A BASELINE STUDY OF THE GEOCHEMICAL VARIABLES IN THE AGRICULTURAL SOILS OF THE PROPOSED NUCLEAR POWER PLANT AREA IN BANGLADESH

M. A. Halim^{a*}, R. K. Majumder^a, S. Hossain^a, M. K. Jahan^b, M. N. Zaman^c, A. F. M. M. Rahman^d, I. Khalil^d, M. A. Razzaque^d, J. U. Ahmad^b, and M. R. Islam^e

 ^aIsotope Hydrology Division, Institute of Nuclear Science and Technology, Atomic Energy Research Establishment, Savar, Dhaka-1000, Bangladesh
 ^bDepartment Chemistry, Jahangirnagar University, Dhaka-1342, Bangladesh
 ^cInstitute of Mining, Mineralogy and Metallurgy, Bangladesh Council of Scientific and Industrial Research, Science Laboratory Road, Khonjonpur, Joypurhat-5900, Bangladesh
 ^dNuclear Minerals Unit, Atomic Energy Research Establishment, Savar, Dhaka-1000, Bangladesh
 ^eDepartment of Civil and Resource Engineering, Dalhousie University, Halifax, NS B3J 2X4, Canada

ABSTRACT

The geochemical compositions of topsoil and subsoil samples collected from proposed Rooppur nuclear power plant site were analyzed in order to generate baseline data for assessing future contamination. The examined soils are mainly silty clay type; and quartz, K-feldspar, albite, muscovite, vermiculite and calcite are major minerals constituting the soil compositions. Silicon is the dominant element in all assorted samples followed by Al, Fe, K, Ca, Na, Mg and Ti. On contrary, the order of trace element abundances in the soils is Mn>S>Zr>Zn>Cr>Sr>Rb>V>Ce>Pb>Y>As>Cu>Co>Th. The calculated enrichment factors, geoaccumulation index and contamination factors suggest that the soils are none to very lightly polluted with respect to most metals and only sample #9 is moderately to highly polluted by As, Pb, S and Zn. The calculated pollution load index (PLI) varied between 0.98 and 1.24 with a mean of 1.08. Correlation, hierarchical cluster and principal component analyses suggest that the enrichment of As, Pb, S and Z are probably caused by human activities, mainly due to agricultural production, which has directly affected the chemical compositions of topsoils. The very low correlation of total organic carbon with As, Co, Cr, Cu, Pb and Cu, and negative

^{*} E-mail: halim1972@gmail.com

relationship with Rb, S, Sr, Th, Y, Zn and Zr indicates organic carbon is irrelevant to the accumulation of these elements in soils.

Keywords Soils, Baseline data, Soil quality, Arsenic, Lead, Correlation analysis.

INTRODUCTION

Soil plays a vital role in socioeconomic development of rapid population growing countries like Bangladesh through food production. In Bangladesh, more than 80% of the population depends on agriculture for its livelihood.

The land of this country is divided into three main units, the Holocene floodplains (80%), Pleistocene terraces (8%) and Tertiary hills (12%) (Saheed 1984; Rahman et al. 2005). Floodplains are subdivided into several areas according to the sediments transported by different rivers.

The Ganges River sediments originating from the Himalayas are calcareous and silt loams to silty clay loams (Saheed 1984). Soils of the proposed Rooppur nuclear power plant site are mainly alluvium deposited by the Ganges River. The geochemical characterization of these soils is environmentally important, because the high concentrations of geochemical constituents in soil may enhance the levels of toxic metals as well as it can reduce soil fertility and finally it can increase input to food chain, which leads to accumulate toxic metals in foodstuffs and ultimately can endanger human health (Madrid et al. 2002). Moreover, quantity of toxic metals available for release or sorption in soil is influenced by pH, organic matter, texture and cation exchange capacity (CEC) of the solid phase (Skordas and Kelepertsis 2005).

The natural pedo-geochemical background, which represents the concentration of metal derived from parent materials (Baize and Sterckeman 2001); and anthropogenic contamination, which can involve direct deposition on soil (slag and smelter dust) and agricultural inputs like animal manure (Xue et al. 2003), mineral fertilizer (Gray et al. 1999), compost (Pinamonti et al. 1997), sewage sludge (Cornu et al. 2001), or diffuse contamination via aerosol deposition on soil surface (Hernandez et al. 2003) are the major sources of metals in soil.

Although some studies have been focused on mineralogy of soils in Ganges River Floodplain soil (Ripon et al. 2004; Rahman et al. 2005), but very rare information is available on geochemical composition of these soils (Egashira et al. 2004).

In addition, with agriculture and rapidly increasing anthropogenic activities after the establishment of nuclear power plant in the study area, there would be a need for baseline geochemical information, both from the standpoint of understanding soil fertility and for assessing potential soil contamination in future.

Therefore, the main objectives of this study are (i) to determine the range, distribution and behaviour of elements in soils of investigated area as a basis for future geochemical surveys, (ii) to asses the soil quality by calculating a number of indices, (iii) to identify the main physicochemical properties controlling the factors of their distribution by analyzing their mutual relationships and (iv) to highlight their natural or anthropogenic origin by enrichment factor analysis, cluster analysis (CA) and principal component analysis (PCA).

MATERIALS AND METHODS

Study Site and Sampling

The study area covers at about 400 km² land areas of Iswardi, Bheramara and Mirpur upazilas (sub-district) and the area extends on both northern and southern banks of the river Ganges (Padma) flowing from northwest to southeast direction (Figure 1). Geographically the area extends from 23°56′ to 24°16′ N latitude and 88°57′ to 89°12′ E longitude. Iswardi and surrounding areas has a tropical wet and dry climate. The climate is generally marked with monsoons, high temperature, considerable humidity and moderate rainfall. The hot season commences early in March and continues till mid July. The maximum mean temperature is about 32 to 36 °C during the months of April, May, June and July and the minimum temperature recorded in January is about 7 to 16 °C. The highest rainfall is observed during the months of monsoon. The annual rainfall in the study area is about 1,448 mm (http://www.bbsgov.org/urban/rajshahi.htm).

The usage of land around the study area is similar to that of other parts of Bangladesh. Major part of the land is used for the cultivation of agricultural products and the rest is used for housing. The soil in the area is mainly alluvial sand (silty clay and fine sand) deposited by the Ganges river.

The principal agricultural products of the area are sugarcane, paddy, turmeric, mustard, spices, pulses, various kinds of vegetables and fruits etc (Rashid 1991).

Geologically the area is located in the Ganges Floodplain and the area is formed of interstream channel deposit that is later turned into a part of floodplain. The site mainly comprises a smooth landscape of ridges, basins and old channels.

The relief is locally irregular alongside the present and former river courses comprising a rapidly alternating series of linear low ridges (old channel bar) and depressions (Ox-bow Lakes). The floodplain deposits derived from the river Ganges is characterized by larger contents of mica (both muscovite and biotite) and it is predominately of calcareous sediments. Moreover, the deposits are composed of monotonous fine sand with little amount of silt and clay. Clay soils predominate in depressions with loamy soils (and occasionally sands) occur mainly on ridge crests (Brammer 1996).

A total of 20 topsoil samples (depths 0-20 cm) and 4 subsoil samples (21a-21d at depths 0-80 cm) were collected from the study area in clean polyethylene bags and were sealed in double bags (Figure 1).

Two topsoil samples were also collected from an agricultural land at a distance of about 15 km from the study area to calculate the enrichment factor of each element. The geographic coordinates of each sampling point were determined in the field with Global Positioning System (GPS) receiver.

Prior to analysis, in the laboratory, large items in soil, such as grass, pieces of wood, etc., were manually removed and samples were air dried at room temperature for 7 days. Dried samples were crushed in a mechanical agate grinder until fine particles (<2 mm) were obtained and sample was homogenized for analysis.



