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Elemental composition of crop field soil by X-Ray fluorescence (XRF) spectroscopy, Bangladesh subject

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Elements are important for soil that can yield information on soil nutrient content. Soil samples were collected from crops area in four different districts (Dhaka district, Narsingdi district, Mymensingh district and Kishoreganj district) in Bangladesh. Direct analysis of soil was carried out by X-ray fluorescence spectrometry with wavelength dispersion. Only total nitrogen was carried out by Kjeldhal method. The results showed that the order of major elements concentrations are Si>Al>Fe in the investigated areas. Trace amount of Ni, Y and Ba were found in the samples from all the study areas.

Key words: Soil element, x-ray fluorescence spectrometer (XRF), heavy metal and trace element.

INTRODUCTION

The soil is considered as a fundamental part of the global ecosystem having the crucial role of supplier of nutrients and mechanical support to plants. Furthermore, soils act as a sink for various chemical compounds including pollutants from anthropogenic activities. Pollution of the environment has an unfavorable effect on physicochemical properties of soil and its protective function. Observation of changes in chemical composition of soil plays an important role in estimating its pollution grade and permits choosing such methods of agricultural exploitation which delimit excessive passage of trace elements from soils to plants. Currently there exists a need to determine not only total concentration of elements in examined samples, but also concentrations of various forms in which these elements could exist. Bioaccumulation and influence on living organisms of these elements depends on their physicochemical forms. Examination of element distribution in soil is very important because under environmental conditions it can accumulate or release them (Ouddane et al., 1997). Various methods have been proposed for speciation analysis of soils. We met the methods based on calculation of element speciation, thanks to application of ready counting programs, such as: MICROQL (Boudot et al., 1994; Geiger et al., 1996) and WHAM program (WHAM 2012). These methods are based on knowledge of total concentration of elements, ligands and thermodynamic stability constants. NMR, XAFS and

SEM/EDX (Welter et al., 1999) are often in use as direct methods for speciation analysis of elements, whereas single and sequential extraction procedures are applied as indirect methods. Al, Fe, Zn, Mn for instance were examined using AAS (Chen et al., 2000; Davidson et al., 1999; Yaman, 2000), S by IC (Chen et al., 1997), Pb by DPASV (Sauve et al., 1998), Cr by photometric method (Rudel and Terytza 1999). The major part of Bangladesh is on the Delta formed by the three major rivers Brahmaputra, Ganges and Meghna. These rivers and many of the country's other minor rivers originate outside the national boundary of the country and make up the Ganges-Brahmaputra-Meghna river system.

The system drains a basin of some 1.76 million sqkm and carry not only snowmelt water from the Himalayas but also runoff water from some of the highest rainfall areas of the world. Over millennia, the sediments carried by the huge discharges of these rivers have built a broad Delta, forming most of the large area of Bangladesh and the submerged Delta-plain in the Bay of Bengal. These huge sediments are the major sources of formation of 80% soils of the country. The remaining 20% of soils have been formed in Tertiary and Quaternary sediments of hills (12%) and in uplifted pleistocene terrace (8%).

The Soil Resources Development Institute (SRDI) has identified about 500 soil series in Bangladesh. Soil series is a group of soils formed from the same kind of parent material under similar conditions of drainage, vegetation,

crop, climate and time, and having the same sequence of soil horizons with similar differentiating properties. Each soil series is known after a name of locality (eg Tejgaon series, Sara series, Ishwardi series, etc) (Brammer, 1996).

Only rural areas crop field soil was study for elemental analysis by XRF in four districts of Bangladesh. These areas farmer didn't understand why their crop products day by day decrease. For this, I decided find out the problem. The goal of this study to determine the elemental composition for discovering the deficiency of soil. To the best of my knowledge there is no published report on the elemental composition of study areas soil.

Geology of study area

Dhaka district

Total area of Dhaka District is 1,463.6 km². Main rivers flowing through this district are Padma, Kaliganga, Dhaleshwari, Ichamati, Shitalakshya, Buriganga and numerous smaller rivers including Bangshi, Turag, Balu, Elamjani, Alam, Bherujkha, Ramkrishnadi, Elisamari, Tulsikhali. Major lakes ("beels") include Belai, Saldaher, Labandaher, Churain, Damsharan and Kiranjir Beel. Annual average temperature of the district is maximum 34.5°C, minimum 11.5°C; average annual rainfall 1931 mm.

Dohar Upazila

The total area of Dohar Upazila is 161.49 km². One of the largest rivers of Bangladesh, the Padma, is situated in the southern and south-western part of Dohar. The land of the Dohar Upazila is formed mainly deeply flood phases soil and grey floodplain soils.

Nawabganj Upazila

The total area of Nawabganj Upazila is 244.81 km². The land of the upazila is formed mainly grey floodplain soils. Total cultivable land 18208.01 ha, fallow land 6272.76 ha; single crop 47.5%, double crop 37.8% and treble crop land 14.7%.

Keraniganj Upazila

Keraniganj stands on the southwest side of Dhaka City on the bank of the Buriganga river. The total area of Keraniganj Upazila is 166.87 km². The land of the upazila is formed mainly Madupur tract soils.

