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Sorption and lability of cadmium and lead in different soils from Egypt and Greece

Sabry Mohamed Shaheen *

Department of Soil Sciences, Faculty of Agriculture, University of Kafrelsheikh, 33 516-Kafr El-Sheikh, Egypt

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ABSTRACT

Reactions of heavy metals with soils are important in determining their availability and fate in the environment. Mono-metal sorption and lability of sorbed cadmium (Cd) and lead (Pb) in different representative soils from Egypt and Greece as influenced by their properties were investigated in this study. For this purpose eleven surface soil samples varying widely in their origin and properties were selected. Four of them were from Egypt representing the main soil orders i.e., Entisols and Aridisols and the rest, seven, from different sites of Greece belonging to the orders Entisols, Alfisols, Vertisols, Mollisols, and Histosols. In these samples sorption isotherms were developed from which sorption parameters, and distribution coefficient (K_d) of Cd and Pb were determined. In addition lability of these metals was estimated by DTPA extraction following their sorption.

The results showed that Freundlich model described satisfactorily sorption of both metals. In all the soils studied K_d values of Pb were higher than that of Cd indicating that this was retained by the soils stronger than Cd. Sorption parameters (k_f, n) and K_d values of Egyptian Entisol developed on lacustrine deposits showed higher affinity for Pb, Greek Histosol for Cd while acidic Alfisols showed the lowest affinity for both metals studied. Permanent charge clayey soils with relatively low Fe, Al and Mn oxides content sorbed more Cd and Pb than the variable charge red soils with higher content of these oxides. In variable charge red soils with similar sesquioxides content, Pb and Cd sorption was pH dependent. However, in variable charge soils with similar soil pH, no significant differences were recorded for Pb sorption, while Cd sorption capacities differed significantly depending on the active ratios of Fe and Al oxides. Sorption parameters of Cd were correlated to clay content, cation exchange capacity, organic matter content, total free and amorphous aluminum oxides, amorphous iron oxides and $CaCO_3$ content while Pb sorption parameters were correlated with clay content, total free and amorphous silica oxides, and amorphous aluminum oxides content as well as cation exchange capacity (CEC).

Lability of the adsorbed Cd was higher than Pb in all the studied soils and may pose more threats to the ground water and plants. The Greek acidic Alfisols (Rhodoxeralf) showed the lowest lability of sorbed Cd, while the alkaline one exhibited the highest Cd lability. The lowest lability of sorbed Pb was in Greek Histosols and the highest in acidic Alfisol (Typic Haploxeralf). Labile Cd was negatively correlated only with $CaCO_3$ content in all the soils studied while labile Pb was negatively correlated with CEC, clay, organic matter, total free aluminum oxides and the amorphous iron and aluminum oxides content.

1. Introduction

The environmental hazards derived from the recent increasing disposal of heavy metals into soils particularly cadmium and lead, which are highly toxic to humans even at low concentrations have arisen growing concern in recent years (USEPA, 1992). The interest in heavy metals existence and behaviour in soil arises from the fact that soil is the main source for human food and from the possibility of soil pollution due to industrial wastes. Like other heavy metals, Cd and Pb in soils come from both soil parent materials and anthropogenic activities (Alloway, 1995). Lead and Cd are used in many industrial, urban, and agricultural applications (Kabata-Pendias and Pendias, 1992; Adriano, 2001) and are often found together at sites contaminated with heavy metals. Therefore, it is important to understand the chemistry of Pb and Cd in soils in order to assess their bioavailability.

Heavy metals in soil are to a large extent sorbed to soil particles. Sorbed heavy metals can be desorbed into soil solution, and thus uptaken by plants or move down to lower soil horizons and groundwater. The fate of Cd and Pb that reaches soil from anthropogenic sources depends essentially on its sorption and lability in the host medium, which in turn depends on soil properties such as pH, organic matter and clay content. Heterogeneous soil systems consist of both organic and inorganic constituents with different affinities for heavy metals. In addition, heavy metals themselves exhibit varying affinities for soil surfaces. Variability in heavy metals affinity for soil sorption sites has been attributed to a given metal's hydrolysis constant (pK_H),

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* Tel.: +20 473247324, +20 104525256(mobile); fax: +20 473232032.
E-mail address: smshaheen1973@yahoo.com.

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electronegativity, Lewis acidity, charge density and solubility (K_{SP}) of precipitates, including hydroxide and carbonate (McBride, 1994; Pardo, 2000; Sparks, 2003). Hence, sorption and lability of Cd and Pb in different soil types is of potential interest for determining their loading capacity and distribution in the soil profile. These data can be used to predict the environmental impact of Cd and Pb from anthropogenic sources, as well as to establish government policies on the usage of metals containing materials in agricultural soils.

Sorption of heavy metals onto soil components can be described by a linear (McLaren et al., 1990), Langmuir, or Freundlich sorption model (Sposito, 1989). The Freundlich equation is often useful for modeling sorption of metals onto solids with heterogeneous surfaces and has frequently proved superior than the Langmuir equation for cations or anions sorption by soils (Sposito, 1980; Arias et al., 2005). Although, there is disagreement regarding the effectiveness of Langmuir and Freundlich models to interpret sorption of metal cations in soils (Sparks, 1995), some parameters of these models, such as maximum sorption quantity and the distribution coefficient are widely acceptable in characterizing Pb and Cd sorption capacity of soils (Basta and Tabatabai, 1992a; Gomes et al., 2001; Holm et al., 2003; Usman, 2008).

Distribution coefficient is a useful parameter for comparing the sorptive capacity of different soils or materials for any particular ion, when they are measured under the same experimental conditions (Alloway, 1995). The mobility of metals in the soil environment are directly related to their partitioning between soil and solution (Sparks, 1995) and, therefore, are directly related to their distribution coefficients, which indicate the capability of a soil to retain a solute and the extent of its movement to the liquid phase (Reddy and Dunn, 1986).

