A Study of Elemental Profile of Soil of EPZ area, Savar, using PIXE Technique

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Abstract: *The well-established powerful ion beam analytical technique, particle induced X-ray emission (PIXE) has been utilized for the determination of the elemental concentration of soil of Savar EPZ area, Dhaka. In this work 9 soil samples have been collected from different location of Savar EPZ area. The adequate modernized facilities available in the accelerator laboratory of Atomic Energy Centre (AEC), Dhaka have been used for the research work, from sample preparation to data analysis and also for research writing. The proton beam energy 2.2 MeV and the current range 10-15 nA are used in my experiments. Microprocessor control Freeze Drying system, Oven (0-220 V), Microbalance and pellet maker have been used for sample preparation. A [Si (Li)] detector with associated other equipments such as amplifier, pre-amplifier, MCA Buffer, PC are used for data acquisition. The energy of the emitted X-rays indicates the identity of the elements and the intensity of the X-rays emission gives a measure of the concentration of the element present in the samples. The software MAESTRO-32 has been used for data acquisition and the collected spectrum data has been analyzed using GUPIX/DAN-32 software. The thickness of Beryllium (Be) window of the detector is 25 µm. The scattering chamber has 19 different ports, one CCTV camera, light inside the chamber, electron suppressor, faraday cup, vacuum pumping system etc and a computer controlled sample wheel, which is electrically isolated from the chamber.*

The detected elements in soil samples and their concentration are Aluminium (2110 to 8384 µg/g), Chlorine (28 to 423 µg/g), Potassium (5009 to 8485 µg/g), Calcium (1430 to 8040 µg/g), Scandium (41 to 150 µg/g), Titanium (1454 to 3588 µg/g), Vanadium (45 to 148 µg/g), Chromium (65 to 147 µg/g), Manganese (237 to 929 µg/g), Iron (8620 to 19554 µg/g), Nickel (10 to 746 µg/g), Copper (3 to 44 µg/g), Zinc (22 to 108 µg/g), Germanium (7 to 25 µg/g), Selenium (2 to 8 µg/g), Rubidium (84 to 902 µg/g), Strontium (60 to 207 µg/g), Yttrium (5 to 43 µg/g) and Zirconium (126 to 835 µg/g).

It is shown that Concentration of Iron is in large amount among all elements present in the soil samples. This is an alarming signal for soil and environment pollution. Also the presence of Chromium and Titanium, though the concentrations are very small, are very harmful for harvest.

Keywords: *Elemental profile of soil, PIXE technique, Functions of soil, Trace element of soil, Toxicity, Gamma ray spectrometry.*

I. Introduction:

Soil is one of the three major natural resources alongside air and water. It is one of the marvelous products of nature and without which there would be no life. It is made up of three main components- minerals that come from rocks below or nearby, organic matter which is the remains of plants and animals that use the soil and living the organisms that reside in the soil. It performs four important functions: it is a medium for plant growth; it is a means of water storage, supply and purification; it is a modifier of the atmosphere of earth; and it is a habitat for organisms that take part in decomposition of organic matter and the creation of a habitat for living organisms.

Soil is considered to be the "skin of the earth" with interfaces between the hydrosphere, atmosphere of earth, and biosphere. Soil consists of a solid phase of minerals and organic matter) as well as a porous phase that holds gases and water. Accordingly, soils are often termed as a three state system.

Soil is the end conduct of the influence of the climate, relief (elevation, orientation, and slope of terrain), biotic activities (organisms), and parent materials (original minerals) interacting over time. Soil continually undergoes development by way of numerous physical, chemical and biological processes, which include weathering with associated erosion.

So it is necessary to promote more extensive investigation on major, minor, and trace elements, particularly in Bangladesh due to the demand and availability. An element is considered to be essential if its deficiency consistently results in the impairment of the function of a human organ from optimal to sub-optimal [1]. In general trace element can be considered as [2] present in all healthy tissues of all living things, its withdrawal from the body induces reproducibly the same physiological and structural abnormalities, its addition either reverses or prevents these abnormalities, biochemical changes can be prevented or cured through addition of trace elements.