Savar Upazila

The total area of Savar Upazila is 280.13 sq/km (108.16 sq mi). The land of the upazila is composed of

alluvium soil of the Pleistocene period. The height of the land gradually increases from the east to the west. The southern part of the upazila is composed of the alluvium soil of the Bangshi and Dhalashwari rivers. Main rivers are Bangshi, Turag, Buriganga and Karnatali.

Dhamrai Upazila

The total area of Dhamrai Upazila is 307.4 km². Dhamrai Upazila is composed of the alluvium soil of the Bongshi and Dholessshori rivers. Other rivers are Kolmai and Gazikhali.

Narsingdi district

Narsingdi district with an area of 1140.76 sq km. Annual average temperature: maximum 36°C, minimum 12.7°C; annual rainfall 2376 mm. Main rivers are Meghna, Arial Khan, Haridhoa, Kalagachhia and Paharia. There are high hills with red soil on the northern region of the district.

Mymensingh district

The total area of Mymensingh district is 4363.48 sq km. The main river is Old Brahmaputra. Besides, there are small rivers, marsh, canals and forestry in the district. The soil formation of the district is flood plain, grey piedmont, hill brown and terrace. There are small valleys between the high forests; annual average temperature maximum 33.3°C, minimum 12°C; annual rainfall 2174 mm.

Kishoreganj district

The total area of Kishoreganj district is 2688.62 sq km. The soil formation of the district is alluvial sand coming from Brahmaputra, Meghna and other small rivers. The soil is fertile. Annual average temperature- maximum 33.3°C, minimum 12°C; annual rainfall 2174 mm. There are hills and hillocks on the northern and depressions on southern parts of the district. Main rivers are old Brahmaputra, Meghna, Kalni, Dhanu, Ghorautra, Baurii, Narasunda, Piyain.

MATERIALS AND METHODS

Study area

The study area (Figure 1) are situated in Dhaka district (without Dhaka city), Narsingdi District, Mymensingh District and Kishoreganj District in Dhaka division of Bangladesh.

Sample size

Samples were collected from four districts in Bangladesh.

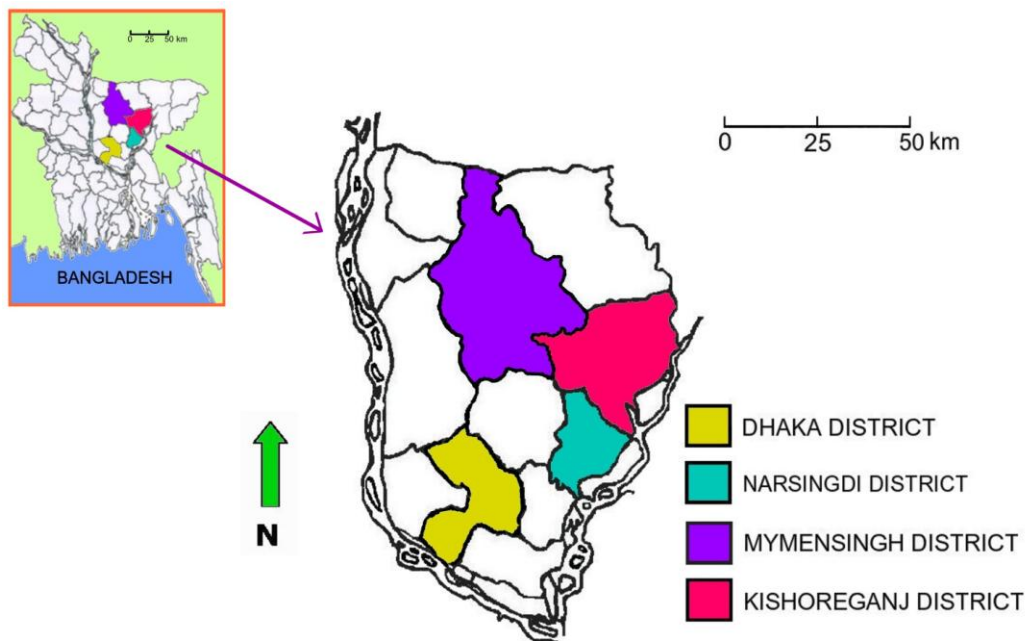


Figure 1. The four districts of the study area.

