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Arsenic fractionation in agricultural acid soils from NW Spain using a sequential extraction procedure

Juan Carlos Nóvoa-Muñoz [a,*], José Manuel G Queijeiro [a], Daniel Blanco-Ward [a], Cristalina Álvarez-Olleros [a], Eduardo García-Rodeja [b], Antonio Martínez-Cortizas [b]

[a] *Área de Edafoloxía e Química Agrícola, Facultade de Ciencias de Ourense, Universidade de Vigo. As Lagoas s/n. 32004 Ourense, Spain*

[b] *Departamento de Edafoloxía e Química Agrícola, Facultade de Bioloxía, Universidade de Santiago de Compostela. Rua Lope Gómez de Marzoa s/n. 15782 Santiago, Spain*

Abstract

Arsenic fractionation has been studied in nine vineyard soils from a wine-producing area in Galicia (NW Spain) characterized by an unusually high As content. Total As concentrations are 7 to 10 times higher the maximum values allowed by the legislation, reaching maximum value of 200 mg kg^{-1}. The study of As fractionation revealed that those fractions showing strong correlations to crystalline Fe and Al hydrous oxides ($r > 0.69$, $p < 0.01$ and $r > 0.71$, $p < 0.01$ respectively) represented, on average, higher than the 80% of total As. The low levels of mobile and potentially toxic As fractions (<4% of total As) suggest that its toxicity is partially minimized in these soils, although the modifications induced by soil management could promote an increase of As availability.

Keywords: Agricultural soils; Vineyard; Arsenic; Sequential extraction; Soil use change

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1. Introduction

The geochemical behaviour of arsenic (As) in soils has become an increasingly important environmental concern due to their potential risks for human health. Thus, in several countries, a total As content (As_T) above 50 mg kg^{-1} is considered dangerous and above this concentration soil remediation procedures are recommended (Adriano, 2001), whereas in Galicia (NW Spain) the upper As_T limit allowed in soils for agricultural use is 25–30 mg kg^{-1} (CICDXI.XG, 1996). In our area, new vineyards are being planted in soils where the presence of arsenopyrite (FeAsS) is known and its dissolution in aerobic environments may result in the release of dangerous mobile As species (Lumsdon et al., 2001).

Since As_T content only gives a poor indication about its availability and potential toxicity risks for living organisms (Taggart et al., 2004), multi-step sequential procedures are usually applied to estimate As fractions in soils (Lombi et al., 2000; Wenzel et al., 2001) and to assess the potential effects of As in soil pollution and human health. However, it is well know that an extractant cannot remove all of a targeted solid-phase component without any effect on other soil compounds. Moreover, redistribution and readsorption during the sequential extraction procedure can also take place. Despite these shortcomings, as happen with other chemical extractions procedures, this technique still

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* Corresponding author. Tel.: +34 988 387091; fax: +34 988 387001.

E-mail address: edjuanca@uvigo.es (J.C. Nóvoa-Muñoz).

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Table 1
Mean values and deviation of selected soil properties

Depth (cm)	n	pH (H_2O)	CEC	C (g kg^{-1})	Al_o (g kg^{-1})	Al_d (g kg^{-1})	Al_n (g kg^{-1})	Fe_o (g kg^{-1})	Fe_d (g kg^{-1})
0–10 cm	9	5.0±0.8	6.9±4.0	3.1±2.0	1.9±1.5	2.2±1.3	3.6±2.7	2.2±0.8	15.5±8.8
10–30 cm	9	5.1±0.8	7.1±4.7	2.4±1.2	1.7±1.3	3.1±1.3	3.2±2.5	2.3±0.8	14.6±8.1
>30 cm	9	5.1±0.7	6.7±3.2	2.3±1.1	1.8±1.2	2.0±1.1	3.4±3.0	2.4±0.9	15.5±9.6

CEC is expressed in $cmol_c$ kg^{-1}.

furnishes more useful information on metal binding, mobility, and availability that can be obtained with a single extractant (Belzile et al., 1989).

Thus, this work was focused on As distribution in vineyards soils, also considering the vertical variation of different As fractions and their potential risk of mobility.

