



## Soil interaction and fractionation of added cadmium in some Galician soils



D. Arenas-Lago<sup>a</sup>, F.A. Vega<sup>a</sup>, L.F.O. Silva<sup>b</sup>, M.L. Andrade<sup>a,\*</sup>

<sup>a</sup> Department of Plant Biology and Soil Science, University of Vigo, Lagoas, Marcosende, 36310 Vigo, Spain

<sup>b</sup> La Salle University Centre, Canoas, UNILASALLE, Av. Victor Barreto, 2288 Canoas, Brazil

### ARTICLE INFO

#### Article history:

Received 22 July 2013

Received in revised form 9 August 2013

Accepted 11 August 2013

Available online 23 August 2013

#### Keywords:

Soil  
Cadmium  
Sorption  
Fractionation  
Mineral alteration  
FE-SEM/EDS

### ABSTRACT

The surface and subsurface horizons of four different soils – an Ultisol (U), a Fluvent (F), an Inceptisol (I) and a Fluvaquent (Fa) – were treated with an acidic solution of Cd<sup>2+</sup> with the aim of establishing their sorption capacity, the distribution of Cd in the different geochemical phases of the soil, and to determine the possible mineralogical changes resulting from the treatment. The Cd fractionation process was carried out by means of a sequential chemical extraction. XDR and FE-SEM/EDS were used to determine the mineralogical composition of all of the horizons before and after the treatment with Cd. The majority of the Cd that was added was not sorbed by the soils, which retained between 10.22% in Fa and 16.09% in F. The horizons with the highest content of Fe, Mn and Al oxides, organic matter and high mineralogical variety in the clay fraction were those that absorbed the most Cd. The percentage of exchangeable Cd was the highest in all of the soil, while the fraction of metal associated with crystalline Fe oxides and the residual fraction were very low. The acid treatment affected the mineralogy of all of the soils, reducing the percentage of the most labile minerals and leading to the formation of amorphous phases capable of sorbing Cd. The images obtained by FE-SEM and EDS confirmed the formation and fixation of Cd gels on muscovite, as well as the formation of Cd(NO<sub>3</sub>)<sub>2</sub> · 4H<sub>2</sub>O in Fa.G.

© 2013 Elsevier B.V. All rights reserved.

### 1. Introduction

Cadmium (Cd) is a naturally occurring heavy metal that is widely distributed in low concentrations in rocks, soils, waters, plants and animals. It has no essential biological function, although at high concentrations it can be toxic to soil biota, plants, animals, and humans [1].

A large amount of wastewater containing cadmium, mostly from industries, is discharged into soil. The causes of these effluents include the production of zinc, phosphate minerals and manure bio-industries. Cadmium can also enter the air through the burning of waste and fossil fuels and reach the soil by wet or dry deposition.

Approximately 75% of the cadmium that is produced is used in the manufacture of batteries, especially nickel–cadmium batteries. A significant amount is used in electroplating (as a coating), and some salts are used as pigments and in certain alloys with low melting points. Because of its low friction coefficient and high resistance to fatigue, it is used in alloys for bearings. Also, many types of welding fluxes contain cadmium, and it is used in control rods in nuclear fission and some semiconductors. Cadmium compounds are used as stabilizers for plastics such as PVC, and the element is also applied as a pigment in the manufacture of acrylic and oil paints, amongst others.

Cadmium mainly enters humans through soils from which plants and animals take up Cd, and through the processes of the food chain

that lead it to accumulate. Cadmium accumulates in soil by pedogenic processes from parent materials and anthropogenic sources such as atmospheric deposition, the application of agricultural materials such as phosphate fertilizers and farmyard manure, biosolids, and industrial wastes [2–6]. As a result, cadmium is one of the most common heavy metals in the soil environment, and its concentrations have increased dramatically over the last few decades. Therefore, concerns about soil and water pollution have highlighted the importance of understanding the processes or factors that control the retention and release of Cd in soils [7].

