CADMIUM SORPTION-DESORPTION BY TROPICAL SOILS AS AFFECTED BY CULTIVATION

[1]*Pardo M.T., [1]López-Fando, C., [2]Kileo, E. and [2]Maliondo, S.M.S.

[1]Centro de Ciencias Medioambientales (CSIC), Serrano 115-B, Madrid, 28006-Spain, email: mt.pardo@ccma.csic.es; tel. +34 917452500; Fax +34 915640800)
[2]Sokoine University of Agriculture, PO Box 3000, Morogoro, Tanzania e mail: maliondo@suanet.ac.tc,tel. +255 56604944, fax + 255 56604648

Abstract:

The sorption of Cd by two soils from Tanzania with different cultivation histories: Mkindo site and Mafiga site was studied. Samples were collected at both virgin and cultivated sites. The two virgin soils showed similar abilities to bind Cd. Mkindo soil (16.3 g C kg^{-1}) presented the highest affinity for Cd. Yet, Mafiga soil (12.3 g C kg^{-1}) sorbed almost the same amount amount. Mafiga soil had higher cation exchange capacity and Mn and Fe oxide content and these characteristics seemed to counteract the effect of lower organic matter. Once cultivated, the two soils behaved quite differently. In Mkindo, 10 years of cultivation have led to a noticeable increase in the maximum Cd sorption capacity. In Mafiga, on the contrary, after 30 years of cultivation the soil Cd retention ability had decreased. These changes in Cd sorption have been related to the effect of cultivation in some important soil characteristics affecting metal sorption. In both virgin and cultivated sites, the reversibility of the sorption reaction was very low. More than 70% of the sorbed Cd was apparently strongly bonded.

Introduction:

Sorption of heavy metals by soils and soil materials has been the subject of extensive research, and many authors have reported on the relationships between a wide range of soil chemical and physical properties and metal sorption. Cadmium sorption by soils and soil materials has been correlated positively to pH (Boekhold et al., 1993), cation exchange capacity (Zachara et al., 1992), and crystalline and poorly crystalline oxides of Fe and Mn (Cowan et al., 1991). With regard to the OM, although no positive correlation has been found between OM content and metal retention in a wide variety of soils, retention of metals by both insoluble humic and soluble fulvic acids has been clearly established (Taylor and Theng, 1995).

In tropical soils, management practices are focused on low technology, low input agriculture, including addition of animal manures and crop residues. Such land treatments lead in the long run, to significant changes in the soil properties particularly pH and OM content (Almendros et al., 2005) which, in turn, affects the availability of the soil matrix to sorb metals. Changes in OM are of special concern because of the strong dependence of the cation exchange capacity in tropical soils on OM levels. In addition, liming to rise the pH is a common practice and this also affects metal sorption. As very little information is available about the effect of cultivation on metal retention in tropical soils, this research has been focused to determine the effect of clearing and cultivation on the sorption of Cd by two important agricultural soils from Eastern Tanzania.

Materials and Methods:

Two soils with different cultivation histories: Mkindo (Mvomero district) and Mafiga (Morogoro district) were selected for the study. Mkindo (classified as Eutric Fluvisol, FAO) is located at Mkindo village, 800 m East of Dakawa-Turiani Road. This soil has been cultivated for 10 years without the use of mineral fertilizers. Mafiga (classified as Ferric Lixisol) is located at Sokoine University Farm, 420 m East of Morogoro-Iringa highway and has been cultivated for over 30 years with periodic fallows and regular fertilizer use based mainly on NP composition. The samples were collected from virgin and cultivated areas (0-20 cm surface horizon), air-dried and sieved (< 2mm). Clay minerals were identified by X-ray diffraction. Particle size was determined by the pipette method (Gee and Bauder, 1982). The pH was measured in a 1:2.5 (wt/vol) soil:water suspension. Available phosphorus was extracted following the Bray-Kurtz (1945) procedure. Available Ca, K and Mg with 1 mol dm^{-3} NH_4Ac (pH 7) and available micronutrients with ethylenediaminopentaacetic acid (Lyndsay and Norwell, 1978). The OM was determined by the Walkley and Black method (Nelson and Sommers, 1982) and the effective cation exchange capacity (ECEC) by the method of Juo et al., 1976. The oxide content was determined by extraction with dithionite-citrate-bicarbonate (Mehra and Jackson, 1970). The data obtained are given in Table 1. Each value represents the average of four samples.

