September 2007 *Volume 2 Issue 3*

Trade Science Inc.

Environmental Science

An Indian Journal

Current Research Paper

ESAIJ, 2(3), 2007 [200-204]

A Determination Of Arsenic In Sugar Cane Soils And Foliar Tissue From Municipio, Lara State, Venezuela By Hydride Generation Atomic Absorption Spectroscopy

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Received: 3rd July, 2007 ; Accepted: 8th July, 2007

ABSTRACT

The total arsenic levels were determined in sugar cane soils and foliar tissue from crops of the Municipio Palavecino, Lara State, Venezuela using the method of hydride generation atomic absorption spectrometry. The samples were taken from six farms of the zone. In the preparation procedure optimized amounts of KI and HCl were added to the soil slurry in order to perform the predigestion and prereduction of the arsenic. Foliar tissue samples were analyzed after a wet digestion procedure following a similar procedure as for the soils for the pre-reduction step. After that sodium borohydride 3% in NaOH 1% was added to produce the arsine. An Argon flow was used to transport the arsine to the quartz cell of the spectrometer. Measurements were carried out in a Perkin Elmer 3110 spectrometer with hydride generation module. The arsenic levels in the soil were in the range of 5.75 to 12.13μg/g, the accuracy was verified analyzing the NIST standard reference materials San Joaquin Soil and Buffalo River Sediment. The arsenic levels in the foliar tissue samples were in the range of 0.24 to 0.29μg/g . The accuracy was verified with the NIST Standard reference material 1573 Tomato leaves. The proposed soil slurry preparation method avoids the possible losses of the traditional digestion procedures with adequate analytical quality. A good agreement was found between the certified values and those obtained with the proposed procedure. The arsenic levels in the soils are lower than the average toxicity threshold value for crop plants. Eventhough the sampled sites are under risk of contamination due to the intensive use of pesticides containing this toxic element. The Arsenic levels in the foliar tissue indicate absorption and transport of this toxic element and the necessity of further studies for the evaluation of the associated risk. Nevertheless, the arsenic concentration in foliar tissue is significantly lower than those values found in risk zones.

KEYWORDS

Arsenic; Sugar cane; Soil; Foliar tissue.

INTRODUCTION

The arsenic could be found in soils and waters as a consequence of natural sources (dissolution of minerals from volcanic or sedimentary rocks as well from the dilution of geothermal waters)[1-3] or due to anthropogenic factors(industrial and agrochemical discharges)[4,5].The quantification of arsenic in soils plays an important role in the determination of the environmental impact. Its mobility in the environment can lead to the income in the food chain through the adsorption desorption processes in soils[6,7]. The agrochemical discharges are an important source of arsenic contamination. The arsenic compounds sodium methylarsenate, disodium methylarsenate and dimethyl arsenic acid are used as herbicides in sugar cane crops[8] and can contaminate the soils. The bioavailability to crop plants of arsenic depends on several physical and chemical factors in the soil. The texture and chemical composition of the soil are important factors that govern the availability of arsenic to plants[6].

The element can be absorbed by plants and transported to leaves, steam and fruits[6,7,9]. High levels of the element in surface waters could be accumulated also by aquatic plants, algaes and fishes. The toxic nature of the element and its compounds lead to damages of the living organism and humans[10,11].

There is a necessity of the evaluation of sugar cane soils arsenic levels by means of simple methods with adequate analytical quality, as the slurry analysis, for the monitoring of the environmental impact of the arsenic agrochemical discharges in the west center region of Venezuela, Barquisimeto-Cabudare, Lara state. The importance of this study is enhanced by the fact that the sugar cane production is the main agricultural activity in the region under evaluation. The potential risk on the population or sugar consumers must be also evaluated, since the element could be uptaken from soil by the sugar cane plants and enter into the food chain of humans and animals. This fact is evaluated in a first approach by the determination of the element in the foliar tissue.

