STUDY ON VINASSE DYNAMICS IN SOIL USING ENERGY DISPERSIVE X-RAY FLUORESCENCE WITH RADIOISOTOPIC EXCITATION[1]

S.M. SIMABUCO
Hydraulics and Sanitation Department, FEC/UNICAMP - P.O.Box 6021 - CEP: 13080-970 - Campinas,SP - Brasil
V.F. NASCIMENTO FILHO
Department of Physics and Meteorology - ESALQ/USP - P.O.Box 9 - CEP:13418-900 and Center for Nuclear Energy in Agriculture, CENA/USP - P.O.Box 96 - CEP: 13400-970 - Piracicaba,SP - Brasil

SUMMARY: The distribution of S, Cl, K and Ca along the profiles of two soils of different texture (Red Yellow Podzolic and Dark Red Latosol) treated with amounts of vinasse equivalent to 4000 m³/ha were studied using energy dispersive X-ray fluorescence, observing a significant increase in the contents of these elements. The same effect was observed for Cu, Zn, Rb and Sr contents in soils treated with vinasse as compared to the control. The concentrations of Al, Si, Ti, Mn, Fe and Zr could also be evaluated but no significant variation was observed due to the high soil initial concentrations of these elements as compared to the low concentrations in the vinasse. Annular radioactive sources of Fe-55 and Cd-109 were employed for the excitation of these elements in the soil samples, treated or not with vinassse. For the detection of the characteristic X-rays, a Si(Li) semiconductor detector was used, coupled to a multichannel emulation card inserted in a microcomputer.
Key words: X-ray fluorescence, energy dispersive, radioisotopic excitation, vinasse.

ESTUDO DA DINÂMICA DA VINHAÇA EM SOLO UTILIZANDO A FLUORESCÊNCIA DE RAIOS X POR DISPERSÃO DE ENERGIA COM EXCITAÇÃO RADIOISOTÓPICA

RESUMO: A distribuição de S, Cl, K e Ca ao longo de perfis de dois solos de diferentes texturas (Podzólico Vermelho Amarelo e Latossolo Vermelho Escuro), tratados com uma dose de vinhaça equivalente a 4000 m³/ha, foi estudada utilizando a fluorescência de raios X por dispersão de energia, observando-se um acréscimo significativo dos teores destes elementos. O mesmo efeito foi observado nos teores de Cu, Zn, Rb e Sr nos solos tratados com vinhaça em relação às testemunhas. As concentrações de Al, Si, Ti, Mn, Fe e Zr também puderam ser avaliadas, mas não houve variação nos perfis, devido à alta concentração inicial nos solos acompanhada de baixa concentração na vinhaça. Na excitação dos elementos presentes nas amostras de solo tratados ou não com vinhaça foram empregadas fontes radiativas anelares de Fe-55 e Cd-109, e na detecção dos raios X característicos um detector semicondutor de Si(Li), acoplado a uma placa analisadora de pulsos multicanal, inserida em um microcomputador.
Descritores: fluorescência de raios X, energia dispersiva, excitação radioisotópica, vinhaça.

INTRODUCTION

One of the main residues of the alcohol industry is the vinasse, whose production is in average 13 liters per liter of alcohol. The effect of pollution caused by its disposal whithout suitable pre-treatment has been intensively discussed in the past years. There is a great interest in the utiliza-tion of this subproduct as a complement of mineral fertilization of various crops, mainly sugar cane, due to the presence of nutrients in its chemical composition, specially potassium and sulfur. On the other hand, its use as irrigation water in regions with hydric deficiency has also been studied, as it contains a large percentage of water in its composition.

Among the effects due to the long term application of vinasse to soils, soil salinity and ground water contamination can be pointed out as the most important and therefore it is necessary to understand the dynamics of the distribution of the largest possible number of soil ions.

The aim of this work was to show the feasability of the use of the energy dispersive X-ray fluorescence analysis with radioactive sources for instrumental and simultaneous determination of the elemental concentrations in soil samples treated or not with vinasse.

