



## Heavy metal contamination of surface soils in southern part of Bangladesh

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### Abstract

To assess contamination levels of the heavy metals, concentrations of Sc, Cr, Fe, Co and Zn in surface soils at various locations of southern part of Bangladesh were determined by Instrumental Neutron Activation Analysis (INAA) technique. In this study, concentrations of the Sc, Cr, Fe, Co and Zn elements in surface soil were found in the range of 2.56-16.7 µg/g, 12.9-112 µg/g, 6911-48642 µg/g, 2.59-22.7 µg/g and 37.7-322 µg/g, respectively. The measured concentrations were compared with average concentration of worldwide soil and observed that most of the samples contain much higher concentration of heavy metals except Cr and Fe. Analysis based on soil utilization type showed that the samples collected from roadside and residential area experienced much higher metal contamination than open area. A significant correlation was observed between Cr-Fe, Cr-Co, Cr-Sc, Fe-Co, Fe-Sc and Co-Sc.

**Keywords:** Metal contamination, surface soil, INAA, research reactor, Bangladesh

### Introduction

Soil is a vital component of the biosphere. It is known as a geochemical sink for contaminants, and it also transports the chemical elements and substances to the various stages of biosphere (atmosphere, hydrosphere, and biota) as a natural buffer (Kabata-Pendias and Pendias, 2001; Wu *et al.*, 2015; Kumar *et al.*, 2019). Recently due to the human activities, natural balance of biogeochemical cycles is significantly altered. It elevates the mobilization of chemical elements into the atmosphere in contrast to the natural process. Therefore, the important processes may become potentially harmful under natural condition. The soil has an absorption capacity to hold and accumulate trace metal to some extent. Migration can be started significantly by changing the condition that controls the mobility of adsorbed metals (Salmons and Frostner, 1995; Harfouche *et al.*, 2016; Lian *et al.*, 2019). The perseverance of contaminants in soil is much higher compared to other compartments of the biosphere and contamination of soil caused by trace elements. Thus, the contamination of soil seems to be virtually permanent. So, it is the responsibility of the mankind to maintain the ecological and agricultural functions of the soil (Kabata-Pendias and Pendias, 2001). The regional contamination of soils due to heavy metals

occurs mainly in industrial areas (factories, smelter, motor vehicles, and municipal wastes dumping sites) (Krishna and Govil, 2007; Mandal and Sengupta, 2006; Li *et al.*, 2015). Moreover, the soil can be contaminated by other sources of metal pollutants, pesticides, fertilizers and materials derived by sewage and these are added as the trace element pool in soils. Soil contamination in some industrial areas can be occurred by an important source like mobilization of windblown dust. Heavy metals are being deliberately used by industrialized and non-industrialized countries for their industrial, agricultural, and domestic purposes without any treatment of remnant metals in prior. As a result, the environment is being elevated due to the deposition of heavy metals (Salmons and Frostner, 1995).

Khalishpur Thana is one of the industrial areas in Khulna district of Bangladesh. A study by World Bank identified the spatial distribution of the most polluted six 'hot spots' in Bangladesh and Khulna is one of them. There are many large industries (steel manufacturing, ship building industry, cable industries, jute mills, hardboard mills, pipe factories etc.) located in the southern region especially in Khalishpur Thana. These industries produce a considerable amount of solid wastes and effluents, which spread over the adjacent farmland, water body and to

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immediate locality. The saline characteristics of water and soil in this region also influence the accumulation of heavy metals that in turn may be harmful for indigenous flora and fauna.

In general, the hazardous contaminants spread into the environment through various media such as soil, mineral, water and vegetation from industrial area. The human body is being affected by several diseases due to the accumulation of these hazardous contaminants while it passes through the food chain. It is essential to create the base line data for the toxic elements and radionuclides in the contaminated area of industrial zone in order to save the population and to take the remedial action (Sultana *et al.*, 2003; Latif *et al.*, 2009; Islam *et al.*, 2011; Khademi *et al.*, 2019). However, a limited number of research works are found in Bangladesh due to lack of sophisticated techniques and appropriate facilities for the assessment of natural radionuclides and heavy metals in the environmental matrices.

