finishing, mining, paint and dye, textiles, pharmaceuticals, pesticides, etc, discharge heavy metals like Ni with their effluents and wastes.

Heavy metals are widely distributed in the environment, in soils, in plants and animals. The concentrations of individual metals in living tissue are ordinarily very low and must be maintained within narrow limits to permit the optimum biological performance of most organisms. Some heavy metals are essential in trace amounts, namely Co, Cu, Fe, Mn, Mo and Zn for plants and in addition Cr, Ni, Sn for animals (Greenland and Hayes, 1981).

Pollution by heavy metals is a new threat to Bangladesh agriculture. As s consequence of anthropogenic activities there is a progressive increase in soil and water pollution by heavy metals, such as nickel (Ni), Cu, Cd, Pb, Cr, Fe, Mn, Zn etc. Their uptake and accumulation in plants have been known to results in negative effects on plant growth (Trivedi and Erdei, 1992). Inhibition of plant growth could be caused by the effect of heavy metals on different plant processes i.e. photosynthesis (Moya *et al.,* 1993); respiration (Keck, 1978); carbohydrate metabolism (Greger ang Lindberg, 1986) and water relations (Becerril *et al.,* 1988). Additionally, it has been reported that heavy metals may interfere with the uptake and distribution of essential mineral nutrients in plant (Brecle and Khale, 1992). Applied Ni had an antagonistic effect on nitrogen (Singh *et al.,* 1990) and potassium concentration (Faroughi *et al.*, 1975). Nickel was not toxic to wheat up to 50 µg N g^{-1} soil. Nutrient medium containing toxic concentration of NiCl2 (300, 400 and 500 µg ml^{-1} exhibited stunted growth with a decrease in internode length and fresh and dry matter weight of wheat CV. ML 711 plants (Setia *et al.,* 1988).

The uptake of heavy metals by plants is often poorly correlated with the total concentrations of heavy metals in soils. Determining factors for plant availability are type and concentration of heavy metal species in the soil solution (intensity factor) and rate of transfer from solid phase to the soil solution (rate factor) for replenishment of the heavy metals taken up by plant roots. In the soil solution heavy metals are present in different physico-chemical forms (Brümmer *et al.,* 1986a). Root exudates may mobilize heavy

metals from the solid phase by forming complexes and thus increase availability to the plants. The formation of such complexes, however, may also decrease heavy metal uptake by plants if the complexes have a high molecular weight (Steric hindrance) or a high stability (Dunemann *et al.,* 1991).

Trace metal composition of soil varies widely depending on the sources, industrial wastes type (He *et al.,* 1992) and geographical location (Krogmann, 1999). The levels of heavy metals in municipal solid waste have been reported for many countries in the world by several authors (He *et al.,* 1992; Krogmann, 1999; Koivula *et al.,* 2000). Like soils, sediments and sludge, trace metals can exist in a variety of forms in soil. These forms include (i) water soluble, (ii) exchangeable, (iii) linked to organic substances, (iv) occluded or co-precipitated with oxides, carbonates and phosphates, or other secondary minerals and (v) ions in the crystalline lattices of the primary minerals (Petruzzelli, 1989; He *et al.,* 1992; Iwegbue *et al.,* 2006a,b). The first three chemical forms are considered to be balanced among themselves; this equilibrium is influenced by pH and the concentrations of metals and ligands. The metals present in these forms are considered to be most available forms of plant nutrition, each successive form representing less availability (Petruzzelli, 1989; Iwegbue *et al.,* 2006b).

The distribution of metals between the specific forms varies widely according to the individual metal and the characteristics of the wastes. These parameters include pH, temperature, oxidation-reduction potential and the presence of complexing ligands.

Total trace metal composition of soil is of little importance in determining its uptake by plants and consequently, in contaminating the food chain since the different forms have different mobilities, bioavailabilities and potential environmental contamination potential. It is more important to know the distribution of each trace metals in the different forms, than just the total content (Petruzzelli, 1989). The various techniques used to estimate heavy metal distribution in soils, and sewage sludge has been adopted for fractionation of heavy metals in soils. There are two basic techniques. These techniques include (i) physical fractionation based on particle size and density, and (ii) chemical extraction based on selective dissolution of trace metals in different reagents. In order to asses the speciation or binding forms of heavy metals in solid materials, different analytical procedures involving successive extractions have been developed. These procedures are based on the assumption that the following species of heavy metals exist in soils (Iwegbue, 2007):

1. Water-soluble (i.e. in the soil solution)

2. Exchangeable

3. Organically bound

4. Occluded in iron and manganese oxides

5. Definite compounds (e.g. heavy metal carbonates, phosphates, sulphides)

6. Bound in silicate structure (i.e. the residual fraction)

The heavy metals in the soluble fraction can be determined in the saturation extract of soil samples or by extracting soil material with deionized water at a certain ratio (Sposito *et al.,* 1982).

