DOI: 10.15415/jnp.2014.12018

Elemental Analysis of Soil Samples Using Thick Target-Particle Induced X-Ray Emission (TT-PIXE) Technique

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Abstract In this work thick target-proton induced x-ray emission (TT-PIXE) technique has been employed for the elemental analysis of soil samples collected from Budha nullah region of Ludhiana city, Punjab. TT-PIXE analysis of samples has been carried out using 3 MeV proton beam from 3 UD pelletron (9SDH2 from NEC, USA) facility at the Institute of Physics (IOP), Bhubaneswar, Orissa. The emitted x-rays were detected using Si(Li) detector (CANBERRA US, FWHM = 180 eV at 5.9 keV) positioned at 90° to the beam line and using suitable electronics. The trace elements $_{15}$P, $_{16}$S, $_{19}$K, $_{20}$Ca, $_{22}$Ti, $_{24}$Cr, $_{25}$Mn, $_{26}$Fe, $_{29}$Cu, $_{30}$Zn, $_{33}$As, $_{37}$Rb, $_{38}$Sr, and $_{82}$Pb were quantified in the soil samples. The quantitative estimation of PIXE spectrum of the soil samples was performed using GUPIX computer code. The presence of $_{24}$Cr, $_{33}$As, and $_{82}$Pb toxic elements in soils is likely to be due to the pollution caused by seepage of the water at the breached locations of nullah. The present study brings to focus the need to improve the effluent treatment of the industrial wastes and repair of the breached Budha nullah. In comparison to other analytical techniques for elemental analysis, PIXE is sensitive and its multi-elemental character brings advantage to investigators for the determination of minor and trace elements in a variety of soil samples.

1. INTRODUCTION

Major factors interfering with biosphere are the industrial developments, as well as excessive agriculture farming using additives, like fertilizers and pesticides. Moreover, the plant leftovers in the agriculture fields decay to produce humic acids and carbon dioxide gas at excessive pressures in the soils, which results in carbonic acid after its dissolution in the irrigation water. These acids add chemicals to the ground water by leaching metals from soils. In fact the excessive agriculture farming is also a dominating contributor to soil and ground water pollution. The contamination of soil by heavy metals represents one of the most pressing threats to water and soil resources as well as human health. Plants grown on soil can absorb the contaminants because of their similar chemical behavior to other minerals needed for growth. These toxic contaminated elements enter into human beings through food chain and lead to many metabolic disorders.

There are a large number of trace elements in soils, at concentration values in the range of parts per billion and tenths of parts of million. Therefore, it is extremely important to have analytical methodologies that allow us to quickly quantify the metal contents of the mineral wastes and are also highly sensitive to detect heavier

Journal of Nuclear Physics, Material Sciences, Radiation and Applications
Vol. 1, No. 2
February 2014
pp. 225–237

elements, like $_{33}$As, $_{48}$Cd, $_{82}$Pb, $_{80}$Hg which are highly toxic to the human body even at trace level. From this point of view, a large number of analytical techniques have been developed for quantitative elemental analysis of environmental, biomedical and geological samples. Despite the significant advances which have been made lately in already established techniques, no technique can be considered a panacea to tackle all types of samples and determine all elements. So the selection of the appropriate technique for a particular analytical problem has become a difficult task.

Some techniques, namely, atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectrometry (ICP-MS) and chemical analysis destroys the identity of the sample and hence are destructive. Neutron activation analysis (NAA) is another widely used technique for nondestructive bulk analysis. This technique induces radioactivity in the sample and require accurate measurements and correction factors especially for thick samples. Other analytical methods, including particle induced x-ray emission (PIXE) and x-ray fluorescence (XRF) are based on the x-ray emission and have several features in common [1–4]. These techniques work on the same principle of creation of inner-shell vacancies in the target element and measurements of the fluorescent x-rays emitted from the sample using semiconductor detectors. In PIXE, particle beam usually proton beam, and in XRF, x-ray of higher energy are used for the creation of inner shell vacancies in the target atom. Due to their ability of rapid, simultaneous, and nondestructive multi-element analysis, these techniques have been well established to determine the concentrations of various kinds of samples [1, 4]. These techniques can only be used for detection of elements in the range $11 \leq Z \leq 92$ because the energy of the characteristic x-rays emitted by low-Z elements is so low to be detected by presently available detection system. In these techniques, elements with $11 \leq Z \leq 50$ are generally determined through their K x-rays and the other heavy elements are measured through their L x-rays due to large L_i (i = 1-3) subshell cross-sections. Certainly, each analytical technique commercially available have their own limitations, however, since 1993 the PIXE has being used successfully in various analytical applications. The XRF technique produces huge amount of continuous background in the spectrum and hence the spectra is difficult to analyze. But PIXE has the advantage that the cross-section for x-ray production is large and the background contribution from bremsstrahlung is low [5-9]. PIXE is a highly sensitive method [10] for the multi-elemental analysis and is generally performed using ~ 3 MeV proton beam. The atomic spectrometric PIXE technique is a matured analytical technique for minor element analysis in complex matrices, such as metallurgical and environmental samples.

