

The influence of soil organic matter content on soil surface charge and cadmium mobility in soil

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Abstract Rapid solute and particle transport in structured soils may be reduced by adsorption of ions and chemical material on soil adsorption sites. The influence of soil organic matter content on cadmium adsorption onto soil adsorption sites was studied for chernozem soils of the Danubian Lowland in equilibrium batch experiments (pH 3.5, 7.0, 9.0). The back-titration method was employed to obtain pH-dependent surface charge in conjunction with a potentiometric titration method. The soil surface charge and amount of Cd adsorbed increased with increasing organic carbon content. The experiments enable the prediction of the effect of changes of soil surface properties on cadmium transport in soil.

Key words adsorption; back-titration; cadmium; organic matter; soil surface charge

INTRODUCTION

Cadmium is probably the most dangerous heavy metal because of its high solubility in water and its mobility, and also its highly toxic effect on soil biota, animals and humans (Christensen, 1989; Boekhold, 1991). Soils with negatively charged surfaces have a great ability to sorb relatively large amounts of metal ions. The sorption of cadmium by soil has been widely studied (Elliott, 1983; Naidu *et al.*, 1997). At concentrations below the threshold value required for solid-phase formation, cadmium adsorbs on organic and inorganic surfaces. The objective of this study was to investigate soil surface charge and cadmium sorption characteristics in relation to soil pH and organic carbon content.

MATERIALS AND METHODS

Soil samples were taken near Kutniky in the Danubian Lowland (Slovakia) and had an organic carbon content of 1.97% and a carbonate content of 0.7%. Samples were dried at room temperature, crushed, and passed through a 2-mm sieve before use. For additional experiments, organic carbon contents were adjusted by addition of humic acids and fulvic acids, or by treatment with H₂O₂. The humic and fulvic acids were

extracted from peat. Organic carbon content (C_{ox}) was measured by oxidation with $K_2Cr_2O_7-H_2SO_4$ and titration of non-reduced chromate. Five soil samples with varied content of organic carbon, namely 1.33, 1.69, 1.97, 2.50, 2.83% C_{ox} , were obtained.

Cadmium nitrate $Cd(NO_3)_2$ solutions with 10.0, 30.0, 70.0 and 100.0 $mg\ Cd\ l^{-1}$ were used for a study of Cd(II) sorption in acid, neutral and alkaline conditions (pH 3.5, 7.0, 9.0). One gram of fine-grained soil and 50 ml of $Cd(NO_3)_2$ solution were added to 100 ml plastic bottles, and this suspension was shaken on a laboratory shaker for 2 h, left at rest for 24 h, and then shaken once more for 2 h. The solid phase was separated by centrifugation (30 min, 3500 r.p.m.) and filtration through paper filters. The amount of adsorbed cadmium is the difference between the initial and final cadmium concentrations, and these were determined by an ion-selective method (potentiometer, WTW, Germany).

The sample back-titration was performed as follows (Duguet & Hendershot, 1993): 0.2 g of soil sample was weighed into a 100 ml beaker. Then 40 ml of electrolyte solution (0.01 M $Ca(NO_3)_2$) was added and the suspension was stirred until a constant pH was obtained. The suspension was then titrated with 0.1 ml of standardized 0.1 M HNO_3 , with 2-min equilibration periods between each addition, until a pH of 3 was reached. The suspension was then allowed to equilibrate for 2 min and then back-titrated with standardized 0.005 M $Ca(OH)_2$ at a titration rate of 1 $ml\ min^{-1}$ to pH 10, and the pH was recorded. The reference titration was performed as follows: the suspension was prepared and titrated to pH 3 as described above. Then the suspension was filtered through 0.1 μm filters. The supernatant solution was allowed to equilibrate for 10 min with continuous stirring. Then the solution was back-titrated as described above. The changes in pH-dependent surface charge due to different pH and different organic carbon content were calculated based on back-titration data by subtracting the OH^- consumption of the original sample (organic carbon content of 1.97%) from the samples with modified organic carbon contents at the same pH.

RESULTS

Back-titration curves were obtained for different organic carbon contents (Fig. 1(a, b)). Calculated changes in pH-dependent soil surface charge were strongly influenced by organic carbon content and soil pH (Fig. 1(c)).

Sorption isotherms for Cd are shown in Fig. 1(d–f). The Cd(II) adsorption in soil increased with increasing total organic carbon content in the soil, with cadmium concentration in solution, and with pH. Reversal of the slope of the sorption isotherm for the largest addition (Fig. 1(f)) probably indicates precipitation of solid phase.

For initial concentrations of 10–70 $mg\ Cd\ l^{-1}$, Langmuir adsorption parameters (Table 1) were calculated using a linear form of the equation:

$$c/x = 1/kx_m + c/x_m$$

where c is equilibrium concentration, x is amount adsorbed per unit mass of sorbent, and k and x_m are constants related to bonding energy and maximum sorption, respectively. The coefficient k increased with increasing total organic carbon content in soil and pH. Adsorption isotherms enable the prediction of cadmium transport in soil through transport equations.