MATERIAL AND METHODS

For the detection of X-rays a Si(Li) semiconductor detector coupled to a multichannel emulation card was used, employing Fe-55 and Cd-109 annular radioactive sources for excitation. A source-sample-detector arrangement was made in transparent acrilic allowing an excitation/detection under vacuum condition and inserting Al collimators in the central holes of the radioactive sources (SIMABUCO, 1993; SIMABUCO & NASCIMENTO, 1994).

Two different texture soils were used: a clayey Dark Red Latosol, "Iracema" series, and a sandy Red Yellow Podzolic, collected in Tupi and Ribeirão Claro districts of the Piracicaba county, SP, Brazil, respectively. Surface soil layers of 30 cm were collected, air dried, crushed and passed through 2 mm sieve.

Soil columns of 30 cm were packed using transparent acrilic cylinders (5.7 cm internal diameter), which were slowly satured from the botton with distiled water, until obtaining an approximately 0.2 cm water head on the soil surface. After the saturation, 1 liter of vinasse, equivalent to 3,930 m^3/ha was added on the top of the columns.

After vinasse percolation, the columns were sectioned in layers of 1 cm thickness, dried in an oven at 60° C, for approximately 24 hours, and powdered to obtain particles with diameters less than 0.053 mm (270 mesh). The samples were diluted with boric acid in 1:4 ratio and then portions of 500 mg were submitted to a pressure of 2.03×10^8 Pa (2.9×10^4 psi), for 5 minutes, obtaining 2.5 cm diameter pellets of 100 mg/cm^2 superficial density. Three replications were made for each soil layer sample.

To evaluate the element concentrations in the soil, it was necessary to convert intensity data in concentration. This was carried out using elemental sensitivities of the characteristic X-ray emitted by elements present in the sample and correcting for the matrix absorption.

The determination of the sensitivity curves for Fe-55 and Cd-109 sources was done through the fundamental parameter method, based on the mathematical relationship derived from the physical properties and characteristics of the elements and the efficiency of detection system. Therefore, the determination of the sensitivity for the energy range from 1 up to 17 keV was possible using standard pellets containing Al, Si, S, K, Ca, Ti, V, Cr, Mn, Cu, Zn, Sr and Zr, prepared in the laboratory from pure elements and chemical coumponds, under similar conditions as described for the soil samples.

The standard samples were measured from 300 to 1,200 s, but this time could be substantially reduced if the samples were not diluted with boric acid.

The characteristic X-ray absorption correction in the soil samples was performed through the transmission method, which was based on the measurement of attenuation of X-ray intensities emitted by the elements present in a target, placed in the adjacent position to the sample. Initially the intensity of the fluorescence radiation is measured at various energies emitted by the target (irradiator) and then the measurement is repeated placing the sample between the radioactive source and the target (GIAUQUE et al., 1973).

Thus, the transmission method could only be used for thin and intermediate samples, and in this way, the absorption correction by this method could only be applied for Cd-109 excitation, allowing the determination of element concentrations in range of atomic numbers from 22 up to 42 (Ti to Mo).

For the elements of atomic numbers 13 to 23 (Al to V) excited with Fe-55 source, the sample could be considered of infinite thickness, not being transparent to incident and emergent X-rays for this range of energy. In this case, the transmission method cannot be applied and then another procedure based on absorption edges must be used (HALLAK & SALEH, 1983).

In order to obtain the total absorption coefficient with Cd-109 excitation, for the range of energies from 5 up to 17 keV (Ti to Mo), an iterative procedure is performed using the experimental values of the attenuation.

With these absorption coefficient values it was possible to determine the total absorption coefficient for Fe-55, through another iterative process associated with the absorption edges for the elements in the range of energies from 1.5 up to 5.0 keV, i.e., from Al up to V (SIMABUCO, 1993). A multielemental thick target, in pellet form, containing V, Mn, Cu, As, Br, Sr e Zr was prepared for the transmission measurement.

The measuring time for the soil samples was fixed to obtain a total significative count, minimizing the deviation on the area calculation below the characteristic X-ray peaks. In this way the samples excited by Cd-109 were measured for four hours and one hour when excited by Fe-55.