Several groups have demonstrated use of the PIXE technique [4-6, 11,12] for elemental analysis to understand correlation with altered soil chemistry, or elements deposition and sedimentation phenomena [13, 14]. The aim of present investigation is to establish TT-PIXE analysis of soil samples and perform a comparative study of heavy elements in soil samples collected from various locations enroute Budha

nullah in Ludhiana city, Punjab. Buddha nullah is a water drain carrying waste from the industries, which runs through thickly populated and industrialized Ludhiana city, once known as Manchester of India. and drains into Sutlej river.

2. EXPERIMENTAL DETAILS

Soil samples from different locations were taken from the Budha nullah region of Ludhiana city. Thirteen soil samples labeled S1-S13 were collected at various locations from regions within ~ 30 m of the nullah. The locations of sample collection sites are shown in Fig. 1. The samples were collected from the top soil, *i.e.*, 10 - 15 cm depth, which is usually contaminated, to study the anthropogenic sources of pollutants.

The samples were collected using wooden tools and stored in self-locking polythene bags kept at 30°C. Care is taken that the collected portion is not from the visibly contaminated region. The collected soil samples from specific regions were air dried, cleaned and subsequently grounded into fine powder by using an Agate pestle and mortar. The powdered samples were weighed and thoroughly mixed with equal amount of graphite powder (Hi-MEDIA Product) in the ratio 1:1 by weight. The graphite powder acts as binder as well as conductor which is necessary for charge integration with better accuracy and eliminating the problems associated with charging during PIXE measurements. Then self-supporting pellets of 9 mm diameter and uniform thickness of about 2 mm from the finely pulverized sample were made using a die of stainless steel. A constant pressure of ~20 kN/cm^2 was applied to the die head by using hydraulic press (Paul-Otto-Weber Co., Germany), so as to get pellet of uniform thickness and to reduce the surface effects. The die is covered with mylar to minimize contamination from die. The pellets of powder Montana soil (SRM-2710) mixed with graphite powder were also prepared. It was used as a reference target for the elemental determination of the present soil samples. The Montana soil standard is made from soil collected from the top 10 cm of pasture land located at Latitude 46° 01' and Longitude 112° 47' along Silver Bow Creek in Butte, Montana area [15]. The Montana soil is highly contaminated with quite high concentration of $_{25}$Mn, $_{29}$Cu, $_{30}$Zn, $_{33}$As, and $_{82}$Pb.

The PIXE experiment was performed at the IOP, Bhubaneswar, using 3 UD pelletron (9SDH2 from NEC, USA) facility [16]. The 3 MeV proton beam [17] was collimated onto the target position in the scattering chamber. Among various ancillary devices housed in the chamber, the most important are the x-ray detection system and a Faraday cup for monitoring the proton current incident on the specimen. In the present case, the beam current was integrated in the sample equipped with electron suppressor (- 200 V) as the targets were thick enough to stop the beam. The schematic diagram of multipurpose scattering chamber with special arrangement for PIXE studies is shown in Fig. 2.

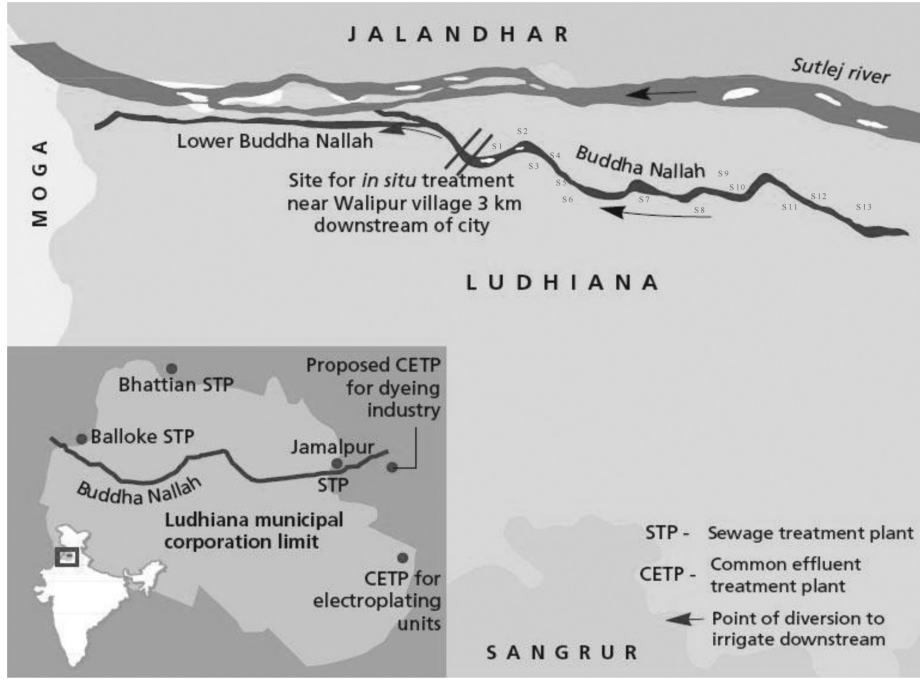

Figure 1: Different locations of the sample collection along the Budha nullah from regions within ~ 30 m.