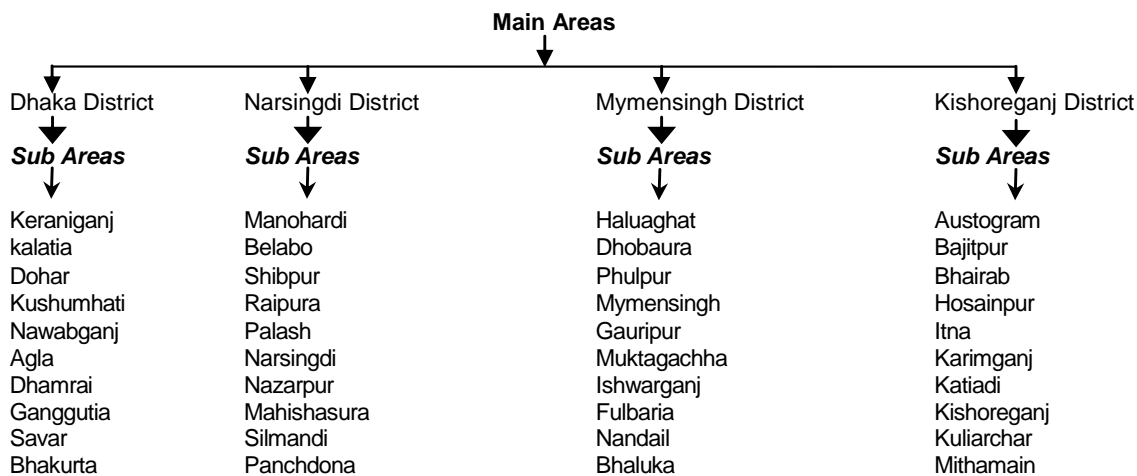


Figure 2. Flow chart of sampling area in Bangladesh.

Every district divided ten sub-areas and each sub-area has ten different areas. The ten different areas soils were collected and mixed and were made one sample for each sub-area. So, total hundred samples were collected for each district and, ten samples were analyzed for each district (Figure 2).

Soil sampling

Samples were collected from surface layer of soil (20 cm) and sampling dates were: January - March 2009. The sample of bulk soils were air-dried, crushed and

powdered to pass a No. 180 sieve. The powdered samples of soil were stored in clean polyethylene bottles until analysis.

pH, organic matter and total nitrogen

pH of analyzed soil samples was measured potentiometrically in water (soil and water ratio 1:2) using a potentiometer. Organic matter of soil samples was analyzed by loss on ignition method (Rowell, 1994). Obtained results are gathered in Figure 3. The total nitrogen of soil was carried out by Kjeldhal method

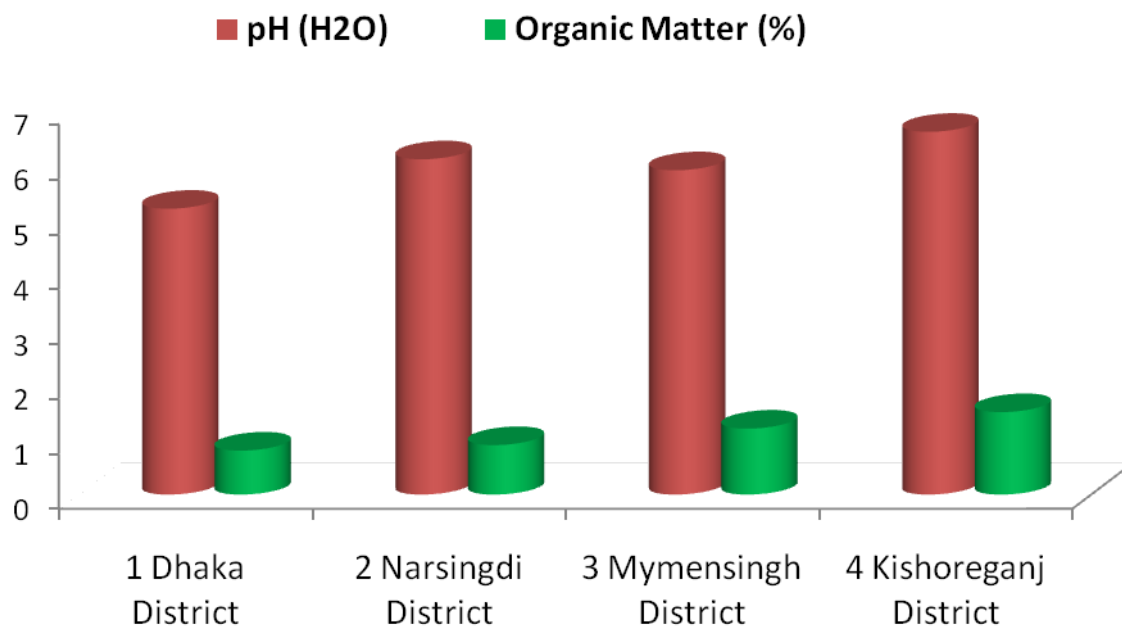


Figure 3. pH (H₂O) and organic matter of examined soils (mean).

(Didar-UI-Alam et al., 1991). Analytical or reagent grade solvents and chemicals (Sigma, E. Merck) were used in the analyses.

Pellets preparation

Pellets were prepared by mixing 4 g of moisture free soil powder with 0.4 g of pure stearic acid (as a binder) and homogenizing the mixture by using an agate mortar. These prepared samples were put down by the presser machine dice and add its upper 8 g pure boric acid as a base. These prepared samples were pressed at 12 tons for 60 s to obtain a cylindrical pellet 40 mm in diameter. Every sample was prepared three times for analysis. The condition for the preparation of the pellets was experimentally standardized.