Metal sorption experiments:

Batch experiments were performed to quantify Cd sorption. Stock solutions containing increasing amounts of Cd as $Cd(NO_3)_2$, were prepared in a 0.01 mol dm^{-3} $NaNO_3$ background and standardized against atomic absorption reference standards. Nitrate was chosen in order to minimize specific sorption effects and inorganic binding of the metals. Triplicate 1-g soil samples were placed in 30 cm^{-3} pre-weighed centrifuge tubes with 10 cm^3 of 0.01 mol dm^{-3} $NaNO_3$ solutions containing increasing amounts of Cd (ranging from 0 to 7.12 µmol cm^{-3}). The reaction between the metal and the soils was allowed to proceed for 1h at $24 \pm 1°$ C with continuous stirring using the TTA80 titration assembly of the ETS822 end-point titration system. The pH was maintained at a constant value, i.e. at the pH of the respective zero-metal treatment. At the end of the stirring process the suspensions were centrifuged and the concentrations of metals in the supernatant solutions measured by inductively coupled plasma emission spectrometry or graphite furnace atomic absorption spectrophotometry depending on the metal concentration. Isotherms were computed by subtracting the amount of metal remaining in solution from the original and assuming the difference represented the sorbed. The zero metal treatments were used as background for the sorption experiments, and these values were subtracted from the others to correct for the metal released from the untreated soil. The final data were fitted to the Langmuir equation and regression analysis was used to find the best-fitting straight line from which sorptium maximun (b_{max}) was determined. To establish the immediate reversibility of the sorption process (desorption), the tubes containing the solid residue were

weighed to determine the amount of entrapped solution, and equilibrated for 1 h under all the same experimental conditions described above. After centrifuging the supernatants were used to determine Cd concentrations, and the values obtained were corrected taking into account the weight and metal concentration in the entrapped solution. The percent desorbed was defined relative to the amount of apparent sorption.

Table 1. Soil characteristics of uncultivated and cultivated sites

		Mkindo			Mafiga		
		Virgin	Cultivated	LSD	Virgin	Cultivated	LSD
Clay minerals*		K,I	S,I,K		K,S,I,G	K,S,I	
Clay		12	19	2	44	27	4
Silt	%	14	15	2	10	14	2
Sand		74	66	6	46	59	4
pH (H$_2$O)		6.8	7.8	0.1	6.4	6.6	0.2
pH (KCl)		5.4	6.0	0.1	5.0	5.2	0.2
N		0.9	0.6	0.2	1.1	0.9	0.2
C	g kg^{-1}	16.3	7.6	2.4	12.3	8.3	2.1
C/N		18.1	12.7	0.6	12.3	10.8	2.9
P		27	2	2	7	6	1.4
Ca		1293	693	226	1367	1047	303
K		208	90	8	243	275	35
Mg		106	268	24	303	217	25
Fe	mg kg^{-1}	210	101	6	48	26	9
Mn		144	43	3	191	93	34
Zn		0.0	0.0	0.2	0.7	0.2	1.2
Cu		2.0	2.4	1.5	2.0	0.6	1.3
ECEC**		81	103	12	101	69	21
Ca		65	35	11	68	52	9
K		5	2	0.2	6	7	3.5
Na	mmol$_c$ kg^{-1}	1	44	2.4	1	0.9	0.2
Mg		9	22	1.9	25	9.4	1.3
H		0.6	0.0	3.2	0	0	0
Al		0.1	0.1	1.7	0	0	0
ESP***	%	1.4	43	1.4	1.3	1.3	0.2
SiO$_2$		54	54	2	59	61	3
Al$_2$O$_3$	g 100g^{-1}	13	15	3	17	15	3
Fe$_2$O$_3$		3	4	1	7	4.4	0.6
MnO		0.07	0.03	0.0	0.4	0.1	0.0

*K = Kaolinite; I = Illite; S = Smectite; G = Goethite; ** ECEC = Effective cation exchange capacity; ***ESP = % Na saturation.

