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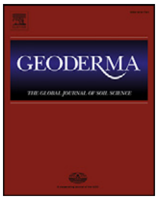

Using time of flight secondary ion mass spectrometry and field emission scanning electron microscopy with energy dispersive X-ray spectroscopy to determine the role of soil components in competitive copper and cadmium migration and fixation in soils

B. Cerqueira, D. Arenas-Lago *, M.L. Andrade, F.A. Vega

Department of Plant Biology and Soil Science, Faculty of Biology, University of Vigo, Lagoas, Marcosende, 36310 Vigo, Pontevedra, Spain

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ABSTRACT

The bioavailability of heavy metals mainly depends on their sorption in soils, as the sorption/desorption processes determine their concentration in surface or underground water. The sorption and desorption of cations predominantly involve negatively charged soil surfaces such as organic matter, clays and metallic oxides or hydroxides. The distribution of metals among the soil components depends on the intrinsic properties of the metal species involved, the properties of the soil, and the amounts of metal added. Relatively new spectroscopic imaging techniques can help determine the distribution of contaminants on soil surfaces such as natural minerals and organic matter. Competitive Cu^{2+} and Cd^{2+} sorption and desorption experiments were performed by the batch method in all of the horizons (A and B) of five natural soils: Umbric Cambisol, Endoleptic Luvisol, Mollic Umbrisol, Dystric Umbrisol, and Dystric Fluvisol. The competitive sorption and desorption capacity, hysteresis and migration throughout the profile were determined. The influence of soil components on retention capacity was investigated by means of the pairwise Pearson correlation analysis. It was found that the A horizons sorb and retain more Cu^{2+} than B, and more Cd^{2+} than A. The hysteresis indices show that the competitive sorption of Cd^{2+} is more irreversible than that of Cu^{2+}. Correlation analysis shows that both Cu^{2+} sorption and retention capacities are positively correlated with the effective cation exchange (ECEC) and organic carbon content, while Cd^{2+} sorption and retention capacities are strongly correlated with the pH, the ECEC and the Fe and Mn oxide and clay contents. The migration indices indicate that the largest proportions of Cu^{2+}, are retained in the A horizons. A small proportion of Cd^{2+} is retained in the B horizons, but the largest proportion migrates out of the soil profile. The time of flight secondary ion mass spectrometry (TOF-SIMS) images show that in the treated soils, the signal intensity of Cu^{2+} is high, while that of Cd^{2+} is very low, indicating that Cu^{2+} is retained in larger quantities than Cd^{2+}, also demonstrating how intensively Cu^{2+} interacts with organic matter. The association between Cu^{2+} and Fe ions is very low and is not associated with the Mn ions. In contrast, the scarcely retained Cd^{2+} interacts with the Fe and Mn ions. Soil analysis by field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FE-SEM/EDS) showed that Cu^{2+} retention depends on the formation of organic matter and vermiculite aggregates or associations. Cd^{2+} is retained on vermiculite associated with gibbsite and amorphous Fe oxides. We confirmed the coexistence of amorphous Fe oxides, vermiculite, gibbsite and organic matter aggregates containing Cu^{2+}, and vermiculite and gibbsite aggregates containing Cd^{2+}. These results confirm the differences between the Cu^{2+} and Cd^{2+} sorption sites, and the competence in favour of the first, especially in the A horizons, as the organic matter has higher affinity for Cu^{2+} than for Cd^{2+}. The combined use of TOF-SIMS with FE-SEM/EDS makes it possible to visualise the associations between soil components which jointly retain the metals we studied, rather than individually.

1. Introduction

The availability of heavy metals for plant uptake and the risk of these metals finding their way into surface or underground waters both depend on their sorption and desorption in soil (Vega et al., 2006; Loganathan et al., 2012). Copper and cadmium enter the soil not only through urban solid wastes but also via sewage sludge. Furthermore, Cd and Cu can reach soils via fertilizers, pesticides, liming agents, acid water drainage from mining activities, sewage sludge and urban and industrial waste (Yanqun et al., 2005; Nagajyoti et al., 2010; Selim, 2013).

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* Corresponding author.
E-mail address: darenas@uvigo.es (D. Arenas-Lago).

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Studies on the behaviour of Cu^{2+} and Cd^{2+} in soil have largely focused on interactions with solutions containing either metal, and have therefore ignored the potential effects of their mutual competition.

The migration of a heavy metal through a soil profile is a complex process that depends on multiple factors, namely soil pH and other soil characteristics, such as Fe and Mn oxide contents, clay and carbonate contents, clay mineral and the amount of organic matter types, textures and structures, as well as the intrinsic properties of the metal, its concentration in the soil solution and the presence of other metals (Simpson et al., 2004; Vega et al., 2011).

The heterogeneity of soil makes it very difficult to predict the potential mobility and distribution of even single metals, so experimental data are usually essential for this purpose. Consequently, sorption tests on soil should invariably be followed by desorption tests. Sorption and desorption isotherms reveal whether sorption is reversible or wholly or partially irreversible (hysteretic).

This paper examines the influence of soil characteristics on competitive Cu^{2+} and Cd^{2+} sorption, desorption and migration in five different soils. To this end, the capacities of soil horizons jointly polluted by Cu^{2+} and Cd^{2+} were comprehensively assessed and compared; this involved determining not only two general indicators of sorption and retention capacity (adimensional parameters) Kr,s and Kr,r but also the hysteresis and migration indices (HI, MI) defined by Vega et al. (2008, 2009a, 2011); as a result, it was possible to make an accurate comparison of the soil horizons in terms of Cu^{2+} and Cd^{2+} competitive sorption, retention, hysteresis, and migration.