Equipment and instrumental conditions

Samples were analyzed using a commercial WDXRF (Wavelength dispersive X-ray fluorescence spectrometer) in which calculate and fixed calculation methods were used in PW 2404 (specification: X-Ray tube with Rh target and also maximal 4 filter) WDXRF (PHILIPS, Netherlands). The X-ray generator was 4 KW with 60 KV, 125 mA (in steps). The generator was solid state based on 'Switch Mode Power Supply' design to respond fast the changes sought in X-Ray tube power. The scintillation detector was duplex (Xenon filled detector for mid range in tandem with flow counter). The P10 gas (is normally 90% Ar and 10% CH₄; gas output pressure 80 kpa) used

in flow detector as the quench gas. The recorded spectra were evaluated by the fundamental parameters method using the software linked to the equipment. Applied measurement parameters are depicted in Table 1.

Statistical analysis

The data was analyzed statistically using SPSS Ver. 12 for windows. The significance of differences among means was carried out using ANOVA test at $p < 0.05$. The results are expressed as the mean (g kg^{-1}) \pm SE (standard error).

RESULTS

Soil collected from various places of Bangladesh province and from the character of crop areas were analysis using the XRF method. Results of direct analysis of soil samples are presented in Table 2.

In Dhaka district, the value of silicon, phosphorus and zirconium were detected significantly higher ($p < 0.001$) in sample 1 between the sample 2, 3 and 4. Calcium in sample 1 showed higher significant ($p < 0.001$) value among the sample 2 and 3. The value of manganese was found significantly higher ($p < 0.001$) in Dhaka soil than in the Mymensingh and Kishoreganj soil. On the other hand, sample 1 in total nitrogen was showed higher significant ($p < 0.001$) value between the sample 3 and 4. In contrast, sodium, magnesium, aluminium, sulfur, potassium,

Table 1. Parameters of measurement program.

Compound formula	Elements	XRF Line	Crystal	Collimator	Detector
Na ₂ O	Na	K α	PX 1	550 μ m	Scintillation
MgO	Mg	K α	PX 1	550 μ m	Flow
Al ₂ O ₃	Al	K α	PE	550 μ m	Flow
SiO ₂	Si	K α	PE	550 μ m	Flow
P ₂ O ₅	P	K α 1	Ge	550 μ m	Flow
SO ₃	S	K α	Ge	150 μ m	Flow
Cl	Cl	K α	Ge	150 μ m	Flow
K ₂ O	K	K α	LiF 200	150 μ m	Flow
CaO	Ca	K α	LiF 200	150 μ m	Flow
TiO ₂	Ti	K α	LiF 200	150 μ m	Flow
MnO	Mn	K α	LiF 220	150 μ m	Flow
Fe ₂ O ₃	Fe	K α	LiF 220	150 μ m	Flow
NiO	Ni	K α	LiF 220	150 μ m	Flow
Rb ₂ O	Rb	K α	LiF 220	150 μ m	Flow
SrO	Sr	K α	LiF 220	150 μ m	Flow
Y ₂ O ₃	Y	K α 1	LiF 220	150 μ m	Flow
ZrO ₂	Zr	K α	LiF 220	150 μ m	Flow
BaO	Ba	K α	LiF 220	150 μ m	Flow

titanium and iron did not show significant differences in the soils samples of Dhaka district. Trace amount of nickel, rubidium, strontium, yttrium and barium were found in sample 1. Chlorine was not detected in sample 1. The pH and organic matter were found 5.2 and 0.8% in sample 1 respectively.

Narsingdi soil of pH and organic matter identified 6.1 and 0.9% respectively. Sodium, magnesium, potassium and iron of sample 2 showed significantly higher ($p < 0.001$) value than in sample 1. Silicon, calcium and zirconium in Narsingdi soil showed significantly higher ($p < 0.001$) value than in Mymensingh soil. Aluminium and titanium in sample 2 was showed significantly higher ($p < 0.001$ and $p < 0.001$, $p < 0.01$ respectively) value between sample 1 and 4. On the other hand, Narsingdi soil in total nitrogen was showed higher significant ($p < 0.001$) value between sample 1, 3 and 4. Phosphorus and rubidium did not show significant differences in the soils samples of Narsingdi. Trace element of sulfur, chlorine, manganese, nickel, strontium, yttrium and barium were found in sample 2.

In Mymensingh soil, the value of potassium ($p < 0.001$, $p < 0.01$ and ($p < 0.001$ respectively), Aluminium and iron ($p < 0.001$) were found significantly higher in sample 3 than in the sample 1, 2 and 4. Titanium in sample 3 was found significantly higher ($p < 0.001$ and $p < 0.01$) value among the sample 1 and 4. The value of sodium in sample 3 was showed significantly higher ($p < 0.001$) among the sample 1. Magnesium in sample 3 was found significantly higher ($p < 0.001$) value than in the sample 1 and 2. On the other hand, the value of phosphorus and manganese were found significantly higher ($p < 0.001$) in sample 3 than in the sample 2 and 4, respectively. In contrast, nitrogen, silicon, calcium, rubidium, strontium

and zirconium did not show significant differences in the soils samples of Mymensingh. Trace element of sulfur, chlorine, nickel, yttrium and barium were found in sample 3. The pH and organic matter showed in sample 3 were 5.9 and 1.2% respectively.