LSD = least significant difference between spatial replicates

Results and Discussion :

As seen in Table 1, in the two soils clearing and cultivation have affected some important characteristics related to metal retention. After cultivation, clay content at Mafiga site has decreased by 30 %. The organic carbon has decreased by 40% relative to the original soil and because of the strong dependence on OM in this type of soils with low-activity clays, the ECEC has also decreased. In this soil, the pH value has not been modified due to agricultural practices. In Mkindo cultivated soil, on the contrary, the pH value has increase by a unit. The relative OM status is below 60% from that of the original soil. Nevertheless, in this soil the ECEC increased after cultivation as a result of the noticeable increase in the concentration of Na and Mg in the exchange complex. In Mkindo soil, clearing and cultivation have also induced an increase in clay content (from 12% to 19%) and a shift in the mineralogical characteristics of the topsoil. In uncultivated sites, kaolinite, and illite were the dominant clay minerals, whereas in the cultivated area the presence of noticeable amounts of smectite was clearly detected.

Metal sorption and desorption:

Cadmium sorption by the soils in the presence of 0.01m dm^{-3} NaNO$_3$ background electrolyte and determined at the pH of the zero-metal treatments is depicted in Figure 1. Under the experimental conditions used in this study, sorbed amounts increased continuously with increasing amounts of metal added. Isotherms as those in Figure 1 seldom reach a well-defined plateau from which a value for the sorption maxima can be observed. The maximum sorption capacities (b$_{max}$) calculated from the slopes of the Langmuir plots were similar to, or only slightly higher tan the amounts of metal sorbed at the higher concentrations used in these experiments (Table 2).

Table 2. Cadmium sorption maxima (x$_m$), bonding energy (k) and Cd desorption maxima

Soil	Equation	Correlation coefficient	x$_m$ mmolkg^{-1}	k mlmmolCd^{-1}	Cd desorbed % Cd sorbed
Mkindo virgin	Y=1.55+20.07x	0.98	43.8	12.94	13
Mkindo cultivated	Y=5.24+18.14x	0.98	59.1	3.46	19
Mafiga virgin	Y=5.93+24.83x	0.97	40.2	4.19	16
Mafiga cultivated	Y=13.6+29.14x	0.95	34.3	2.15	26

In their original state, i.e., not cleared-nor cultivated, the two soils exhibited noticeable and similar capacities to sorb Cd. Thus, maximum Cd sorption capacities, as determined by the Langmuir equation, were 43.8 mmol Cd kg^{-1} and 40.2 mmol Cd kg^{-1} for Mkindo and Mafiga, respectively (Table 2). The Mkindo soil contained the highest amount of OM (16.3 g C kg^{-1}), yet, the Mafiga soil in spite if its lower OM level (12.3 g C kg^{-1}) had higher

ECEC and Mn and Fe oxide content, and these characteristics seemed to have counteracted the effect of lower OM. After 10 years of continuous cultivation, the maximum Cd sorption capacity of Mkindo soil had noticeably increased. In Mafiga, on the contrary, the soil Cd retention ability had decreased. Apparently, in the two soils, clearing and cultivation had affected some important characteristics related to metal sorption. In Mkindo, the OM status in the cultivated areas was below 60% relative to that of the virgin soil. In this type of soils with low-activity clays, OM represents most of the bulk of the metal sorption sites, and consequently, as a result of the severe loss of OM, Cd sorption should have decreased.