In the present research, sequential extraction methods are frequently used to characterize and predict the mobility and bioavailability of heavy metals in soils. The extractants commonly used include deionized water (H_2O), ammonium acetate (NH_4OAC), potassium chloride (KCl), DTPA (diethyl-ene-triamine-penta-acetic acid), and hydrochloric: nitric acid mixture called aqua regia ($HCl:HNO_3=3:1$). Each extractant is targeted on a single form of each metal, for example, H_2O for soluble species, NH_4OAC for exchangeable species, DTPA for plant available species and aqua regia for total, non-crystalline form of each metal species (He *et al.,* 1992). For nickel (Ni) there have been very few studies so far on the chemical speciation in soil. During the course of the present research, soils samples were collected and analyzed by various independent extractant for characterization of the nickel (Ni) species in soils.

Materials and Methods

Description of the sampling areas

The study area consisted of two distinct areas (Plate 1 and 2). One was the lagoon bordering Tejaon industrial area. This area received the drainage residue of the industrial area, Gulshan model town, Niketan Housing Society, Begunbari and other adjoining residential and slum areas including numerous classified/unclassified industries. The other consisted of the canal which received the inflow from the lagoon and drained into Balu river. In the rainy season the pollution was lowest because of heavy rainfall; most of the suspended materials, which were not complexed and precipitated with soil, organic matter and other compounds, were flushed out through the canal into the adjoining vast flood zone. As the rainy season receded the soils and water were enriched with the pollution load.

The main focus of the study is Tejgaon industrial area which is located within the Dhaka City Corporation and about 5 km north of the city centre. The effluents from many diverse industries in Tejgaon industrial area flow into a lagoon where the residue settles into a thick muck. It overflows through a sluice gate at Rampura into a channel which flows east for about 10 km to Balu river which in turn flows into Sitalakhya river. The whole area is really a flood drainage zone which originally connected Buriganga river on the west of Hazaribagh

Table I. Description and location of different samples collected during rainy season (September 2006)

Location	Location name	Longitude, north	Latitude, east	Samples type
1	Begun bari. Lal Tanki	$23^O45.7$	$90^O24.5$	Soil
2	Boubazar	$23^O45.8$	$90^O24.6$	Soil
3	G S G	$23^O46.0$	$90^O24.7$	Soil
4	Back side of Arong	$23^O46.2$	$90^O24.8$	Soil
5	Iron Bridge	$23^O46.3$	$90^O24.9$	Soil
6	Flood plain	$23^O46.2$	$90^O25.0$	Soil
7	Flood plain	$23^O46.1$	$90^O25.1$	Soil
8	Rampura Bridge	$23^O46.1$	$90^O25.4$	Soil
9	Ullan	$23^O46.1$	$90^O24.9$	Soil
10	Mahanagar Project	$23^O45.9$	$90^O24.8$	Soil
11	Madhubag	$23^O45.6$	$90^O24.6$	-
12	Ha-Meem Garments	$23^O45.7$	$90^O24.4$	Soil
13	Nasirabad	$23^O45.7$	$90^O27.8$	-
14	Nasirabad ghat	$23^O45.7$	$90^O27.8$	Soil
15	Nasirabad	$23^O45.7$	$90^O27.9$	Soil
16	Nasirabad	$23^O45.7$	$90^O28.1$	Soil
17	Guronagar bottala	$23^O45.7$	$90^O28.4$	Soil
18	Guronagar	$23^O45.6$	$90^O28.7$	Soil
19	Balu river	$23^O45.6$	$90^O28.7$	Soil
20	Nalchata ghat	$23^O46.6$	$90^O28.9$	Soil
21	Nalchata	$23^O45.5$	$90^O28.9$	Soil
22	Balu river	$23^O45.55$	$90^O29.0$	-
23	Dasher Kandi	$23^O45.9$	$90^O27.8$	Soil
24	Trimohini	$23^O45.6$	$90^O27.5$	Soil
25	Trimohini	$23^O45.6$	$90^O27.2$	Soil
26	Aongargora Meradia	$23^O46.6$	$9^O26.8$	Soil
27	Meradia	$23^O45.7$	$90^O26.5$	Soil
28	Aftab nagar	$23^O45.8$	$90^O26.2$	-
29	Banashere	$23^O45.8$	$90^O25.9$	-
30	Rampura Bridge	$23^O46.0$	$90^O25.6$	-

through a canal passing through Jhikatala, Dhanmondi, Kalabagan, and Hatir Jheel into Balu river. The canal between Jhikatala and Dhanmondi was closed during the middle of the last century. Overflowing rainwater used to discharge through this canal. Dhanmondi-Kalabagan portion was closed about 20 years ago. Other parts of the vast flood drainage zone are fast being filled up to cater for the development of Dhaka city. The common

Plate 1. Location of sampling sites during September, 2006.

agricultural crop is rice with substantial amount of various vegetables like chilli, capsicum, carrot, cauliflower, cabbage, coriander, water gourd, and tomato. There are abundance of water hyacinth and natural grasses inside the embankment, which are used as fodder for domestic animals.

Sample collection and preservation

Soil samples were collected from the study area at two dates, September, 2006 (wet season) and January, 2007 (dry season). Arial photographs were downloaded from Google Earth website (Plate 1). The sampling sites

were georeferenced with GPS and marked on the map (Plate 2). The location of sampling sites is given in Tables II and III respectively. All samples were collected from the field in required amounts, wrapped in polyethylene bags and transported to laboratory and preserved at $+4^O$C for processing next day.