Figure 1. Location map of the study area showing soil sampling points.

Particle Size Analysis

Particle size distribution of examined soil samples was carried out following the modified methodology outlined by Kettler et al. (2001) where 30 g soil (<2 mm) was mixed with 90 mL water at a ratio of soil:water was 1:3. After dispersion, the soil slurry was sieved through nested standard 0.063-mm mesh sieves to separate sand particles. During sand-particles separation, the solution and particles (silt + clay) passing through sieve were collected in a beaker and was stirred thoroughly to achieve suspension of all soil particles. While stirring, a 45 mL sub-sample was collected from the suspension and was shaken vigorously, and then left undisturbed at room temperature with a vertical orientation for at least 90 min to allow silt particles to settle. After the sedimentation period, the solution containing the suspended clay was decanted into a pre-weighed drying pan. The settled silt particles were then rinsed into another pre-weighed drying pan, and both are dried at 105 °C to constant weight. Finally, the contents of sand, silt and clay were calculated.

Mineralogical Analysis

The minerals present in each soil sample were identified using a PHILIP X'pert PRO Xray diffractometer at the Magnetic Materials Division, Atomic Energy Centre, Dhaka, Bangladesh. The powder diffraction technique was applied with a primary beam power of 40 kV and 30 mA for Cu radiation. A nickel filter was used to reduce CuK_{β} radiation and finally CuK_{α} radiation was only applied as the primary beam. Individual scans were obtained from 0 to 50° 20 with a dwell time of 1.0 second. Scans were collected electronically and processed using the "X'PERT HIGHSCORE" pattern processing software.

Determination of Ph, Electrical Conductivity and Total Organic Carbon

The soil pH was determined following the procedure outlined by Islam and Weil (2000). 10 g of the air dried sample was mixed with 25 mL distilled water (soil: water at a ratio of 1: 2.5) and was stirred. The mixture was allowed to stand for 30 min for allowing it to settle. The slurry was decanted and pH was measured with calibrated pH meter (Sension1, HACH, USA). The electrical conductivity (EC) was measured using a conductivity meter (Sension5, HACH, USA) in the soil suspension having a soil: water at a ratio of 1:40, after 30 min shaking. Total organic carbon (TOC) was measured by dry combustion method. Approximately 1.0 g aliquot of the ground soil was placed in porcelain crucibles, moisture was determined by oven drying for 24 h at 100 °C, and then the crucible was placed in a muffle furnace and heated to 550 °C for 4 h to combust organic carbon. The weight loss was calculated as organic carbon content (Carbonell-Barrachina et al. 1999).

Chemical analysis

Total concentrations of geochemical chemical variables in soil samples were measured by X-ray fluorescence spectroscopy (XRF) at the Institute of Mining, Mineralogy and Metallurgy, Bangladesh Council of Scientific and Industrial Research (BCSIR), Joypurhat following the procedures outlined by Goto and Tatsumi (1996) by using Rigaku ZSX Primus XRF machine equipped with an end window 4 kW Rh-anode X-ray tube (Table 1). The samples were mixed with binder (steric acid: sample at a ratio of 1:10) and pulverized for two minutes.

The resulting mixture was spooned into an aluminum cap (30 mm). The cap was sandwiched between two tungsten carbide pellets using a manual hydraulic press with 10 tons/sq. in for 2 minutes and finally pressure was released slowly. Measurements of major and trace elements were carried out using 40 kV voltage and 60 mA current, and 30 kV voltage and 100 mA current, respectively. The standards used in the analyses were the Geological Survey of Japan (GSJ) stream sediments (JSD) series. The precision was better than $\pm 5\%$ for all analyzed elements.

Soil Quality

The quality of proposed nuclear power plant site soils in Bangladesh was evaluated by calculating a number of indices:

Major	Major variables (%)											Trace elements (mg/kg)														
Sand	Silt	Clay	TOC	Al	Na	Κ	Ca	Mg	Fe	Ti	Si	As	Ce	Co	Cr	Cu	Mn	Pb	Rb	S	Sr	Th	v	Y	Zn	Zr
28.3	70.3	1.4	8.6	5.3	1.5	2.9	2.6	1.1	3.9	0.5	24	27	88	14	243	15	682	122	99	240.5	139	10	89	30	98	303
30.8	65.6	3.6	4.9	5.4	1.4	3.0	1.9	1.0	3.9	0.5	24	21	92	13	227	15	655	94	102	416.8	136	10	91	31	101	297
8.3	85.3	6.4	6.3	3.2	1.9	3.1	2.1	2.1	4.2	0.5	19	15	90	14	148	15	703	67	91	360.7	109	9	95	26	95	214
19.0	77.2	3.9	6.6	5.2	1.6	3.0	2.3	1.3	4.0	0.5	23	17	91	13	183	15	707	76	98	336.7	131	10	94	30	102	305
10.9	84.2	4.9	5.8	6.2	1.0	3.3	2.7	1.1	4.9	0.5	20	14	98	14	155	17	882	61	109	332.7	135	10	110	30	125	237
34.6	63.1	2.3	4.2	5.5	1.2	3.0	2.2	0.9	4.1	0.5	23	14	91	13	165	16	763	62	104	308.6	135	10	97	31	119	280
32.1	64.3	3.6	4.9	5.7	1.3	3.0	1.2	0.9	4.4	0.5	23	14	97	14	184	16	675	63	108	364.7	127	11	102	32	117	357
71.7	27.0	1.3	2.2	4.7	1.6	2.6	1.6	0.7	3.3	0.3	26	19	82	12	240	14	586	86	100	200.4	137	10	77	30	91	269
47.8	50.7	1.4	3.6	5.0	1.8	2.8	2.4	1.0	3.7	0.4	23	15	87	13	124	15	663	67	100	2605	137	10	87	30	596	302
31.1	66.0	2.9	4.1	5.3	1.5	2.8	1.7	0.9	3.8	0.5	24	14	91	13	136	15	680	63	102	773.5	134	10	90	31	270	309
22.9	75.0	2.1	3.9	5.5	1.4	3.1	2.4	1.0	4.0	0.5	22	13	93	13	149	15	700	61	104	569.1	136	10	91	31	202	303
52.3	45.2	2.5	3.1	5.2	1.5	2.9	2.0	0.9	3.6	0.5	23	14	88	12	151	15	649	63	102	477	139	10	91	31	199	317
17.0	80.8	2.2	2.1	4.4	1.6	2.5	3.2	0.9	2.8	0.4	24	13	84	11	141	14	521	61	91	316.6	167	11	76	31	152	368
11.4	85.4	3.2	3.2	5.5	1.4	3.1	1.5	0.9	3.9	0.5	23	14	95	13	141	16	719	63	108	376.8	132	10	96	32	151	321
NA	NA	NA	3.2	3.1	2.6	2.8	1.6	1.5	3.3	0.4	23	13	87	12	108	14	580	57	94	336.7	120	9	82	28	115	272
10.9	83.8	5.3	4.5	5.8	1.3	3.1	2.4	1.2	4.3	0.5	22	13	95	14	113	16	790	61	105	356.7	132	10	101	31	135	267
NA	NA	NA	2.8	5.0	1.9	2.9	2.1	1.2	3.5	0.5	24	16	90	12	104	15	643	74	101	597.2	135	10	88	31	167	312
14.8	81.5	3.7	6.0	4.5	1.8	2.8	2.3	1.4	3.8	0.5	23	13	90	13	125	16	678	60	100	657.3	136	10	91	30	119	294
21.4	74.8	3.7	5.1	5.2	1.5	3.0	2.5	1.0	3.7	0.5	23	13	91	13	133	16	688	61	104	581.2	142	11	91	31	143	287
29.2	68.1	2.7	5.9	6.3	1.2	3.3	0.8	1.0	4.8	0.6	22	14	102	15	148	17	716	64	116	448.9	120	11	110	32	134	266