The position of beam on the sample was adjusted properly using a quartz target. The vacuum obtained inside the experimental chamber was of the order of 10^{-6} Torr. The target was positioned at 45° to the beam direction and distance between the target and detector was 11 cm. The characteristic x-ray spectra were taken using an Si(Li) detector (CANBERRA US, FWHM = 180 eV at 5.9 keV) at 90° to the beam line having 25 μm mylar window. The energy spectrum was stored and displayed using a multichannel analyser (CANBERRA Series 88). The beam current for thick soil samples was integrated using current integrator. Each sample was irradiated for approximately 20μC charge to ensure good statistics.

The beam current was kept low to limit the count rate and dead time correction. The typical x-ray spectra recorded for soil samples is shown in Fig. 3. The PIXE spectrum shows peaks corresponding to the *K* x-rays of $_{15}$P, $_{16}$S, $_{19}$K, $_{20}$Ca, $_{22}$Ti, $_{24}$Cr, $_{25}$Mn, $_{26}$Fe, $_{29}$Cu, $_{37}$Rb, $_{38}$Sr, and *L* x-rays of $_{82}$Pb element present in soil. For the reliable calibration of the analytical system, *viz.*, x-ray yield observed by the detector per unit charge per unit mass of the element, thin $_{28}$Ni and $_{47}$Ag foils (thickness ~ 200 μg/cm^2) and thick Montana soil were used.

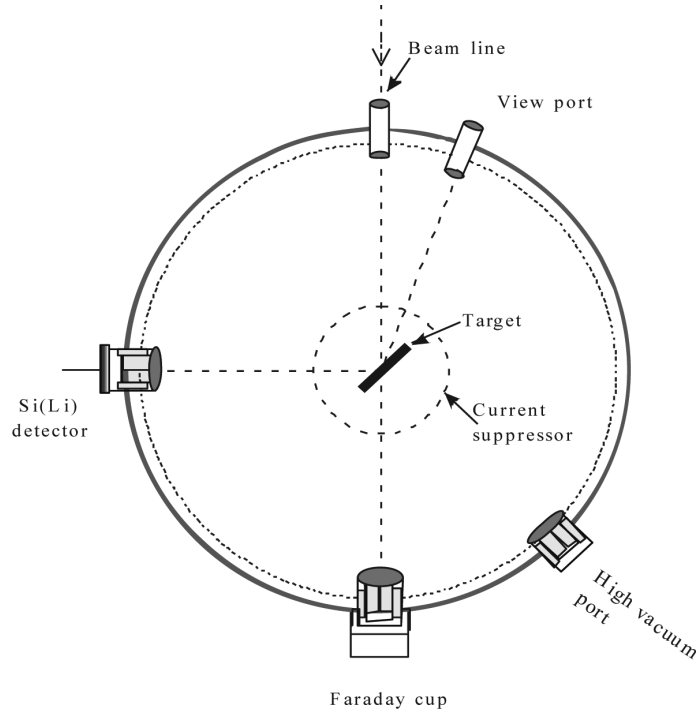

Figure 2: Schematic of the ion beam, target, and detector arrangement in the PIXE scattering chamber used for the present measurements.

Typical PIXE spectra showing elemental composition of Montana soil (SRM 2710) and graphite powder are shown in the Fig. 4. Graphite spectrum shows *K* x-ray peak due to $_{26}$Fe.

3. DATA ANALYSIS

In present work thickness of soil samples is sufficient to stop 3 MeV proton beam. Therefore, the measured x-ray yield is related to mass thickness of element present in the sample as

$$Y(Z) = \frac{N_A \varepsilon_Z N_P C_Z}{A_Z} \int_{E_0}^{0} \frac{\sigma_Z^X(E) T_Z \; E}{S(E)} dE \qquad (1)$$

where $Y(Z)$ is the number of counts in a characteristic x-ray line of the element with atomic number Z, N_A is Avogadro's number, $\sigma_Z^X(E)$ (E) is the x-ray production cross-section for the line p at the incident energy E_0, ε_Z is the absolute detection efficiency including all absorbing components of the set-up for the x-ray line, N_P is the number of incident protons, C_Z the concentration of the analyte element in the specimen, A_Z the