Copper and **Zinc** absorption is closely related, and although copper is also needed in relatively small amounts, some discussions are under way on the optimum need of this mineral. Acute Copper poisoning occurs in man when grams of Copper Sulfate are ingested accidentally [3]. If Copper is deficient in the body, iron is also normally in short swallow leading to anemia as well as the likelihood for infections, osteoporosis, thinning of bones, thyroid gland dysfunction, heart diseases as well as nervous system problems. Systematic toxic effects of Copper poisoning include hemolysis, hypatic necrosis, gastrointestinal bleeding, oligureia, azotemia, hemglobinuria, hematuria, proteinnuria, hypotension, tachycardia, convulsions and death [4].

Fluorine is a constituent of bones and teeth. It is beneficial in most cases in preventing dental caries, but the addition of fluoride to drinking water has become a controversial subject in some societies. The enamel of teeth normally contains a small percentage of fluorine. If during the period of tooth development, children drink water that contains about 1 part per million of fluoride, the tooth decay is markedly reduced, compared with similar situation in which the drinking water contains no fluoride. This was first observed in the communities where the water supply naturally contained a small percentage of dissolved fluorides [5].

Boron is distributed throughout the tissues and organs of the animal at concentrations mostly between 0.5 and 1.5 ppm dry basis in the soft tissues and several times these levels in the bones. Human being and other animals take boron through fruits and vegetables at the ppm level. An optimum concentration of boron in soil is very essential for the growth and production of rice, potato, oat, Soya bean, tomato, and some other plants [6].

Normally if the concentration is more than 2.0 ppm, it is considered as toxicity. The excess of boron may cause gastrointestinal and pulmonary disorders in animals. A shortage of boron might negatively influence the balance of calcium, magnesium and phosphorus resulting in bone loss, and increasing the risk of arthritis and elevated blood pressure [7].

Molybdenum is a component of three different enzymes, which is involved in the metabolism of nucleic acids- DNA and RNA- iron as well as food into energy. These three enzymes are sulfite oxidase, xanthine oxidase, and aldehyde oxidize. The deficiency of this element and the metabolic disorders are accompanied by abnormal excretion of sulfur metabolites, low uric acid concentrations, and elevated hypoxanthine and xanthine excretion. A causative relationship between high intake and gout in some areas of Armenia, USSR, has been reported. [8]

Selenium used to be treated as a very toxic substance, but modern science now regards it as essential – but in small quantities. The toxic effects of selenium have been recognized for a long time. An isolated instance of selenium poisoning by well water containing 9 ppm selenium was reported [9]. It is helpful in fighting infections since it stimulates increased antibody response to infections, promotes more energy in the body, and while it helps with alleviating menopausal symptoms in women, it assists the male in producing healthy sperm. In certain cases selenium has also proven effective in helping to fight cold sores and shingles, which are both caused by the herpes virus [10].

Chromium is an essential nutrient required for normal sugar and fat metabolism and works primarily by potentiating the action of insulin. It is present in the entire body but with the highest concentrations in the liver, kidneys, spleem and bone [11].

Nickel occurs in low concentrations in all animal tissues and fluids that have been examined by sufficiently sensitive and reliable analytical methods. High concentrations nickel can result in DNA damage. Demerits is most commonly associated with industrial exposure. High level occupational exposure has been associated with renal problems and effects such as vertigo and dyspnoea have been observed [12].

Sodium is important for conducting nerve impulses. It's the major electrolyte of extra cellar fluyid. The minimum requirement of sodium for an adult is about 500 mg per day [13]. However, according to FDA

food leveling rules the daily need for Na is 2400 mg. It has been observed experimentally that almost all plants contain sodium in conciderable quantity. But there is no sufficient information about its role in plant metabolism. However, the essentiality of sodium as a micronutrient has been established for the halophyte Atriplexvesicaria [14].

Developments of complementary techniques are, therefore, always desirable and sometimes become essential or the analysis of all groups of elements present in a sample. In the present study we used PIXE technique. For a long time X-ray emission has been used for analytical purposes, mainly in the form of charged particle induced X-ray emission analysis (PIXE). This analysis provides high Z elemental analysis such as Calcium, Titanium, Manganese, Iron, Cobalt, Nickel, Copper, Zinc, Gallium, Bromine, Rubidium, lead etc. It is known that X-ray spectra arise when electron vacancies occur in the inner orbital in the atoms. These vacancies are created principally in bombardment by electrons or high energy charged particles, irradiations by photons X-ray tubes or radioisotopes. PIXE is generally used for the determination of elements from Z number 11 to the rest.