2. Materials and methods

Composite soil samples were collected at 0–10, 10–30 and >30 cm depth intervals in nine vineyard soils from D.O. Ribeiro (Galicia, NW Spain) developed from schists (6), alluvial sediments (2) and granites (1). The following analyses were performed, in duplicate, using air dried fine earth fraction (<2 mm): soil pH was measured in distilled water suspensions (1:2.5 w/v ratio) using a pHmeter BasiC 20 Crison, whereas total C was determined in finely ground samples using a C analyzer (Thermo Finnigan Flash EA 1112 NC); cation exchange capacity at soil pH (CEC) was estimated as the sum of base cations (K, Na, Ca, Mg) extracted in 1 M NH_4Cl and Al extracted with 1 M KCl. The fractionation of Al and Fe in vineyard soils was studied following the selective dissolution methods used by García-Rodeja et al. (2004): bound to non-crystalline components (extracted in 0.2 M oxalic acid-ammonium oxalate at pH 3.0, Al_o, Fe_o); total free Fe and associated Al (extracted in Na-dithionite-citrate, Fe_d, Al_d) and total free Al (extracted in 0.5 M NaOH, Al_n). All measurements of base cations, Fe and Al were performed by flame-AAS (Varian SpectrAA 220).

For As distribution a sequential extraction procedure developed recently by Wenzel et al. (2001) was used allowing us to define the following As fractions: non-specifically adsorbed As (As_{NEA}; extracted with $(NH_4)_2SO_4$ 0.05 M); specifically sorbed As (As_{EA}; extracted with $(NH_4)H_2PO_4$ 0.05 M); As associated with amorphous Fe and Al oxyhydroxides (As_{AM}; extracted with NH_4-oxalate buffer 0.2 M, pH 3.25, in the dark); As associated with crystalline Fe and Al oxyhydroxides (As_{CR}; extracted with NH_4-oxalate buffer plus 0.1 M ascorbic acid, pH 3.25, at 96 °C in a water bath) and residual As (As_{RD}; digested with $HCl+HNO_3$). Arsenic measurements in soil extracts were carried out using ICP-AES (Perkim-Elmer, Optima 4300DV). Arsenic measurements by ICP have a detection limit of 0.012 mg L^{-1} which results, take into account the soil: solution ratio used in the sequential extraction procedure, in a minimum As content of 0.3 mg kg^{-1}. During ICP measurements, internal As standards were run every 20 samples and the values obtained were within 5% of the certified values. The recovery of the final sequential extraction procedure (SEP) was estimated comparing the sum of the five fractions with a single digestion by strong acids ($HCl+HNO_3+HF$) which was tested using certified reference materials (NIST 1633b, NIST 2711 and NIST 2709).

The relationships between As fractions and soil components were evaluated using correlation analysis. The software used for the purpose of statistical analysis was SPSS v 12.0.

3. Results and discussion

3.1. Soil characteristics

The studied soils are acidic (average water pH <5.1), have low CEC at the soil pH (6.7–7.1 $cmol_c$ kg^{-1}) and have a total organic carbon content ranging from 23 to 31 g kg^{-1} (Table 1). Amorphous Al (Al_o) and free Al

Table 2
Mean values and standard deviation in mg kg^{-1} of As fractions and total As for the studied soils

Depth (cm)	n	As_{NEA}	As_{EA}	As_{AM}	As_{CR}	As_{RD}	As_T
0–10	9	<0.30	2.7±2.8	18.5±10.6	29.8±17.8	23.6±19.4	98.1±55.0
10–30	9	<0.30	1.4±1.3	16.5±8.7	31.9±22.8	27.7±16.2	93.5±45.9
>30	9	<0.30	1.9±1.6	19.5±10.6	34.4±24.6	26.4±25.6	100.6±59.7

As_{NEA}: non-specifically adsorbed As; As_{EA}: specifically sorbed As; As_{AM}: As associated with amorphous Fe and Al oxyhydroxides; As_{CR}: As associated with crystalline Fe and Al oxyhydroxides; As_{RD}: residual As.