The soil samples were collected from 0-15 cm depth. Next day analyses of water soluble, NH_4OAC extractable, DTPA extractable fractions and determination of moisture percentage in samples were done. Rest of the

Table II. Description and location of different samples during dry season (January, 2007).

Location	Location name	Longitude, north	Latitude, east	Samples type
31	Nasirabad ghat	$23^O45.7$	$90^O27.8$	Soil
32	Nasirabad	$23^O45.6$	$90^O27.9$	Soil
33	Nasirabad	$23^O45.7$	$90^O27.9$	Soil
34	Nasirabad	$23^O45.7$	$90^O28.1$	Soil
35	Nasirabad	$23^O45.7$	$90^O28.5$	Soil
36	Guronagar	$23^O45.6$	$90^O28.8$	Soil
37	Guronagar	$23^O45.6$	$90^O28.8$	Soil
38	Guronagar	$23^O45.6$	$90^O28.8$	Soil
39	Nalchata	$23^O45.5$	$90^O28.8$	Soil
40	Nalchata	$23^O45.6$	$90^O29.0$	Soil
41	Balu river	$23^O45.8$	$90^O29.0$	-
42	Meradia	$23^O45.7$	$90^O28.8$	Soil
43	Banashree ghat	$23^O45.6$	$90^O27.5$	-
44	Rampura bridge	$23^O45.7$	$90^O26.7$	-
45	Tejgaon. Begun Bari	$23^O45.7$	$90^O24.6$	Soil
46	Boubazar	$23^O45.8$	$90^O24.6$	Soil
47	Arong	$23^O46.0$	$90^O24.7$	Soil
48	Niketon	$23^O46.2$	$90^O24.8$	Soil
49	Residential area	$23^O46.2$	$90^O24.9$	Soil
50	Ullan	$23^O46.2$	$90^O25.0$	Soil
51	Rampura bridge	$23^O46.1$	$90^O25.4$	Soil

Plate 2. Location of sampling sites during January, 2007.

samples was air dried and ground to pass through 2-mm sieve for subsequent physical and chemical analysis.

Metal extraction and determination

i.   Water soluble : Soil samples were extracted with deionized water at a soil:water ratio of 1:10 according to Sparks, *et al.* (2001).

ii. NH$_4$OAC extractable: Soil samples were extracted with NH$_4$OAC at a ratio of soil:NH$_4$OAC solution ratio of 1:10 according to Sparks, *et al.* (2001).

iii. DTPA extractable: Soil samples were extracted with DTPA solution at a ratio of soil:DTPA solution ratio of 1:2 according to Sparks, *et al.* (2001).

iv. Total (non-crystalline fraction): Soil samples were digested with aqua regia (HCl:HNO$_3$= 3:1) according to Blum, *et al.* (1996).

Nickel (Ni) in the extracted solutions were determined by atomic absorption spectrophotometer (Perkin Elmer, 3110) (level of detection limit up to ppb)in Centre for Advanced Research in Physical, Chemical, Biological and Pharmaceutical Sciences, D.U.

Statistical Analysis

The results of experiments reported were statistically evaluated by the DMRT (Duncan's Multiple Range Test). Different letters were used to signify the statistically different results at 5% level of significance.

Results and Discussion

At Tejgaon soil the minimum pH value was 5.3 and the maximum 7.6. High buffering capacity resulting from high soil organic matter content (4.87-11.55%) probably influenced soil. Electrical conductivity (EC) (25-551 μS/cm) and organic matter (OM) (4.87-11.55%) contents were also influenced by the industrial wastes and effluents of the factories. General soil data during wet season and in dry season are presented in Table III and IV.

Samples collected during wet season (1st sampling)

The water soluble fraction is certainly the most biologically active. The high toxicity potential of this fraction is proven by the higher sensitivity exhibited by plants grown in hydroponic media. The water soluble fraction has highest potential of contamination of food chain, surface water and groundwater (He *et al.,* 1992).

The concentration of Ni found in all fractions of extraction of the 1st collected samples (wet season), ranges from 0.23-5.85, 0.16-9.05, 1.0-37.0 and 15.50-160.50 mg kg^{-1} Ni in water-soluble, NH$_4$OAC extractable, DTPA extractable and total fractions respectively (Table V).

The Ni concentration decreased from point source to distance in all respect but total Ni concentration at sampling points 1 to 12 was

Table III. General soil data during wet season (September, '06, 1st sampling)