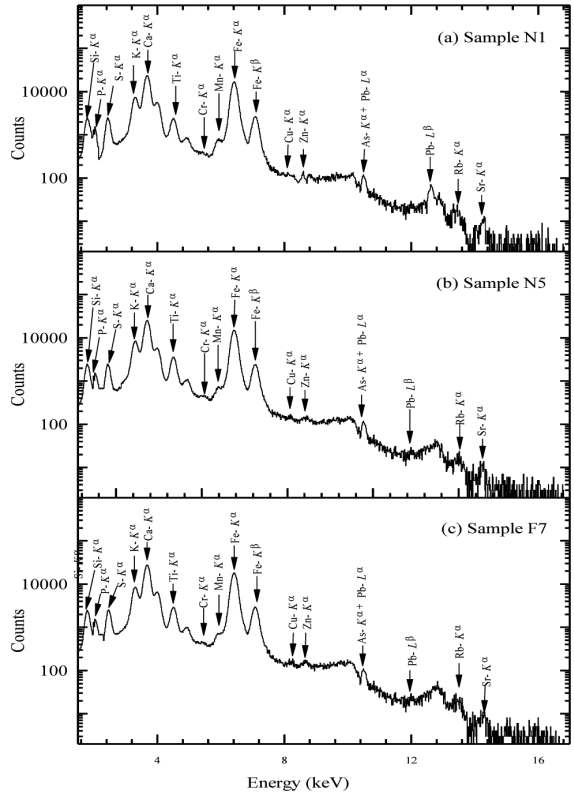

Figure 3: Typical PIXE spectra showing elemental composition of soil samples from (a) sample N1, (b) sample N5, and (c) sample F7. Only the major peaks are marked.

atomic mass of the analyte element, and $S(E)$ is the stopping power in the soil matrix. The transmission of the x-rays from successive depths in the specimen, $T_Z(E)$, is given by the relation [4],

$$T_Z(E) = \exp\left(\frac{-\mu_Z \cos\theta}{\sin\phi}\int_{E_0}^{E}\frac{dE}{S(E)}\right) \tag{2}$$

where μ_z is the mass attenuation coefficient for the x-rays in the sample matrix, θ = 45° is the angle between the incident proton beam and the specimen surface and ϕ is the angle between target surface and detector axis. The absorption of x-rays leaving the target from different depths in a direction to the detector is taken into account. The absorption of x-rays in the mylar window is calculated using the formula

$$\frac{I}{I_0} = e^{-\mu t} \tag{3}$$

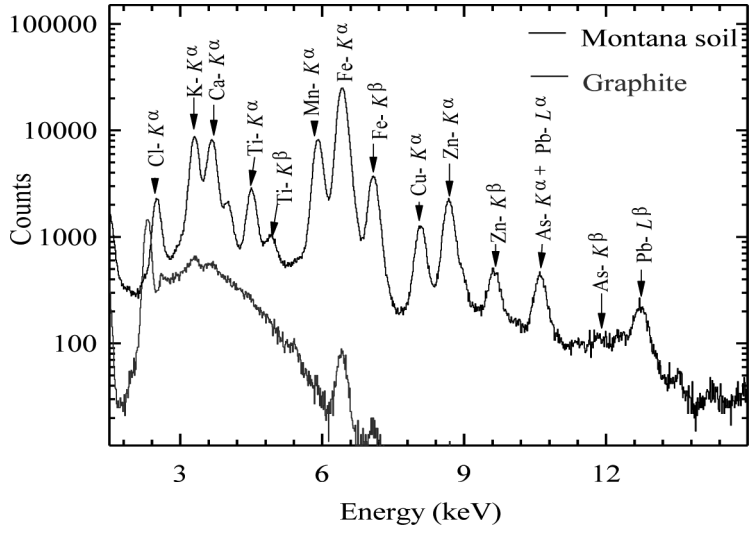

Figure 4: PIXE spectrum of standard reference material of Montana soil standard-SRM 2710 and the graphite powder.