Multi-elements can be determined in a broad range of matrices by the most powerful non-destructive neutron activation analysis technique. Instrumental neutron activation analysis (INAA) is one of the most extensively used methods for determination of elemental concentration due to its high sensitivity, precision, versatility and multi-elemental character (Greenberg *et al.*, 2011; Tamim *et al.*, 2016; Islam *et al.*, 2017). Particularly INAA is the most suitable for solid matrices, e.g. soil, because no digestion is needed in this technique. For these reasons, the NAA technique is the best among the methods- Inductively Coupled Plasma Mass Spectrometry (ICP-MS), X-ray Fluorescence (XRF), Atomic Absorption Spectrometry (AAS), etc. (Ehmann and Diane, 1991). In view of the above considerations, the present work was undertaken to study the contaminations of heavy metals in surface soils around the industrial area of Khalishpur Thana in Khulna, Bangladesh using INAA.

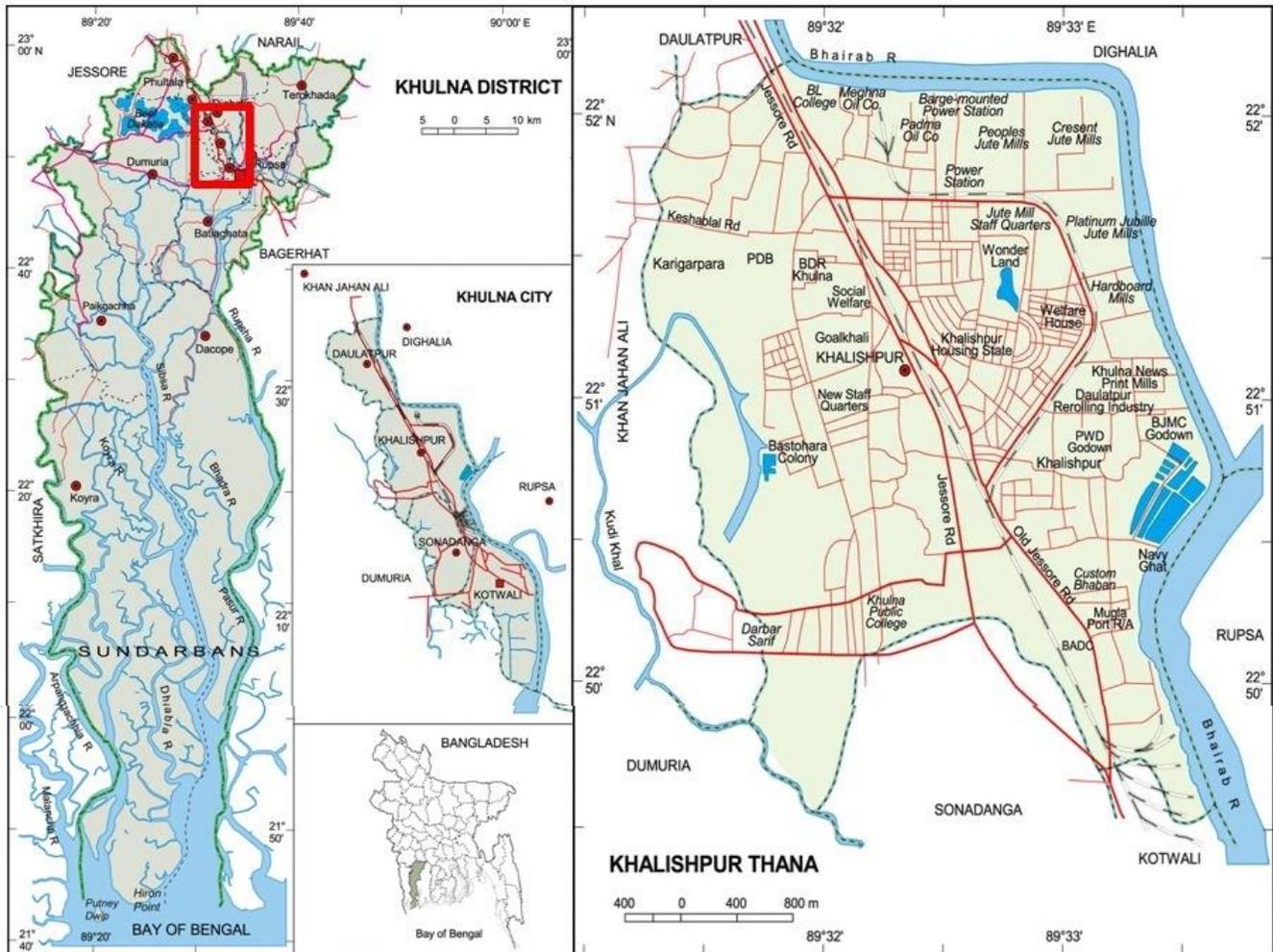


Fig. 1: Geographical location of the study area



## Materials and Methods

The soil samples were collected randomly from various sites of Khalishpur industrial area (89°30' to 89°35' E and 22°47' to 22°55' N), Khulna, Bangladesh. The geographical location of the sampling area is shown in Fig. 1. In this study the sampling sites were selected in the uncultivated areas assuming that the pollution arises only from the atmospheric deposition not from other sources like utilization of fertilizer or irrigation. Twenty-six surface soil samples (from 0-10 cm) were taken from the high lands mainly from the open areas, roadsides and residential areas of Khalishpur Thana in Khulna district at 26<sup>th</sup> May 2007. An oven was used for drying the samples at a temperature of about 70° C until they attained constant weight. An agate mortar was used to make powder samples from the dried soils for ensuring the homogeneity. About 50 mg of each sample was packed into a polyethylene bag. IAEA certified reference materials (CRM) e.g. soil-7 and SL-1 were also packed in a clean small polyethylene bag. The soil sample were doubly heat sealed by polyethylene bags. The samples and standards were placed in a vial for irradiation.