RESULTS AND DISCUSSION

Using standard samples, the relationships between elemental sensitivity and atomic number were obtained for Fe-55 and Cd-109 excitations and could be described by equations (1) and (2), with correlation coefficients equal to 0.9999 and 0.9978, respectively, significative at the 1% level:

$$S_i(Fe-55) = -1.40 \times 10^7 + 3.48 \times 10^6 Z$$
$$-3.16 \times 10^5 Z^2 + 1.20 \times$$
$$x \, 10^4 Z^3 - 1.47 \times 10^2 Z^4$$

(1)

$$S_i(Cd-109) = 2.20 \times 10^5 + 2.35 \times 10^4 \, Z -$$
$$-9.78 \times 10^2 \, Z^2 + 18.38 \, Z^3$$

(2)

Thereafter, soil samples were irradiated and, for illustration purpose, figures 1 and 2 show the pulse spectra obtained for the control of the Dark Red Latosol, excited with Fe-55 and Cd-109, respectively.

For the transmission and absorption edge methods the absorption effects of the matrix were corrected and by this procedure it was possible to calculate the concentration for several elements in the sandy (TABLE 1) and clayey (TABLE 2) soil samples, not treated with vinasse. Standard deviations and the coefficients of variation were also determinated of three replications for each soil layer sample.

The detection limit was established as being equal to three times the standard deviation of

the area under the characteristic X-ray peaks, obtained through the spectrum adjust of the AXIL *software* (ESPEN et al., 1977). Thus, the detection limit for S was 370 ppm and for the Cl 330 ppm, in the case of the sandy soil (TABLE 1).

It can be seen in this TABLE that the elements which show high values of coefficients of variation were Br, Rb, Sr and Nb, due to their very low concentrations in the soil.
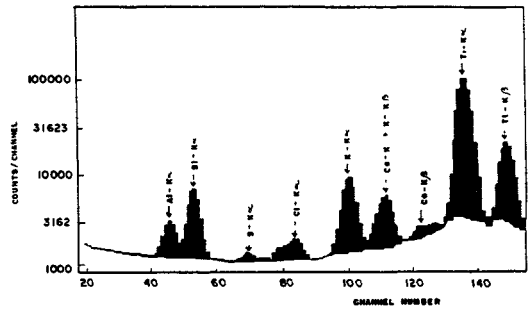

Figure 1. Characteristic X-ray pulse spectrum for the Dark Red Latosol, without addition of vinasse and excitated with Fe-55 source.
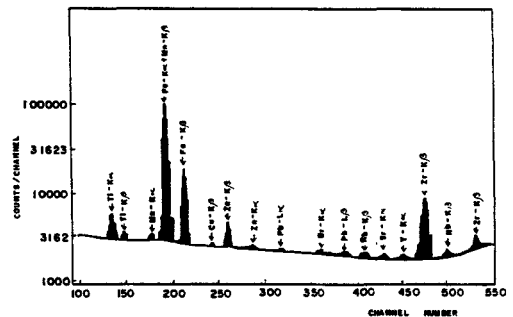

Figure 2. Characteristic X-ray pulse spectrum for the Dark Red Latosol, without addition of vinasse and excitated with Cd-109 source.

TABLE 1. Elemental concentrations for the Red Yellow Podzolic soil, with Fe-55 and Cd-109 excitation.

Element	1st.rep	2nd.rep	3rd.rep	Mean±Deviation	CV(%)
Al	10.72%	0.60%	11.55%	10.96±0.52%	4.72
Si	19.89%	20.87%	24.02%	21.59±2.16%	10.00
S	<370ppm	<370ppm	<370ppm	<370ppm	----
Cl	<330ppm	<330ppm	<330ppm	<330ppm	---
K	0.10%	0.10%	0.12%	0.11±0.01%	11.13
Ca	0.10%	0.11%	0.11%	0.11±0.01%	6.43
Ti	0.70%	0.73%	0.78%	0.75±0.04%	5.81
Mn	693ppm	692ppm	724ppm	703±18ppm	2.59
Fe	3.90%	4.10%	4.17%	4.06±0.14%	3.45
Cu	43ppm	38ppm	38ppm	40±3ppm	7.29
Zn	236ppm	244ppm	233ppm	238±6ppm	2.40
Br	32ppm	30ppm	25ppm	29±4ppm	12.43
Rb	23ppm	20ppm	26ppm	23±3ppm	13.04
Sr	16ppm	23ppm	17ppm	19±4ppm	20.04
Zr	1079ppm	1266ppm	1184ppm	1177±94ppm	7.96
Nb	10ppm	17ppm	14ppm	14±4ppm	28.57

