Studying the spatial variability of Cr in agricultural field using both particle induced X-ray emission (PIXE) and instrumental neutron activation analysis (INAA) technique

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Abstract

In the field of soil physics, a technique which permits a non-destructive, accurate and fast elemental analysis with a minimum of sample preparation effort is often desired. Although trace elements are minor components of the solid phase, they play an important role in soil fertility. Cr is of nutritional importance because it is a required element in human and animal nutrition. The immobility of Cr may be responsible for an inadequate Cr supply to plants. This work not only demonstrates the suitability of PIXE as a fast and non-destructive technique, useful to measure Cr content in soil samples, but also outlines a study of spatial variability of that element in agricultural field. To demonstrate the capability of the method soil samples were collected in a 5000 m^2 agricultural field. The soil samples were analyzed using both PIXE and INAA techniques. Besides, a Fourier interpolation technique was used to verify the distribution of Cr along of the sampled field. INAA was carried out by means of the γ-ray emitted by ^{51}Cr(320 keV). Results shows that there is a good linear relationship between the elemental concentration of Cr obtained using those techniques, i.e. a correlation coefficient of $r^2 = 0.82$ was achieved.

1. Introduction

An appreciation of the physical, chemical, and biological factors determining the supply, availability, and movement of trace-elements in soil/plant ecosystems, together with suitable techniques for the measurement of the concentration and identification, is essential to the development of an understanding of the mechanisms and dynamics of transport and their biological implications. One serious difficulty encountered in attempts to relate trace-elements to plant response is the fact that their concentration in the agricultural zone varies spatially and in time. Thus, in order to study trace-elements concentration in an agricultural field it is used to use a large number of samples, or at least to have a representative sampling grid of the experimental field. Furthermore when working with a large number of either soil or plant samples, the choice of the analytical technique to measure and identify trace-elements is another critical point, in terms of optimizing sample preparation, matrix corrections, requested time required for each sample analysis, and non-destructive characteristics. Certainly, all analytical

techniques commercially available have their own limitations, however the proton induced X-ray emission technique has been used successfully in agronomic applications [1–3]. In the field of soil physics, a technique which permits a non-destructive, accurate and fast elemental analysis with a minimum of sample preparation effort is often desired. The composition of soils is extremely diverse despite being governed by many different factors, such as climatic conditions, and parent material being most predominant. Although trace elements are minor components of the solid phase, they play an important role in soil fertility. A knowledge of the association of trace elements with particular solid phase and their affinity to each soil constituent is the key to a better understanding of the principles governing their behavior in soils. There are a large number of trace elements in soils, at concentration values in the range of parts per billion and tenths of parts per million. As for biological samples many of them are of great importance for the nutrition of the plants, while others are toxic, and others play an unknown role. Moreover the knowledge of the behavior of polluting trace elements is far from complete.

Chromium (Cr), for example, is of nutritional importance because it is a required element in human and animal

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nutrition [14]. It has been shown that most of the soil Cr occurs as Cr^{3+} and is within the mineral structures or forms of mixed Cr^{3+} and Fe^{3+} oxides. Cr behavior is governed by both soil pH and redox-potential. The behavior of Cr in soils may be modified by organic complexes, however, the dominant effect of organic matter is the stimulation of the reduction of Cr^{6+} to Cr^{3+}. Cr^{6+} is very unstable in soils and is easily mobilized in both acid and alkaline soils. On the other hand the compounds of Cr^{3+} are considered to be very stable in soils. The immobility of Cr may be responsible for an inadequate Cr supply to plants.

Particle Induced X-ray Emission (PIXE) is an analytical technique based on the ionization of the sample atoms by the incidence of, for instance, a proton beam and the subsequent emission of X-rays characteristic of the elements present in the sample. The number of X-ray photons of a given element provides information on the amount of the element in the sample [4,5]. The PIXE technique is also able to analyze very small sample quantities down to 10^{-4} g for solids and around 1 μl for liquids. In addition, it allows the simultaneous detection of all elements heavier than Na, a non-destructive and rapid analysis [6]. Recent developments have expanded the usefulness of PIXE in applications such as geology and material science by combining part per million (ppm) elemental sensitivity and sub-millimeter spatial resolution [7,8]. For PIXE analysis the X-ray yield can be obtained using the ionization cross section energy dependence according to the relation:

$$Y_p(E) = (4.968) \times 10^{-17} N_2 x \sigma_p^x(E) Q \Omega \left(\frac{\varepsilon}{\sin \theta_i} \right). \qquad (1)$$

where $Y_p(E)$, in Eq. (1) is the number of X-ray counts in a peak p for an incident ion energy E, $\sigma_p^x(E)$ is the X-ray production cross section for a peak p, N_2 is the number of target atoms/cm³, x is the target thickness (μg/cm²), Q is the total charge hitting the target (μC), Ω is the detector solid angle (sr), ε is the total detection efficiency and θ_i is the angle between the surface normal and the beam direction [9,10]. Also, some correction factors are required. The first is a loading correction that reflects the transmission of X-rays through a uniform layer of a filter. The second is a particle size diameter correction associated with a spherical particle of a given diameter and composition [13]. The latter correction may become important for quantitative analysis of soils.