Table 1. Characteristics of distributions of the physicochemical parameters measured in top-soil and sub-soil samples (values of depth and EC are in cm and µS/cm, respectively)

				Major	Major variables (%)										Trace elements (mg/kg)															
ID	Depth	pН	EC	Sand	Silt	Clay	TOC	Al	Na	K	Ca	Mg	Fe	Ti	Si	As	Ce	Co	Cr	Cu	Mn	Pb	Rb	S	Sr	Th	v	Y	Zn	Zr
Subsoil	samples																													
21(i)	0-20	8.5	37.8	12.0	83.4	4.6	3.7	5.6	1.1	3.1	2.2	0.9	4.1	0.5	21	41	94	20	120	17	749	189	109	268.5	136	11	97	31	125	283
21(ii)	20-40	8.5	41.4	5.4	87.3	7.3	4.2	6.2	1.0	3.3	2.6	1.1	4.7	0.5	20	19	95	15	80	17	807	87	109	204.4	133	10	107	30	113	241
21(iii)	40-60	8.6	37.5	15.9	81.1	3.0	1.9	5.0	1.3	2.8	2.9	0.9	3.5	0.4	22	17	87	13	90	15	621	79	103	152.3	151	10	88	30	99	282
21(iv)	60-80	8.6	40.4	15.6	81.1	3.2	2.5	5.4	1.2	3.0	3.0	0.9	4.0	0.5	21	16	87	13	103	16	689	82	105	160.3	143	10	93	30	105	273

Enrichment Factor

Enrichment factor (EF) is one of the useful tools to speculate on the origin of elements in the soils (Loska et al. 1997). It was calculated using the following relation (Yaqin et al. 2008):

$$EF = ([M]/[Fe])_{Sample}/([M]/[Fe])_{Background}$$
(1)

where $([M]/[Fe])_{Sample}$ is the ratio of the concentration of test element (M) to that of Fe in the sample and $([M]/[Fe])_{Background}$ is the same ratio in reference soils of the study area. Iron (Fe) was used as the reference element for geochemical normalization because Fe is associated with fine solid surfaces, its geochemistry is similar to that of many trace metals and its natural concentration tends to be uniform (Daskalakis 1995). Data from two samples collected from an agricultural land at approximately 15 km far from the study area are used as reference soils composition in EF calculations (Yaqin et al. 2008). The EF values close to unity indicate crusted origin, those less than 1.0 suggest a possible mobilization or depletion of metals (Zsefer et al. 1996), whereas EF >1.0 indicates that the element is of anthropogenic origin.

Geoaccumulation index

Geoaccumulation index (*Igeo*) was calculated following the procedure proposed by Muller (1981) and Ruiz (2001):

$$I_{geo} = \log_2 \left(C_n / (1.5 \times B_n) \right) \tag{2}$$

where C_n is the measured concentration of trace metal in sample, B_n the background value for the same metal, and 1.5 a multiplying factor intended to offset potential oscillations in background data resulting from lithological variations (Ruiz 2001). I_{geo} on the other hand provides a classification system for the degree of pollution when compared to the background (Ruiz 2001): $I_{geo} < 1$ – uncontaminated; $1 < I_{geo} < 2$ – very lightly contaminated; $2 < I_{geo} < 3$ – lightly contaminated; $3 < I_{geo} < 4$ – moderately contaminated; $4 < I_{geo} < 5$ – highly contaminated and $I_{geo} > 5$ – very highly contaminated.

Contamination Factor

Contamination factor (CF) is the ratio obtained by dividing the concentration of each metal in the sample by the background value:

$$CF = (C_M)_{Sample} / (C_M)_{Background}$$
(3)

The contamination levels may be classified based on their intensities on a scale ranging from 1 to 6 (0 = none, 1 = none to medium, 2 = moderate, 3 = moderately to strong, 4 = strongly polluted, 5 = strong to very strong, 6 = very strong) (Muller 1969). The highest

number indicates that the metal concentration is 100 times greater than what would be expected in the crust.

Pollution Load Index

Pollution load index (PLI) was determined in the studied area as the nth root of the product of the n CF (Usero et al. 2000):

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$
(4)

where CF_n is the contamination factor of metal n in sample. This empirical index provides a simple, comparative means for assessing the level of trace metal pollution.

Statistical Analysis

Correlation and multivariate statistical processes such as principle component analysis (PCA) and cluster analysis (CA) were performed using Statistica 7.0 for Windows (StatSoft Inc. USA 2006) in order to investigate associations among the physicochemical properties of soils. All physicochemical variables were used for correlation analysis while a dataset of trace elemental concentrations were used for PCA and CA.

RESULTS AND DISCUSSION

Major Physicochemical Variables

The observed soil mineralogy is dominated by silicate phase mainly quartz, aluminosilicates albite, muscovite and vermiculite. The carbonate mineral calcite (CaCO₃) is also identified in most of the soil samples. The contents of sand, silt and clay in the examined soils vary from 5.4 - 71.7%, 27.0 - 87.0% and 1.3 - 7.3% with the mean values of 24.7, 71.9 and 3.4\%, respectively, which indicates the studied soils are mainly silty type (Tables 1 and 2).

The major physicochemical parameters measured in soils of the study site (Figure 1) are shown in Table 1. Statistical summary of major variables together with the mean values of major elements in topsoils from various countries are presented in Table 2. The values of pH ranging in a narrow interval (8.1 - 9.1) with a median of 8.4, which suggests sub-alkaline to alkaline conditions for all samples while the value of EC varying from 20.8 to 66.1 μ S/cm with a median content of 37.4%. Contents of total organic carbon (TOC) in the examined soils vary from 1.9 to 8.6%, with a median value of 4.2% and standard deviation of 1.88%. These relatively abundant TOC contents in studied soils, where historic and traditional agricultural practices have taken place for several decays.

Silicon (mean 22.6%) is the dominant element in all soil samples followed by Al (mean 5.2%), Fe (mean 3.9%), K (mean 3.0%), Ca (mean 2.2%), Na (mean 1.5%), Mg (mean 1.1%), and Ti (mean 0.5%). All these values are slightly higher than those observed in topsoils of different countries (Guvenc et al. 2003; Liao et al. 2007) (Table 2). The investigated soils

show chemical imprints of Calcareous Grey Floodplain soils (Rahman et al. 2005). Quartz (SiO₂) is the most common source of Si while Al, Fe and K in the soils come mostly from potassium feldspars [KAl₂(AlSi₃O₁₀)(OH)₂], albite (NaAlSi₃O₈), vermiculite, chlorite and muscovite (KAl-Si₃O₈). However, clay mica (illite, (K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,(H₂O)]) is the other major source of K and Al, particularly in the fine grained soil. In contrast, carbonate mineral calcite (CaCO₃) is the main source of Ca in studied soils.