Regarding to the analytical procedures,[12]; studied the adsorption-desorption dynamic of the As(V) in soils. The determination of arsenic by HG-FAAS was performed after the digestion of the soils with a mixture of concentrated HNO_3 and H_2O_2. [13,14]determined the element in slurry samples of volatile ashes, diatomeas and cement, after a prereduction step with HCl and KI followed by sonication and HG-FAAS. This procedure was adapted for the determination of arsenic in soil samples.

TABLE 1 : Sampling sites

Farms	Longitude East(UTM)	Latitude North(UTM)
GA-12	477110	1108559
SN-12	484577	1110344
LD-12	467340	1111925
PA-12	472600	1112414
BA-12	472598	1111548
SA-12	473298	1111779

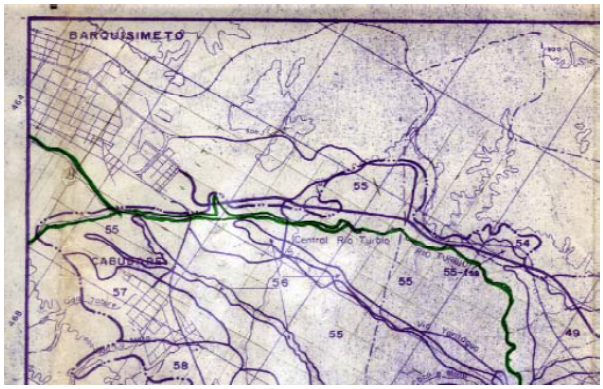

Figure 1 : Map of the Rio Turbio Valley region with sample sites (Numbers 55, 56, 57, 58, 49 in the map)

EXPERIMENTAL

Sampling procedure

The soil samples were collected taking into account the soil classification given by Mendoza et al[15] and Graterol et al[16], to ensure that the soil samples had similar physical and chemical characteristics. Using a map, the soils were located in the respective farms of the region under study (Cabudare, Edo.Lara, in the Rio Turbio Valley). The coordinates were determined using a GPS instrument. The sampling site coordinates are given in TABLE 1. The figure 1 shows the sample sites in a map. Sites correspond to the numbers 55,56,57,58 and 49 in the map or soil units.

The soil samples were taken at two deeps: 0-20cm and 20-40cm, according to the procedure employed by the Laboratorio de Suelos y Aguas del Ministerio del Ambiente(MARN-Lara), In all the cases sampling was random and composite. Samples were stored in plastic bags. The sample preparation involves the sieving, drying at room temperature,

milling, and grinding, following the procedures of the Environment and Natural Resources Minister in Venezuela (Ministerio de Ambiente y Recursos Naturales Renovables) to ensure the sample homogeneity and representativity. Only the fine fraction of the soil (< 2mm) was analyzed. The humidity correction was performed separately, by weighing samples before and after drying at 110°C in oven.

The foliar tissue samples were collected in the same sample sites as the soils according to the TABLE 1 and figure 1. Whole sugar cane plants (leaves and steams), aprox. 2 meters hight, were taken from sample sites. Three specimens were collected from every site. Only the young green leaves without the central nerve were taken into account. Composite samples were prepared for soils as well for foliar tissue, and then divided in 4 replicates for the slurry preparation and/or digestion procedures.

Sample preparation

Slurries

The optimized sample mass of 200mg (see TABLE 2) is taken after an optimized milling time of 10min. Then the sample is carry on to a vessel for the reaction with Potassium iodide (KI 2%) in HCl(Riedel de Haen, Merk, Germany) 5M in a final volume of 25mL. The reaction mixture is sonicated in Ultrasonic Bath for 5min. An aliquot of 200µL of the supernatant is aphorized to 10 ml with HCl 0.5M and taken to the reaction vessel of the Hydride Generation module in order to perform the hydride generation with sodium borohydride 3% w/V in NaOH 1% w/V.