In this work besides using the PIXE technique the determination of the total Cr content was also obtained by means of instrumental neutron activation analysis technique (INAA). This technique allows to obtain information about concentrations of a large number of elements simultaneously and it has been applied to the analysis of soil by several researchers during the last years [11,12].

This work demonstrates not only the suitability of PIXE as a fast and non-destructive technique useful to measure the Cr content in soil samples and a comparison of results with INAA but also its spatial variability in a typical agricultural field.

2. Material and methods

PIXE analysis of the samples was carried out using a Pelletron accelerator, model 5SDH, installed at the Physics Institute of the University of São Paulo, São Paulo, Brazil. This accelerator provides proton energies up to 2.4 MeV. The detector used to obtain a suitably high sensitivity for each element is a Si(Li) from Kevex, model 3000, with a resolution of 175 eV in 5.9 KeV. The instruments used for signal processing were a standard electronic pulse handling system, and a ADCAM Analyst, model 100U multichannel analyzer form EG&G ORTEC. Data were accumulated in either a VAX or PC-compatible computer, and the AXIL code was used [15], giving both a spectrum of characteristic X-ray and a smooth background. Absolute accuracy of the analysis system was established through the use of gravimetric thin film standards. Therefore in order to have accurate measurements for the soil samples analysis a standard reference material from National Bureau of Standards was used. This reference material, i.e., NIST-SRM no. 1646, is a sediment standard and it is intended primarily to calibrate and use in the analysis of sediments, soils, or materials of a similar matrix (National Bureau of Standards, 1984). The certified concentration of the elements in that standard reference material was obtained using X-ray fluorescence spectrometry. An average analysis normally requires 400 s of beam time and about 25 s of computer time. Sodium and heavier elements are routinely detected with minimum detectable limits (MDL) ranging from a few ppm of several hundred ppm, when interferences are present.

The soil samples were analyzed using an incident 2.4 MeV proton beam with a typical beam current of 15 nA and a charge of 8 μC. Because the 2.4 Mev proton beam cannot penetrate the target deeper than tens of microns all soil samples were crushed identically before analysis. The soil samples were crushed to allow both the penetration of the 2.4 MeV proton bean and to decrease the effects of X-ray attenuation by the aggregates of the soil. Nucleopore filter with a thickness of approximately 0.01 mm was used to hold the crushed soil as a thin layer for PIXE analysis.

INAA was carried out by means of a thermal neutron flow of 5×10^{12} n cm^{-2}s^{-1} for a period of eight hours. Irradiations have been carried out at the IEA-R1 swimming pool type reactor at IPEN-CNEN/SP. Samples and standard of Cr were irradiated together in aluminum tubes. After a cooling time of ten days the γ-ray emitted by ^{51}Cr(320 keV) was measured. Samples and standard were placed in close geometry using a solid state EG&G ORTEC model GMX 20190 Ge detector, with a resolution of 1.9 keV for the 1332 keV peak of ^{60}Co, coupled to an ADCAM 918A multichannel buffer. Analysis of the γ-ray

P.E. Cruvinel et al. / Nucl. Instr. and Meth. in Phys. Res. B 000 (1995) 000–000
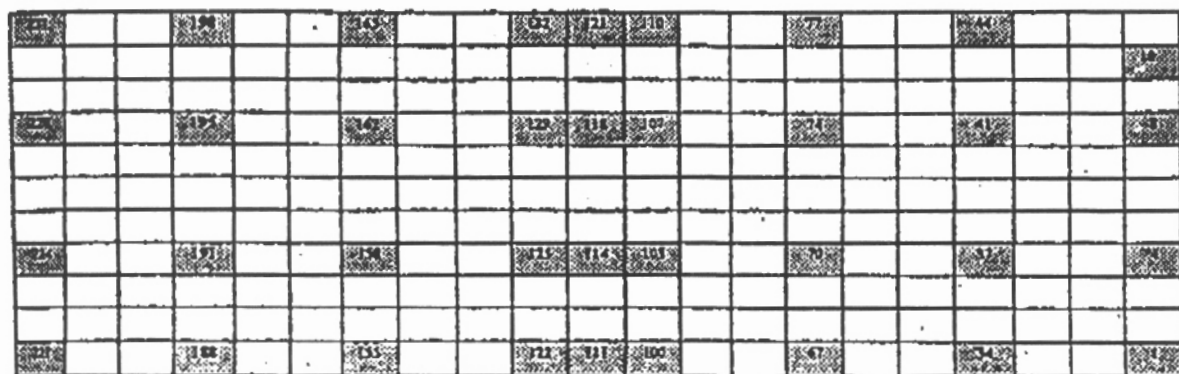
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Fig. 1. The schematic diagram of the experimental field. On the striped points are located the soil samples used in the PIXE analysis.