In the present study 3MW TRIGA Mark-II research reactor of Bangladesh Atomic Energy Commission was applied for the irradiation purposes of both soil samples and standards. The IAEA Soil-7 & SL-1 were used as standards in this work. The samples and standards were irradiated with neutron flux about  $1.52 \times 10^{13}$  n/cm<sup>2</sup>/s for 40 minutes at 250 kW in Dry Central Thimble (DCT) of 3MW TRIGA Mark-II research reactor. To check the variation of neutron flux three iron (Fe) foils were irradiated along the stacked samples simultaneously at bottom, middle and top of stack samples. High Purity Germanium (HPGe) gamma-ray spectrometry

system and gamma-ray acquisition software were used for the measurement of the activities of the irradiated samples. The irradiated samples were allowed for two days decay to reduce the high activity before start radioactivity measurement. To avoid radioactive contamination the outer envelopes of irradiated samples were replaced by new polyethylene bags before radioactive counting. The geometry was same for both samples and standards gamma-ray spectra measurements. Normally the dead time was maintained below 10% and the uncertainty of peak area was less than 5% during radioactive counting. To avoid the interference of overlapping gamma-lines from undesired radioactive nuclides sufficient cooling time was allowed between each sample radioactivity measurement. In this study each sample was counted three times.

## Results and Discussion

The concentrations of the elements Sc, Cr, Fe, Co and Zn in surface soils of Khulna, which is in the southern part of Bangladesh, were determined by relative method using INAA. The Sc, Cr, Fe, Co and Zn elements of soils were identified with the gamma-ray energies from the decay of the <sup>46</sup>Sc, <sup>51</sup>Cr, <sup>59</sup>Fe, <sup>60</sup>Co and <sup>65</sup>Zn radionuclides, respectively, which were produced via (n,  $\gamma$ ) reaction on the corresponding target isotopes. The decay characteristics of the above radionuclides are quoted in Table 1. The detection limits (3 $\sigma$ ) determined under the present experimental conditions for Sc, Cr, Fe, Co and Zn were 0.29  $\mu$ g/g, 1.0  $\mu$ g/g, 147  $\mu$ g/g, 0.61  $\mu$ g/g and 11.37  $\mu$ g/g, respectively. To investigate the reliability of the analysis of the data quality assurance (QA) test was performed by measuring Sc, Cr, Fe and Zn concentration level in certified reference materials Soil-7 relative to another certified