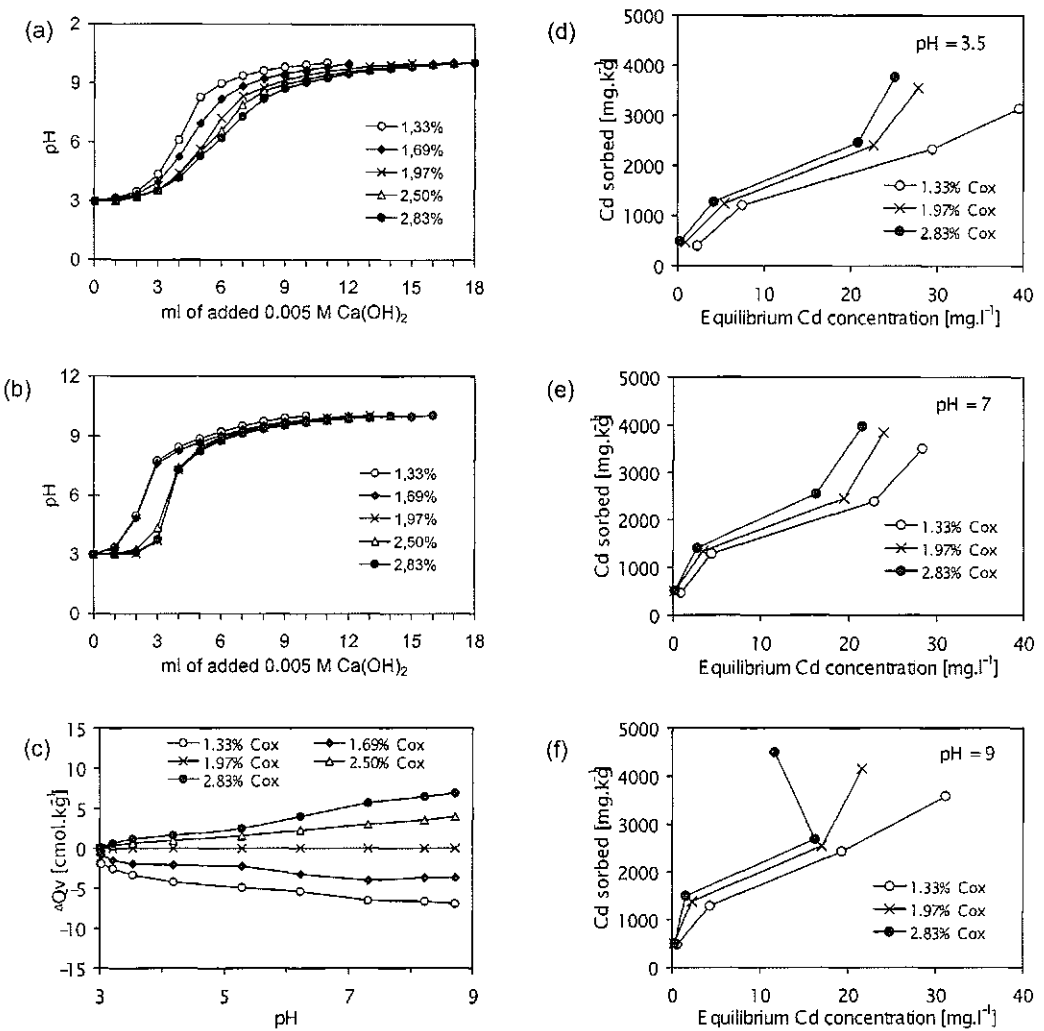


Fig. 1 (a) Titration curves for soil sample suspensions; (b) titration curves for soil sample supernatants; (c) computed change in soil surface charge as function of organic carbon content; and Cd sorption isotherms for different contents of organic carbon at pH 3.5 (d), 7.0 (e), and 9.0 (f).

Table 1 Langmuir adsorption parameters for soils with different organic carbon content and different pH. (C_{ox} is organic carbon content, k and x_m are constants related to bonding energy and maximum sorption, respectively, and r is correlation coefficient.)

pH	1.33% C_{ox}			1.97% C_{ox}			2.83% C_{ox}		
	x_m (mg kg ⁻¹)	k (dm ³ mg ⁻¹)	r	x_m (mg kg ⁻¹)	k (dm ³ mg ⁻¹)	r	x_m (mg kg ⁻¹)	k (dm ³ mg ⁻¹)	r
3.5	3811	0.06	0.992	3037	0.16	0.992	2776	0.34	0.986
7.0	2921	0.20	0.999	2675	0.51	0.991	2818	0.56	0.995
9.0	2918	0.24	0.993	2769	0.62	0.998	2942	0.65	1.000

From the results of these adsorption and back-titration experiments, it is possible to conclude that cadmium immobilization in the soil may be encouraged primarily by increasing organic matter content while simultaneously treating the soil with lime.

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