| Location | pH
Soil: water | EC
Soil: water=1 : 10) | Texture | | | | O.C. | OM. |
			Sand	Silt	Clay	Class		
	1:10	μS/cm	%	%	%		%	%
1	6.60 cd	84.00 de	13.51	43.66	42.84	Silty clay	5.01n	8.64 n
2	6.50 c	251.00i f	47.44	32.05	20.51	Loam	4.72 j	8.13 j
3	6.00 b	125.00 g	9.62	46.91	43.47	Silty clay	4.80 l	8.28 l
4	6.70 de	163.00 g	60.35	17.70	21.95	Syndy loam	2.82 a	4.87 a
5	6.70 de	58.00 b	26.35	30.82	42.84	Silty clay	4.17 f	7.19 f
6	5.30 a	61.00 bc	38.83	32.36	28.80	Loam	5.27 p	9.08 p
7	6.50 c	213.00 h	57.93	29.51	12.56	Loam	6.70 u	11.55 u
8	6.60 cd	81.00 cde	45.00	40.59	14.41	Silt loam	4.72 j	8.13 j
9	6.50 c	163.00 g	41.96	39.29	18.75	Silt loam	6.53 t	11.26 t
10	5.90 b	61.00 bc	51.51	33.75	14.75	Loam	5.73 r	9.88 r
11	6.80 ef	90.00 e	16.70	38.01	45.29	Silty clay	5.14 o	8.86 o
12	6.90 f	330.00 j	18.88	60.13	20.99	Silt loam	5.94 s	10.24 s
13	7.20 gh	30.00 a	17.11	54.26	28.63	Silt loam	4.55 i	7.84 i
14	6.90 f	2368.00 k	2.51	53.76	43.73	Silty clay	4.97 m	8.57 m
15	7.10 g	93.00 e	15.20	56.40	28.40	Silt loam	5.39 q	9.29 q
16	7.10 g	125.00 f	0.72	69.61	29.67	Silty clay loam	ND	ND
17	7.10 g	65.00 bcd	8.91	78.26	12.83	Silt loam	3.24 b	5.59 b
18	7.10 g	75.00 b-e	23.09	43.47	33.44	Clay loam	3.96 e	6.83 e
19	7.30 h	95.00 e	11.75	77.99	10.26	Silt	3.45 c	5.95 c
20	7.60 i	162.00 g	1.63	54.25	44.12	Silty clay	5.01 n	8.64 n
21	6.80 ef	162.00 g	0.00	67.51	32.19	Silty clay loam	3.66 d	6.32 d
22	6.80 ef	160.00 g	6.06	70.94	23.00	Silt loam	4.51 h	7.77 h
23	6.80 ef	201.00 h	23.67	43.14	33.19	Clay loam	4.30 g	7.41 g
24	6.70 de	220.00 h	10.39	36.81	52.80	Silty clay	4.76 k	8.21 k
Maximum	7.60	2368.00	60.35	78.26	52.80		6.70	11.55
Minimum	5.30	30.00	0.00	17.70	10.26		2.82	4.87
Mean	6.73	225.13	22.88	47.97	29.14		4.75	8.20

ND- not done

Mean values with the same letter (s) in a column is not significantly different at 5% level by DMRT.

Table IV. General soil data during dry season of January '07 (2nd sampling)

Location	pH		EC	Texture				O.C.	OM.
	Soil: water (1:10)	Soil:KCl (1 : 10)	Soil:water (1 : 10)	Sand	Silt	Clay	Class		
			μS	%	%	%		%	%
1	7.49 ij	6.91	120 i	29.55	47.5	22.95	Loam	4.12 k	7.1 k
2	5.71 cd	4.91	101 h	24.55	20.0	55.45	Clay	3.88 i	6.68 i
3	5.87 de	4.58	34 c	9.55	32.5	57.95	Clay	3.84 h	6.62 h
4	6.77 g	6.39	290 l	7.05	70.0	22.95	Silt loam	5.36 p	9.23 p
5	6.92 g	5.89	98 g	9.55	55.0	35.45	Silty clay loam	6.08 q	10.48 q
6	5.67 c	3.94	154 j	12.05	52.5	35.45	Silty clay loam	4.96 n	8.55 n
7	6.92 g	5.73	24 a	2.05	25.0	72.95	Clay	2.76 d	4.76 d
8	6.2 f	5.63	312 n	7.05	52.5	40.45	Slty clay	3.56 f	6.13 f
9	7.62 j	6.86	25 a	4.55	65.0	30.45	Silty clay loam	2.4 b	4.14 b
10	5.06 b	4.51	298 m	5.55	50.0	44.45	Silty clay	4.36 l	7.51 l
11	7.41 i	6.63	27 b	13.05	47.5	39.45	Silty clay loam	4.64 m	7.99 m
12	7.17 h	6.45	173 k	33.05	50.0	16.95	Silt loam	4.96 n	8.55 n
13	7.15 h	5.97	56 d	25.55	30.0	44.45	Clay	2.6 c	4.48 c
14	7.86 k	6.7	67 e	18.05	40.0	41.95	Slty clay	3.68 g	6.34 g
15	4.68 a	3.96	100 h	18.05	32.5	49.45	Clay	5.16 o	8.89 o
16	6.02 ef	5.25	551 p	30.55	57.5	11.95	Silt loam	4.0 j	6.89 j
17	4.79 a	4.55	494 o	35.55	52.5	11.95	Silt loam	3.4 e	5.86 e
18	7.19 h	6.7	78 f	65.55	25.0	9.45	Sandy loam	1.96 a	3.38 a
Max	7.86	6.91	551	65.00	12.0	23.0	Sandy clay loam	6.08	10.4
Min	4.68	3.94	24	2.05	20.0	77.95	Clay	1.96	3.38
Mean	6.49	5.64	166.78	19.49	44.72	35.78	Silty clay loam	3.98	6.86

Mean values with the same letter (s) in a column is not significantly different at 5% level by DMRT.