The soil pH value, however, had increased after cultivation by more than a unit, and it has been clearly established that metal sorption is highly pH- dependent, increasing sharply as the pH rises (Naidu et al., 1994, Barrow and Wheland, 1998). In addition, soil ECEC had also increased as a result of a noticeable increment in the concentration of Na and Mg in the exchange complex. In Mafiga cultivated soil, on the contrary, the original soil pH value had not been modified. Soil OM had decreased by 40% and the ECEC had also proportionally decreased. Consequently, in Mafiga, cultivation had led to a decrease in the capacity of the soil matrix to retain Cd.
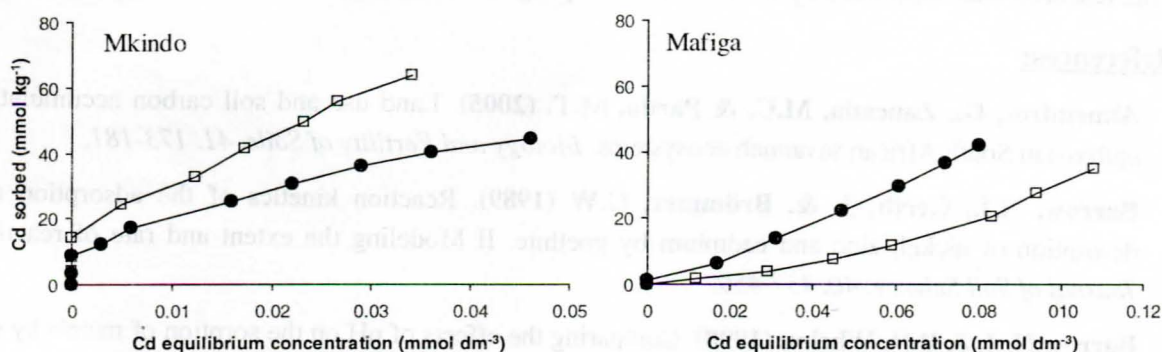

Fig. 1. Comparison of the sorptive behaviour of Cd onto the two virgin soils (●) and their cultivated counterparts ( ).
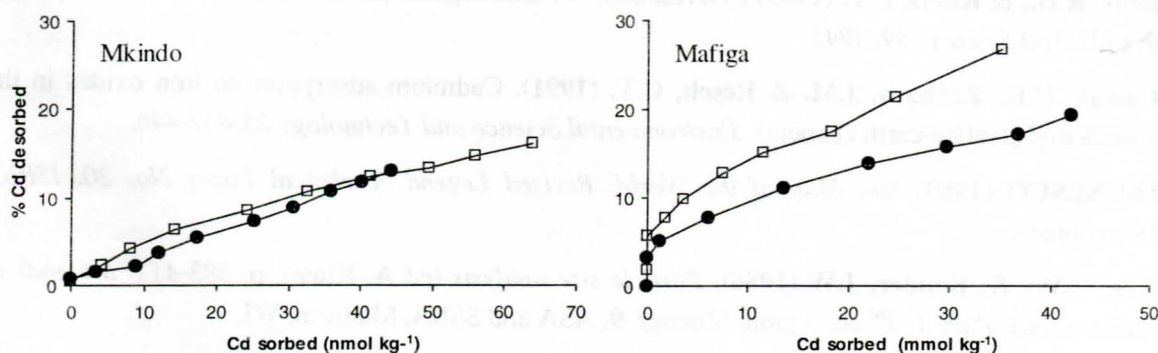

Fig. 2. Cadmium desorption isotherms. Virgin soils (●). Cultivated soils ( ).

Data for the backward reaction showed that, in the two virgin soils, the reversibility of the sorption process was low (13% and 19% of the total Cd sorbed for Mkindo and Mafiga, respectively). In the two cultivated soils, the Cd immediately released slightly increased, amounting 16% (Mkindo) and 26% (Mafiga) of the metal initially sorbed. These results indicated that in the two soils studied most Cd retained was strongly bonded. Some studies (Barrow et al., 1989) have indicated that the apparent irreversibility of the sorption process observed for some metals is not associated with the nature of the initial sorption reaction, and it is only a consequence of the slow reaction that follows sorption. In the present study, Cd was measured after only 1 h; under such conditions, the slow reaction would hardly count, and hence Cd would be expected to be readily desorbed.

The observed results can be interpreted by considering the effect of anthropogenic activities on the metal sorption related characteristics of the soil under study. These findings are significant in relation to the fate of Cd applied as a possible contaminant in phosphate-fertilizers and waste materials.

Acknowledgement:

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