The detection limit for S in clayey soil (TABLE 2) was 300 ppm and for Cl 150 ppm; V, Cu and Rb did not present a good reprodutibility. With regard to V, probabily the high concentration of Ti interferred in the determination, and for Cu, contamination of this element in the Al collimator caused an over estimation of the Cu fluorescence intensity in the sample.

The elemental concentrations of Al, Si, K, Ca, Mn, Ti and Fe obtained for the soils here studied agree with those reported by VERDADE (1972) for a Red Yellow Latosol (var. Marília), a Dark Yellow Podzolic (var. Orto), "Terra Roxa Legítima" and a Purple Latosol.

The dynamics of several ions of vinasse in soil were evaluated by determining the elemental concentration from Al to Nb, in all soil columns treated with vinasse. The results were compared with those of the control soil. Results of the 0-1, 1-2, 2-3, 9-10, 14-16 and 28-30 cm layers, for the two soils, are presented in TABLES 3 and 4. The figures 3 to 6 show the elemental changes of the concentrations of S, Cl, K and Ca, respectively, for the sandy soil, treated and not with vinasse.

In figure 3 it can be observed that the S concentration in the clayey soil increases up to the 10 cm depth and then decreases, and in the last layer, the concentration still does not reach the

values showed in the control column (370 ppm). The S behaviour in clayey soil was quite different than in the sandy soil. Although the S concentration in the original control columns has been almost the same, it could be observed that in the sandy soil treated with vinasse, the concentration of the first layer reached 2,200 ppm, while in the sandy soil this value was half, i. e., 1,100 ppm.

In a general way, the S in the sandy soil was concentrated in the first 10 cm of the column, while in the clayey soil it concentrated in the first layer (0-1 cm) and its concentration almost did not change below the 3 cm depth.

With regard to Cl (figure 4) it can be verified that its concentration increases up to 2-3cm layer, reaching the value of 2365ppm, and then decreases to 1700 ppm at the 28-30 cm layer. As the detection limit for Cl was estimated as being 330 ppm, this value was considered for the sandy soil samples not treated with vinasse. On the other hand average values of Cl concentration in the samples treated with vinasse was very high about 2000ppm.

TABLE 2. Elemental concentrations for the Dark Red Latosol soil, with Fe-55 and Cd-109 excitation.

Element	1st.rep	2nd.rep	3rd.rep	Mean±deviation	CV(%)
Al	12.09%	13.22%	12.10%	12.47±0.65%	5.21
Si	12.39%	13.51%	12.01%	12.64±0.78%	6.17
S	303ppm	479ppm	<300ppm	391±8ppm	22.51
Cl	<150ppm	198ppm	169ppm	184±15ppm	8.15
K	0.20%	0.21%	0.20%	0.20±0.01%	3.54
Ca	0.12%	0.11%	0.12%	0.12±0.01%	5.89
Ti	2.28%	2.33%	2.23%	2.23±0.08%	3.55
V	0.15%	0.12%	0.14%	0.14±0.02%	11.29
Mn	0.15%	0.15%	0.13%	0.14±0.01%	8.75
Fe	13.01%	13.05%	12.99%	13.02±0.03%	0.24
Cu	36ppm	30ppm	38ppm	35±4ppm	11.95
Zn	275ppm	57ppm	265ppm	266±9ppm	3.39
Br	51ppm	50ppm	50ppm	50±1ppm	1.41
Rb	34ppm	34ppm	25ppm	31+5ppm	16.76
Sr	38ppm	36ppm	35ppm	36±2ppm	4.39
Y	16ppm	14ppm	16ppm	15±1ppm	8.16
Zr	902ppm	880ppm	875ppm	886±14ppm	1.62
Nb	41ppm	41ppm	40ppm	41 ±1 ppm	1.72

TABLE 3. Elemental concentrations for several layers of the sandy Red Yellow Podzolic soil column, treated with vinasse.