The agricultural soils of Egypt and Greece are one of the oldest agricultural areas in the world, having been under continuous cultivation for at least 5000 years. The soils in these two countries differ widely in their origin and properties. Most of the Egyptian soils are classified as Entisols and Aridisols. The Egyptian Entisols were developed on different deposits i.e., (fluvial, lacustrine and sandy marine deposits) differ widely in their physico-chemical properties, while the Aridisols were developed on calcareous deposits. Most of the Greek soils belong to the orders Entisols, Inceptisols, Alfisols, and Vertisols, and in a less extent to the orders Mollisols and Histosols. These soils differ in pH, sesquioxides content and the other physical and chemical properties, which affect heavy metals sorption and mobility.

Sorption of Cd and Pb by soils has been studied by several researchers (Gomes et al., 2001; Appel and Ma, 2002; Appel et al., 2008) but usually in soils developed under different than the Mediterranean conditions. Few relevant studies have been conducted in Egyptian and Greek soils but mainly on one soil group such as fluvial deposits (Usman, 2008), calcareous soils (Elkhatib et al., 1991) and Rhodoxeralf (Ponizovsky and Tsadilas, 2003). In addition, either in Egypt or Greece Cd and Pb sorption and lability characteristics as influenced by soil properties in different soil types are limited. So, the main objective of this study was to investigate the influence of soil properties in different soil types from Egypt and Greece on (i) sorption characteristics and distribution coefficient of Cd and Pb, (ii) lability of sorbed Cd and Pb in the studied soils.

2. Materials and methods

2.1. Soil selection and characterization

Eleven surface soil samples varying widely in their origin and properties were selected for this study corresponding to the dominant soil orders from Egypt and Greece. Four of them were from Egypt representing belonging to the orders Entisols (developed on fluvial, lacustrine and sandy marine deposits) and Aridisols (calcareous deposits). The rest seven soils were from Greece belonging to the orders Entisols, Alfisols, Vertisols, Mollisols, and Histosols (Table 1). Soil samples were air-dried, ground to pass through a 2-mm sieve and analyzed for their basic physical and chemical properties according to Sparks (1996). Soil pH was measured in deionized water with a soil solution ratio of 1:1. Organic matter content was determined by the wet oxidation procedure. Cation exchange capacity (CEC) was measured by the 1 M ammonium acetate (pH 7.0) method. Total calcium carbonates equivalent (TCCE) were determined by using Collins calcimeter. Particle size analysis was performed according to Gee and Bauder (1986). Total free iron (Fe_d), aluminum (Al_d), silicon (Si_d) and manganese (Mn_d) oxides content were extracted with 3 M sodium citrate + 1 M sodium bicarbonate + 1 g sodium dithionite (CBD) in a water bath heated at 85 °C (Mehra and Jackson, 1960). Amorphous iron (Fe_o), aluminum (Al_o), silicon (Si_o) and manganese (Mn_o) oxides content were extracted with 0.175 M ammonium oxalate + 0.1 M oxalic acid adjusted to pH 3.0. Alkaline soils were pre-treated with 1 M ammonium acetate (pH 5.5) to remove carbonates according to Loeppert and Inskeep (1996).

2.2. Sorption experiment

A batch equilibrium experiment was conducted using Cd and Pb solutions as follows: 2 g of soil samples were equilibrated with 20 mL of 0.01 M $NaNO_3$ solutions containing 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 and 2.0 mM Cd as cadmium nitrate or 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 mM Pb as lead nitrate in 50-mL centrifuge tubes (pre-weighed) for 24 h on a reciprocating shaker at room temperature. Some drops of toluene were added to suppress microbial activity. A relatively high initial Cd and Pb concentration range was used in this study, because after a preliminary experiment it was shown that the large initial Cd and Pb concentrations range were necessary for the alkaline soils with high Cd and Pb sorption capacity. After equilibration the samples were centrifuged and the supernatant was filtered through a Whitman No. 42 filter paper. Two replicates were used for collecting each data point. Cadmium and Pb concentrations in the supernatant were measured by atomic absorption spectrometry (Varian, SpectrAA-400 Plus, Australia). The amount of Cd and Pb sorbed was calculated as the difference between the initial and final concentration. Cadmium and Pb sorption data were fitted to Freundlich equation using the formula:

$$q = k_f\, c^n$$

where q is the sorbed Cd and Pb amount in mg kg^{-1}; c is the equilibrium solution concentration in mg L^{-1}. From this equation, the following sorption parameters were determined: k_f, which represents the Cd and Pb sorbed at $c = 1$ mg L^{-}, n which is an empirical parameter expressing the Cd and Pb sorption intensity. To fit the data, the model was linearized by using the logarithmic transformation resulting in the predictive equation log $(q) = \log(K_f) + n \log(c)$. The linearized model fitted to each soil using analysis of covariance to estimate log (K_f) and n and test if the log (K_f) and n coefficients differed across the tested treatments. Estimates of K_f were obtained using exp (log (K_f)). The distribution coefficient (K_d) values were calculated according to Alloway (1995), Anderson and Christensen (1988), and Gomes et al. (2001) by using the formula:

$$\text{Distribution coefficient}(K_d) = q\,/\,c = k_f c^n\,/\,c = k_f c^{n-1}$$

2.3. Lability of sorbed Cd and Pb

Lability of sorbed Cd and Pb was evaluated at the end of sorption experiment by DTPA extraction (Cottenie et al., 1982). A 10-mL DTPA solution was added to each centrifuge tube containing Cd or Pb sorbed samples from the sorption experiment after washing with isobutyl