Table V. Concentration of nickel in soils with different extractions during wet season (September, 2006) (in mg kg^{-1})

Location	Water soluble	NH$_4$OAC Extractable	DTPA Extractable	Total
1	1.42 o	4.48 n	11.00 h	140.50 i
2	2.94 u	4.25 m	12.10 l	100.00 g
3	4.61 w	7.63 v	14.30 p	95.00 g
4	1.37 n	1.57 d	3.90 b	118.50 h
5	1.35 m	1.61 e	5.80 c	97.50 g
6	2.47 t	2.74 i	7.40 e	117.50 h
7	2.20 s	8.19 w	11.80 k	124.00 h
8	4.15 v	6.62 t	13.10 n	150.00 j
9	5.85 x	6.19 q	17.90 q	124.50 h
10	0.60 f	6.36 r	12.50 m	160.50 k
11	1.76 q	2.06 g	8.20 f	68.00 e
12	0.45 c	6.60 s	9.30 g	96.50 g
13	0.98 i	4.80 o	5.90 c	48.50 d
14	0.23 a	0.28 b	1.00 a	15.50 a
15	0.50 d	4.89 p	6.70 d	63.50 e
16	1.70 p	9.05 x	12.00 l	35.00 c
17	0.73 g	1.49 c	11.20 i	34.60 c
18	1.91 r	3.10 j	11.40 j	22.80 b
19	0.80 h	0.16 a	14.00 o	30.00 c
20	1.06 j	3.45 l	11.50 j	123.87 h
21	1.30 l	3.25 k	22.00 r	95.00 g
22	0.52 e	1.86 f	23.00 s	75.00 f
23	1.22 k	6.66 u	34.00 t	141.50 i
24	0.37 b	2.50 h	37.00 u	146.00 ij
Max	5.85	9.05	37.00	160.50
Min	0.23	0.16	1.00	15.50
Mean	1.69	4.16	13.21	93.12

Mean values with the same letter (s) in a column is not significantly different at 5% level by DMRT.

variable and in most cases above the tolerable limit value of 50 mg kg^{-1} (Kloke, 1980) (Table V).

Water soluble Ni concentrations in different sampling points were significantly different from each other. The lowest concentration of water soluble Ni was found in the sampling point 14 and the highest was in the location point of 9. On the other hand the highest concentration of NH$_4$OAC and DTPA extractable Ni was found in the sampling point 16 and 24 which differed significantly from other sampling points.

Samples collected during dry season (2nd sampling)

In the 2nd collected samples, the concentration of Ni found in all fractions of extraction, ranges from 0.14-13.32, 0.11-12.22 and 25.5-532.5 mg kg^{-1} Ni in NH$_4$OAC extractable, DTPA extractable and total fractions respectively (Table VI). The average Ni concentrations in different soil fractions were 3.07, 4.29 and 223.89 mg kg^{-1} Ni in NH$_4$OAC extractable, DTPA extractable and total fractions respectively (Table VI). Comparing 1st and 2nd sampling data, Ni concentrations in different soil fractions were higher in the 2nd sampling data which might be due to flooding or dilution effect during wet season.

The Ni concentration decreased from point source (1 and 12) to distance in all respect but total Ni concentration at different sampling points were significantly variable and

in most of the cases above the tolerable limit value (Kloke, 1980) (Table VI).

NH$_4$OAC and DTPA extractable Ni concentration at different sampling points were significantly different from each other. The lowest concentration of NH$_4$OAC extractable Ni was found at the sampling point 29 and the highest was found in the sampling point 40 i.e. near the Rampura bridge point. The lowest concentration of DTPA extractable Ni was found in the sampling point 31 and the highest was found at the point 40.

In case of total Ni concentration in soil, the lowest value was in point 33 and the highest was in the sampling point 41 which was above the tolerable limit value (Kloke, 1980). Total nickel concentration in all sampling points differed significantly from each other except some points (Table VI). Total Ni concentration at some sampling points were above the maximum tolerable limit (50 mg kg^{-1}) according to Kloke (1980).

As a whole, the Tejgaon industrial area soils had the highest concentration of total, water soluble, NH$_4$OAC extractable and DTPA extractable Ni in some points which might be due to discharge of liquid wastes, flocculated sludge and other solids with excessive metals coming from different industrial processes. The highest concentration of Ni and other metals in this area is not only a problem with respect to plant nutrition and the food chain, they may constitute a direct health hazards as well. The area is not only

Table VI. Concentration of Ni in soil during dry season (January 2007) (in mg kg^{-1}).