Element	DEPTH (cm)					
	0-1	1-2	2-3	9-10	14-16	28-30
Al	11.36%	12.63%	12.63%	12.10%	12.44%	13.44%
Si	14.16%	18.32%	17.15%	20.44%	19.98%	18.24%
S	2224ppm	2069ppm	2053ppm	2505ppm	1893ppm	1269ppm
Cl	1886ppm	2295ppm	2365ppm	2321ppm	2004ppm	1704ppm
K	0.76%	0.80%	0.83%	0.94%	0.97%	0.79%
Ca	0.29%	0.31%	0.29%	0.35%	0.33%	0.23%
Ti	0.73%	0.76%	0.74%	0.74%	0.85%	0.82%
Mn	658ppm	701ppm	641ppm	558ppm	727ppm	639ppm
Fe	4.97%	5.16%	4.77%	4.40%	5.05%	5.78%
Cu	166ppm	155ppm	117ppm	151ppm	151ppm	116ppm
Zn	897ppm	870ppm	853ppm	865ppm	905ppm	876ppm
Br	46ppm	44ppm	46ppm	39ppm	51ppm	54ppm
Rb	41ppm	37ppm	33ppm	33ppm	35ppm	39ppm
Sr	37ppm	39ppm	28ppm	21ppm	25ppm	32ppm
Zr	529ppm	649ppm	591ppm	957ppm	934ppm	756ppm
Nb	11ppm	12ppm	13ppm	15ppm	14ppm	20ppm

In relation to the concentration of this element in the clayey soil it can be observed that in the control samples its value was 184 ppm, while the first layer soil treated with vinasse, reached 1100 ppm. It is important to point out that from 2 cm depth on the Cl concentration remained constant, not reaching the control soil values, even at 28-30 cm layer.

Comparing the Cl concentration values obtained for the two soil types treated with the same vinasse quantity, it can be verified that the sandy soil reached higher values than the clayey soil at all depths, remaining in the range of 1700 to 2400 ppm, while for the clayey soil the range was 500 to 1100 ppm, however with a significant decrease already in the first layer.

Figure 5 shows that the K concentration in the clayey soil control was 0.20%, while for all column layers treated with vinasse this value increased to about 0.60%, having thus an increase of almost three times.

In the sandy soil (figure 5), the K concentration in soils treated with vinasse increased almost 10 times when compared with the sandy soil control (0.11%), remaining at the same level along the whole profile.
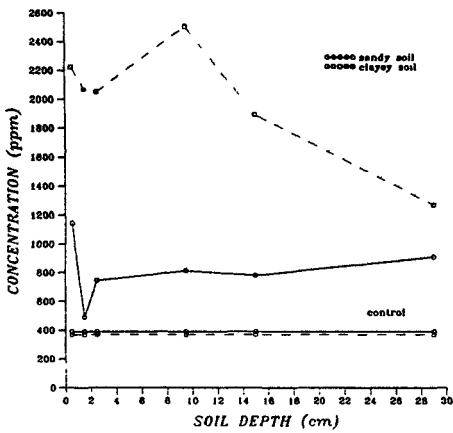
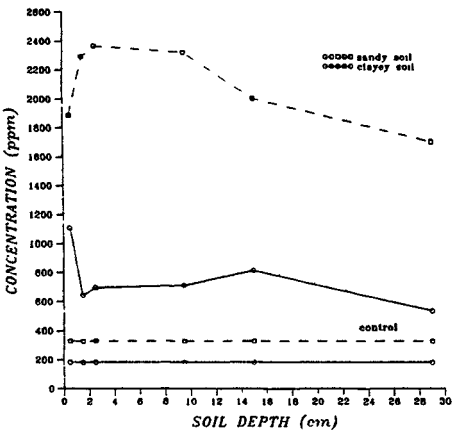Figure 3. Sulfur distribution in the sandy and clayey soils.

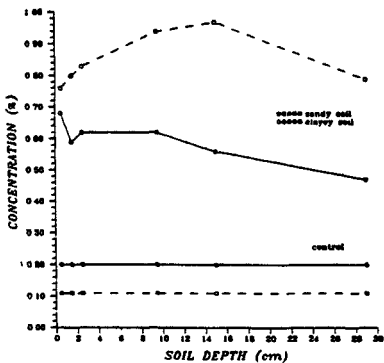Figure 4. Chlorine distribution in the sandy and clayey soils.

