Enrichment of Cr, Mn, Ni and Zn in Surface Soil

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Abstract-The textile industry produces highly coloured effluents containing polar and non-polar compounds. The textile mill run by the Assam Polyester Co-operative Society Limited (APOL) is situated at Rangia, about 55 km from Guwahati (26º11' N, 91º47' E) in the northern bank of the river Brahmaputra, Assam (India). This unit was commissioned in June 1988 and started commercial production in November 1988. The installed capacity of the weaving unit was 8000 m/day and that of the processing unit was 20,000 m/day. The mill has its own dyeing unit with a capacity of 1500-2000 kg/day. The western side of the mill consists of vast agricultural land and the far northern and southern side of the mill has scattered human population. The eastern side of the mill has a major road for thoroughfare. The mill releases its effluents into the agricultural land in the western side of the mill. The present study was undertaken to assess the impact of the textile mill on surface soil quality in and around the mill with particular reference to Cr, Mn, Ni and Zn. Surface soil samples, collected along different directions at 200, 500 and 1000 m were digested and the metals were estimated with Atomic Absorption Spectrophotometer. The metals were found in the range of: Cr 50.9 - 105.0 mg kg⁻¹, Mn 19.2- 78.6 mg kg⁻¹, Ni 41.9 -50.6 mg kg⁻¹ and Zn 187.8 – 1095.8 mg kg⁻¹. The study reveals enrichment of Cr, Mn, Ni and Zn in the soil near the textile mill.

Keywords—Cr, Mn, Ni, Zn, soil quality, heavy metal enrichment.

I. INTRODUCTION

TEXTILE industry is one of the oldest and largest industries in India. Ever increasing consumer demand for textile products in domestic as well as in international market has resulted in setting up of more and more industries. The textile mills require large volumes of water of high purity and in turn, they also generate equally large volumes of effluent with complex and highly variable chemical composition. In textile production process, huge quantity of water is used [1] and most of the water go to the environment after use, which pollutes the neighbourhood and influences the soil quality. Environmental pollution by metals became extensive as industrial activities increased in the late 19th and early 20th century.

The metal pollutants, ultimately derived from a growing number of diverse anthropogenic sources (industrial effluents and wastes, urban runoff, sewage treatment plants, boating activities, agricultural fungicide runoff, domestic garbage dumps, and mining operations), have progressively affected the ecosystems more and more [2]. All heavy metals are toxic at higher concentrations [3], [4]. The chemical form of heavy metals in soil solution is dependent on the metal concerned, pH and the presence of other ions [5].

II. OBJECTIVES

The objectives of the present study were to determine environmental effects of a textile mill on soil with respect to concentrations of the toxic heavy metals Cr, Mn, Ni and Zn.

III. STUDY AREA

The textile mill run by the Assam Polyester Co-operative Society Limited (APOL) is situated at Rangia, Kamrup district of Assam, which is 55 km away from Guwahati (26° 28' 11" N, 91° 37' 47"E) in the northern bank of the river Brahmaputra. The mill was established in 38.04 acre of agricultural land in June 1988 with an installed capacity of 2000 tonnes of viscose and 3000 kg of acrylic and polyester spinning yarn per day; 8000 m weaving capacity of cloth per day. The mill has its own cloth printing and yarn dyeing facilities for which it requires different dyes, chemicals, reducing and finishing agents. The western side of the mill is a vast agricultural land while scattered human population could be found in far northern and southern sides of the mill. The eastern side of the mill contains the main road for communication. The mill releases its effluents into the agricultural land in the western side of the mill.