Where I is intensity of the x-rays after passing through the mylar window, I_o is the initial intensity of the x-rays, μ is the attenuation coefficient of mylar and t is thickness of the mylar foil used. The computer code XCOM was used to calculate the values of attenuation coefficient (μ) of mylar. Absorption of x-rays in the mylar window comes out to be 91% for 1 keV x-rays, decreases to 30% for 2 keV x-rays and 0.3% for 10 keV x-rays. The PIXE analysis of soil samples presents difficulties as soil contains a multitude of trace and minor elements. Each of these elements may give rise to one or more x-ray peaks due to various *K*, *L,* and *M* shell x-ray transitions in the energy region of interest. Thus, a large number of peaks are expected in the spectrum and there is a good probability that a number of the x-ray peaks will be overlapping and interfering with each other. However, the significance of *K*, *L,* and *M* shell x-ray peaks depends upon the atomic number of the elements. The low energy background is largely due to the bremsstrahlung caused by the secondary electrons ejected from the target atoms during the collision process. This deteriorates the detection limit for the elements being detected using low energy x-rays. The GUPIX code [18] was chosen for the quantitative analysis of the PIXE spectrum. This package has the provision to convert the x-ray peak intensities into elemental concentrations using a standardization technique involving fundamental parameters like x-ray ionization cross section, mass attenuation coefficient, fluorescent yields, solid angle, charge collected, geometrical factor, and predetermined instrumental constants (Eq. 1). The continuous background [19] is dealt by applying simple digital filter operator [20] prior to least squares fitting. Using this software program the elemental concentrations were estimated. The pellets of soil samples are infinitesimally thick for 3 MeV

protons; therefore, matrix effects for infinitesimally thick target were applied. The most practical approach to estimate the concentration values would be to run the GUPIX program for PIXE spectrum from thick pellet of a standard reference of soil under identical experimental conditions. Optimum values of various parameters related to the detector efficiency, geometrical factors, and absorption in the target matrix were obtained using the certified concentration values for various elements. The measured x-ray yield per unit charge per unit mass of the element from pure thin $_{28}$Ni and $_{47}$Ag foils of thickness ~ 100 μg/cm^2 were also used to enhance reliability of the analysis. The corrections due to $_{26}$Fe present in the graphite were estimated from its spectrum and have been incorporated in the quoted values of concentration.

4. RESULTS AND DISCUSSION

The estimated uncertainties in the concentrations of trace elements in the present work are ~ 8-15% depending upon the concentration value. The error in the present measured values are propagated through the x-ray cross-section values as a function of the proton energy which continuously decreases in soil matrix, detection efficiency, incident ion beam current, and x-ray absorption coefficients. The elements $_{15}$P, $_{16}$S, $_{19}$K, $_{20}$Ca, $_{22}$Ti, $_{25}$Mn, $_{26}$Fe, $_{29}$Cu, $_{30}$Zn, $_{37}$Rb, and $_{38}$Sr were quantified in the soil samples. The concentration of various elements found in the present soil samples is listed in Table 1. The elements $_{24}$Cr, $_{33}$As, and $_{82}$Pb have also been observed in the soil samples. The presence of these toxic elements in soils is likely to be due to the pollution caused by seepage of the water at the breached locations of nullah. The concentration of different elements observed in the soil samples are plotted in Fig. 5 and Fig. 6. In a separate study by the EDXRF laboratory at Panjab University and Punjab Pollution Control Board, revealed that water samples of the nullah were contaminated with toxic elements like $_{24}$Cr, $_{33}$As, and $_{82}$Pb, from the industrial wastes.

The average concentration of the elements in the nullah water are evaluated using EDXRF set-up and given in the Table 2. The breaching of nullah need to be repaired to decrease the contamination of surrounding soils due to recharge from nullah. Generally, the ratio $_{37}$Rb/$_{38}$Sr is expected to be nearly same in the soils over wide regions, which are produced by weathering of same kinds of rocks. This ratio is observed to be in the range 0.9-2.1 in the present samples. However, frequent exposure of soils to the ground water can change the ratio due to the presence of varying significant amounts (~ few hundred ppb) of $_{38}$Sr and small amounts of $_{37}$Rb in these waters. Further elemental analysis of soil samples collected from the breached nullah regions as a function of distance and at the depth below the general level of nullah water is required to look for its pollution spread.

5. CONCLUSION

In this work, the main objective was to demonstrate the suitability of TT-PIXE for determining and measuring elements present in the soil samples. In the present