The concentration of Cd in the soil solution, as well as its downward transport, bioavailability and toxicity, is mainly controlled by sorption–desorption processes at the surfaces of both inorganic and organic soil colloids. It is a well-known fact that pH is the most important soil parameter determining the mobility of Cd in soils, which generally decreases with increasing soil pH [7–10]. Furthermore, other factors such as the soil organic carbon content, cation exchange capacity, clay content, Fe and Mn oxyhydroxide contents and solution composition have a pronounced effect on the retention and mobility of Cd in soils [11,12].

Cadmium added to soil from different sources undergoes a series of reactions that include sorption to inorganic and organic colloidal materials, precipitation and complexation with organic and inorganic ligands in soil solution, and the subsequent sorption of some of these ligand complexes to the soil particles.

Total cadmium contents are of limited importance in evaluating its mobility and bioavailability in soils. The mobility and bioavailability of cadmium depend strongly on its chemical forms associated with

\* Corresponding author. Tel.: +34 986 812630; fax: +34 986 812556.

E-mail address: [mandrade@uvigo.es](mailto:mandrade@uvigo.es) (M.L. Andrade).

inorganic and organic soil components. Various analytical approaches have been used to determine the different chemical forms of Cd, many of which rely on the desorption of the element from the solid phase using chemical reagents. Two groups of tests should be considered: (i) single extraction procedures using one extraction reagent and (ii) sequential extraction procedures using a series of progressively stronger reagents to dissolve increasingly refractory forms [13–15].

The aim of this study was to investigate the fractionation of Cd added to four different soils (in all of the horizons). We also studied the suitability of the sequential extraction that was carried out to assess the bio-availability of Cd in these soils. Finally, as the fractions obtained by sequential extraction produce artifacts, we decided to use the FE-SEM and EDS techniques to examine Cd fractionation in these soils and to compare the results obtained with both methods.

## 2. Material and methods

### 2.1. Selection and analysis of the soils

We selected four soils: an Ultisol (U), a Fluvent (F), an Inceptisol (I) and a Fluvaquent (Fa) [16], respectively on quaternary sediments, amphibolites, slate and two mica granites. Each of the horizons was sampled (U.A, U.Bw, F.A, F.Bw, I.A, I.Bw, Fa.A, Fa.G, respectively), and then analyzed and characterized extensively to assess the influence of its components and properties on Cd<sup>2+</sup> sorption. Using an Eijkelkamp sampler, six samples were collected from the surface and subsurface horizons of each soil and then stored in polyethylene bags. The samples were pooled, air dried, passed through a 2 mm sieve and homogenized in a Fritsch Laborette 27 rotary sample divider. Of the six samples into which each pooled sample was divided, three were used for soil analyses and three for sorption and sequential extraction experiments, as well as for XRD and FE-SEM analysis.

Soil pH was determined with a pH electrode in 2:1 water/soil extracts [17]. Particle size distribution was determined after oxidizing the organic matter with hydrogen peroxide, separating the upper fraction (down to 50 mm) by sieving and using the lower fraction for the internationally endorsed procedure [18]. Clay mineralogy was determined by powder X-ray diffraction in a SIEMENS D-5000 Bragg-Brentano ( $\theta/2\theta$ ) apparatus with a Cu anode, using 0.05 steps and 10 s per step.

Total organic C and dissolved organic C were determined with a TOC analyzer-V CSH/CSN Shimadzu apparatus which performs the analysis by applying the principle of catalytic combustion oxidation and detection by non-dispersive IR.

Exchangeable acidity was determined using 1 M KCl as an extractant and titration to a phenolphthalein endpoint [19]. The cation exchange capacity (CEC) and exchangeable cation content were determined using Hendershot and Duquette's method [20]. Al, Ca, K, Mg and Na were extracted with 0.1 M BaCl<sub>2</sub>, and their concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) in a Perkin Elmer Optima 4300 DV apparatus.

Mn and Al oxide contents were determined using the dithionite-citrate method [21,22]: samples were shaken with a solution of sodium hydrosulfite (0.5 g per gram of soil) and sodium citrate (0.27 M), and the Fe, Al and Mn contents of the extract were determined by ICP-OES as above.