In the soil of Kishoreganj, the value of sodium and calcium were found significantly higher ($p < 0.001$) in sample 4 than in the sample 1, 2 and 3. Kishoreganj soil of silicon and phosphorus were showed significantly higher ($p < 0.001$) value than sample 2 and 3. The value of strontium in sample 4 were found significantly higher ($p < 0.001$) than in sample 3. Kishoreganj soil of aluminium, potassium and iron were found significantly higher ($p < 0.001$) value than in sample 1. On the other hand, magnesium in sample 4 was showed higher significant ($p < 0.001$) value than in sample 1 and 2. In contrast, nitrogen, sulfur, titanium and manganese did not show significant differences in the soils samples of Kishoreganj. Trace element of chlorine, nickel, rubidium, yttrium and barium were found in sample 4. The organic matter and pH showed in sample 4 were 6.6 and 1.5% respectively.

Discussion

Regarding soil formation, two distinct conditions occur in Bangladesh: alternating seasonal wet or inundated and dry conditions, as prevalent on most of the floodplain areas, and intermittently wet or moist or dry conditions, as on the upland areas of hills and Terraces. This is due to variation of agroclimatic parameters in different seasons. The soil formation process differs significantly between floodplain, hill and uplifted terrace.

The study areas are mainly floodplain and rainfall areas.

Table 2. Element concentrations (g kg^{-1} , dry weight) of soil samples obtained by calibration curves ($n = 100$ for each main area).

Compound formula	Elements	1 Dhaka District	2 Narsingdi District	3 Mymensingh District	4 Kishoreganj District
-	O	497.28±0.48	481.23±0.42	478.59±0.39	482.32±0.25
-	N**	1.25±0.02 ^a	1.58±0.02 ^d	1.07±0.01	1.12±0.01
Na ₂ O	Na	1.70±0.09	5.05±0.01 ^e	5.14±0.02 ^h	5.79±0.13 ⁿ
MgO	Mg	5.86±0.03	16.44±0.13 ^e	18.70±0.2 ⁱ	18.76±0.15 ^o
Al ₂ O ₃	Al	79.25±0.17	108.38±0.27 ^f	113.52±0.19 ^j	98.40±0.27 ^p
SiO ₂	Si	341.95±0.60 ^b	297.57±0.13 ^g	286.30±0.17	300.19±0.23 ^q
P ₂ O ₅	P	3.92±0.04 ^b	0.301±0.01	0.712±0.01 ^k	1.63±0.07 ^q
SO ₃	S	0.945±0.01	tr	tr	1.17±0.03 ^p
Cl	Cl	ND ^s	tr	tr	tr
K ₂ O	K	19.77±0.1	27.55±0.12 ^e	28.33±0.24 ^{βj}	27.38±0.14 ^p
CaO	Ca	10.69±0.03 ^c	9.54±0.08 ^g	8.47±0.08	11.42±0.07 ⁿ
TiO ₂	Ti	5.44±0.04	5.93±0.01 ^{βf}	5.99±0.13 ^{βl}	5.61±0.09
MnO	Mn	0.844±0.01 ^a	tr	0.807±0.004 ^m	0.602±0.01
Fe ₂ O ₃	Fe	31.77±0.09	47.60±0.15 ^f	53.05±0.15 ^j	46.37±0.14 ^p
NiO	Ni	tr ^t	tr	tr	tr
Rb ₂ O	Rb	tr	0.166±0.01	0.17±0.002	tr
SrO	Sr	tr	tr	0.028±0.01	0.127±0.01 ^r
Y ₂ O ₃	Y	tr	tr	tr	tr
ZrO ₂	Zr	0.583±0.01 ^b	0.236±0.01 ^g	0.193±0.003	0.223±0.004
BaO	Ba	tr	tr	tr	tr

Results expressed as mean ± standard error; ANOVA test with superscripts in each row indicate significant statistical difference at $\alpha = p < 0.001$; $\alpha = p < 0.002$ and $\beta = p < 0.01$; ** N of soil sample was analyzed by Kjeldhal method; ^asample 1 vs. sample 3 and 4; ^bsample 1 vs. sample 2, 3 and 4; ^csample 1 vs. sample 2 and 3; ^dsample 2 vs. sample 1, 3 and 4; ^esample 2 vs. sample 1; ^fsample 2 vs. sample 1 and 4; ^gsample 2 vs. sample 3; ^hsample 3 vs. sample 1; ⁱsample 3 vs. sample 1 and 2; ^jsample 3 vs. sample 1, 2 and 4; ^ksample 3 vs. sample 2; ^lsample 3 vs. sample 1 and 4; ^msample 3 vs. sample 4; ⁿsample 4 vs. sample 1, 2 and 3; ^osample 4 vs. sample 1 and 2; ^psample 4 vs. sample 1; ^qsample 4 vs. sample 2 and 3; ^rsample 4 vs. sample 3; ^snot detected; ^tstands for a trace element with peak intensity, the significance is too low for quantification.

The soil contains the bulk of nutrients for plants. It consists of the mineral or inorganic portion accounting for 90 to 99% in most soils and the organic portion which is a major factor of their fertility. The average elementary composition of the soil was estimated in the investigation (four areas soil) that the oxygen accounts for almost half of the soil, silicon for a second, aluminium and iron for more than 10% and the rest of the elements accounting for only 7% (Table 2), it was comparable to Vinogradov (Yagodin, 1984).