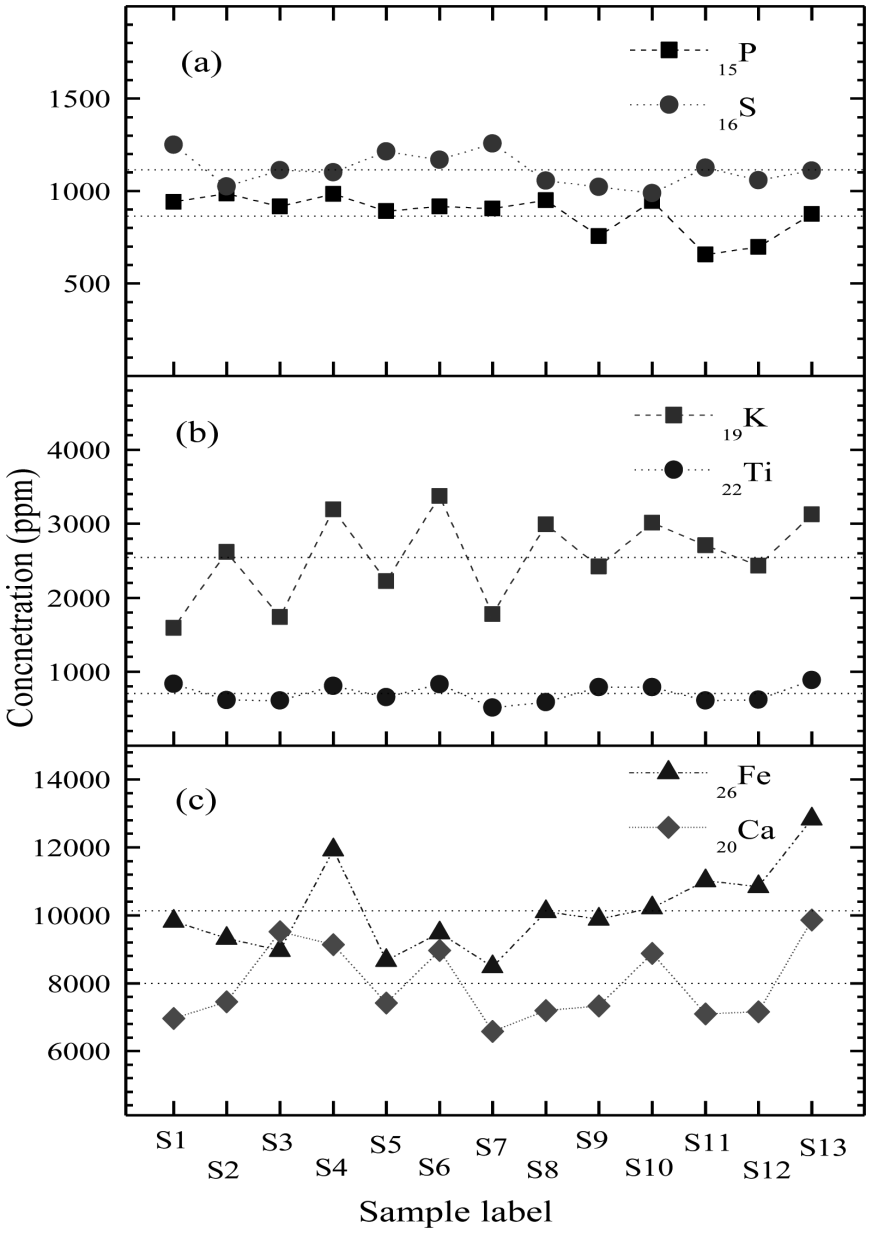

Figure 5: The plot showing the variation of elemental concentration of (a) $_{15}$P and $_{16}$S, (b) $_{19}$K and $_{22}$Ti, and (c) $_{20}$Ca and $_{26}$Fe in soil samples. Horizontal lines indicate the average value of the metal for each element.