spectra was carried out by using appropriate computer programs. In addition, for the INAA analysis a stock solution containing 9.31 mg Cr/ml was prepared by dissolution of metallic chromium (Johnson Matlhey, Materials Technology UK) in a mixture of HF, H_2O, H_2SO_4. Then, the standard solution containing 93.1 μg Cr/ml was prepared by dilution of the stock solution. From this solution an aliquot of 25 μl was pipetted onto a small sheet of Whatman paper filter and dried at room temperature. The sheet of paper filtered was placed in polyethylene bags for irradiation.

Cr was analyzed from a set of 36 samples collected in the experimental field of Pindorama-SP, Brazil, part of the Agronomic Institute of Campinas, with coordinates of 48°55′W, and 21°13′S, inside an area of $50 \times 100 \ m^2$. Fig. 1 shows the schematic diagram of the experimental field, where the sampling points were 5 m apart. For comparison, the samples from points marked with stripes, in Fig. 1, were analyzed experimentally by both PIXE and INAA. In addition, in order to analyze the spatial variability of Cr along of the sampled field, an average filter was used to interpolate, with window moving operation, in between neighboring sampled points of soil, whose concentration were determined by PIXE.

3. Results and discussion

A typical PIXE spectrum emitted from a soil sample is shown in Fig. 2. Fe, Si and Al are predominant with respect to Cr, Cl, Ca, K and other trace elements.

The pile-up pulse shown in Fig. 2 occurred because during signal processing each pulse must be measured individually with reference to a zero level and cannot be measured when superimposed upon either the leading edge or the trailing edge of a nearly coincident pulse, i.e., the fact that pulses from a radiation detector are randomly spaced in time can lead to interfering effects between pulses when counting rates are not low. These effects,

called pile-up, can be minimized by making the total width of the pulses as small as possible. The resulting PIXE spectra were analyzed to provide the absolute concentration in (μg/g) of the measured elements. Besides, matrix correction was also implemented. Uncertainties in the concentrations range from 2% for heavy elements to 20% for light elements. Moreover, the resulting INAA spectra were also analyzed to provide the absolute concentration in (μg/g).

Table 1 shows the concentration in (μg/g) for Cr, i.e., respectively, for PIXE and INAA methodologies. Fig. 3 shows a comparison between PIXE and INAA analyses, for results of Cr concentration measurements in soils. Considering the errors given in Fig. 3, the Cr concentration obtained by PIXE seems to correlate well with that obtained by INAA, i.e., $y = 22.61 + 0.76x$ with a coefficient of linear correlation $r^2 = 0.82$. These results confirm the use of PIXE as a complementary method to investigate total Cr in soils as well as to measure, at the same time, other elements present in soil samples of potential interest to investigators.
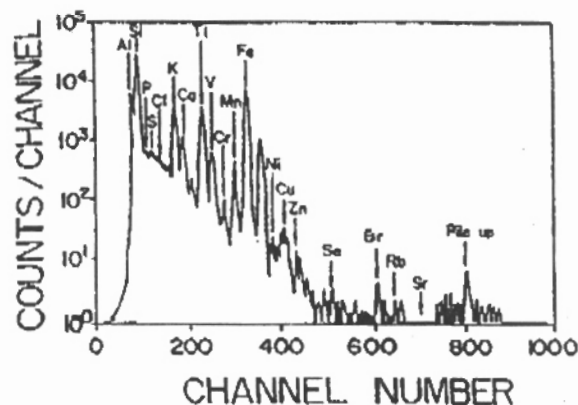

Fig. 2. A typical PIXE spectrum of a soil sample from the Pindorama's Experimental Station.