In recent years, sorption processes have been studied (Sastre et al., 2006; Lair et al., 2007; Covelo et al., 2008b; Rees et al., 2014) in order to determine the influence of soil components on heavy metal fixation, mainly using statistical analysis such as linear regression and regression tree analyses (Covelo et al., 2008a; Vega et al., 2009b). However, little attention has been focused on providing information about the interactions between heavy metals and soil components using various techniques such as field emission scanning electron microscopy with energy dispersive X-ray spectroscopy (FE-SEM/EDS) and time of flight secondary ion mass spectrometry (TOF-SIMS) (Sipos et al., 2009; Cerqueira et al., 2011b). The starting hypothesis of this study is that the use of both techniques will provide very precise information on the nature of soil components as well as their interactions with heavy metals.

Therefore, the aims of the present study were to assess and compare the competitive sorption and desorption capacity and the sorption hysteresis of Cu^{2+} and Cd^{2+}, as well as the migration of both cations through the horizons of each soil. Another objective was to determine the interactions between the main soil components and Cu^{2+} and Cd^{2+} by TOF-SIMS and FE-SEM/EDS. An understanding of how Cu^{2+} and Cd^{2+} migrate through soil profiles will make it possible to propose measures to control their mobility and prevent pollution problems, given that the mobilization of Cu^{2+} and Cd^{2+} leads to plant uptake and leaching into groundwater; but this can be minimized by reducing the bioavailability of these metals.

2. Material and methods

2.1. Soil sampling

To carry out this work five natural soils developed on different parent matter were selected in Galicia (NW Spain). The soils studied were an Umbric Cambisol (UC), an Endoleptic Luvisol (EL), a Mollic Umbrisol (MU), a Dystric Umbrisol (DU) and a Dystric Fluvisol (DF) (IUSS Working Group WRB, 2014) developed on quartzite, amphibolites, slates, schists and amphibolites respectively. Samples from the horizons (UC.A, UC.Bw, MU.A, MU.Bw, EL.A, EL.Bt, DU.A, DU.Bw, DF.A and DF.Bw) were analyzed and characterized. Using an Eijkelkamp sampler, 6 samples were collected from the 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. Each pooled sample was split into twelve sub-samples, three of which were used for soil analyses, three for sorption and desorption experiments, three for FE-SEM/EDS and three for TOF-SIMS.

2.2. Soil analyses

The soils were characterized by determining their particle size distribution, pH, total organic carbon content, dissolved organic carbon, oxide content and effective cation exchange capacity (ECEC) and also by mineralogical analysis of the clay fraction.

Soil pH was determined with a pH meter using 2.5:1 water/soil suspensions according to Slattery et al. (1999). Particle size distributions were determined after oxidising the organic matter with hydrogen peroxide; the >50 μm fraction was further fractionated using sieves, and the <50 μm fraction by the international procedure (Day, 1965). Mineralogical analysis of the clay fraction was carried out by means of powder diffractometry 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 carbon and dissolved organic carbon were determined with a total organic carbon analyser-V CSH/CSN Shimadzu apparatus, which performs the analysis by applying the principle of catalytic combustion oxidation and detection by non-dispersive IR (according to UNE-EN 1484).

The ECEC and exchangeable cation content were determined using the Hendershot and Duquette (1986) method. Aluminium, Ca, K, Mg and Na were extracted with 0.1 M $BaCl_2$, and their concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) in a Perkin-Elmer Optima 4300 DV apparatus.

Iron, Mn and Al oxide contents were determined using the dithionite–citrate method (Soil Conservation Service, 1972; Sherdrick and McKeague, 1975). The samples were shaken with a solution of sodium hydrosulphite (0.5 g/g of soil) and sodium citrate (0.27 M), and the Fe, Al and Mn concentrations in the extract were determined by ICP-OES as above.

2.3. Sorption and desorption experiments

Data for isotherm construction were obtained in batch experiments following the method described in Vega et al. (2010). Competitive sorption was evaluated using multi-metal ($Cd^{2+} + Cu^{2+}$) nitrate solutions at concentrations of 0.01, 0.05, 0.1, 0.5, 1, 3 mmol L^{-1} of each ion, containing 0.01 M $NaNO_3$ as a background electrolyte. The heavy metals were used in the form of nitrates because of the high solubility of these salts, and the concentrations were chosen to range from normal values to values representative of severe pollution. Triplicate suspensions of 6 g soil samples in 100 mL of solution in polyethylene tubes were shaken in a rotary shaker for 24 h at 25 °C and then centrifuged at 5000 rpm; the resulting pellet was set aside for use in the desorption stage of the experiment. The supernatant was then filtered through Whatman 42 paper and the filtrate was analysed by ICP-OES in a Perkin-Elmer Optima 4300 DV apparatus (USA). The quantity of each metal that had been sorbed was calculated from the difference between its concentrations in solution before the addition of soil and after equilibration (shaking) with the soil.

Sorption isotherms for each metal were constructed by plotting the sorbed metal content of the soil horizon (μmol g^{-1} dry soil) against the metal concentration in solution at equilibrium (μmol L^{-1}).

Following Vega et al. (2010), desorption experiments were conducted using the pellets obtained in the sorption phase of the experiments. They were dried at 45 °C and weighed; each pellet was shaken for 24 h in a polyethylene tube with 100 mL of 0.01 M $NaNO_3$ solution at 25 °C, which was then centrifuged at 5000 rpm. The supernatant was filtered through Whatman 42 paper and the resulting filtrate was analysed by ICP-OES. The quantity of each metal that had been retained in the soil sample was calculated from the quantity sorbed (determined in the sorption stage of the experiment) and the concentration of the metal in solution following desorption.