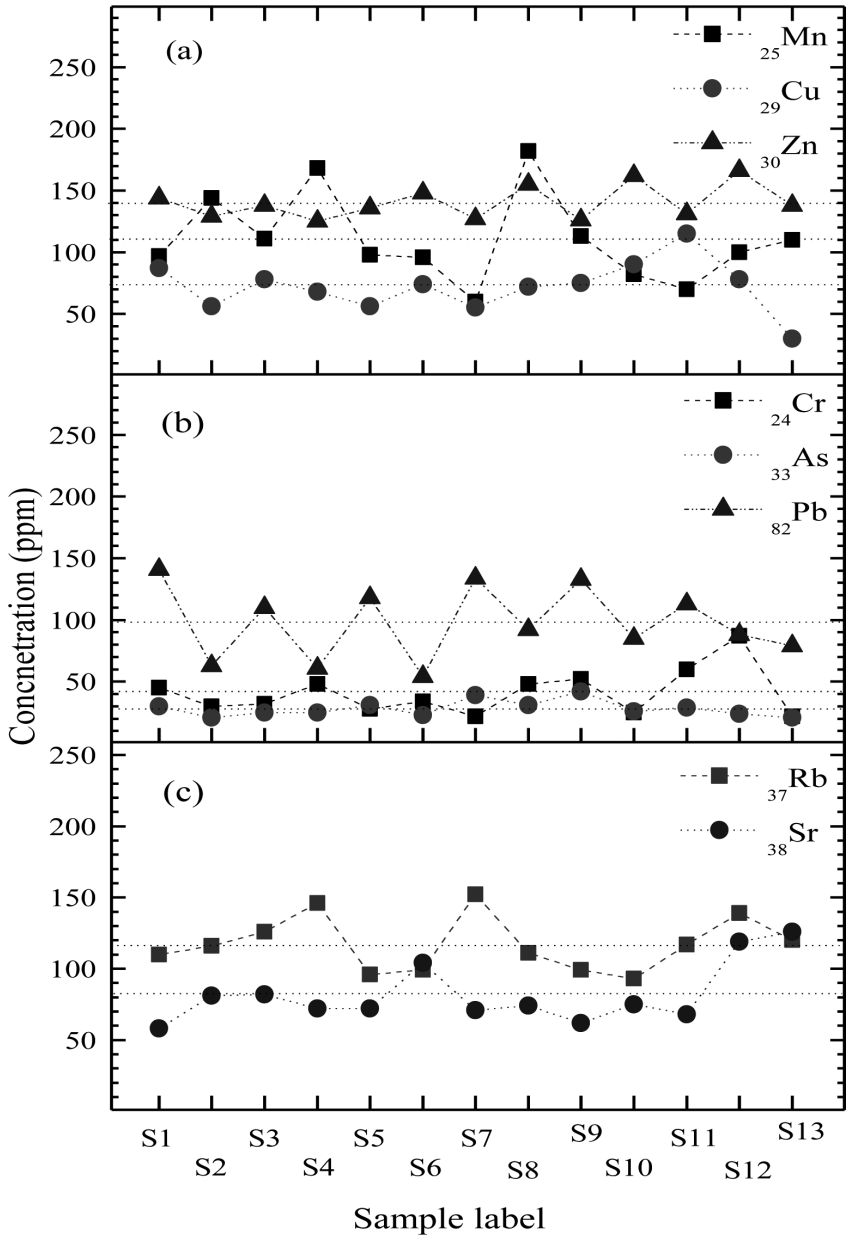

Figure 6: The plot showing variation of elemental concentration (a) $_{25}$Mn, $_{29}$Cu, and $_{30}$Zn, (b) $_{24}$Cr, $_{33}$As, and $_{82}$Pb (c) $_{37}$Rb, and $_{38}$Sr in soil samples. Horizontal lines indicate the average value of the metal for each element.

Table 1: Elemental concentration of soil samples in the vicinity of Budha nullah, Ludhiana, Punjab.

Element	Concentrations (ppm) of various elements												
	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11	S12	S13
$_{15}$P	941	985	917	983	892	915	904	951	756	946	657	698	875
$_{16}$S	1251	1025	1112	1102	1215	1169	1256	1057	1023	988	1126	1058	1109
$_{19}$K	1591	2620	1740	3196	2221	3373	1778	2992	2421	3013	2710	2434	3127
$_{20}$Ca	6968	7456	9523	9142	7414	8969	6581	7201	7334	8881	7103	7161	9865
$_{22}$Ti	835	616	609	807	656	833	512	586	789	790	613	622	884
$_{24}$Cr	45	30	32	48	28	34	22	48	52	25	60	87	22
$_{25}$Mn	97	144	111	168	98	96	60	182	113	82	70	100	110
$_{26}$Fe	9824	9318	8968	11932	8675	9476	8489	10109	9891	10221	11016	10850	12832
$_{29}$Cu	87	56	78	68	56	74	55	72	75	90	115	78	30
$_{30}$Zn	144	129	138	125	136	148	127	155	126	162	131	166	138
$_{33}$As	30	21	25	25	31	23	39	31	42	26	29	24	21
$_{37}$Rb	110	116	126	146	96	99	152	111	99	93	117	139	120
$_{38}$Sr	58	81	82	72	72	104	71	74	62	75	68	119	126
$_{82}$Pb	141	63	110	61	118	54	134	92	133	85	113	88	79

Table 2 Average concentration of elements present in the water samples of Budha nullah, determined using EDXRF set-up [21].

Average elemental concentration (μg/L) in water samples										
$_{20}$Ca	$_{24}$Cr	$_{25}$Mn	$_{26}$Fe	$_{27}$Co	$_{29}$Cu	$_{30}$Zn	$_{33}$As	$_{37}$Rb	$_{38}$Sr	$_{82}$Pb
122307	575	121	13052	111	497	601	3	9	228	21

work, the elemental analysis of soil samples collected from Budha nullah region of Ludhiana city, Punjab, was performed using the PIXE technique. The elements $_{15}$P, $_{16}$S, $_{19}$K, $_{20}$Ca, $_{22}$Ti, $_{24}$Cr,$_{25}$Mn, $_{26}$Fe, $_{29}$Cu, $_{37}$Rb, $_{38}$Sr, and $_{82}$Pb were quantified in the soil samples. PIXE supported by GUPIX software has been applied for the elemental analysis of thick soil samples. The measurements exhibit analytic power of the ion-beam based method. The EDXRF analysis of Budha nullah water samples has shown presence of the toxic elements like $_{24}$Cr, $_{33}$As, and $_{82}$Pb, which are likely from the industrial waste water seepage from the breached parts of nullah. The present study brings to focus the need to improve the effluent treatment of the industrial wastes and repair of the breached Budha nullah. This work demonstrates the suitability of PIXE as a fast and non-destructive technique, concerning to the preservation of the inorganic matrix of the samples and useful to measure heavy metals content in soil samples. In comparison to other analytical technique for elemental analysis, the multi-elemental character of PIXE brings advantage and potentialities to soil science investigators.