**Table 1: The investigated elements, product nuclides and their decay characteristics**

Element	Reaction	Half-life	Gamma-ray energy (keV)	Branching ratio (%)
Sc	<sup>45</sup> Sc(n, $\gamma$ ) <sup>46</sup> Sc	83.8 d	889.3	100
Cr	<sup>50</sup> Cr(n, $\gamma$ ) <sup>51</sup> Cr	27.71 d	320	9.8
Fe	<sup>58</sup> Fe(n, $\gamma$ ) <sup>59</sup> Fe	44.6 d	1099	56
Co	<sup>59</sup> Co(n, $\gamma$ ) <sup>60</sup> Co	5.272 y	1173.2	99.9
			1332.5	100
Zn	<sup>64</sup> Zn(n, $\gamma$ ) <sup>65</sup> Zn	243.7 d	1115.5	49.8

**Table 2: Comparison of elemental concentrations ( $\mu$ g/g) determined in this study with certified values of the IAEA-CRM-Soil-7**

Element	This study	Certified value	Deviation <sup>a</sup> (%)
Sc	8.83	8.3	6.00
Cr	105.56	104.00	1.48
Fe	25060	25700	2.35
Zn	112.97	104.00	7.94

<sup>a</sup>Deviation indicates deviation of this study value from the certified value of the CRM.



reference materials SL-1. The analytical results for the certified reference materials are given in Table 2. The experimental results had 1-8 % deviations from the

16.7 µg/g, 12.9-112 µg/g, 6911-48642 µg/g, 2.59-22.7 µg/g and 37.7-322 µg/g, respectively (Table 3). The highest mean concentration was observed 37981 µg/g for Fe. The lowest

**Table 3: Measured elemental concentrations (µg/g) of the investigated elements in soil**

Soil utilization pattern	Location	Elements				
		Cr	Zn	Fe	Co	Sc
Open area	Kashipur	47.7	153	22367	9.33	6.75
	Karigarpara	62.2	160	29887	14.4	10.7
	Crescent jute mill	66.3	92.7	26414	8.66	7.45
	Mujgunni (Mollapara)	42.7	167	18307	9.82	6.49
	Goalkhali	62.9	162	28475	14.5	10.6
	Khalishpur	12.9	37.7	6911	2.59	2.56
	Hard board mill	52.8	49.0	22538	6.28	5.73
	Boyra	51.8	140	20055	10.4	5.87
	Range	12.9—66.3	37.7—167	6911—29887	2.59—14.5	2.56—10.7
	Average	49.9	120	21869	9.50	7.02
	STD	17.0	53.1	7260	3.94	2.67
	Coefficient of variation	0.341	0.441	0.332	0.415	0.380
	Road side	Kashipur	71.2	231	32009	15.5
Karigarpara		86.8	171	43873	19.1	15.1
Pabla		96.1	156	45955	22.7	15.9
Peoples jute mill		105	186	48642	19.2	14.6
Mujgunni		48.7	176	22153	11.4	6.66
Goalkhali		78.0	179	37524	16.5	13.7
Khalishpur		100	107	46991	18.8	16.8
Khalishpur		76.0	89.4	37437	14.4	12.7
Newsprint mill		65.3	322	33440	9.11	6.45
Boyra (Raermahal)		78.1	146	44015	19.7	15.4
Moddhopara		64.1	322	25749	10.5	9.00
Range		48.7—105	89.4—322	22153—48642	9.11—22.7	6.45—16.7
Average		79.1	189.6	37980.7	16.1	12.5
STD	17.0	75.7	8868	4.33	3.66	
Coefficient of variation	0.215	0.400	0.233	0.270	0.292	
Residential area	Karigarpara	65.4	152	29574	13.5	11.0
	Pabla (Shahapara)	96.1	156	45955	22.7	15.9
	Mujgunni (Dakhinparar)	47.8	144	21401	10.7	7.36
	GoalKhali	89.1	160	47702	18.9	15.6
	Charerhat	112	83.3	48131	19.0	16.4
	Boyra	54.4	134	22568	11.6	6.41
	Gabtala	35.6	92.3	16485	5.71	5.35
	Range	35.6—112	83.3—160	16485—48131	5.71—22.7	5.35—16.4
	Average	71.5	132	33117	14.6	11.1
	STD	28.1	31.3	13788	5.89	4.83
	Coefficient of variation	0.393	0.237	0.416	0.404	0.434