Parameter	Min	Max	Mean	Median	10th	90th	SD^{a}	Worldwide ^b
pН	8.1	9.1	8.5	8.4	8.3	8.6	0.2	
EC	20.8	66.1	37.0	37.4	26.1	46.9	10.7	
Sand	5.4	71.7	24.7	20.2	10.9	46.5	16.2	
Silt	27.0	87.3	71.9	76.1	52.0	85.2	15.1	
Clay	1.3	7.3	3.4	3.2	1.5	5.3	1.5	
TOC	1.9	8.6	4.3	4.2	2.3	5.9	1.7	
Al	3.1	6.3	5.2	5.3	4.4	6.1	0.8	3.0 ^c
Na	1.0	2.6	1.5	1.4	1.2	1.9	0.4	1.19 ^c
K	2.5	3.3	3.0	3.0	2.8	3.2	0.2	1.6 ^d
Ca	0.8	3.2	2.2	2.2	1.5	2.8	0.6	0.9 ^d
Mg	0.7	2.1	1.1	1.0	0.9	1.4	0.3	0.8 ^d
Fe	2.8	4.9	3.9	3.9	3.4	4.6	0.5	3.46 ^d
Ti	0.3	0.6	0.5	0.5	0.4	0.5	0.0	0.52 ^d
Si	19.4	26.3	22.6	22.9	20.5	24.0	1.6	
As	13.0	41.0	16.6	14.0	13.0	19.0	6.1	20.0
Ce	82.0	102.0	91.0	91.0	87.0	96.4	4.6	55.0
Со	11.0	20.0	13.4	13.0	12.0	14.7	1.7	10.0
Cr	80.0	243.0	146.3	141.0	103.3	183.7	43.6	67.0
Cu	14.0	17.0	15.5	15.0	14.3	17.0	0.9	24.0
Mn	521.0	882.0	689.4	685.0	596.5	781.9	76.3	558.0
Pb	57.0	189.0	76.0	63.5	61.0	86.7	28.3	29.0
Rb	91.0	116.0	102.7	102.5	95.2	109.0	5.8	73.0
S	152.3	2605.2	476.8	358.7	201.6	639.3	480.4	303 ^d
Sr	109.0	167.0	135.1	135.5	122.1	142.7	10.8	190.0
Th	9.0	11.0	10.1	10.0	10.0	11.0	0.5	8.0
V	76.0	110.0	93.1	91.0	83.5	105.5	8.8	100.0
Y	26.0	32.0	30.4	31.0	30.0	31.7	1.3	18.0
Zn	91.0	596.0	153.0	122.0	98.3	201.1	103.1	67.0
Zr	214.0	368.0	290.0	290.5	248.5	319.8	34.4	307

Table 2. Statistical summary of properties for the soil samples of Rooppur power plant site (contents of Sand to Si are in % and from As to Zr are in mg/kg, except pH and EC is in µS/cm)

$$NaAlSi_{3}O_{8} + 4H_{2}O + 4H^{+} = Na^{+} + Al^{3+} + 3Si(OH)_{4}$$
(5)

Albite Soluble silica

$$Al^{3+} + 3Si(OH)_4 + 1/2H_2O = 3H^+ + 1/2Al_2Si_2O_5(OH)_4$$
(6)

Kaolinite

where one mole hydrogen ion is consumed and the pH becomes slightly alkaline. Moreover, the pH of examined soils mostly controlled by carbonate minerals like calcite as observed in XRD analysis. In the soil solution, calcite reacts with water to produce hydroxide ions, rise soil pH.

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^-$$
(7)

The alkali and alkaline earth cations (mostly Na, K, Mg and Ca), the halites and silicates tend to remain in solution. The K, Mg, and Si move more slowly than Na and Ca. Meanwhile, the Fe, Ti, and Al precipitate and accumulate in soils (Bohn et al. 1985).

Trace Element Contents

The concentrations of various trace elements in the studied soils are presented in Table 1 and statistical summary along with the mean contents of these elements in surface soils worldwide listed in Table 2 were extracted from data tabulated by Kabata-Pendias and Pendias (2001).

The range of concentrations (mg/kg) is as follows: As(13.0 - 41.0), Ce (82.0 - 102.0), Co (11.0 – 20.0), Cr (80.0 – 243.0), Cu (14.0 – 17.0), Mn (521.0 – 882.0), Pb (57.0 – 189.0), Rb (91.0 - 116.0), S (152.0 - 2605.2), Sr (109.0 - 167.0), Th (9.0 - 11.0), V (76.0 - 110.0), Y (26.0 – 32.0), Zn (91.0 – 596.0) and Zr (214.0 – 368.0). The most abundant trace elements are Mn, S, Zr and Zn (mean values of 689.4, 476.8, 290.0 and 153.0 mg/kg, respectively), with Th, Co and Cu having the lowest concentrations (mean values of 10.1, 13.4 and 15.5 respectively). The order of trace element abundances mg/kg, is Mn>S>Zr>Zn>Cr>Sr>Rb>V>Ce>Pb>Y>As>Cu>Co>Th.

In comparison, concentrations of Ce, Co, Cr, Pb, Rb, Th, Y and Zn in all examined soils and average values of Mn and Zr (Table 2) are greater than those reported by Kabata-Pendias and Pendias (2001) for the worldwide topsoils. The average concentration of S found in this study is also higher than in Chinese soils Liao et al. (2007). Moreover, concentrations of As (27, 21 and 41 mg/kg) and V (110, 102, 101 and 110 mg/kg) in the some examined soils are also greater than world average values (Table 1) though the mean values of these two elements are lower.

This result may suggest that these soils are either contaminated with anthropogenic sources or influence from pedogenic factors.

The Vertical Distribution of Multi-Elements

The vertical distributions of multi-elements investigated in four soils (sample #21(i), 21(ii), 21(iii) and 21(iv)) at different depths (0 - 20, 20 - 40, 40 - 60 and 60 - 80 cm, respectively) are presented in Table 1.

Concentrations of Al, Fe, K, Mg, Ti, Ce, Mn, V and TOC in subsoil #21(ii) (depth 20 – 40 cm) are higher than those in topsoil and other two subsoils (depths 40 – 60 and 60 – 80 cm). This indicates that the above major elements are strongly associated with organic carbon (Figures. 2a, b), which reflects mainly the geogenic origin of these elements (Lobe et al. 1998), thus they accumulate to high levels in subsoil.



Figure 2. Comparison of total organic carbon (TOC in mg/kg) with (a): Al, Fe, K, Mg and Ti (in %), and (b) Ce, Cu, Mn and V (in mg/kg) in the studied subsoil samples.



Figure 3. Vertical distribution of (a): As, Pb, Cr and Cr, and (b): Th, Y, Zr and Cr in the investigated subsoils. Data presented as mean values of each element.

Topsoil of agricultural land is very often enriched, due to atmospheric fallout, agriculture practices and biogeochemical cycles (Baize 1997).

In addition, the mobility of As is low in soils, thus it mainly accumulates in the surface layers of soil (Kalbitz and Wennrich 1998). The maximum concentrations of As, Co, Cr, Pb, S, Th, Y, Zn and Zr are also found in topsoil (sample #21(i); depth 0 - 20) in the study area (Figures. 3a, b). Concentrations of these elements show almost the same trend within the depth profile. However, organic carbon sink effect does not appear to apply to these elements, which show high surface enrichment and no apparent link to organic carbon. Moreover, higher concentrations of these elements in surface than in subsoil layers indicate that the stored input is higher than the accumulative losses.

From this result it may, therefore, be concluded that there were substantial inputs of these elements from agriculture into the soils compared with the losses.

Soil Quality

The calculation of enrichment factor (EF), geoaccumulation index (I_{geo}), contamination factor (CF) and pollution load index (PLI) are carried out for all observed elements in order to evaluate soil quality in the study area. Statistic summary of these indices are presented in Table 3. The mean values of EF for most of the elements are close to 1, which suggests a natural source for these elements in the studied soils.

The natural distribution of these elements in soil has not been changed by pedogenesis or human activity, and because of their geochemical stability. On the other hand, Sr and Zr are slightly enriched in few top-soils (1.5 and 1.59, respectively), suggesting a natural concentration of these metals during weathering and/or pedogenesis processes (Manta et al. 2002), while As (1.61 and 2.33) and Pb (1.56 and 2.29) are moderately enriched in two topsoils (samples #1 and 21(i)), possibly due to anthropogenic inputs (Cancès et al. 2005). Moreover, the highest EF values for S and Zn (6.96 and 3.98, respectively) occur in same sample #9. These high soil enrichment factors are probably caused by human activity, mainly agricultural production which has directly affected the chemical compositions of topsoils.