II. Procedure And Methodology

The fundamental purpose of the PIXE technique is to determine the concentrations (relative or absolute) of elemental constituents in the sample under investigation. The calibration of PIXE system, in which sensitivity factors are determined for the use in assigning number of count on the X-ray peak to absolute concentration data as a function of atomic number, has been the subject of a number of articles [15].

In PIXE technique during concentration calibration process we mainly followed the H value method described in [16], which is based upon the equation,

$$Y(Z, M) = Y_1(Z, M) QC_z T(Z)\varepsilon_z H$$

Where $Y(Z, M)$ is the measured X-ray yield computed by the fitting program, $Y_1(Z, M)$ is the theoretical X-ray yield per unit beam charge, per unit solid angle and per unit concentration computed from the GUPIX database, Q is the measured beam charge or some value proportional to the charge, C_z is the concentration of the element quoted by the manufacturer or measured by some other method, $T(z)$ is the fractional transmission of X-ray through any absorber, ε_z is the intrinsic detector efficiency, and H is the product of detector solid angle and any correction factor for the charge measurement. It also includes the imperfection in the various database used in GUPIX [17].

Uses of PIXE technique: PIXE technique is now used in many laboratories around the world for elemental analysis of the samples of environmental, biological, human health, geological and archeological interest. In Atomic Energy Center, Dhaka, the PIXE technique has already been used several times for trace elemental analysis.

To provide sufficiently good statistics due to practical experimental reasons (cross-section, detection efficiency etc.) some techniques requires higher currents than other. So they are divided into high current techniques and low current techniques sometimes called imaging techniques.

Among the different IBA techniques, the Proton Induced Gamma Emission (PIGE) method in particular, is suitable for the analysis of light elements in the range of $3<Z<21$ [18] and the Proton Induced X-rays Emission (PIXE) method in particular, is suitable for the analysis of heavy elements in the range of high Z regions ($Z \geq 11$).

Particle-induced X-ray emission or proton-induced X-ray emission (PIXE) is a technique used in the determining of the elemental make-up of a material or sample. The block diagram of sample irradiation and X-ray detection system under IBA setup is shown in figure-2 below.
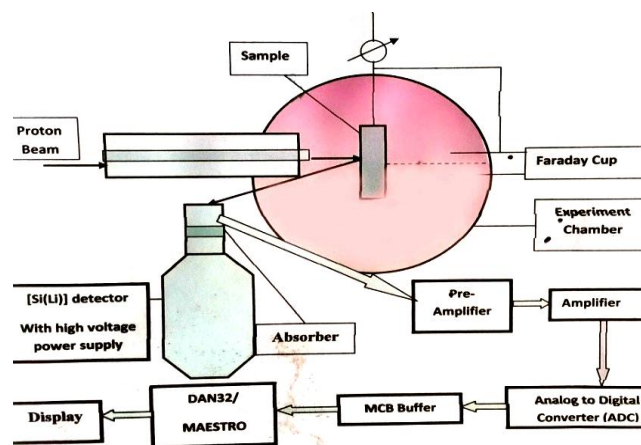

Fig. 2: Block diagram of PIXE technique under IBA setup with basic physical parameters

Radiation Detection and Assessment: When charged particles hit a sample with sufficient energy a vacancy in the inner shells of an atom may be created. The probability of creating a vacancy is higher when velocity of the incoming ions matches the velocity of the inner shell electrons. For MeV ions, the probability (cross-section) for ejecting inner shell electrons is quite high (of the order of barns) [19].

Gamma ray spectrometry: Gamma ray photons are uncharged and create direct ionization or excitation of the material through which they pass. The detection of gamma ray is therefore depending on causing the gamma ray photon to undergo an interaction that transfers all or part of the photon energy to an electron in the absorbing material. Although a large number of possible interaction mechanisms are known for gamma-ray in matter, only three major types play an important role in radiation measurements. They are photoelectric effect, compton effect and pair production. All these process partially or completely transfer gamma ray energy to electrons in the atom of the interacting medium. These processes are strongly depending on photon energy and the atomic number Z of the interacting materials. Other effects such as Rayleigh scattering, Thomson scattering and others are much less important [20] and so ignored in detection process.