ACKNOWLEDGEMENT

The author is thankful to the pelletron staff for providing the smooth beam during the experiment. The author is also thankful to Prof. M. L. Garg, Dr. B.P. Mohanty and Dr. P. Balouria, Department of BioPhysics, Panjab University, Chandigarh for the guidance and help during the experiment.

REFERENCES

[1] A.A. Markowicz, Handbook of X-ray Spectrometry, edited by R.E. Van Grieken and A.A. Markowicz, Vol. **14,** p. 53, Marcel Dekker Inc., New York (2002).

[2] T.A. Cahill, Nucl. Instr. and Meth. B **109/110,** 402 (1996). http://dx.doi.org/10.1016/0168-583X(95)00965-5

[3] G.M.B. Marcazzan, X-Ray Spectrom. **27,** 247 (1998). http://dx.doi.org/10.1002/(SICI)1097-4539(199807/08)27:4<247::AID-XRS294>3.0.CO;2-5

[4] S.A.E. Johansson, J.L. Campbell, and K.G. Malmqvist, Particle-Induced X-ray Emission Spectrometry, John Wiley and Sons (1995).

[5] R. Jenkins, R.W. Gould, and D. Gedcke, Quantitative X-ray Spectrometry, Marcel Dekker Inc. (1981).

[6] S.A.E. Johansson and J.L. Campbell, PIXE: A novel technique for elemental analysis Wiley, Chichester (1988).

[7] F. Folkmann, G. Gaarde, T. Huus, and K. Kemp. Nucl. Instr. and Meth. B **116,** 487 (1974).

[8] S.A.E. Johansson and T.B. Johansson, Nucl. Instr. and Meth. **137,** 473 (1976). http://dx.doi.org/10.1016/0029-554X(76)90470-5

[9] J. D. Garcia, R. J. Fortner, and T.M. Kavanagh, Rev. Mod. Phys. **45,** 111 (1973). http://dx.doi.org/10.1103/RevModPhys.45.111

[10] T.B. Johansson, R. Akselsson, and S.A.E. Johansson, Nucl. Instr. and Meth. **84,** 141 (1970). http://dx.doi.org/10.1016/0029-554X(70)90751-2

[11] A.H. Legge, H.C. Kaufmann, and J.W. Winchester, Nucl. Instr. and Meth. B **3,** 507 (1984). http://dx.doi.org/10.1016/0168-583X(84)90428-2

[12] K. Pernestal, B. Jonsson, J.E. Hallgren, and H.K. Li, Int. J. PIXE **1,** 281 (1991). http://dx.doi.org/10.1142/S0129083591000202

[13] R. Checci, G. Ghermandi, and R. Zonta, Nucl. Instr. and Meth. B **5,** 6 677 (1991).

[14] M.A. Respaldiza, R. Garcia-Tenorio, and F. El-Daoushy, Nucl. Instr. and Meth. B **64,** 538 (1992). http://dx.doi.org/10.1016/0168-583X(92)95529-Z

[15] Standard Reference Material SRM 2710, National Institute of Standard and Technology, Certificate of Analysis.

[16] M. Hajivaliei,, M.L. Garg, D.K. Handa, K.L. Govil, T. Kakavand, V. Vijayan, K.P. Singh, and I.M. Govil, Nucl. Instr. and Meth. B **150,** 645 (1999). http://dx.doi.org/10.1016/S0168-583X(98)01066-0

[17] K. Sekar, P.V. Satyam, G. Kuri, D.P. Mahapatra, and B.N. Dev, Nucl. Instr. and Meth. B **73,** 630 (1993). http://dx.doi.org/10.1016/0168-583X(93)96054-G

[18] J.A. Maxwell, W.J. Teesdale, and J.L. Campbell Nucl. Instr. and Meth. B **95,** 407 (1995). http://dx.doi.org/10.1016/0168-583X(94)00540-0

[19] J.L. Campbell, W. Maenhaut, E. Bombelka, E. Clayton, K. Malmqvist, J.A. Maxwell, J. Pallon, and J. Vandenhaute Nucl. Instr. and Meth. B **14,** 204 (1986). http://dx.doi.org/10.1016/0168-583X(86)90045-5

[20] F.H. Schamber, in X-ray fluorescence analysis of environmental samples, ed. T.G. Dzubay (Ann Arbor Science, Michigan, 1977).

[21] Uranium in drinking water: Scientific opinion and fact sheet, Available from: http://physics.puchd.ac.in/dmehta.