The calculated values for I_{geo} suggest that in generally the soils are very lightly to lightly contaminated with respect to most elements. However, some of the soils are moderately contaminated with Na, Ca, Fe, Co, Cr and Mn, and very highly polluted with As, Pb, S and Zn (Table 3).

This results further support that the high concentrations of As, Pb, S and Zn in some soils might be caused of fertilizer and insecticide used in this study area for agricultural production. Pollution load index (PLI) was calculated by taking the contamination factors of the multiple elements at each soil sample. The calculated PLI values are very close to 1 for all soils apart from sample #9 (PLI value 1.236) showing their unpolluted nature.

Correlation Analysis

It is quite common that environmental geochemical phenomena, including major and trace metals concentration in soils, are correlated, and it is caused by the physicochemical features of elements and geochemical processes (Zhang and Selinus 1998).

Variable	Index	Range	Mean	Variable	Index	Range	Mean	Sample ID	PLI
Al	EF	0.53-1.07	0.90	Cu	EF	0.81-1.18	0.93	1	1.129
	Igeo	1.43-2.91	2.39		Igeo	2.22-2.69	2.452	2	1.112
	CF	0.65-1.31	1.08		CF	1.00-1.21	1.11	3	1.037
Na	EF	0.46-1.76	0.86	Mn	EF	0.82-1.04	0.97	4	1.097
	Igeo	1.43-3.86	2.19		Igeo	1.99-3.67	2.632	5	1.107
	CF	0.65-1.74	0.99		CF	0.89-1.52	1.19	6	1.056
K	EF	0.83-1.10	0.95	Pb	EF	6.2-2.29	0.97	7	1.075
	Igeo	2.07-2.75	2.50		Igeo	2.04-6.75	2.713	8	0.987
	CF	0.93-1.24	1.13		CF	0.92-3.05	1.23	9	1.236
Ca	EF	0.29-1.97	0.96	S	EF	0.40-6.96	1.24	10	1.114
	Igeo	0.95-3.70	2.50		Igeo	1.03-17.63	3.228	11	1.114
	CF	0.43-1.67	1.13		CF	0.47-7.96	1.46	12	1.079
Mg	EF	0.79-1.93	1.08	Sr	EF	0.62-1.50	0.88	13	1.021
	Igeo	1.89-5.50	2.83		Igeo	1.80-2.76	2.233	14	1.072
	CF	0.85-2.49	1.28		CF	0.81-1.25	1.01	15	0.983
Fe	EF	1.0-1.0	1.00	Th	EF	0.67-1.29	0.86	16	1.086
	Igeo	1.88-3.31	2.66		Igeo	1.99-2.43	2.242	17	1.1
	CF	0.85-1.50	1.20		CF	0.90-1.10	1.01	18	1.09
Ti	EF	0.82-1.16	0.94	V	EF	0.91-1.11	0.96	19	1.094
	Igeo	1.82-2.91	2.48		Igeo	2.08-3.01	2.545	20	1.081
	CF	0.82-1.32	1.12		CF	0.94-1.36	1.15	21(i)	1.177
Si	EF	0.54-1.12	0.77	Y	EF	0.61-1.11	0.78	21(ii)	1.066
	Igeo	1.72-2.32	2.00		Igeo	1.80-2.21	2.105	21(iii)	0.991
	CF	0.78-1.05	0.90		CF	0.81-1.00	0.95	21(iv)	1.021
As	EF	0.67-233	1.00	Zn	EF	0.56-3.98	1.00	Min	0.983
	Igeo	2.06-6.45	2.630		Igeo	1.61-10.55	2.711	Max	1.236
	CF	0.92-2.93	1.19		CF	0.73-4.77	1.22	Mean	1.08
Ce	EF	0.67-1.01	0.78	Zr	EF	0.58-1.59	0.91		
	Igeo	2.04-2.54	2.265		Igeo	1.73-2.97	2.344		
	CF	0.92-1.15	1.02		CF	0.78-1.34	1.06		
Со	EF	0.78-1.32	0.94	Rb	EF	0.73-1.11	0.89		
	Igeo	2.03-3.69	2.476		Igeo	2.08-2.65	2.344		
	CF	0.92-1.67	1.12		CF	0.94-1.19	1.06		
Cr	EF	0.39-1.67	0.87						
	Igeo	1.24-3.76	2.266						
	CF	0.56-1.69	1.02						

Table 3. Statistical summary of soil quality as determined from the calculation of enrichment factor (EF), Geoaccumulation index (Igeo), contamination factor (CF) and pollution load index (PLI)

Para- meters	Sand	Silt	Clay	pН	EC	TOC	Al	Na	К	Ca	Mg	Fe	Ti	Si
Sand	1.0													
Silt	-1.0	1.0												
Clay	-0.7	0.65	1.0											
pH	-0.2	0.21	0.2	1.0										
EC	-0.4	0.43	0.23	0.38	1.0									
TOC	-0.4	0.38	0.29	0.3	0.21	1.0								
Al	0.00	0.01	- 0.12	0.3	0.30	0.04	1.0							
Na	0.12	0.1	- 0.08	0.19	0.26	0.03	0.8	1.0						
К	-0.5	0.48	0.56	-0.5	0.15	0.49	0.52	0.6	1.0					
Ca	-0.3	0.33	0.05	0.75	0.60	0.03	-0.3	0.22	0.3	1.0				
Mg	-0.5	0.50	0.67	-0.1	0.34	0.56	-0.6	0.48	0.33	0.16	1.0			
Fe	-0.4	0.32	0.49	-0.6	0.11	0.52	0.56	-0.6	0.91	0.4	0.28	1.0		
Ti	-0.6	0.56	0.46	-0.4	0.08	0.37	0.65	-0.6	0.84	0.3	0.12	0.84	1.0	
Si	0.70	0.7	0.73	0.06	0.28	0.4	0.00	0.18	-0.7	0.2	0.7	0.6	0.6	1.0

 Table 4. Correlation between the major physicochemical parameters in the studied topsoils

The correlations that exist between major and trace elements in the proposed nuclear power plant site topsoils are inherited from their parent materials and are also affected by anthropogenic activities. Understanding the relationship between the elements and the soil parameters could help clarify the behavior of these elements in soil.

The correlation among major physicochemical properties, between trace elemental concentrations and major soil properties of 21 topsoils (Figure 1) and among trace elements are carried out in this study (Tables 4, 5, 6).

Correlation among Major Physicochemical Properties

Silicon is strongly correlated with sand particle ($R^2 = 0.70$) in studied topsoils indicating origin of Si is mainly quartz. Concentrations of K, Mg and Ti are moderately strongly correlated with the contents of both silt and clay particles (Table 4).

Positive relationships between the major variables EC, TOC and Fe and the soil particles silt and clay are also observed in the examined samples suggesting association of these parameters with organic matter present in topsoil. Surprisingly, there is no significant correlation between major elements apart from Ca and soil pH (Table 4), having little influence on elemental behavior. On contrary, soil pH is strongly correlated with Ca ($R^2 = 0.75$), possibly due to the presence of carbonate mineral calcite (CaCO₃) in topsoils at the study area (Figure 1). The absence of correlation between K and major elements could be explained by presence of potassium-feldspars which may obscure the relation between K and clays.