Sample preparation and data acquisition: The study area of this research is selected in Export Processing Zone (EPZ) areas, Savar that are located near Dhaka city. Many Garment industries are established at this area. These industries are continually discharging their washes in the open natural canals and sometimes directly into the ground without any treatment, which pollutes the soil. Three specific locations are selected in the EPZ area, Savar for my research work. Soil samples have been collected from different depths. The details of sample collection procedure are shown in the Table 1.

Table 1: Selected Area, Depth and Quantity of Soil Sample

Sl No.	Selected Area	Depth (ft)	Quantity of Sample
1	Around EPZ main road, Savar	1	2
2	Around EPZ main road, Savar	2	2
3	EPZ residential area, Savar	1	3

Concentration calibration: In the case of PIXE analysis, the concentration calibration is defined as the number of X-ray per ppm of the element of interest per micro coulomb vs. its atomic number. The concentration calibration curves were constructed from the average peak areas obtain from the irradiation of 0.025 gm standard pellets. The typical curves obtained from these standards for 10 μC irradiation with 2.2 MeV proton beam. In this research the samples and the respective standards were assumed to be similar in matrix composition on the ground. This assumption is again verified experimentally.

Calculation procedure: The main objective of the PIXE experiment is to identify the presence of unknown elements signature in the X-ray and the quantitative calculation of their concentration from the measured X-ray yields. There are many programs that are used for unfolding the X-ray spectra such as AXIL, MAESTRO, and GUPIX etc. In this research work we have used well established MAESTRO-32 software for unfolding the X-ray spectra. Then we analyzed the spectrums data into concentration of different elements present in the samples using GUPIX software. The typical PIXE spectrum of soil sample is shown in fig.3.
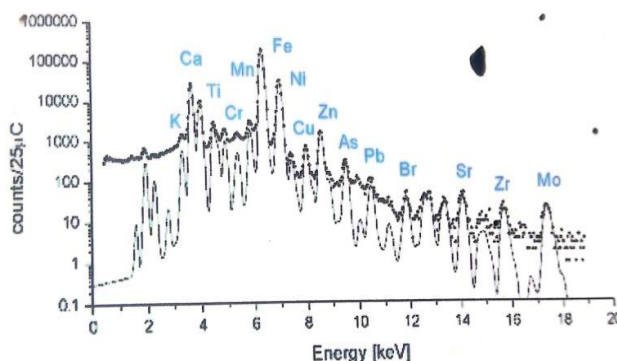

fig.3: Typical PIXE spectrum of soil sample

Qualitative Analysis: The analytical information on the presence and concentration of separate elements in a sample is confined in a complex spectrum of characteristic X-ray peaks sitting on an energy dependent continuum.

In PIXE analysis, frequently X-ray line spectra for twenty or more elements are simultaneously recorded. Such complex spectra contain more than thirty X-ray lines and often complicated by multiple interferences, depending on the nature of analytical samples. The ideal spectrum consists of Gaussian peak situated on a continuum background. But in practice, however, spectral analysis is complicated by presence of sum and escape peaks and plus distortion in the basic Gaussian shape and interference between the characteristic peaks of different elements. Inter-element interferences can occur either as an interference between the K_β signal from element Z and K_α signal from element (Z+1) or (Z+2) or as an interference between a particular K-line of a low or medium Z element with a L-line of a high Z element.

Commonly encountered interferences include the K K_β - Ca K_α, Mn K_β - Fe K_α, Ni K_β - Cu K_α, Br K_β - Ru K_α and As K_α - Pb L_α interferences. Fortunately, only a few combinations of elements which have the potential to interferences, are found in naturally in sufficient concentrations.

The qualitative analysis of different elements in a spectrum is performed by identifying the intense peak originating from a particular X-ray line of the constituent element at the corresponding X-ray energy. One or two X-ray lines are normally sufficient for the positive identification of an element in qualitative terms.

Quality assurance assessment of the PIXE technique: In PIXE analysis, it was customary to use the standard samples to established the cross-section or reaction yield for the specific experimental conditions and then to use the stopping power corrections to measurements of the unknown samples. For the samples of similar in composition, the correction for matrices was negligible for the absolute measurements requiring only the determination of the yield and the charged collected. No attenuation correction was required. It should be noted that such approximations introduce symmetric errors is the sample in homogeneity.