Location	Water soluble	NH$_4$OAC Extractable	DTPA Extractable	Total
25	tr	6.46 m	1.93 c	187.00 efg
26	tr	1.6 f	7.57 f	253.00 gh
27	tr	1.72 h	4.18 d	235.00 h
28	tr	5.19 l	3.26 d	217.33 gh
29	tr	0.14 a	1.79 c	176.50 ef
30	tr	1.08 e	4.26 d	106.00 d
31	tr	0.98 d	0.11 a	157.50 e
32	tr	0.88 c	1.77 c	32.50 ab
33	tr	0.78 b	0.99 b	25.50 a
34	tr	1.68 g	5.25 e	69.00 c
35	tr	0.88 c	2.00 c	289.00 i
36	tr	1.97 i	4.87 de	451.50 k
37	tr	0.98 d	0.42 ab	222.00 gh
38	tr	4.78 k	4.47 d	194.00 fg
39	tr	3.67 j	12.01 h	375.50 j
40	tr	13.32 o	12.22 h	477.00 k
41	tr	8.36 n	8.56 g	532.50 l
42	tr	0.78 b	1.75 c	62.50 bc
Min		0.14	0.11	25.5
Max		13.32	12.22	532.5
Mean		3.07	4.29	223.89

Mean values with the same letter (s) in a column is not significantly different at 5% level by DMRT.

tr=Trace

occupied by industries but there are many slums' people around the complexes and on the bank of waste discharging channel. Recently many urban area/housing projects namely, Aftab Nagar, Banasri housing project, Niketon project etc. have developed on the bank of waste discharging channel. So, these may be ecological implications associated with metal poisoning to the slums living children because they have direct contact with the contaminated soil and effluents (Kashem and Singh, 1998). The highest concentration of total and extractable Ni, is also due to effluents and solid wastes of textile dying industry.

Water soluble, NH_4OAC extractable and DTPA extractable Ni have been considered as available Ni (Lindsay and Norvell, 1978). These Ni species should measure available concentration of Ni in the contaminated soils of Tejgaon industrial area. Considering the critical limits of DTPA-extractant for Ni (Lindsay and Norvell, 1978), some of the sampling points were above the critical limits. The concentration of Ni in the soil solution phase strongly increased with decreasing pH and increasing total content of this metal in the different sampling points. The similar results were also reported by many authors (Ullah *et al.,* 1999; Chamon *et al.,* 2005).

Extent of contamination by Ni in soils

Expeditions to collect samples were extremely difficult due to the foul smell and unknown nature of gases emitting out of the water body. The soil, water and air were unfit of any kind of human habitation. But a vast number of populations were living and working in the area disregarding the existing severe health hazards. Results show that the soil, water and plant were of extremely low quality in the rainy season. Their quality deteriorated several fold in the dry season.

The pH dependence of the solution concentration of Ni showed that the mobility and availability of the metals is high at strongly to extremely acid soil reaction. This was also reported by Brümmer *et al.,* (1986b).

The extent of contamination due to heavy metal deposition at Tejgaon industrial sites are presented in Table IX. The total Ni content of the soils, water and plant samples showed wide range of values from background to a level considered to reflect severe contamination. The extent of contamination (in %) was identified by using information of background levels of total Ni in soils (Singh and Steinnes, 1994) and background levels of Ni for Bangladesh soils (Domingo and Kyrzma, 1983). The tolerable and in excess of tolerable level was calculated on the information of Kloke (1980).

Background concentration for Ni of Bangladeshi soils is 22 mg kg^{-1} (Domingo and Kyuma, 1983). Tolerable total concentration of Ni in soil is 50 mg kg^{-1} (Kloke, 1980). The total Ni concentration of the soil samples at different points showed wide

range of values from background to a level considered to reflect severe contamination. The extent of contamination was identified by using information of background levels of total Ni in soils (Domingo and Kyruma, 1983; Singh and Steinnes, 1994; Ullah *et al.* 1999 and Chamon *et al.* 2005). The tolerable and in excess of tolerable level was calculated on the information of Kloke (1980).

Concentration of total Ni in soils during wet season was found above the natural background level with few exceptions. Only 4% of Ni (≤ 22 mg kg^{-1}) samples in the normal range. Ni concentration in the group of tolerable level was 21% (>022-≤ 50 mg kg^{-1}) and 75% (≥ 50 mg kg^{-1}) soil samples were found in the group of in excess of tolerable level during wet season (Table VII).

On the other hand, during dry season, no Ni (≤ 22 mg kg^{-1}) samples were in the normal range. Ni concentration in the maximum tolerable level was 11% (>22 mg kg^{-1}) and 89% (>50 mg kg^{-1}) were found in excess of tolerable level during dry season (Table VII).

One of the most alarming facts is that some sampling points under investigation were apparently far from the pollution source. Bumper crops were being produced in the vicinity of Balu river. Consumers have no idea that locally produced crops with attractive appearances have high pollution content of heavy metals like Ni. Elevated levels of heavy metals in plants at Tejgaon industrial area have been demonstrated by other investigators (Ullah *et al.,* 1999 and Chamon *et al.,* 2005).

Distribution of total, water soluble, NH$_4$OAC extractable and DTPA extractable Ni with Distance

The extent of contamination due to heavy metal deposition in different sampling points in the study area is presented in Fig. 1. Concentration of total Ni was found to be above the natural background level at all points at 1st sampling with few exceptions in the Tejgaon industrial sites (Fig. 1 and 2). Background concentration of Ni in Bangladeshi soils is 22 mg kg^{-1} (Domingo

Table VII. Extent of contamination according to total Ni concentration in soils (mg kg^{-1}) during wet and dry season. Percentage of sampling locations in parentheses

Metals	Group 1	Group 2	Group 3
Ni (wet season)(n=24)	≤ 22 (4)	>22-≤ 50 (25)	≥ 50 (75)
Ni (Dry season)(n=18)	≤ 22 (0)	>22-≤ 50 (11)	≥ 50(89)

Group 1 = Background level, group 2= Maximum tolerable level and group 3 = In excess of tolerable level.