Correlation between Trace Elements and Soil Properties

No significant correlations between the content of sand particle and trace elements are found in topsoils. It is reported that soil particles with large surface areas such as clay minerals and metal oxy-hydroxides exhibit higher tendency for trace element adsorption than other soil particles (Adriano 1986). Among the trace elements, the concentrations of Ce, Co, Cu, Mn and V are moderately to strongly correlate with the contents of Clay, Al, K, Fe and Ti in the studied soils (Table 5), which indicates strong affinity of these trace elements for these major soil properties. On the other hand, silt particle is also positively correlated with these trace elements. Sterckeman et al. (Sterckeman et al. 2004) found good correlations between the concentrations of Cu, and V, amongst others, and concentrations of Al and Fe in the surface soils of France. Apparently, total Fe, Al and K are significant in controlling metal concentrations in studied soils. Huisman et al. (1997) have already shown that Al and Fe contents can help to determine the trace element background values in soils from the Netherlands.

In present study, As and Pb are not correlated with major soil properties. Moreover, no correlation between soil pH and trace element content except Sr is observed for analyzed soils (Table 5). These results are consistent with those obtained by Tume et al. (Tume et al. 2006) for natural surface soils of Catalonia, Spain, and also by Manta et al. (Manta et al. 2002) for non-stratified soils from Sicily.

It is well known that organic matter sorbs trace elements from solution and may be strongly related to metal content. But in arid or/semiarid environments, its presence is minimal (Graf et al. 1991) and it may be considered irrelevant (Taylor and Kesterton 2002). The very low correlation of total organic carbon (TOC) with As, Co, Cr, Cu and Pb and Cu, and negative relationship with Rb, S, Sr, Th, Y, Zn and Zr found in this study indicates that organic carbon (OC) is irrelevant to the accumulation of these metals in topsoil. Agricultural activities alter the OC content significantly, compliancy thus lowering or/negative correlation between TOC and these elements. However, TOC is moderately correlated with Ce, Mn and V (Table 5), suggesting association of these metals with organic matter present in the studied soils. Among these elements, adsorption of Mn is found to be increased with higher soil organic carbon content (Bradl 2004).

Correlation among the Contents of Trace Elements

Arsenic is linearly correlated with Pb ($R^2 = 1$) and strongly correlated with Co ($R^2 = 0.76$) in topsoils (Table 6). Among these three metals, the spatial distribution of As and Pb is shown in Figures. 4a and b, respectively. This variation patterns and the inter-element correlations between As and Pb strongly suggest that there is a common source of these metals in examined topsoils, most likely the lead arsenate (PbHAsO₄), which corresponds to the main pesticide manufactured at the pesticide plant (Cancès et al. 2005).

The trace elements Ce, Cu, Mn, Rb and V are strongly correlated with each other. Copper and V have similar ionic radii (Dean 1992); thus, they may exhibit similar geochemical behavior during pedogenic processes.

Element	Sand	Silt	Clay	pН	EC	TOC	Al	Na	Κ	Ca	Mg	Fe	Ti	Si
As	-0.06	0.06	0.08	0.02	-0.03	0.10	0.09	-0.23	0.12	0.04	-0.10	0.04	-0.03	-0.08
Ce	-0.43	0.41	0.46	-0.53	-0.16	0.40	0.67	-0.54	0.84	-0.47	0.13	0.86	0.92	-0.44
Со	-0.36	0.34	0.44	-0.30	-0.07	0.22	0.34	-0.43	0.59	-0.16	0.12	0.54	0.50	-0.50
Cr	0.55	-0.55	-0.45	-0.23	-0.21	0.39	-0.12	0.22	-0.24	-0.37	-0.08	-0.15	-0.37	0.65
Cu	-0.50	0.48	0.54	-0.38	0.14	0.24	0.66	-0.67	0.81	-0.16	0.05	0.82	0.85	-0.63
Mn	-0.47	0.44	0.61	-0.36	0.16	0.40	0.58	-0.56	0.86	-0.02	0.26	0.87	0.77	-0.65
Pb	-0.08	0.08	0.08	0.04	-0.03	0.06	0.09	-0.25	0.11	0.08	-0.12	0.03	-0.04	-0.10
Rb	-0.10	0.10	0.15	-0.50	-0.29	-0.01	0.88	-0.77	0.66	-0.42	-0.40	0.69	0.72	-0.24
S	0.32	-0.31	-0.30	-0.07	0.07	-0.04	-0.10	0.47	-0.19	-0.02	0.01	-0.12	-0.13	0.12
Sr	0.05	-0.02	-0.42	0.79	0.28	-0.52	-0.03	-0.04	-0.64	0.64	-0.59	-0.69	-0.44	0.32
Th	0.03	-0.01	-0.20	0.05	-0.16	-0.13	0.40	-0.32	-0.07	-0.15	-0.55	-0.06	0.19	0.23
V	-0.46	0.42	0.60	-0.50	-0.04	0.41	0.66	-0.62	0.91	-0.29	0.22	0.97	0.94	-0.64
Y	0.18	-0.15	-0.38	-0.11	-0.34	-0.24	0.69	-0.43	-0.01	-0.34	-0.78	0.01	0.29	0.43
Zn	0.34	-0.33	-0.34	0.05	-0.03	-0.19	-0.02	0.36	-0.21	0.02	-0.13	-0.16	-0.12	0.12
Zr	0.24	-0.20	-0.57	0.27	-0.13	-0.23	-0.02	0.20	-0.56	-0.08	-0.51	-0.55	-0.20	0.62

 Table 5. Correlation of trace element contents with soil properties in the study area

Element	As	Ce	Со	Cr	Cu	Mn	Pb	Rb	S	Sr	Th	V	Y	Zn	Zr
As	1.00														
Ce	0.00	1.00													
Со	0.76	0.53	1.00												
Cr	0.18	-0.11	-0.12	1.00											
Cu	0.22	0.80	0.69	-0.29	1.00										
Mn	0.12	0.72	0.55	-0.15	0.82	1.00									
Pb	1.00	-0.01	0.76	0.14	0.23	0.11	1.00								
Rb	0.16	0.77	0.53	-0.14	0.83	0.62	0.17	1.00							
S	-0.17	-0.11	-0.12	-0.13	-0.1	-0.08	-0.2	-0.10	1.00						
Sr	0.06	-0.46	-0.28	-0.06	-0.2	-0.35	0.09	-0.13	-0.01	1.00					
Th	0.23	0.32	0.32	0.06	0.39	0.00	0.25	0.49	-0.02	0.43	1.00				
V	0.02	0.91	0.56	-0.17	0.89	0.87	0.02	0.76	-0.15	-0.45	0.18	1.00			
Y	0.02	0.39	0.08	0.09	0.33	0.09	0.03	0.64	0.01	0.39	0.74	0.21	1.0		
Zn	-0.16	-0.13	-0.12	-0.19	-0.2	-0.09	-0.2	-0.06	0.96	0.09	0.00	-0.16	0.1	1.00	
Zr	-0.08	-0.19	-0.32	0.18	-0.4	-0.53	-0.1	-0.14	0.16	0.52	0.48	-0.41	0.6	0.22	1.0

Table 6. Correlation among trace element concentration in the study area

Chromium did not correlate with any other trace metal, which may indicate different origin or controlling factors of Cr in analyzed topsoils. On contrary, Zn is very strongly correlated with S ($R^2 = 0.96$) (Figures. 4c, d), indicating source of both these elements is sphalerite (ZnS), which could be released Zn into the environment by oxidization through the reaction below (Eq. (8) (Bhuiyan et al. 2010):

$$ZnS(s) + 2O_2(aq) \rightarrow Zn^{2+} + SO_4^{2-}$$
(8)

Positive relationships observed among the trace metals Sr, Th, Y and Zr, indicating these metals are associated with the mineral phase in topsoils of study area.



Figure 4. Spatial distribution of enrichment factors of (a): As, (b): Pb, (c): Zn and (d): S in the examined topsoil samples .