The amount of material exposed to the beam is small. Therefore, most of the yield comes from the part of the proton range were the energy is the highest. The volume analyzed the typical of the order of 1000 d^2 cm^3 (d = beam diameter) for 2 to 3 MeV protons. Accordingly analysis carried out under these conditions implies a high degree of homogeneity of the sample. It was also implicit that standards used to test such analytical methods should be equally homogeneous.

In-homogeneities with dimensions of the order of (100 d) μm will have a significant effect on the observed concentrations. Lateral in homogeneities was easily checked by charging the beam position and observing the effect on the scatter of the result [21].

III.   Results :

Experimental results of concentrations of elements in PIXE analysis are given below.

Table 1.1: Concentration of the Elements of Soil Sample 1 of Around EPZ Main Road, Savar (1 ft Depth)

Z Number	Name of the element	Concentration in µg/g	Limit of detection	Error in percentage
13	Al	2455	5521	80.52
14	Si	703	265	38.21
17	Cl	38	27.1	41.7
19	K	5376	18.4	0.71
20	Ca	6040	35.3	1.21
22	Ti	2871	10.6	0.81
23	V	105	30.2	11.07
24	Cr	70	8.9	6.99
25	Mn	498	9.4	1.75
26	Fe	10647	10.1	1.82
28	Ni	19	5.3	18.60
29	Cu	4	4.9	172.91
30	Zn	40	4.6	9.63
32	Ge	9	8.0	62.16
37	Rb	89	22.6	16.30

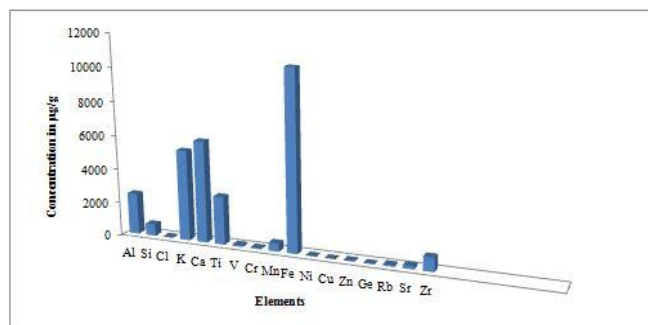| 38 | Sr | 196 | 10.4 | 8.48 |
| 40 | Zr | 835 | 28.8 | 4.81 |

Figure 1.1 : Bar Diagram of the concentration of the elements of soil sample 1 of around EPZ main road, Savar (1 ft depth)
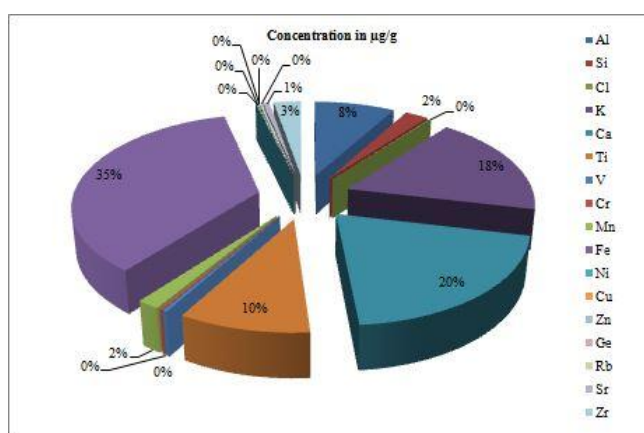

Figure 1.2 : Pie chart of the concentration of the elements of soil sample 1 of around EPZ main road, Savar (1 ft depth)

Table 1.2 : Concentration of the Elements of Soil Sample 2 of around EPZ Main Road, Savar (2 ft Depth)