Soil: Background concentration for Ni = 22 mg kg^{-1} of Bangladesh soil, (Domingo and Kyuma, 1983). Tolerable total concentrations are 50 ppm for Ni (Kloke, 1980).
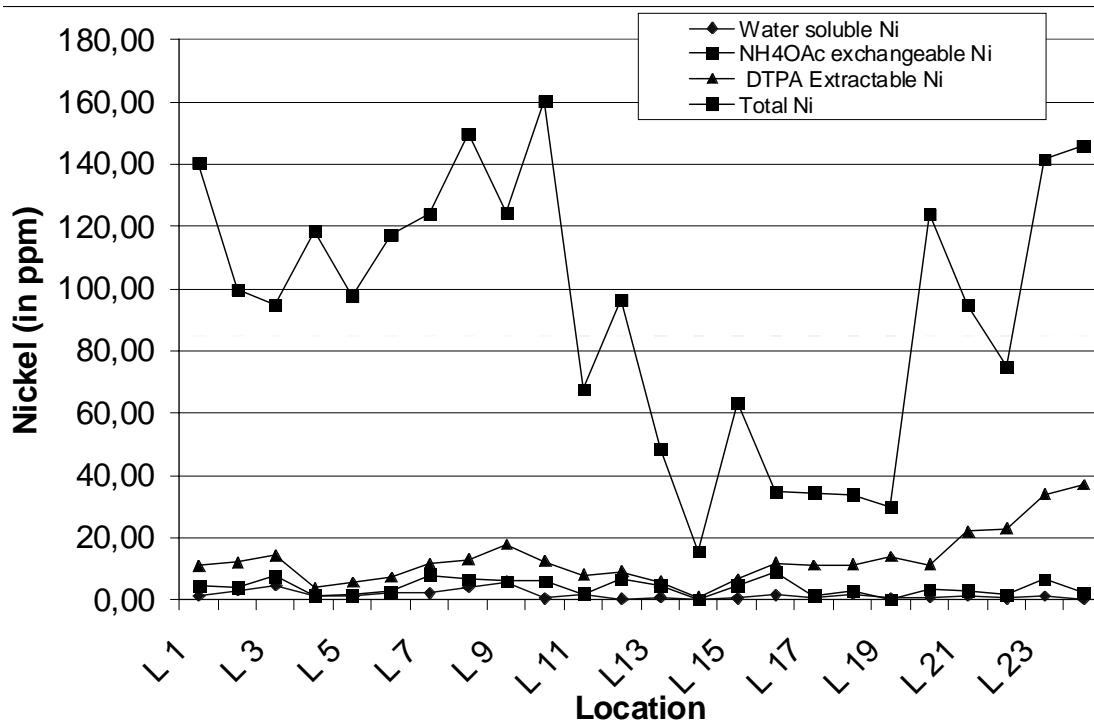
Fig. 1. Distribution of different Ni fractions with distance with during the wet season

and Kyuma, 1983). Tolerable total concentrations are 50 mg kg^{-1} for Ni (Kloke, 1980). Ni concentration during 2nd sampling in different extraction i.e in NH$_4$OAC extractable, DTPA extractable and in total fraction was found to decrease with distance away from the disposal point source due to dilution of the effluent and water (Fig. 2). The decreasing tendency with distance indicates the accumulation of metals by the industrial operations. Similar findings were also observed by other investigators (Blom, 1986) reported a very drastic decrease in metal concentration away from the source point i.e from an electro-metallic industry in south-eastern Norway. The Tejgaon industrial area is low-lying and wet through most part of the year. This part is influenced by the battery, biscuit, paper and pulps, textiles, carbides, pharmaceuticals, pesticides, mining, distilleries etc, where all effluents and wastes converse and the zone under investigation is designated as the confluence zone by which the heavy metals were elevated. Low pH values in the respective sites could possibly increase to solubility and mobility of metals in the soils. Increased solubility of metals is likely to lead to increased availability of the metals for plant uptake, and it might cause Ni toxicity. These results indi-
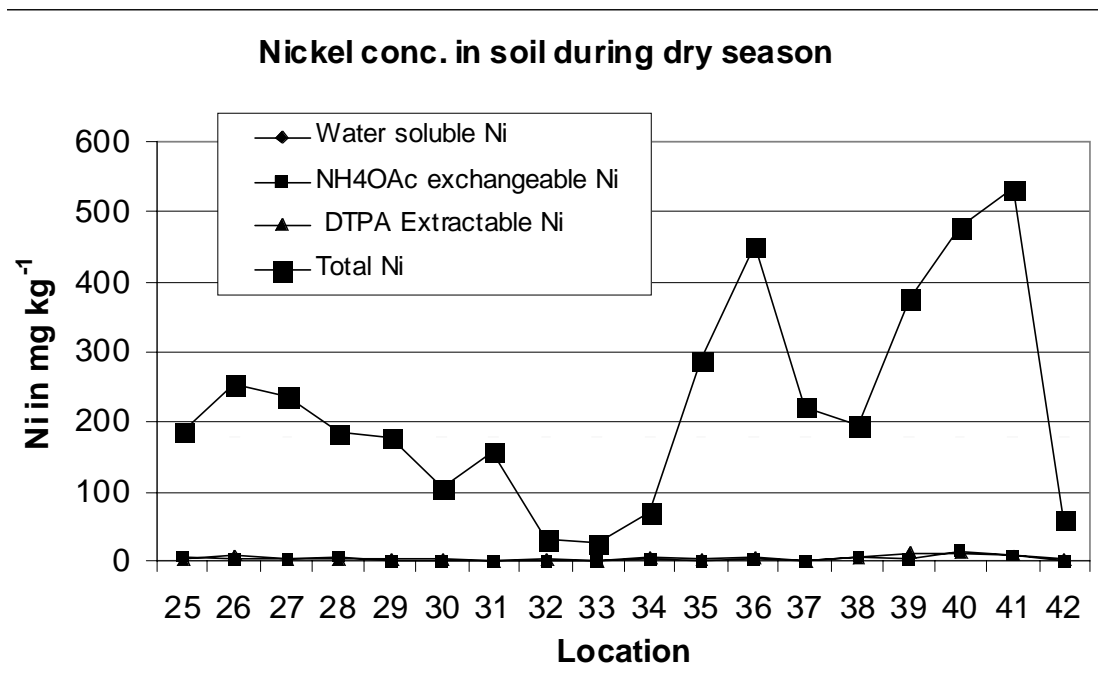
Fig. 2. Distribution of different Ni fractions with distance during dry season