Hierarchical Cluster Analysis

An explorative hierarchical cluster analysis was performed on measured dataset with Ward's method and the Pearson r as a similarity measure in order to discriminate distinct groups of metals as tracers of natural or anthropogenic source (Manta et al. 2002). The obtained results (Figure 5) enabled the identification of two main groups (I and II) of

variables and clustered at level of similarity 3.5, discriminating the trace elements As, Pb, Co, Ce, V, Mn, Cu, and Rb (Group–I) from Cr, Sr, Zr, Th, Y, S, and Zn (Group–II). Each of these two main groups is further divided into two sub-groups (A and B).



Figure 5. Hierarchical clustering results (dendrogram) of the heavy metal concentrations in soil samples of study area.

Group–IA includes elements As, Pb and Co, which were previously discussed as contaminants derived from anthropogenic sources such as schultenite, a lead arsenate (PbHAsO4) (Cancès et al. 2005).

The result is consistent with elemental relationships indicating that the metals Ce, V, Mn, Cu, and Rb of Group–IB strongly correlate with the alumino-silicate phases, thus supporting a natural origin for these elements. Group–IIA contains trace metals Cr, Sr, Zr, Th and Y, which may be derived by chemical weathering of some metal bearing minerals. Group–IIB contains S and Zn may derive from anthropogenic activities as calculated their enrichment factor in previous section.

Principal Component Analysis

Principal component analysis (PCA) was performed with examined data (Table 1) to reduce the high dimensionality of the sample/variable space, following standard procedure outlined in literature (Dragovi'c et al. 2008). PCA procedures are based on linear combinations of the variables and their correlations. The obtained factors were rotated using a

varimax normalized algorithm, which allows an easier interpretation of the principal component loadings and the maximization of the variance explained by the extracted factors. In this study, five principal components (PCs) with eigenvalues greater than 1 were extracted, explaining a total variance of approximately 85% (Table 7).

Principal component 1 (PC1) has high positive loadings of Ce, Cu, Mn, Rb and V, and moderately positive loadings of Co and explains for the highest 35.89% of variance. Based on earlier discussions it is obvious that the distribution of these elements is mainly controlled by natural materials and the PC1 can be inferred as a lithogenic component (Figure 6). In contrast, PC2 having high positive loading of Y, Th and Zr, and moderately positive loadings of Sr and Rb, accounts for 19.05%. Rubidium is highly correlated with PC1 and moderately correlated with PC2, indicating the source of this element is also lithogenic inputs. PC3 has high positive loading of As, Pb and Co, accounts for 16.91% of variance can be identified as a tracer of anthropogenic pollution. Cobalt shows relatively high values in PC1, but it is also represented in PC3. An explanation for this may be that the distribution of Co is affected by both lithogenic and anthropogenic control.

The S and Zn are negatively correlated with PC4, which explains 12.03% of variance and can be considered as the agriculture factor. For irrigation purposes, the farmers use the chemical fertilizers and pesticides, which often release some elements including Zn and S in soil. PC5, which accounts for 6.96% of the total variance, is characterized by high negative loadings of Cr can be considered as the different origin in topsoils.

Parameter	PC 1	PC 2	PC r 3	PC 4	PC 5
As	0.01	0.04	0.99	0.08	-0.09
Ce	0.94	0.09	-0.04	0.04	-0.10
Со	0.57	-0.05	0.79	0.01	0.07
Cr	-0.16	0.08	0.10	0.13	-0.92
Cu	0.90	0.10	0.23	0.07	0.24
Mn	0.86	-0.22	0.12	0.02	0.10
Pb	0.01	0.06	0.99	0.10	-0.04
Rb	0.84	0.36	0.13	0.03	0.05
S	-0.07	0.00	-0.08	-0.98	0.03
Sr	-0.46	0.67	0.06	0.07	0.36
Th	0.25	0.84	0.23	0.01	0.01
V	0.97	-0.08	0.00	0.09	0.03
Y	0.33	0.89	-0.05	-0.04	-0.10
Zn	-0.08	0.08	-0.08	-0.98	0.10
Zr	-0.36	0.78	-0.13	-0.15	-0.19
Eigenvalues	5.38	2.86	2.54	1.80	1.04
% Total variance	35.89	19.05	16.91	12.03	6.96
% Cumulative	35.89	54.94	71.85	83.88	90.85

 Table 7. Varimax normalized principal component factor loadings; values of dominant elements in each factor reported in bold



Figure 6. Bvariate plots showing the relationship between (a): PC 1 and PC 2, (b): PC 1 and PC 3, and (c): PC 2 and PC 3 in the topsoils.

CONCLUSIONS

An integrated analysis has been performed to generate a baseline geochemical data of soils collected from the proposed Rooppur nuclear plant site in Bangladesh. The mineralogical analyses of soils indicate the presence of quartz, alumino-silicates albite, muscovite, vermiculite and carbonate (calcite) can release high levels of the measured elements. The studied soils are mainly silty type (mean 71.9%) and their pH (mean 8.4) is mainly controlled by carbonate minerals like calcite (CaCO₃). The results of soil quality indices analysis suggest that all major elements (Si, Al, Fe, K, Ca, Na, Mg and Ti) and most of the trace elements (Mn, Cr, Rb, V, Ce, Y, Cu, Co and Th) are mainly controlled by lithogenic origin, whereas As, Pb, S and Zn are inferred to derive from anthropogenic sources in some soils. Moreover, Sr and Zr are slightly enriched in two topsoils (1.5 and 1.59, respectively), which are interpreted as natural enrichment by weathering and pedogenesis processes.

Correlation matrix, hierarchical cluster analysis (CA) and principal component analysis (PCA) used in this study provide important tools for better understanding of the sources and dynamics of geochemical variables. The PCA applied on the investigated trace elements are extracted as five components. Among them, PC1, PC3 and PC5 are loaded with Ce, Cu, Mn, Rb, V, Co, Sr, Th, Y, Zr and Cr are related to the geogenic sources. The same results are also obtained from cluster analysis. On contrary, correlation analysis, CA and PCA suggests that the main source of As, Pb, S and Zn in some topsoils are chemical fertilizers and pesticides most likely the lead arsenate (PbHAsO₄). Therefore, the data obtained in this study demonstrate that the major and trace element concentrations of examined soils can be used as powerful geochemical tracers for future environmental monitoring and assessment the impact of anthropogenic activities in the proposed power plant site soils.

ACKNOWLEDGEMENTS

The authors would like to grateful acknowledge Bangladesh Council of Scientific and Industrial Research to provide WD-XRF facility for elemental analysis. We are also extremely grateful to Professor Bidyut Baran Saha for his thorough revision of this manuscript. The authors wish to thank Dr. Dilip Kumar Saha Materials Science Division, BAEC for his kind support to carry out XRD analysis.

REFERENCES

Adriano DC (1986) Heavy Metals in Terrestrial Environment. Springer, Berlin.

- Baize D (1997) Teneurs totales en éléments traces métalliques dans les sols. Institute National de la Recherche Agronomique, Paris, pp 409.
- Baize D, Sterckeman T (2001) The necessity of knowledge of the natural pedo-geochemical background content in the evaluation of the contamination of soils by trace elements. *Sci. Total Environ.* 264:127–139.