Amorphous and crystalline Fe oxides were determined using 0.25 M NH<sub>2</sub>OH·HCl + 0.25 M HCl and 0.2 M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.1 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.1 M citric acid respectively as extractants. The Fe content was analyzed by ICP-OES.

### 2.2. Sorption experiments

100 mL of 0.5 mM Cd(NO<sub>3</sub>)<sub>2</sub> in NaNO<sub>3</sub> background electrolytes (1 mM) was added to 12 g of soil in a pre-weighed polyethylene

centrifuge tube. The suspension was then equilibrated on a rotary shaker for 24 h at 25 °C.

Preliminary kinetic studies [24] showed that a 24-h reaction period was sufficient to achieve apparent equilibrium under these conditions. The sample then was centrifuged (15 min) at 5000 rpm. The supernatant was filtered through Filter-Lab 1244 paper (pore size = 0.45  $\mu$ m), and refrigerated at 4 °C for subsequent analysis of the amount of Cd sorbed by ICP-OES in a Perkin-Elmer Optima 4300 DV apparatus, which was determined from the difference between its concentrations in solution before adding the soil and after equilibration (shaking) with the soil.

The pellets obtained in the sorption phase of the experiments were used for the Cd fractionation and the XRD and FE-SEM study.

### 2.3. Cd sequential extraction experiments

The cadmium fractionation study was carried out by adapting the sequential method [23,25], with the modifications suggested by [26] in the proposed method for the dissolution of amorphous iron oxides [27]. The Cd content was determined in all of the fractions in order to identify its distribution amongst the soil components, making it possible to establish the availability of the metal in the short or medium term, without chemical meteorization processes of the primary minerals having to occur for its release. Sequential extraction was carried out according to the scheme shown in Fig. 1, using the soils treated with the acidic Cd solution.

### 2.4. X-ray diffraction

The mineralogical composition of all of the horizons before and after treatment with Cd was determined. The samples were measured in a Philips-type powder diffractometer fitted with a Philips PW1710 control unit, Vertical Philips PW1820/00 goniometer and FR590 Enraf Nonius generator. The instrument was equipped with a graphite diffracted beam monochromator and copper radiation source [ $\lambda$  (K $\alpha$ 1) = 1.5406 Å], operating at 40 kV and 30 mA. The X-ray powder diffraction pattern (XRPD) was collected by measuring the scintillation response to Cu K $\alpha$  radiation versus the  $2\theta$  value over a  $2\theta$  range of 2–65°, with a step size of 0.02° and counting time of 4 s per step.

The determination was carried out according to the RIR procedure (Reference method intensity/radium) (Chung, 1975) using corundum as the reference material. The crystalline phases were identified and quantified using the program "Match!" Copyright © Crystal Impact, Bonn, Germany [28].

### 2.5. Field emission scanning electron microscopy

The morphology, structural distribution and particle chemical composition of samples containing ultrafine crystalline and/or amorphous particles and minerals were investigated using a Zeiss Model Ultra Plus FE-SEM with charge compensation for all applications in both conductive and non-conductive samples. The FE-SEM was equipped with an EDS, and the mineral identifications were made based on their morphology and grain composition using both secondary electron and back-scattered electron modes [29,30]. The samples were dried at 45 °C, and suspensions were prepared in hexane to prevent possible mineralogical changes. The samples were placed on a standard aluminium slide with carbon adhesive, coating them with 20 nm-thick layers of gold/palladium.

EDS spectra were recorded in FE-SEM imaging mode. The electron diffraction patterns of the crystalline phases were recorded in SAED or MBD mode, and the d spacing was compared to that of the International Center for Diffraction Data [31] inorganic compound powder diffraction file (PDF) database in order to identify the crystalline phases.

Download English Version:

<https://daneshyari.com/en/article/7644186>

Download Persian Version:

<https://daneshyari.com/article/7644186>

[Daneshyari.com](https://daneshyari.com)