Sorption of Cu and Zn in low organic matter-soils as influenced by soil properties and by the degree of soil weathering

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HIGHLIGHTS

- Metal sorption in weathered soils was weaker due to pH and low reactivity clay.
- Zn release in alkaline soils was higher than that in acidic.
- Fe oxides slowed metal release in newly developed soils.
- Fe oxides increased metal release in weathered soils.

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ABSTRACT

Copper and Zn sorption and desorption, among other factors, depend on soil pH, but in soils with different degree of weathering the role of other soil properties (*e.g.*, oxides content and the level of their crystallinity) has not been thoroughly examined. We conducted batch sorption and desorption tests using 21 low-organic C soils that belonged to the soil orders of Entisols, newly developed soils, Inceptisols, and Alfisols, the most weathered soils. Zinc sorption was lower than that of Cu, and its desorption faster, confirming that it is a highly mobile metal. Alfisols had the weaker affinity for metals, due to the lower soil pH typical of this soil order, but also due to the low reactivity colloids they contained. Correlation analyses showed that Fe oxides in Alfisols increased metal release from soils, while they decreased metal desorption from Entisols. We conclude that in low organic matter-content soils, where the protective role of organic colloids is not to be expected, high soil pH alone is not sufficient to protect against metal contamination, but the degree of soil weathering is also important, due to the dominant role of other mineral phases (here, Fe oxides).

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1. Introduction

In recent decades heavy metals in soils have increasingly been found in elevated concentrations, mainly due to anthropogenic inputs, such as industrial waste deposits, and sewage sludge application (Bolan et al., 2014). Heavy metal mobility depends on various soil key properties, most important of which is soil pH. Heavy metals, typical to cationic species, decrease mobility as pH increases to neutral–alkaline values, and their availability is enhanced in acidic soil environments (Lim et al., 2013). Although organic matter is another soil property recognized for its binding metal ability, in low organic matter soils, such as those found in the Mediterranean region, organic C is not expected to have a significant role in heavy metal retention.

Another soil key attribute is mineral oxides, mainly those of Al and Fe. Oxides concentration is connected with soil weathering (or soil "age"), as it is expected that oxides content increases in soil with progressing weathering (Zhou et al., 2013). In the southeast Mediterranean region, the most weathered soil order is Alfisols, according to the Soil Taxonomy classification system. Alfisols typically lack $CaCO_3$ in their surface A horizon, thus they are acidic (Fanning and Fanning, 1989). Due to this, one would expect a weaker metal sorption in such soils. In contrast, Entisols, the soil order comprising newly developed soils (*e.g.*, in plains where soils are alluviated faster and in slopes eroded faster than soil genesis process), are expected to have lower oxides content, while Inceptisols are between the two previously mentioned soil orders concerning their weathering and development (Fanning and Fanning, 1989).

Soil oxides at pH lower than *c.* 9 (approximately their point of zero charge, PZC) mainly bear a positive surface charge, and thus

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in usual soil pH values tend to sorb anionic species. However, it has repeatedly been found that oxides are also capable of binding metals, either in works with clear oxides systems (Mahdavi et al., 2012) or in works conducted with bulk soils (Serrano et al., 2009), presumably due to the colloidal dimensions of the oxides, which render them chemically reactive and due to the fact that there still exist some negative-charge sites onto oxide surfaces even at pH < PZC.

Although oxides content increases with soil weathering, so does oxides crystallinity (Mikutta et al., 2009). Increased crystallinity is connected with decreased chemical reactivity per oxide unit mass, while amorphous oxides have high surface area and thus high CEC (Essington, 2004, p. 83). Thus in soils with more progressed weathering, it is not known which of the two factors will have the most decisive role in metal sorption: Higher oxides content or higher crystallinity (and thus lower reactivity). Moreover it is not known what the effect will be in "aged" soils as compared to newly developed soils, which have lower oxides content but higher percentage of amorphous oxides.

Now, there have been some studies concerning heavy metals in soils with different degree of weathering. *E.g.*, Golia et al. (2008) analyzed soils and plants in Entisols, Alfisols and Verisols, but soil orders were merely mentioned—the role of those soil orders in relation to the effect of the weathering process in metal mobility was not discussed. Also Shaheen (2009) studied Cd and Pb sorption in 11 soils of 6 different soil orders, but the number of soils per order was not sufficient to investigate the effect of soil properties within those orders (*i.e.*, there were 4 Entisols, 3 Alfisols and one sample for each of the orders of Aridisols, Mollisols, Vertisols and Histosols). Thus, to our knowledge, there is a void in the literature concerning the sorption behavior of heavy metals in soils where, while some properties (*e.g.*, pH) affect metals in a well established manner, some other properties have not previously been investigated (*e.g.*, oxides, as discussed earlier).