Digested samples

1000 mg of the soil sample were digested with concentrated HNO_3 and H_2O_2(Both reagents Riedel de Haen, Germany) bellow 70°C. The silica residue was filtered and the samples were stored till analysis. The same procedure was performed for the foliar tissue samples, but using a sample mass of 3000mg. For the hydride generation an aliquot of 1ml was prepared as explained in the section above. See TABLE 2.

Standards

The standards were prepared by serial dilution of the 1000mg/L titrisol (Merk, Germany) arsenic (III) stock solution with HCl 0.5M, in the range of 0.001 to 0.01mg/L. Soil and foliar tissue samples were spiked with the standards to evaluate the feasibility of aqueous calibration when slurry samples are analyzed. For the accuracy verification the NIST standard reference materials SRM Buffalo River Sediment (1646a) and San Joaquin Soil(2709) were analyzed. The accuracy of the Determination of As in the foliar tissue was evaluated with the NIST SRM 1573 Tomato Leaves. The standard reference materials were digested in the same fashion as the samples by the procedure explained in the section of digested samples.

TABLE 2 : Optimized conditions

	Soil.	Foliar tissue
Wavelenght	193.7 nm	193.7 nm
Slit	0.7 nm	0.7 nm
Flame	Air/acetylene	Air/acetylene
Carrier gas pressure	39 Psi	39 Psi
Purge time in reaction vessel	30 s	15 s
Aliquot volume (slurry)	200µL	NA
Aliquot volume (digested)	1mL	400µL
Sample mass (slurry)	200 mg	NA
Sample mass (digested)	1000 mg	3000 mg
Milling time	10 min	NA

INSTRUMENTAL

The total arsenic was determined by HG-FAAS, in a PERKIN ELMER® Spectrometer 3110, with Hydride generation module with quartz cell and a single hollow cathode lamp. The experimental optimized conditions are summarized in TABLE 2.

RESULTS

Optimization of the slurry sample preparation procedure

In a first step of the work the milling time, sample mass and supernatant aliquot were optimized. Sample masses of 50, 100 and 200mg respectively were tested for milling times of 10, 20 and 30min. It was found that the best compromise among low preparation time, mass representativity and highest signal was obtained for 10 minutes of milling with a sample mass of 200mg in the prereduction step, when an aliquot of 200µl is taken for the further reduction in the hydride generation module. The aliquot volume that was taken for the reduction was also optimized. Aliquots of 50 till 600µL were tested. It was found that an aliquot of 200µL allows to a high signal value

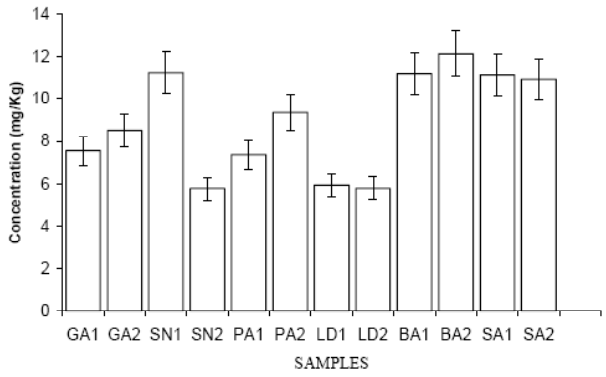

Figure 2 : Total arsenic concentration in sugar cane soils. 1-0-20cm deep and 2-20-40cm deep

TABLE 3 : Concentration of arsenic in soil(1-0-20cm deep and 2-20-40cm deep) and foliar tissue(dry weight)

Sample	[As](μg/g)n=6	
	Soil	Foliar tissue
GA1	7.55	0.260
GA2	8.50	
SN1	11.24	0.290
SN2	5.77	
PA1	7.36	0.239
PA2	9.34	
LD1	5.93	0.260
LD2	5.78	
BA1	11.18	0.243
BA2	12.13	
SA1	11.13	0.259
SA2	10.93	