STD= standard deviation ( $1\sigma$ ).

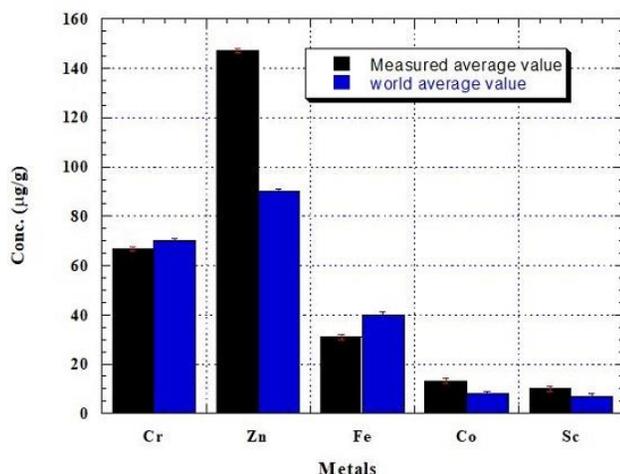
corresponding certified values of the CRM.

The concentration range, average, standard deviation and coefficient of variation for the soil samples are given in Table 3. The concentrations of the Sc, Cr, Fe, Co and Zn elements in surface soil were found in the range of 2.56-

mean concentration was observed 7.02 µg/g for Sc. As shown in Fig. 2 comparing with the average metal concentration of worldwide soil (Bowen, 1979) it is found that most of the samples contain much higher concentration of heavy metals except Cr and Fe. The exception may be due to the mobility of Cr.  $P^H$  of the soil governs the mobility



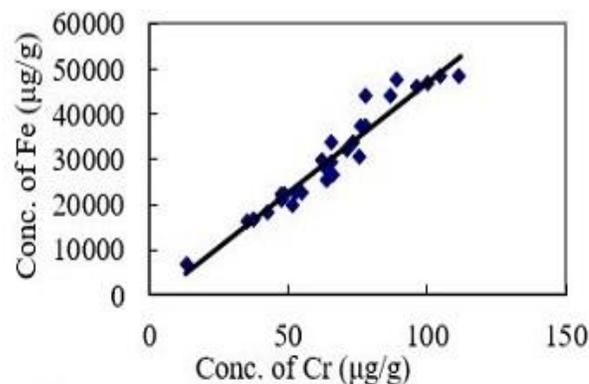
of Cr. Very acidic media is suitable for its mobility. On the other hand, Fe can be substituted by many other metals such as Co, Sc, Al, Pb etc. (Kabata-Pendias and Pendias, 2001). The average upper continental crust (UCC) average values of Sc, Cr, Fe, Co and Zn are 14, 92, 39200, 17.3 and 67  $\mu\text{g/g}$ , respectively, (Rudnick and Gao, 2014). If we compare our metal concentration values with UCC, it is observed that Zn concentrations in most of the soil samples are higher than the UCC values, especially in the samples from road side areas.