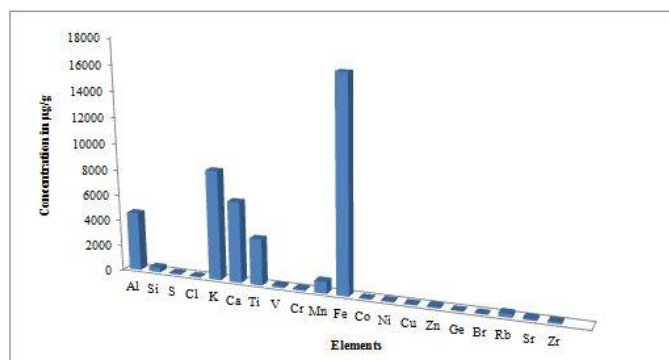| Z Number	Name of the element	Concentration in μg/g	Limit of detection	Error in percentage
13	Al	4546	6785.8	63.10
14	Si	364	308.7	50.98
16	S	80	54.3	41.15
17	Cl	28	31.0	62.88
19	K	8485	17.5	0.78
20	Ca	6266	45.6	1.07
22	Ti	3588	12.4	0.89
23	V	136	35.5	10.16
24	Cr	98	10.6	5.75
25	Mn	929	12.4	1.43
26	Fe	16452	12.3	6.50
27	Co	22	205.9	86.16
28	Ni	70	6.2	7.04
29	Cu	44	4.9	8.69
30	Zn	108	4.7	4.80
32	Ge	20	12.1	33.29
35	Br	14	7.5	43.31
37	Rb	280	54.2	9.05
38	Sr	127	21.6	13.72
40	Zr	126	27.2	16.83

Figure 1.3 : Bar diagram of the concentration of the elements of soil sample 2 of around EPZ main road, Savar (2 ft depth)
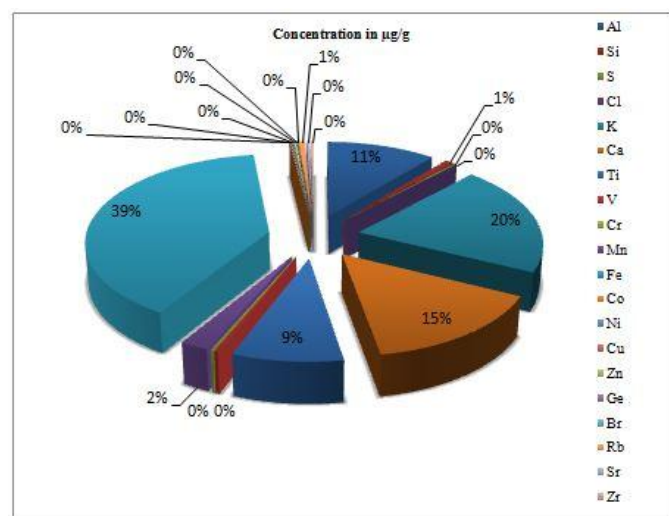

Figure 1.4 : Pie chart of the concentration of the elements of soil sample 2 of around EPZ main road, Savar (2 ft depth)

Table 1.3 : Concentration of the Elements of Soil Sample 3 of around EPZ Residential Area, Savar (1 ft Depth)

| Z Number	Name of the element	Concentration in μg/g	Limit of detection	Error in percentage
13	Al	8023	5895.3	33.13
14	Si	384	263.8	36.75
19	K	6452.8	15.0	0.84
20	Ca	7397	37.9	8.61
21	Sc	41	20.1	24.16
22	Ti	3547	13.2	0.90
23	V	142	35.4	3.70
24	Cr	75	10.5	7.14
25	Mn	475	11.5	2.04
26	Fe	19554	10.7	3.68
28	Ni	52	6.3	8.20
30	Zn	73	4.4	5.99
32	Ge	25	8.7	21.85
34	Se	6	8.1	100.39
37	Rb	183	46.9	13.16
38	Sr	60	19.7	22.50
39	Y	25	23.7	53.56
40	Zr	401	19.7	8.26
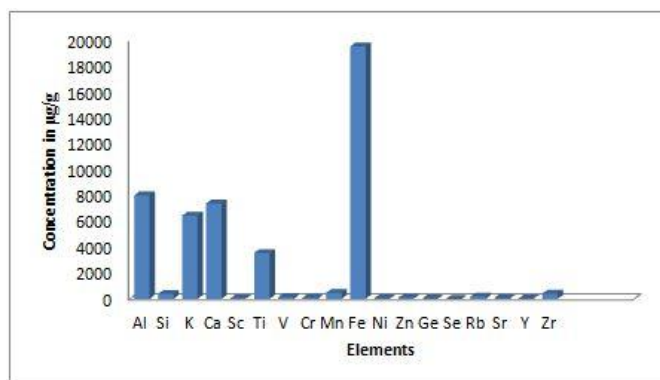
Figure 1.5 : Bar diagram of the concentration of the elements of soil sample 3 of EPZ residential area, Savar (1 ft depth)
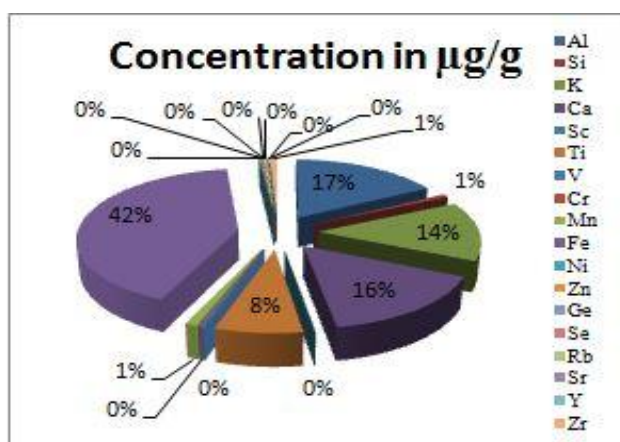