IV. METHODS

Three surface soil (depth 0-10 cm) samples were collected along southern (S1, S2 and S3), northern (N1, N2 and N3) and western (W1, W2 and W3) directions of the mill at 200, 500 and 1000 m distances respectively. The collection and digestion of the soil samples were done according to standard procedures [6]-[8]. Altogether 9 soil samples were collected once in two seasons, pre-monsoon (March-May; B1 and B2) and post-monsoon (Sept-Nov; A1 and A2) for two years. The heavy metals were extracted from the soil as per standard procedure [9]. 1.0 g of the sieved sample was digested with 35 ml of the acid mixture (4 parts conc. H₂SO₄, 2 parts conc. HCl and 1 part conc. HNO₃). The mixture was heated gently and then more strongly until white fumes were no longer evolved. The residue was taken up with 1:1 dil HCl, filtered (Whatman 42) and washed with distilled water for several times. The final volume was made to 100 ml with distilled water. The metals were estimated with Atomic Absorption Spectrophotometer (Varian Spectra AA 220). The study also includes a "Control" soil sample collected from a non-polluted site of distance 3500 m in the southeastern direction from the

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Mill as a reference and analyzed using the same procedures as the test samples. The concentrations were computed as follows:

Metal Concentration, mg/kg =
$$\frac{P \times Q \times R}{W}$$

where,

P = Concentration of metal in digested solution Q = Final volume of digested solution (ml).

R = Further dilution ratio.

W = Amount of soil taken (1 g).

V. RESULTS

In this study, concentration of Cr (Table I) is high in the western direction with a mean value of 100.3 - 105.0 mg/kg, which are \geq the maximum permissible limit of 100 mg/kg, [10]. The Cr concentration has a gradual decreasing trend from first premonsoon to second post-monsoon season. However, the variation with distance was not uniform. The Control site has a mean Cr-content of 14.9 mg/kg. Skin contact with certain chromium (VI) compounds can cause skin ulcers. Some people are extremely sensitive to chromium (VI) or chromium (III). Allergic reactions consisting of severe redness and swelling of the skin have been noted. Several studies have shown that chromium (VI) compounds can increase the risk of lung cancer.

TABLE I CR CONTENT OF THE SOIL

Site	B1	A1	B2	A2	Min	Max	Mean	SD	
Control	15.2	14.8	14.6	15.0	14.6	15.2	14.9	0.3	
S1	116.2	66.8	57.2	62.1	57.2	116.2	75.6	27.4	
S2	92.3	88.7	80.1	69.0	69.0	92.3	82.5	10.4	
S3	62.3	59.0	60.0	64.0	59.0	64.0	61.3	2.3	
N1	78.0	62.8	66.4	43.3	43.3	78.0	62.6	14.4	
N2	74.6	43.8	55.2	30.0	30.0	74.6	50.9	18.9	
N3	71.2	51.6	59.4	54.0	51.6	71.2	59.1	8.7	
W1	103.8	98.5	102.0	97.0	97.0	103.8	100.3	3.1	
W2	129.1	106.2	96.4	86.8	86.8	129.1	104.6	18.2	
W3	115.6	112.0	93.7	98.6	93.7	115.6	105.0	10.5	

Mn is a very important micronutrient in the soil as it is a cofactor of various enzymes and is utilized in photosynthesis. Phytotoxicity from Mn may occur in soil containing low humus and low pH [11]. Manganese toxicity is a serious constraint to many crops grown on acid soils [12]. Manganese (usually present as Mn^{2+} in the soil solution) is an essential nutrient that can be toxic to crops when in excess [3]. Levels of Mn in the soil solution are controlled mainly by a soil's Mn reserve, pH, and the availability of electrons [13] [14]. In this study, Mn was obtained in the mean range of 18.7 - 78.6 mg/kg (Table II), which is much below the World average of 850 mg/kg [15], [16]. The Control value is low. Samples

nearer to the mill in all the directions (S1, W1, N1) have more Mn content. Distinct distance variation is observed. Seasonal variation is not uniform. Maximum values of Mn were found in S1 (101 mg/kg). The Control mean value was 12.9 mg/kg. The values, as a whole, have a decreasing trend away from the Mill.