- Bhuiyan AHM, Lutfar Parvez, Islam MA, Samuel B, Dampare, Shigeyuki Suzuki (2009) Heavy metal pollution of coal mine-affected agricultural soils in the northern part of Bangladesh. J. Hazard Mater. 173:384–392.
- Bohn LH, Mcneal, BL, O'connor GA (1985) *Soil Chemistry*. 2nd ed. A Wiley-Interscience Publication, New York, pp 73.
- Bradl HB, (2004) Adsorption of heavy metal ions on soils and soils constituents. J. Coll. Inter. Sci. 277:1–18.
- Brammer H (1996) The Geography of the Soils of Bangladesh. University Press Limited, Dhaka, Bangladesh.
- Cancès B, Juillot F, Morin G, Laperche V, Alvarez L, Proux O (2005) XAS evidence of As(V) association with iron oxyhydroxides in a contaminated soil at a former arsenical pesticide processing plant. *Environ. Sci. Tech.* 39:9398–405.
- Carbonell-Barrachina AA, Jugsujinda A, Burlo F, Delaune RD, Patrick Jr WH (1999) Arsenic chemistry in municipal sewage sludge as affected by redox potential and pH. *Water Res.* 34:216-224.
- Cornu S, Neal C, Ambrosi C, Whitechead JP, Neal P, Sigolo M, Vachier P (2001) The environmental impact of heavy metals from sewage sludge in Ferrasols (Sao Paulo, Brazil). *Sci Total Environ* 271:27–48.
- Daskalakis KD, O'Connor TP (1995) Normalization and elemental sediment contamination in the Coastal United States. *Environ Sci Tech* 29:470–477.
- Dean JA, (1992) Lange's Handbook of Chemistry. 14th ed. McGraw-Hill, New York.
- Dragovi'c S, Mihailovi'c N, Gaji'c B (2008) Heavy metals in soils: distribution, relationship with soil characteristics and radionuclides and multivariate assessment of contamination sources. *Chemosphere* 72:491–549.
- Egashira K, Aramaki K, Yoshimasa M, Takeda A, Yamasaki S (2004) Rare earth elements and clay minerals of soils of the floodplains of three major rivers in Bangladesh. *Geoderma* 120:7–15.
- Goto A, Tatsumi Y (1996) Quantitative analysis of rock samples by an X-ray fluorescence spectrometer (II). *The Rigaku J*. 13:20-39.
- Graf LW, Clark SL, Kammerer MT, Lehman T, Randall K, Schroeder R (1991) Geomorphology of heavy metals in the sediments of Queen Creek, Arizona, USA. *CATENA* 18:567-582.
- Gray CW, McLaren RG, Roberts AHC, Condron LM (1999) The effect of long-term phosphatic fertiliser applications on the amounts and forms of cadmium in soils under pasture in New Zealand. *Nutri Cyc. Agroeco.* 54:267–277.
- Guvenc N, Alagha O, Tuncel G (2003) Investigation of soil multi-element composition in Antalya, Turkey. *Environ. Inter* 29:631–640.
- Hernandez L, Probst A, Probst JL, Ulrich E (2003) Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. *Sci. Total Environ.* 312:195–219.
- Huisman DJ, Vermeulen FJH, Baker J, Veldkamp A, Kroonenberg SB, Klaver GTh (1997) A geological interpretation of heavy metal concentrations in soils and sediments in the southern Netherlands. *J. Geochem. Explore* 59:163–174.
- Islam KR, Weil RR (2000) Land use effects on soil quality in a tropical forest ecosystem of Bangladesh. *Agri. Eco. Environ.* 79:9-16.
- Kabata-Pendias A, Pendias H (2001) *Trace Elements in Soils and Plants*. 3rd ed. CRC Press, Boca Raton, p 315.

- Kalbitz K, Wennrich R (1998) Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. *Sci. Total Environ.* 209:27-39.
- Kettler TA, Doran JW, Gilbert TL (2001) Simplified Method for Soil Particle-Size Determination to Accompany Soil-Quality Analyses. *Soil. Sci. Soc. Am. J.* 65:849–852.
- Liao Q, Evans LJ, Gu X, Fan D, Jin Y, Wang H (2007) A regional geochemical survey of soils in Jiangsu Province, China: Preliminary assessment of soil fertility and soil contamination. *Geoderma* 142:18–28.
- Lobe IW, Wilcke J, Kobza, Zech W (1998) Heavy metal contamination of soils in Northern Slovakia. *Z Pflanzenernähr Bodenkd* 161:541–546.
- Loska K, Cebula J, Perczar J, Wiechula D, Kwapulinski J (1997) Use of environment, and contamination factors together with geoaccumulation indexes to evaluate the content of Cd, Cu, and Ni, in the Rybnik water reservoir in Poland. *Water Air Soil. Poll* 93:347–365.
- Madrid L, Diaz-Barrientos E, Madrid F (2002) Distribution of heavy metal contents of urban soils in parks of Seville. *Chemosphere* 49:1301–1308.
- Manta DS Angelone M, Bellanca A, Neri R, Sprovieri M (2002) Heavy metals in urban soils: a case study from the city of Palermo (Sicily), Italy. *Sci. Total Environ.* 300:229–243.
- Muller G (1969) Index of geoaccumulation in sediments of the Rhine River. *Geojournal* 2:108–118.
- Muller G (1981) Die Schwermetallbelastung der Sedimente des Neckars und seiner Nebenflusse: eine Bestandsaufnahme. *Chem. Zeitung* 105:157–164.
- Pinamonti F, Stringari G, Gasperi F, Zorzi G (1997) The use of compost: its effects on heavy metal levels in soil and plants. *Res. Conser. Recyc.* 2:129–143.
- Rahman MH, Moslehuddin AZM, Saha DK, Ahmed IU, Egashira K (2005) Mineralogy of soils from different agroecological regions of Bangladesh: Region 12 Low Ganges River Floodplain. *Clay. Sci.* 12:321-326.
- Rashid HEr, (1991) Geography of Bangladesh. University Press Limited, Dhaka, Bangladesh.
- Ripon MNA, Moslehuddin, Hoque AKMM, Ahmed IU, Egashira K (2004) Mineralogy of soils from different agroecological regions of Bangladesh: Region 11–High Ganges River Floodplain. *Clay Sci.* 12:197-203.
- Ruiz F (2001) Trace metals in estuarine sediments from the southwestern Spanish Coast. *Mar Poll Bull* 42:482–490.
- Saheed SM (1984) Soils of Bangladesh. Proceedings of International Symposium on Soil Test Crop Response Correlation Studies, Bangladesh Agricultural Research Council and Soil Science Society of Bangladesh, *Dhaka*, p 107–129.
- Skordas K, Kelepertsis A (2005) Soil contamination by toxic metals in the cultivated region of Agia, Thessaly, Greece: Identification of sources of contamination. *Environ. Geo.* 48:615–624.
- StatSoft Inc., STATISTICA (2006) (Data Analysis Software System), Version 7, USA.
- Sterckeman T, Douay F, Baize D, Fourrier H, Proix N, Schvartz C, (2004) Factors affecting trace elements concentrations in soils developed on recent marine deposits from northern France. App. Geochem 19:89–103.
- Taylor MP, Kesterton RGH (2002) Heavy metal contamination of an arid river environment: Gruben River. *Namibia Geomorpho* 42:311-327.
- Tume P, Bech J, Longan L, Tume L, Reverter F, Sepulveda B (2006) Trace elements in natural surface soils in Sant Climent (Catalonia, Spain). *Eco Eng* 27:145–152.

- Usero J, Garcia A, Fraidias J (2000) Calidad de las aguas y sedimentos del Litoral Andaluz, in: Junta de Andalicia. *Consejeria del Medio Ambiente*, Sevilla, p 164.
- Xue H, Nhat PH, Gachter R, Hooda PS (2003) The transport of Cu and Zn from agricultural soils to surface water in a small catchment. *Adv Environ Res* 8:69–76.
- Yaqin JI, Yinchang F, Jianhui WU, Tan Z, Zhipeng B, Chiqing D (2008) Using geoaccumulation index to study source profiles of soil dust in China. J. Environ Sci. 20:571–578.
- Zhang C, Selinus O (1998) Statistics and GIS in environmental geochemistry–some problems and solutions. J. Geochem. Exp. 64:339-354.
- Zsefer P, Glasby GP, Sefer K, Pempkowiak J, Kaliszan R (1996) Heavy-metal pollution in superficial sediments from the southern Baltic Sea off Poland. *J. Environ Sci. Health* 31A:2723–2754.