Figure 1.6 : Pie chart of the concentration of the elements of soil sample 3 of EPZ residential area, Savar (1 ft depth)

IV. Discussion:

The elements that are found in this study are: Aluminum, Silicon, Phosphorus, Sulfur, Chlorine, Potassium, Calcium, Scandium, Titanium, Vanadium, Chromium, Manganese, Iron, Cobalt, Nickel, Cuprum, Zinc, Germanium, Bromine, Selenium, Rubidium, Strontium, Yttrium and Zirconium. The elemental concentrations have been shown in above tables.

It is shown that concentration of Iron is highest among all elements present in the soil samples and the concentration of Iron varies from 8620 to 19554 μg/g.

The concentration of Aluminum (2110 to 8384 μg/g), Potassium (5009 to 8485 μg/g), Calcium (1430 to 8040 μg/g) and Titanium (1454 to 3588 μg/g) are found relatively high in all these samples comparing with other elements apart from Iron.

Silicon, Phosphorus, Sulfur, Chlorine, Vanadium, Manganese, Cobalt, Nickel, Cuprum, Zinc, Germanium, Bromine, Rubidium, Strontium, Yttrium, Zirconium are found present significantly in most of the soil samples but not constituently in all the samples.

Presence of Chromium (65 to 147 μg/g) and Titanium (1454 to 3588 μg/g) in most of the soil sample are an alarming signal for soil pollution in EPZ area, Savar.

The present experiments have been done at fixed proton energy, 2.2 MeV, in Van de Graaff accelerator. This energy of proton may not sufficient to excite "all the elements in the thick target samples. Proton beam of higher energy (>2.2 MeV) is suitable to excite the elements and isotope present in a sample [22]. As the intensity of the emitted X-ray energy line is weak so the experiment has to be run for a longer time to obtain statistically significant number of counts to result in large and sharp X-ray peaks.

Proper selection of peak areas can reduce the corresponding uncertainties or errors. Sharper the peaks in the spectrum the better would be the selection. Proton beam of higher energy or larger time for an experiment might have been able to overcome these difficulties.

Uncertainties may also arise due to fluctuations in high voltage power supply, inability of the pre-amplifier to amplify properly the weak current signal from the detector, inadequate analyzing power of MCA for which an energy peak may be shifted from its proper position and become broaden.

All soil samples have been irradiated. To get maximum information from the specimen experimentally the data have been analyzed. It is essential to have detailed information on the nature and extent of the actual and potential elemental concentration of soil so that these can be used properly to improve the environment.

V. Conclusion:

The importance of identification of elemental concentrations in the soil samples for environment has significantly stimulated the needs for elemental analysis of soil. A number of sensitive and accurate analytical methods are used world widely for the determination of the elemental concentration.

The PIXE technique is used for its sensitivity, accuracy, precision, simplicity of thick target and the ability to perform multi-elemental analysis of a large number of samples.

In this study MAESTRO-32 software has been used for data acquisition and GUPIX software has been used to analyze the data for the study of elemental profile of soil at the Accelerator Laboratory of Atomic Energy Centre, Dhaka to assure the quality of life.