On the basis of pH measurement (Figure 3) it is possible to divide analyzed samples into the following groups: acid and sub-acid soil (sample 1 and 3) and neutral soils (samples 2 and 4). Acid soils belongs the sandy and neutral to the sandy-loamy soils. Acid soils are prone to increased leaching of important components and decreased assimilation of such macroelements as P, K and Mg by plants. Plants growing on alkaline soils can have troubles with assimilation of Fe, Cu and Mn. The effect of acidifying of soils is visible in decreasing their

saturation with exchangeable cations and successive loss of Ca and Mg and simultaneous activation of toxic compounds of Al, Mn, Fe and accumulation of heavy metals (Pb) by plants.

From the above results it is evident that the organic matter percentage level was 0.8 - 1.5% meaning that there is a low organic matter content in the soils, difficulties would have been faced due to the structural soil water and also the conversion of sulphides into sulphur dioxide, further problems were faced in the organization where an oven was used in the experiment instead of a furnace as specified in the manual.

Soil is classified depending on the size of particles and also the level of organic matter it contains, the loamy sand soils will usually contain less than 1% of organic matter, silt loam will contain 1 to 4% of organic matter and therefore it is clear that due to the low level of organic matter in these soils we can conclude that because it contains less than 1.5% of organic matter then the soil type is loamy sand and silt loam (White, 2006). All the study area soils are needed to increase organic matter percentage, to get the good crop.

Taking into results of speciation analysis describe below:

Solubility of mineral in the soil is an important factor to absorption and translocation of water and inorganic nutrients by root for plant nutrition. All soil samples were found potassium, sodium, chlorine, calcium, magnesium, phosphorus and sulfur, its stay in soil as a salt of carbonate, sulfates, nitrates, chlorides, and phosphates. Most of these salts are readily soluble in water and are present in soils in small amounts. All soils always contain poorly soluble salts of phosphoric acid (Calcium, magnesium, iron and aluminium phosphates).

Plant cannot complete its full life cycle without 17 essential plant nutrients (viz. macronutrients: nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, silicon, micronutrients (trace levels) include: chlorine, iron, boron, manganese, sodium, zinc, copper, nickel, molybdenum). Without boron and molybdenum, all essential nutrients were identified in the entire investigation area sample.

N is observed higher in sample 2. On the other hand lower nitrogen found in sample 3. The range of 1.12 – 1.25 g kg⁻¹ of N was found in crop fields (sample 1 and 4). Because of low level of OM (organic matter) the nitrogen status of Bangladesh soils is substantially low and most crops on all soils respond to nitrogen applications. In fact, nitrogen (N) fertilizers are the most commonly used fertilizers in the country. Compared to production with no fertilizers, a 2 to 3 fold increase is common in most crops including rice with N-fertilizers. Nitrogen may be taken up in two forms, nitrate and ammonium. Nitrogen can be supplied for plant growth from several sources which are atmosphere, biological fixation, atmospheric fixation, precipitation, commercial fertilizers, soil organic matter, crop residues, animal manures. On the other hand, nitrogen is lost from the soil system in several ways

which are leaching, denitrification, volatilization, crop removal, soil erosion and runoff.

P was found higher value in the Dhaka soil. On the other hand, lower value was found in Narsingdi soil. Large amounts of P required by plants. Phosphorus is one of the three nutrients generally added to soils in fertilizers. In contrast to N, P are very insoluble in soil systems. The available phosphorus in Bangladesh soils could be considered between low and medium. Most soils respond to P-fertilisation. Maintaining proper soil pH is critical to providing adequate P for optimum plant growth. Within the range of pH 5.0 to 7.5, P solubility is maximized, but is still low compared to the other primary and secondary nutrients. Study area pH found within the range of pH 5.1 to 7.5. So P solubility of study area soil is high.

Mg and Ca in Mymensingh and Kishoreganj soil were found higher value than other soil samples respectively. This could be connected with a presence of clay. Ca, Mg and Fe are essential nutrient elements for all living cells and play an important role in photosynthesis and carbohydrate metabolism (Malik and Srivastava, 1982). In acid soils there appears worse bioaccumulation of Mg by plants. Calcium is the dominant positively charged molecule in nearly all soil systems except those with a very low pH. In acid soils, however, Ca is subject to leaching and native Ca levels may be low. This situation can be corrected by using a liming material.

Al and Si were found in all soil samples. Al was found in higher concentration in two samples from Narsingdi and Mymensingh soil. Highest concentration Si was found in sample 1 and lowest in sample 3. In acid soils, Al could force out other cations from sorption complex and leads to its degradation. Al could exist in various soluble forms, like: AL³⁺, Al-OH, Al-SO₄. Si in soluble form can occur as orthosilicic acid, whose solubility increases with increase of pH, but the influence of P, Al, Ca and Fe here is important, too.