TABLE II MN CONTENT OF THE SOIL										
Site	B1	A1	B2	A2	Min	Max	Mean	SD		
Control	12.6	13.5	12.9	12.6	12.6	13.5	12.9	0.4		
S1	50.6	62.6	78.0	56.3	50.6	78.0	61.9	11.8		
S2	77.0	76.0	64.0	70.0	64.0	77.0	71.8	6.0		
S3	17.2	20.0	19.4	18.0	17.2	20.0	18.7	1.3		
N1	67.5	74.4	68.0	50.0	50.0	74.4	65.0	10.5		
N2	63.0	70.0	66.0	62.0	62.0	70.0	65.3	3.6		
N3	23.2	32.2	27.6	30.2	23.2	32.2	28.3	3.9		
W1	76.5	86.0	89.0	63.0	63.0	89.0	78.6	11.7		
W2	67.0	58.0	62.0	60.0	58.0	67.0	61.8	3.9		
W3	20.3	24.4	15.4	16.7	15.4	24.4	19.2	4.0		

The primary sources of Ni pollution are the burning of coal and oil, emission of smelters and metal works, municipal wastes, sewage, phosphate fertilizers and pesticides. In this study, Ni was found to be more in each sample. Maximum Ni was found at southern direction (mean range 48.9 - 50.1 mg/kg). These values are even higher than the world average for Ni- content in soil (40 mg/kg) [15], [16]. Ni content in the soil samples (Table III) shows a decreasing trend with distance. A decreasing trend was also observed from first premonsoon to second post monsoon season. The Control mean value was low with a value of 2.5 mg/kg. Nickel is one of the harmful elements [17] although in trace amounts, Ni is essential for mammals as a micronutrient and occurs in many biological systems. At very high concentration, Ni is very toxic inducing carcinogenicity [18]. Higher amount of Ni may cause changes in muscle, brain, liver and kidney functions, and can also lead to cancer [19].

The concentration of Zn in the soil of the study area in every direction is very high. The maximum mean value (1095.8 mg/kg) was obtained at the sample nearer to the Mill (200 m) in the western direction and the minimum (187.8 mg/kg) at the sample (Table IV), 1 km away from the mill in the northern direction. The variation of values along each direction shows uniform decreasing trend. In each case, the amount of Zn was more than the World average value of 50 mg/kg [15], [16] and the Control mean value (12.3 mg/kg). The results thus indicate that while the Control site is zincdeficient, the soil in the proximity of the mill has become enriched with excessive amounts of Zn. The metal, Zn is active in many biochemical processes and is known to be involved in several biological and chemical interactions with several elements present in soil. Excessive Zn in soil may cause damage to plants and at lower pH, the yield is reduced [20].

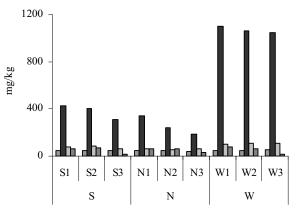
TABLE III NI CONTENT OF THE SOIL

NI CONTENT OF THE SOIL								
Site	B1	A1	B2	A2	Min	Max	Mean	SD
Control	2.5	2.1	2.7	2.5	2.1	2.7	2.5	0.3
S 1	50.0	52.0	50.0	46.0	46.0	53.8	49.5	2.5
S2	52.0	51.5	48.0	49.0	48.0	52.0	50.1	1.9
S3	51.6	50.2	46.8	47.0	46.8	51.6	48.9	2.4
N1	48.0	45.0	45.1	46.0	45.0	48.0	46.0	1.4
N2	54.0	48.0	42.0	38.0	38.0	54.0	45.5	7.0
N3	44.6	44.0	39.0	40.0	39.0	44.6	41.9	2.8
W1	56.7	46.8	46.0	37.9	37.9	56.7	46.9	7.7
W2	49.2	42.8	44.0	37.6	37.6	49.2	43.4	4.8
W3	60.0	52.5	48.0	42.0	42.0	60.0	50.6	7.6