Figure 5. Potassium distribution in the sandy and clayey soils.

It was also observed that the concentration of this element in the clayey soil control (0.20%) was twice as much as the value of the sandy soil (TABLES 1 and 2).

Regarding the vinasse distribution in the two soils of different textures, it can be said that in sandy soil the K concentration after vinasse addition is higher than in the clayey soil and also that the relation between the K concentration with and without vinasse addition is also higher for this type of soil.

According to CAMHI (1979), the K concentration of molasses vinasse *in natura* varies from 0.48 to 0.65%. Thus, the increase in the concentration of this element in soil due to vinasse addition, was the expected.

With respect to Ca in the clayey soil (figure 6), a preferencial distribution was observed over the first 10 cm of the column, decreasing thereafter, reaching the value of the control soil.
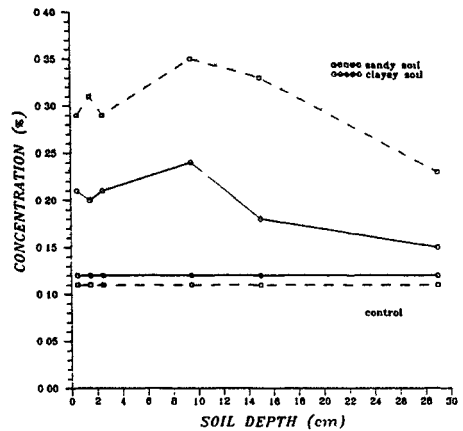

Figure 6. Calcium distribution in the sandy and clayey soils.

As with K, the relation between the Ca concentration with and without vinasse, was higher for the sandy soil.

In the sandy soil treated with vinasse, the Ca concentration in relation to the control, was three times until approximately the 14-16 cm layer (figure 6) and even in the layer of 28-30 cm its concentration did not reach the value of the control soil, which was 0.11%.

In relation to the micronutrients, the discussion of the results must be first addressed to

S.M. SIMABUCO & V.F. NASCIMENTO FILHO

Mn and Fe, and then to Cu and Zn, although they occur in low concentrations in vinasse. The contents of these elements in vinasse of different origins (molasses, juice and mixed must) collected during the season 1978 to 1980 in the Brazilian Northeast region were described by MEDEIROS (1981). The average contents of Cu varied from 0.90 to 3.60 ppm; for the Zn this variation was 2.20 to 4.30 ppm; for the Mn, 5.10 to 6.70 ppm; and for the Fe, 45.20 to 57.20 ppm.

The Mn and Fe contents in soils are higher (TABLES 1 and 2) and therefore it is difficult to measure variations of these elements in the soil due to a treatment with vinasse. The same fact probabily occurs with Al, Si and Ti, present in high concentration in the soil.

TABLE 4. Elemental concentrations for several layers of the clayey Dark Red Latosol soil column, treated with vinasse.

	DEPTH		(cm)			
Element	0-1	1-2	2-3	9-10	14-16	28-30
Al	11.96%	11.51%	13.00%	12.92%	11.90%	12.24%
Si	12.48%	12.20%	13.98%	13.75%	13.87%	13.49%
S	1144ppm	493ppm	747ppm	806ppm	781ppm	909ppm
Cl	1107ppm	646ppm	696ppm	710ppm	815ppm	537ppm
K	0.68%	0.59%	0.62%	0.62%	0.56%	0.47%
Ca	0.21%	0.20%	0.21%	0.24%	0.18%	0.15%
Ti	2.20%	2.25%	2.28%	2.41%	2.33%	2.35%
V	0.16%	0.16%	0.13%	0.15%	0.15%	0.16%
Mn	0.13%	0.13%	0.11%	0.14%	0.15%	0.16%
Fe	13.04%	13.08%	12.73%	13.48%	12.39%	13.38%
Cu	130ppm	127ppm	108ppm	144ppm	99ppm	118ppm
Zn	981ppm	1000ppm	988ppm	026ppm	1007ppm	1006ppm
Br	53ppm	57ppm	60ppm	44ppm	48ppm	63ppm
Rb	46ppm	45ppm	41ppm	49ppm	41ppm	39ppm
Sr	39ppm	48ppm	34ppm	42ppm	42ppm	44ppm
Y	19ppm	22ppm	12ppm	18ppm	21ppm	15ppm
Zr	857ppm	875ppm	800ppm	904ppm	1110ppm	1066ppm
Nb	39ppm	41ppm	40ppm	42ppm	44ppm	43ppm