S in examined soil occurs mainly in sample 1 and 4. Trace amount of S was present in sample 2 and 3. Response to sulphur (S) application is common in most soils except in coastal saline soils, acid sulphate soils and some acidic soils in Bangladesh. Sulfur is taken up by plants as the negatively charged sulfate (SO₄²⁻) molecule. Sulfur availability, therefore, is controlled largely by the amount and rate of organic matter decomposition. In most soils, adequate S for crop plants is supplied through this process and through rainfall. Sulfur may be supplied in many complete fertilizers or may be applied in materials like gypsum (CaSO₄) or elemental S.

K was found in all investigated area soil sample (19.77 – 28.33 g kg⁻¹). The higher value of K was found in sample 3 (28.33 g kg⁻¹). Bangladesh soils are not deficient in potassium (K) although many soils are found to respond to K-fertilisation. These are particularly non-alluvial soils and the coastal saline soils. K is an essential

nutrient element and has an important role mainly accumulates in the green leaves and activates enzymes of carbohydrate metabolism (Malik and Srivastava, 1982). Most K is held as part of the soil minerals structure, or inside layered clay particles, and may become available very slowly. The release of K from K-bearing minerals is usually not sufficient for crop plants. A large amount of K can be taken up by crop plants and this must be replaced by inorganic or organic fertilizers.

Mn found mainly in 3 samples: Dhaka, Mymensingh and Kishoreganj. Trace amount of Mn was identified in Narsingdi. Mn solubility is affected by soil water content. Under waterlogged conditions Mn becomes very soluble and can reach toxic levels. This is most likely to occur in acidic soils with pH levels less than 5.5 (it may be occur in sample 1), although it can happen even when soils are not very acidic. Manganese deficiency can be induced when acidic, low-lying sandy soils are limed to pH levels above 6.5, or when wet, sandy soils are drained.

Fe in soils found lower in Dhaka and Kishoreganj (31.77 and 46.37 g kg⁻¹) and higher in Narsingdi and Mymensingh (47.60 and 53.05 g kg⁻¹ respectively). Solubility of Fe compounds increases with the decrease of pH. Compounds and minerals of Fe and its complex with organic matter are very important in soil forming processes and they influence other elements. All Fe minerals have a large sorption capacity for other metals. Organic compounds increase mobility of Fe and its bioavailability for plants.

Bo and Mo was not identify in the investigation areas. Boron is present in soils as an uncharged molecule that is held weakly by various mineral and organic soil constituents and can be easily leached, particularly from sandy soils. Boron helps in the plant to use of nutrients and regulates other nutrients and also aids to production of sugar and carbohydrates. It is essential for seed and fruit development. The boron was sources of soil, organic matter and borax.

Molybdenum helps in the plant to use of nitrogen. Higher plants require molybdenum in extremely small amounts. Molybdenum is most soluble at high pH levels and is most likely to be deficient in acidic sandy soils. However, Mo deficiencies are sometimes found in moderate pH, fine textured soils. This finding indicates that fertilizer of born and molybdenum would need to the study areas crop field.

Cl was found as a trace element in Narsingdi, Mymensingh and Kishoreganj soil samples. Cl was not detected in Dhaka soil. Cl is essential for plant growth, root formation, photosynthesis and fruiting (Oser, 1979). Chlorine is really deficient in agricultural soils. In fact there are more problems with excess Cl in saline soils than with deficiencies. The functions of Cl are poorly understood, but it appears that Cl is involved in both cold and drought plant tolerance. Chlorine deficiencies (sample 1) may also be involved in disease susceptibility. Adequate Cl is provided by rainfall, air pollution, and in

various fertilizer materials in most situations.

Rb and Sr are observed in all soil samples. Small amount of Rb was found in Narsingdi and Mymensingh areas soil respectively. On the other hand, trace amount of Rb found in sample 1 and 4. However small amount of Sr in Mymensingh (0.028 g kg⁻¹) and Kishoreganj (0.127 g kg⁻¹) was found. On the other hand, trace amount of Sr found in Dhaka district and Narsingdi. Increasing Rb content in crop field could be connected with a large content of organic matter, its acidity and fertilization. In the light acid soils Sr is easy leachable while in neutral soils it could be initiated and bioaccumulated by plants (sample 3).

Fe, Mn, Rb and Sr in acid soils is easily leachable and worse: bioaccumulated by plants. Their organic and mineral-organic compounds are very important in soil-forming processes and influence other elements.

Potentially toxic element like Co, Cd, As, Cr, Pb and Hg were not detected in the investigated areas soil in Bangladesh. On the other hand, serious environmental pollution occurred by the dying and tannery industries at Dhaka City in Bangladesh. Rahman et al. (2007) reported that the content of Pb and Cd in dying (Bamoil, Demra) and tannery (Hazaribagh) industries areas soil were found 28.94 ppm, 32.88 ppm and 1.85 ppm, 1.57 ppm, respectively. Conversely, Kashem and Singh (1999) were investigated that the heavy metal contamination of soil in the vicinity of industries around Dhaka city in Bangladesh. They were collected soil from tannery, ceramic, textile dying and sulphuric acid producing industrial sites. They were found that the concentrations of total Cd, Cu, Mn, Ni, Pb and Zn ranged from 0.1–1.8, 28–217, 106–577, 25–112, 17–99 and 53–477 mg kg⁻¹ soil, respectively among the industrial sites. They were also observed that the concentrations of some heavy metals ranged from background levels to levels in excess of tolerable limits in agricultural soils and the concentrations of total Cu, Mn, Ni, Pb and Zn decreased with increasing distance from the disposal points of the tannery and the textile dying industries.