TABLE IV

ZN CONTENT OF THE SOIL										
B1	A1	B2	A2	Min	Max	Mean	SD			
12.4	12.1	12.5	12.0	12.0	12.5	12.3	0.2			
418.0	470.0	426.0	380.0	380.0	470.0	423.5	36.9			
417.0	423.0	408.0	376.0	376.0	423.0	406.0	20.9			
305.0	328.0	316.0	295.0	295.0	328.0	311.0	14.2			
360.0	372.0	316.0	304.0	304.0	372.0	338.0	33.1			
265.0	248.0	228.0	218.0	218.0	265.0	239.8	21.0			
198.0	206.0	187.0	160.0	160.0	206.0	187.8	20.1			
1119.0	1043.0	1148.0	1073.0	1043.0	1148.0	1095.8	46.8			
1012.0	1192.0	1052.0	995.0	995.0	1192.0	1062.8	89.4			
1053.0	1204.0	1009.0	915.0	915.0	1204.0	1045.3	120.5			
	12.4 418.0 417.0 305.0 265.0 198.0 1119.0 1012.0	B1 A1 12.4 12.1 418.0 470.0 417.0 423.0 305.0 328.0 360.0 372.0 265.0 248.0 198.0 206.0 1119.0 1043.0 1012.0 1192.0	B1 A1 B2 12.4 12.1 12.5 418.0 470.0 426.0 417.0 423.0 408.0 305.0 328.0 316.0 360.0 372.0 316.0 265.0 248.0 228.0 198.0 206.0 187.0 1119.0 1043.0 1148.0	B1 A1 B2 A2 12.4 12.1 12.5 12.0 418.0 470.0 426.0 380.0 417.0 423.0 408.0 376.0 305.0 328.0 316.0 295.0 360.0 372.0 316.0 304.0 265.0 248.0 228.0 218.0 198.0 206.0 187.0 160.0 1119.0 1043.0 1148.0 1073.0	B1 A1 B2 A2 Min 12.4 12.1 12.5 12.0 12.0 418.0 470.0 426.0 380.0 380.0 417.0 423.0 408.0 376.0 376.0 305.0 328.0 316.0 295.0 295.0 360.0 372.0 316.0 304.0 304.0 265.0 248.0 228.0 218.0 218.0 198.0 206.0 187.0 160.0 160.0 1119.0 1043.0 1148.0 1073.0 1043.0 1012.0 1192.0 1052.0 995.0 995.0	B1 A1 B2 A2 Min Max 12.4 12.1 12.5 12.0 12.0 12.5 418.0 470.0 426.0 380.0 380.0 470.0 417.0 423.0 408.0 376.0 376.0 423.0 305.0 328.0 316.0 295.0 295.0 328.0 360.0 372.0 316.0 304.0 304.0 372.0 265.0 248.0 228.0 218.0 218.0 265.0 198.0 206.0 187.0 160.0 160.0 206.0 1119.0 1043.0 1148.0 1073.0 1043.0 1148.0	B1 A1 B2 A2 Min Max Mean 12.4 12.1 12.5 12.0 12.0 12.5 12.3 418.0 470.0 426.0 380.0 380.0 470.0 423.5 417.0 423.0 408.0 376.0 376.0 423.0 406.0 305.0 328.0 316.0 295.0 295.0 328.0 311.0 360.0 372.0 316.0 304.0 304.0 372.0 338.0 265.0 248.0 228.0 218.0 218.0 265.0 239.8 198.0 206.0 187.0 160.0 160.0 206.0 187.8 1119.0 1043.0 1148.0 1073.0 1043.0 1148.0 1095.8 1012.0 1192.0 1052.0 995.0 995.0 1192.0 1062.8			

Overall, it is seen that the metals have a larger presence along the western direction and zinc content is much higher than the other metals in all directions, particularly in the western direction. This is shown in Fig. 1.



 \square Ni mean \square Zn mean \square Cr mean \square Mn mean

Fig. 1 Variation of the mean values of the contents of the metals with distance in different directions.

VI. CONCLUSIONS

The natural soil composition in this study has been affected by the Textile mill operation. The samples in western direction had comparatively more content of all the metals in comparison to the other two directions. This is because of free flow of effluent, towards that direction from exit point. The Mill operations that use different chemical compounds in cloth making process have a definite contribution to its surrounding soil, which has been established by higher concentration of the heavy metals. The comparison of control samples with the samples of the study area indicates that the textile mill effluents have altered the natural content of the metals in the soil. More researches should be done to gain understanding of the relationships between mineral nutrients and toxic heavy metals, their availability in soil, etc.

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