Table 1
Concentration in (μg/g) for Cr, i.e., respectively by using both PIXE and INAA methodologies

Soil Sample #	PIXE analysis [μg/g]	INAA analysis [μg/g]
1	40±9	
4	80±10	
8	75±11	
10	50±4	
34	40±7	
37	60±10	
41	60±7	
44	55±5	
67	50±10	
70	80±15	
74	40±8	
77	75±10	
100	150±8	146±2
103	110±10	115±1
107	100±7	111±1
110	120±5	127±4
111	180±10	195±6
114	95±8	68±2
118	110±10	134±2
121	90±10	101±2
122	100±10	119±2
125	120±10	122±2
129	130±10	142±2
132	120±10	127±2
155	100±10	
158	80±10	
162	100±10	
165	130±15	
188	50±9	
191	80±10	
195	100±10	
198	100±10	
221	115±10	
224	120±10	
228	125±10	
231	100±10	

Fig. 4. The three-dimensional map of the Cr spatial variability along of the experimental field.
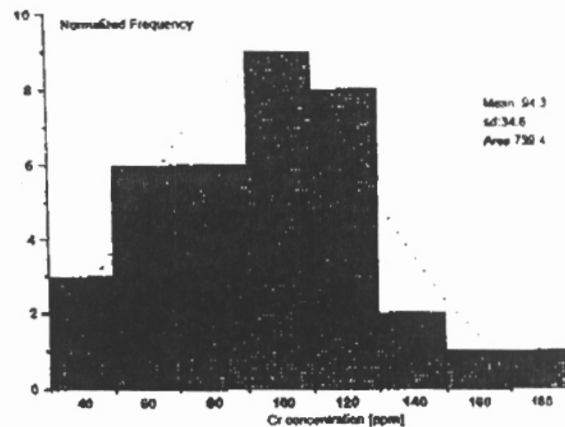
Fig. 5. The histogram of Cr concentrations. Occurrences of 80 μg/g and 100 μg/g were larger than for other concentration values.

Fig. 4 shows a three-dimensional map of the Cr spatial variability along the experimental field. In between the points measured by PIXE, other concentration values were obtained by Fourier interpolation. For the interpolation the technique of sixteen neighbors with a smoothness factor of 0.7 was used, to keep the tendency of the interpolated values.

The histogram presented in Fig. 5 shows that the occurrence of concentrations between 80 μg/g and 100 μg/g was larger than for other concentration values. Moreover, the Gaussian model used on the histogram presented a center in 94.3 μg/g.

4. Conclusions

In the last years, nuclear techniques have given an important contribution in the field of soil physics. In this
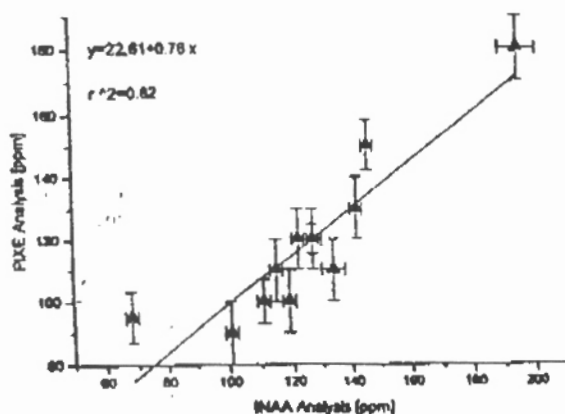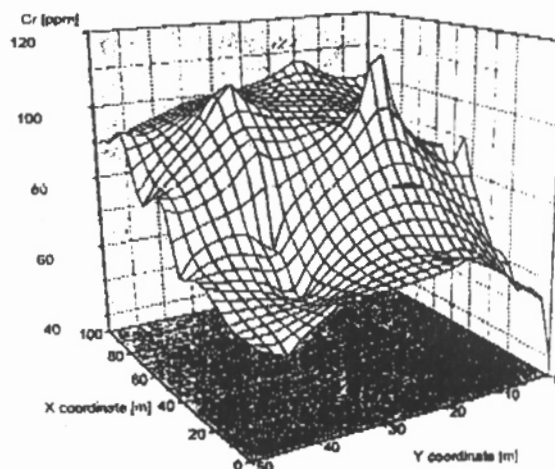

Fig. 3. Comparison between PIXE and INAA analysis, i.e., results for Cr concentration measurements in soils.

work, the main objective was to demonstrate the ability of PIXE in determining and measuring total Cr in soil samples. The PIXE method showed a good correlation with INAA method for analysis of the total Cr in soil samples. Certainly both techniques have their own analytical limitations when applied to soil. For quantitative analysis of total Cr in soils, the PIXE method requires matrix corrections and codes for spectrum reduction. However, it takes a few minutes to carry out a high number of analyses. In addition, detection limits down to 4 μg/g were achieved by the PIXE analysis of total Cr in the soil samples. Furthermore, results of a typical spectrum of soil samples from an experimental field, quantitative concentration in (μg/g) for Cr, and a map of the Cr spatial variability along of the experimental field were outlined.

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