Toxic levels (Cetesb, 2007) were not exceeded in the finding elements of the study areas soil. At present investigated soils quality were not polluted by urbanization and industrialization. It may be occur that the areas situated far distance of urbanizations vehicle and industrial pollution.

Conclusions

Summarizing the obtained results it was found that:

- application of the XRF method gives us the possibility to realize quick multielement soil analysis and speciation analysis. It is reported for the first time in the crop areas soil of Dhaka, Narsingdi, Mymensingh and Kishoreganj district.

- obtained results give us information on the main

contents of the soil elemental composition and its nutrition. Cl was not found in Dhaka. All essential nutrients were identified in the entire investigation areas sample, without boron and molybdenum.

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REFERENCES

- Boudot JP, Merlet D, Rouiller J, Maitat O (1994). Validation of an operational procedure for Al speciation in soil solutions and surface waters. *Science of the Total Environment*. 158: 237-252.
- Brammer H (1996). *The Geography of the Soils of Bangladesh*. UPL, Dhaka.
- Cetesb—Companhia de Tecnologia de Saneamento Ambiental (2007). 'Qualidade do ar no Estado De Sao Paulo – Serie Relatorios'. Sao Paulo. [Internet] Available from: <http://www.cetesb.sp.gov.br/Ar/publicacoes.asp>.
- Chen B, Shan X, Shen D, Mou S (1997). Nature of the HCl-soluble sulfate in the sequential extraction for sulfur speciation in soils. *Fresenius' J. Anal. Chem.*, 357: 941-945.
- Chen ZS, Lee GJ, Liu JC (2000). The effects of chemical remediation treatments on the extractability and speciation of Cd and Pb in contaminated soils. *Chemosphere*. 41(1-2): 235-242.
- Davidson CM, Ferreira PCS, Ure AM (1999). Some sources of variability in application of three-stage sequential extraction procedure recommended by BCR to industrially-contaminated soil. *Fresenius' J. of Anal. Chem.*, 363(5-6): 446-451.
- Didar-Ul-Alam M, Huq SMI, Rahman MS, Anam K (1991). *A Handbook on Chemical Analyses of Soil, Plant and Water*, first ed. Dhaka.
- Geiger G, Gfeller M, Furrer G, Schulin R (1996). Soil bacteria sensitivity towards heavy metals- Experimental system optimisation using chemical speciation calculations. *Analytical and Bioanalytical Chemistry*. 354(5-6): 624-628.
- Kashem MA, Singh BR (1999). Heavy Metal Contamination of Soil and Vegetation in the Vicinity of Industries in Bangladesh. *Water, Air, and Soil Pollution*. 115(1-4): 347-361.
- Malik CP, Srivastava AK (1982). *Plant Physiology*. Kalyant Publisher, New Delhi, India.
- Oser BL (1979). *Hawk's Physiological Chemistry*. Fourth ed. Tate McGraw-Hill, New Delhi, India.
- Ouddane B, Martin E, Boughriet A, Fischer JC, Wartel M (1997). Speciation of dissolved and particulate Mn in the seine river Estuary. *Marine Chemistry*. 58(1-2): 189-201.
- Rahman MM, Haoliang L, Chongling Y, Hoque SS (2007). Heavy Metal Hyper-accumulation in Plants and Metal Distribution in Soil on Tannery and Dying Industries Polluted Area in Bangladesh. *Academic Open Internet Journal*. 21. [Internet] Available from: <http://www.acadjournal.com>
- Rowell D (1994). *Soil science: methods and applications*. Longman press, UK.
- Rudel H, Terytze K (1999). Determination of extractable chromium (VI) in soils using a photometric method. *Chemosphere*. 39(4): 697-708.
- Sauve S, McBride M, Hendershot W (1998). Soil solution speciation of Pb(II): effects of organic matter and pH. *Soil Science Society of America*. 62(3): 618-621.
- Welter E, Calmano W, Mangold S, Troger L (1999). Chemical speciation of heavy metals in soils by use of XAFS spectroscopy and electron microscopical techniques., *Fresenius' J. of Anal. Chem.*, 364(3): 238-244.
- WHAM (Weighted Histogram Analysis Method) (2012). Processing results of UNRES/MREMD simulations, Department of Molecular Modeling, Faculty of Chemistry, University of Gdansk, Sobieskiego 18, 80-952 Gdansk, Poland. [Internet] <http://www.unres.pl/sites/unres/files/v3/whamman-v.3.2.pdf>
- White R (2006). *Principles and practice of soil science*. Blackwell publishers, Oxford.
- Yagodin BA (1984). *Agricultural Chemistry*. First publish, Mir Publishers, Moscow.
- Yaman M (2000). Nickel speciation in soil and the relationship with its concentration in fruits. *Bull. Environ. Contamination and Toxicol.*, 65(4): 545-552.