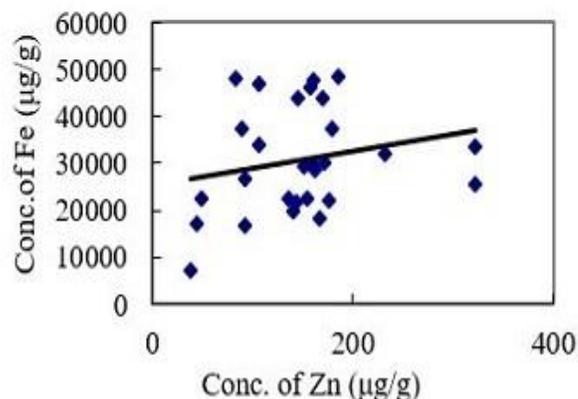
**Fig. 2: Comparison of the average metal concentration in the studied soil samples with the worldwide average value. (Fe concentration values are divided by 1000).**

In the present study, it was found that the concentration of metal in surface soil varies with the soil utilization pattern. Most of the samples collected from road side area contain elevated concentration of heavy metals (Table 3). Average concentrations of the Sc, Cr, Fe, Co and Zn elements in soil are much higher in road side and residential area than open area as given in Table 3. The reason of high concentration of Zn might be mainly due to the industrial activities, traffic densities, activities of roadside artisans, brake wires and radiators wear of studded tires, such as battery charging, vehicle repairs, iron bending, vehicle painting, panel beating, and atmospheric deposition. The concentration of Zn balance in surface soils of various ecosystems illustrates that the atmospheric input of this metal exceeds its output due to both leaching and the production of biomass (Krishna and Govil, 2004; Yarlagadda and Matsumoto, 1995). Other sources of Zn might be emission of zinc oxides from automobiles, brake linings, road salt, metal corrosion etc. Major sources of Sc are the combustion of coal and oil. Sources of Sc due to industrial activities are very limited. Scandium can substitute for  $\text{Fe}^{+3}$  (Kabata-Pendias and Pendias, 2001). So

naturally soil contained higher concentration of Fe may contain elevated concentration of Sc.



**Fig. 3: Correlation between Cr-Fe**



**Fig. 4: Correlation between Zn-Fe**

It was observed that the heavy metals are most closely associated with each other. Strong positive correlation values were observed for Cr-Fe (Fig. 3), Cr-Co, Cr-Sc, Fe-Co, Fe-Sc, and Co-Sc with corresponding values of 0.97, 0.87, 0.92, 0.92, 0.95 and 0.95. These results indicate that the accumulation patterns of Cr, Fe, Co and Sc in soils are correlated with one another to a significant extent. Fe and Co are included subgroup VIII in periodic table with very similar behaviors and due to the small differences in atomic radius; they are likely to form a wide range of mixed crystals. In general,  $\text{Cr}^{+3}$ ,  $\text{Co}^{+3}$ ,  $\text{Sc}^{+3}$  resembles  $\text{Fe}^{+3}$  and also substitutes  $\text{Fe}^{+3}$  in various minerals. Very weak correlation was found between Zn-Cr, Zn-Fe (Fig. 4), Zn-Co, Zn-Sc with the corresponding values of 0.21, 0.21, 0.22, 0.12. Zn-Fe antagonism is widely known, and an excess of Zn leads to a marked reduction in Fe concentration. There are two possible mechanisms of this interaction- the competition between  $\text{Zn}^{+2}$  and  $\text{Fe}^{+2}$  and the interference in chelating

processes. In oxidizing, the mobility of Zn is high at neutral or alkaline condition. But the mobility of Sc, Cr, Fe and Co is very low in such conditions and strongly bound to soil organic matter (Kabata-Pendias and Pendias, 2001).

## Conclusions

In the present study, concentration of Sc, Cr, Fe, Co and Zn were assessed in surface soils of Khalishpur Thana. INAA method was used for the analysis of soil samples and it was found to be very sensitive method. The quality control tests indicate the reliability of the analysis. From the experiment this can be concluded that the average concentrations of heavy metals in the studied area are much higher than the average concentration of worldwide soil except Cr and Fe. Analysis based on soil utilization type shows that samples collected from roadside and residential areas experience much higher metal contamination than open area. So, not only the industrial activities but also traffic sources such as emission from automobiles, vehicles moving without fitness, activities of roadside artisans such as vehicle repairing, welding and uses or disposal of goods that contain metals contributed to the elevated level of metals. A highly significant correlation is observed between Cr-Fe, Cr-Co, Cr-Sc, Fe-Co, Fe-Sc, and Co-Sc.

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