With regards to Cu and Zn (TABLES 1 and 4) differences caused by the addition of vinasse were visualized. The Cu concentration increased from 40 ppm to 116-166 ppm along the profile in the sandy soil and 35 to 99-147 ppm in the clayey soil, while the Zn concentration increased from 238 ppm to 835-905 ppm in sandy soil and from 266 up to 959-1058 ppm in the clayey soils.

A small increase in Rb and Sr concentrations can also be noted in these TABLES, while for the Zr there was a decrease for the sandy soil, reducing from 1177 ppm to 529-957 ppm, which was not observed for the clayey soil.

CONCLUSIONS

Using Fe-55 and Cd-109 radioactive sources, it was possible to evaluate instrumental and simultaneously the concentrations of Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Cu, Zn, Br, Rb, Sr, Y, Zr and Nb in sandy and clayey soil samples.

The behaviours of S and Cl in the clayey soil were different in relation to the sandy soil, when submitted to the same vinasse quantity (about 4000 m^3/ha). The sandy soil presented a significant decrease in their contents after the first 3 cm. In spite of this decrease, the contents of S and Cl along the soil profiles treated with vinasse remained at a higher level as compared to the control soils.

The concentrations of K and Ca along the columns of the two different texture soils practically did not change, indicating that for the quantity of vinasse applied, they reached the saturation level of these elements.

An increase in the contents of Cu, Zn, Rb and Sr in relation to the initial concentrations in the soil due to the addition of vinasse were also observed.

As expected, the Al, Si, Ti, Mn, Fe and Zr concentrations did not vary along the profiles as they are characteristic elements in the soil, occuring in very high initial concentrations in the soil as compared to the vinasse.

ACKNOWLEDGMENTS

REFERENCES

CAMHI, J.D. Tratamento do vinhoto subproduto da destilação de álcool. **Brasil Açucareiro**, Rio de Janeiro, v.94, n.1, p.18-23, 1979.

ESPEN, P.; NULLENS, H.; ADAMS, F. A computer analysis of X-ray fluorescence spectra. **Nuclear Instruments and Methods**, Amsterdam, v.142, p.243-250, 1977.

GIAUQUE, R.D.; GOULDING, F.S.; JAKLEVIC, J.M.; PEHL, R.H. Trace element determination with semiconductor detector X-ray spectrometers. **Analytical Chemistry**, Washington, v.45, n.2, p.671-681, 1973.

HALLAK, A.B.; SALEH, N.S. A new method for matrix corrections by radioisotope excited X-ray fluorescence. **X-Ray Spectrometry**, London, v.12, n.4, p.148-149, 1983.

MEDEIROS, A.P. Composição química de diferentes tipos de vinhaça nos Estados de Pernambuco, Paraíba e Rio Grande do Norte. *Saccharum* STAB, São Paulo, v.4, n.12, p.36-40, 1981.

SIMABUCO, S.M. Emprego da fluorescência de raio-X por dispersão de energia no estudo da dinâmica da vinhaça no solo. São Paulo, 1993. 133p. Tese (Doutorado) - Instituto de Pesquisas Energéticas e Nucleares.

SIMABUCO, S.M.; NASCIMENTO FILHO, V.F. Quantitative analysis by energy dispersive X-ray fluorescence by the transmission method applied to geological samples. **Scientia Agricola**, Piracicaba, v.51, n.2, p.197-206, maio/ago. 1994.

VERDADE, F.C. Análise química total. In: MONIZ, A.C. (Coord.) **Elementos de pedologia**. São Paulo: EDUSP, Polígono, 1972. cap.17, p.209-221.