TABLE 4 : Arsenic in NIST standard reference materials: san joaquin soil, buffalo river sediment and tomato leaves

Sample	Code	Certified value(μg/g)	Experimental value(μg/g)	% error
Buffalo River Sediment	1646a	6.23±0.8	5.85±0.50	6.07
San Joaquin Soil	1709	17.7±0.21	19.06±0.91	7.68
Tomato Leaves	1573	0.27±0.05	0.30±0.04	10.0

in the linear calibration range of the instrument. Higher aliquot volumes were not suitable since the signal values were over the linear range for the concentration level of the samples. The reliability of using aqueous calibration standards for the quantification was also evaluated by comparison of the slope with that obtained by the standard addition procedure. A mean deviation less than 6% of relative standard deviation was obtained. The optimized parameters are shown in TABLE 2.

Arsenic concentration in the soil samples

The arsenic concentration values are shown in figure 2. The arsenic levels are higher than the maximum allowed level of 5mg/Kg, and evidence a risk. Nevertheless, as recommended by Del Rio et al.[4] it would be necessary to evaluate the available fraction of the element and its speciation. On the other hand these values are lower than the threshold levels (40mg/Kg)[4] and 20mg/Kg(soil quality criterion for total arsenic set by the Danish Environmental Protection Agency)[6]. The values of arsenic concentration in the sugar cane soils of the Rio Turbio Valley region are significantly lower than the reported values for contaminated regions[4,6]. Eventhough the periodic monitoring of the arsenic levels in these soils must be performed in order to evaluate the impact of the sugar cane production on the environment and to prevent the contamination of the sugar cane by the accumulation of the elements by the plants. The developed method is faster than the traditional methodology of analysis of digested samples and becomes a reliable alternative for this task. The analytical quality of the results was demonstrated in terms of the accuracy and precision. The precision was evaluated by means of 10 independent replicates of the samples. It was less than 9% of relative standard deviation. A spread was observed in this parameter, but it can be explained by the fact that soil samples have a lack of homogeneity, even when the fine fraction is analyzed.

Regarding to the accuracy, as shown in TABLE 4, a deviation less than 10% of error was found for the standard reference materials. When the slurry method is compared with the method of analysis of digested samples it is found that lower values are obtained when digested samples are analyzed (5.58 +/- 0.50 μg/g by digestion vs. 7.18 +/- 0.65 μg/g by slurry). This could be an evidence of analyte losses during the preparation procedure. When the standard reference samples San Joaquin Soil was analyzed using the digestion procedure lower concentration values were also obtained(13.81 +/- 0.44 μg/g Vs. a certified value of 17.7 +/- 0.21 μg/g).

Arsenic concentration in the foliar tissue samples

The concentration values found for arsenic in

the foliar tissue are in the narrow range of 0.24μg/g to 0.29μg/g, as shown in TABLE 3. These values are lower than those found by other authors in risk zones[19].

The accuracy of arsenic determination in the foliar tissue was verified with the NIST SRM 1573, tomato leaves, being digested in the same fashion as samples. As shown in TABLE 4 a deviation of 10 percent was found respect to the certified value.

CONCLUSIONS

The proposed slurry preparation method avoids the possible losses of traditional digestion procedures with adequate analytical quality and has the advantage of the simplicity. A good agreement was found between the certified value and that found with the proposed procedure. The total arsenic levels in the soils are lower than the usual reported values for contaminated regions. The total arsenic concentrations in the soils of the Rio Turbio Valley are less than the average toxicity threshold values for crop plants, although the sampled sites are under risk of contamination due to the intensive use of pesticides containing this toxic element. The arsenic concentrations in leaf tissue are in a narrow range and are lower than those values found for risk zones. Although it could be necessary the periodic evaluation of the arsenic levels in soil and plants there is non potential risk to population health due to the consumption of sugar form the region.