We chose to study Cu and Zn, two important nutrient metals, which are essential to plants when in low concentrations, but potentially toxic when in elevated concentrations. Yet these metals have a contrasting behavior in soils, with Zn typically being found more mobile and available than Cu (Mehes-Smith et al., 2014). Thus we aimed at studying Cu and Zn sorption and desorption behavior in 21 soils, chosen in such a way as to have contrasting pH values (acidic and alkaline), and to represent the three main soil classification orders of the Mediterranean region, groups identified as newly developed (Entisols), moderately developed (Inceptisols) and progressed in weathering (Alfisols). We chose soils from such cultivated Mediterranean regions, because organic matter is not expected to play a key role in metal retention due to its low content in soils. Thus by choosing such soils we assumed that it is feasible to identify more clearly the effects of pH as related to soil development.

2. Materials and methods

We obtained 21 surface (0–20 cm) soil samples from Thessaly, Central Greece, from the Prefectures of Trikala, Karditsa and Larissa. We selected them so that some may be acidic (9 samples) and some alkaline (12 samples), and so that they may represent the three major soil orders in Greece, along the weathering sequence: 5 samples were Entisols, 7 Alfisols, and 9 Inceptisols. The soil samples were air-dried, sieved through a 2-mm sieve, and analyzed for the following parameters, according to Rowel (1994, reported in Supplementary Table 1): pH (1:2.5 H_2O), $CaCO_3$ (calcimeter), particle size distribution (Bouyoucos hydrometer), organic C (wet oxidation), cation exchange capacity (CEC, 1 M CH_3NOONa, pH 8.2), calculated as $cmol_c$ per kg soil (thereafter, soil

CEC) and per kg clay (thereafter, clay CEC), and amorphous Fe and Al oxides (ammonium oxalate).

With the obtained samples we conducted a 24-h equilibrium batch sorption tests with added metal concentrations of C_0 = 5, 10, 20, 40, 60, 80, and 100 mg L^{-1} of Cu and Zn in multi-metal systems, using their chloride salts in 10 mM $CaCl_2$ background electrolyte at a 1-to-10 solid-to-solution ratio, and measured metal sorbed, q, and metal in equilibrium solution, C. The experimental data were fitted in the two most widely used curve fit isotherm models, *i.e.*, Freundlich ($q = K_F C^N$) and Langmuir [$q = q_{max} K_L C / (1 + K_L C)$], where K_F, N, and K_L are model constants. The two models were linearized appropriately (as per Foo and Hameed, 2010). For comparison of the goodness of fitness of the experimental data to the sorption models, we used the coefficient of determination, R^2 (the closer to unity, the better the goodness of fitness), and the Derivative of Marquardt's Percent Standard Deviation error function (MPSD, Foo and Hameed, 2010). From the sorption isotherms we measured three sorption indices: q_{100} (sorption at C_0 = 100 mg L^{-1}), q_{max} (according to Langmuir), and K_{d-50} (distribution coefficient, equal to q/C, units L kg^{-1}, measured at C_0 = 50 mg L^{-1}). We also measured two desorption indices: $DTPA_{100}$ (extraction for 2 h at 1-to-2 solid-to-solution with the DTPA-TEA-$CaCl_2$ pH 7.3 solution of metals sorbed in soils at C_0 = 100 mg L^{-1} in a single-step procedure), and desorption percentage (%Desorption) of that sorbed at C_0 = 100 mg L^{-1}. These sorption and desorption parameters are reported in Supplementary Tables 2 and 3 for Cu and Zn, respectively.

In order to further examine the soil parameters that affect Cu and Zn sorption and desorption, we performed correlation analyses with sorption and desorption parameters as dependent variables and the studied soil properties as independent variables. Also we estimated the level of significance of the differences between the various soil and metal sorption parameters. All statistical tests were carried out using the Statgraphics Version 2.1 package.

3. Results and discussion

3.1. Soil properties

The 21 studied soils were selected so that they may not differ greatly in other properties than pH and taxonomy. For this reason we obtained medium-textured soils, and also cultivated, so that they may be expected to have low organic carbon (OC) levels. Thus our samples had a narrow clay content (32.21 ± 1.50%), confirming the fact that the samples were medium-textured, and had OC of 0.98 ± 1.50%, a low value, typical to cultivated Mediterranean soils (Table 1).

When soils were divided between acidic and alkaline, clay content was not different, while OC was lower in the acidic than in the alkaline soils ($p < 0.05$). This has probably no connection to soil chemistry, but is rather caused by the fact that acidic cultivated soils are of lower productivity, and thus with lower plant biomass inputs, which in turn leads over the years to the accumulation of smaller quantities of organic matter in soil. Soil CEC and clay CEC were higher in the alkaline soils ($p < 0.01$). Soil CEC is known to increase with pH, because so does the negative charge in the variable charge soil colloidal surfaces (1:1 clay minerals, oxides and organic matter). Even in soils with low content in such colloids, an increase in soil CEC with pH is expected (Wisawapipat et al., 2010). Amorphous Fe oxides were higher in the acidic soils ($p < 0.05$); we assume that this is connected to differences in taxonomy (as we will show later), because most of the acidic soils belonged to the Alfisols order. In contrast to that, Al oxides did not differ, and neither did they exhibit differences in the 3 studied taxonomy soil orders, contrary to what would rather be expected.