The detected elements in soil samples with their concentration range are Aluminum (2110 to 8384 μg/g), Silicon (177 to 521 μg/g), Chlorine (28 to 423 μg/g), Potassium (5009 to 8485 μg/g), Calcium (1430 to 8040 μg/g), Scandium(41 to 150 μg/g), Titanium (1454 to 3588 μg/g), Vanadium(45 to 148 μg/g), Chromium (65 to 147 μg/g), Manganese (237 to 929 μg/g), Iron (8620 to19554 μg/g), Nickel (10 to 746 μg/g), Cuprum (3 to 44μg/g), Zinc (22 to 108μg/g), Germanium (7 to 25 μg/g), Selenium (2 to 8 μg/g), Rubidium (84 to 902 μg/g), Strontium (60 to 207 μg/g), Yttrium (5 to 43 μg/g) and Zirconium (126 to 835 μg/g).

Some Toxic elements have been found in this research such as Chromium and Titanium etc. These are very harmful for environment as well as living being.

The research work shows the elemental concentration of soil samples and indicates the toxic elements that are responsible for soil pollution. Further study like this one will provide sufficient knowledge to evaluate the significance of the importance of elemental analysis.

References:

[1]. Borbely-Kiss, M. Jozsa, A.Z. Kiss, E.Koltey, B. Nyako, E. Somor Jai, Szabo, and S. Self el Nasr, *J. Radioanal. Nucl. Chem., 92/2 (1985) 391.*
[2]. R.A. Cawson, *Essentials of dental surgery and pathology, 3rd edition. Churchill Livingstone, New York, 1978.*
[3]. H.K. Chuttani, P.S. Gupta, S Gulati, and D.W. Gupta, *Acute copper sulfate poisoning, Am. J. Med., 39 (1965) 849.*
[4]. C. Bertrand, *Proc. Int. Congr. Appl. Chem., 28 (1912) 28.*
[5]. J.A. Burton, G.W. Hull, J.C. Severeins, *J. Phys. Chem., 57 (1953) 853.*
[6]. *Trace element in human health and disease, Vol. II, Essential anf Toxic elements*, By Ananda S. Prasad and Donald Oberleas, Academic Press, 1976.
[7]. Walter stiles, *Trace elements in plants, 3rd Edition, Cambridge University press, 1961.*
[8]. V.V. Kovalsky, C.E. Jarovaja and D.M. Shmavonjan, *Zk. Obshch. Biol., 22 (1961) 179.*
[9]. S. Rosenfeld and O.A. Beath, Selenium: *Geobotany, Biochemistry, Toxicity and nutration, Academic Press, New York, 1964.*
[10]. R.F. Burk, Selenium in man. In: *Trace elements in human health and disease, Vol. II. (A.S. Prasad, Ed.) Academic press, New York, 1976, pp. 105-133.*
[11]. H.P. Brinton, E.S. Fraiser and A. L. Koven, *Morbidity and mortality experiences among chromate workers; respiratory cancer and other causes, Public health Rep. 67 (1952) 835.*
[12]. *Commission of European Communities, Trace Metals : Exposure and Health effects, Pergamon Press, Oxford, 1979.*
[13]. G. Karthikeyan, Anitha Pius and B.V. Apparo, *Fluorise, 29 (3) (1996) 151.*
[14]. *Trace element in human health and disease, Vol. II, Essential of Toxic elements*. By Ananda S. Prashad and Donald Oberlease, Academic Press, 1976.
[15]. P.H.A. Mutsaers, *Nucl. Instr. And Meth. B 113 (1996) 323-329.*
[16]. J. A. Maxwell, J.L. Campbell, W.J. Teesdale, *Nucl. Instr. Meth. B95 (1995) 405.*
[17]. L.B. Birks, R.E. Seebold, A.P. Batt and J.S. Grosso, *Excitation of characteristic X-rays by protons, electrons and primary X-rays, J.Appl. Phys., 35 (1964) 2578.*
[18]. J.R. Bird, J. L. Campbell and P.B. Price, *At. Energy Rev. 12 (1974) 275.*
[19]. J.C.Russ (ed.), *American Society for Testing and Materials Special Publication, 485 (1971).*
[20]. R.D. Evans; *The Atomic Nucleus, Mc. Grawhill, New York (1952) p-673.*
[21]. I.S. Giles and M.Peisach, *Cement and Concrete Res., 9 (1979) 591.*
[22]. S.A.E Johanson and J.L Campbell, PIXE, *A Novel Technique for Elemental analysis, John Wiley and Sons, 1998.*