REFERENCES

[1] I.J.Pickering, R.C.Prince, M.J.George, R.D.Smith, G.N.George, D.E.Salt; Plant Physiology, **122**, 1171 (2000).
[2] J.Nriagu; 'Arsenic in the environment', John Wiley & Sons, Inc.New York, USA, **26(1/2)**, (1994).
[3] C.K.Jain, I.Ali; Water Research, **34(17)**, 4304 (2000).
[4] M.Del Rio, R.Font, C.Almela, D.Velez, R.Montoro, A.De Haro Bailon; Journal of Biotechnology, **98**, 125 (2002) .
[5] Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological profile for arsenic (Update). Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service, (2000).
[6] H.Helgesen, E.H.Larsen; Analyst, **123**, 791 (1998).
[7] H.K.Das, A.K.Mitra, P.K.Sengupta, A.Hossain, F.Islam, G.H.Rabbani; Environment International, **30**, 383 (2004).
[8] R.Watts; 'Hazardous Wastes: Sources, pathways, receptors', Edit.John Wiley & Sons, Inc. New York, USA, (1997).
[9] M.E.V.Schmöger, M.Oven, E.Grill; Plant Physiology, **122**, 793 (2000).
[10] J.A.Centeno, F.E.Mullik, L.Martinez, N.P.Page, H.Gibb, D.Longfellow, C.Thompson, E. R.Ladich; Environmental Health Perspectives, **110**, 883-886 (2002).
[11] F.Michael Hughes; Toxicology Letters, 'Arsenic toxicity and potential mechanisms of action', **133**, 1-16 (2002).
[12] J.Alvarez-Benedi, S.Bolado Rodriguez, I.Cancillo Carro, C.Calvo Revuelta; Dinamica de adsorcion-desorcion de arsenico (v) en suelos de cultivo en castillay leon en 'Estudios de la zona no saturada del suelo', J.Alvarez-Benedi, P.Marinero'. www. zonanosaturada. com/publics/V6/pdf, **8**, 331-338 (2003).
[13] J.A.Cortez; Tesis Doctoral Universidad de Murcia, Espana, Suspensiones en Espectrometría de Absorcion Atomica. Analisis de Muestras con Elevado Contenido de Sílice, (1993).
[14] J.Arroyo, L.Gomez, L.M.Marco, R.Rivas; Program and book of abstract, 7th Rio Symposium on Atomic Spectroscopy, Florianopolis, SC, Brasil, (2002).
[15] L.Y.Graterol, J.Venegas; Estudio de suelos semidetallado preliminar Cuencas de los Rios Turbio y Yaracuy, sector Barquisimeto-Chivacoa. Direccion de Informacion Basica. Division de Edafologia. MARN-Lara. Venezuela, (1976).
[16] S.Mendoza, G.Y.Valera, C.Ohep; Estudio de suelos preliminar del eje Moron-Barquisimeto-La Lucia. Estados Falcon, Carabobo, Yacacuy y Lara. Departamento de suelos, vegetación y fauna. MARN-Lara. Venezuela, (1990).
[17] Shaban W.Al Rmalli, Chris F.Harrington, Mohamed Ayub, Parve I.Haris, J.Environ. Monitor; A Biomaterial based approach for arsenic removal from water, 7, 279-282 (2005).
[18] Iris Koch, Li Xia Wang, Chrisa Ollson, William Cullen, Kenneth J.Reimer; Environ. Sci. Technol. The Predominance of Inorganic Arsenic Species in Plants from Yellowknife, Northwest Territories, Canada, 34, 22-26 (2000).
[19] F.Baroni, A.Boscagli, L.A.Di Lella, G.rotano, F.Riccobono; Journal of Geochemical exploration, Arsenic in soil and vegetation of contaminated areas in southern Tuscany Italy, 81, 1-14 (2004).