cate that appreciable soil acidification has taken place in the vicinity of that area. This is an agreement with the result from other investigators (Kashem and Singh, 1998; Chamon *et al.,* 2005).

Interrelationships among the water soluble, NH$_4$OAC extractable, DTPA extractable and total Ni in the Tejgaon industrial soils during wet and dry season

Mean, standard deviation and correlations (r) of soil Ni with different extractions are presented in table   and   during wet and dry season.

A correlation matrix for Ni metal in the soils of Tejgaon industrial sites was calculated to see if some of the Ni fractions were interrelated with each other and the results are presented in Table VIII and IX.

A number of fractions were observed to be significantly (p<0.05) correlated with each other. For example, water soluble fraction of Ni species was positively correlated with total and DTPA extactable species and significantly correlated with NH$_4$OAC species of Ni. The total contents of Ni was found to be positively correlate with their extractable amounts.

Table VIII. Correlation matrix for different Ni extractable species in soil during wet season

Descriptive statistics

	Mean	Std. deviation	N
Watersoluble	1.6904	1.43061	24
NH_4OAC	4.1579	2.54340	24
DTPA	13.2083	8.53652	24
Total	92.6571	44.20480	24

Correlations

	Water soluble	NH_4OAC	DTPA	Total
Watersoluble	1	0.435(*)	0.013	0.273
NH_4OAC		1	0.153	0.367
DTPA			1	0.395
Total				1

*Correlation is significant at the 0.05 level (2-tailed)

Table IX. Correlation matrix for different Ni extractable species in soil during dry season:

Descriptive statistics

	Mean	Std. Deviation	N
Watersoluble	0.0000	0.00000	18
NH_4OAC	3.0711	3.43630	18
DTPA	4.2928	3.65526	18
Total	223.8889	151.41174	18

Correlations

	Water soluble	NH_4O AC	DTPA	Total
Watersoluble	.(a)	.(a)	.(a)	.(a)
NH_4OAC	.(a)	1	0.658(**)	0.632(**)
DTPA	.(a)	0.658(**)	1	0.692(**)
Total	.(a)	0.632(**)	0.692(**)	1

** Correlation is significant at the 0.01 level (2-tailed).

a Cannot be computed because at least one of the variables is constant.

During dry season, water soluble species were present in trace amount, but other fractions of Ni i.e NH_4OAC, DTPA extractable and total Ni fractions were positively and significantly correlate with each other (Table IX).

Conclusion

The distribution of metals between the specific forms varies widely according to the individual metal and the characteristics of the wastes. These parameters include pH, temperature, oxidation-reduction potential and the presence of complexing ligands. Total trace metal composition of soil is of little importance in determining its uptake by plants and consequently, in contaminating the food chain since the different forms have different mobilities, bioavailabilities and potential environmental contamination potential. It is more important to know the distribution of each trace metals in the different forms, than just the total content

The results show that the soil samples were of extremely low quality in the rainy season. Their quality deteriorated several fold in the dry season. Ni concentration during 2nd sampling in different extraction i.e in NH_4OAC extractable, DTPA extractable and in total fraction was found to decrease with distance away from the disposal point source due to dilution of the effluent and water. The decreasing tendency with distance indicates the accumulation of metals by the industrial operations. One of the most alarming facts is that the field under investigation was apparently far from the pollution source. Bumper

crops were being produced in the vicinity of Balu river. Consumers have no idea that locally produced crops with attractive appearances have high pollution content of toxic metals like Ni.

Future research is necessary to delineate the quality and quantity of different organic and inorganic fractions in the total environment. Food quality is an important issue for human survival and should be addressed with immediate urgency.

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