Journal of Chromatography, 643 (1993) 357–362
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2695

Mobility of cadmium as influenced by soil properties, studied by soil thin-layer chromatography

M. Sánchez-Camazano* and M. J. Sánchez-Martín

Instituto de Recursos Naturales y Agrobiologia, CSIC, Cordel de Merinas 40–52, Apdo 257, E-37071 Salamanca (Spain)

ABSTRACT

We studied the mobility of cadmium in various natural soils by soil thin-layer chromatography. The R_F values of the soils varied between 0.14 and 1.00 (mean = 0.64, mode = 0.87). Cadmium was found to be slightly mobile in 27%, moderately mobile in 14%, mobile in 41% and highly mobile in 18% of the soils studied. A statistical analysis of the results obtained revealed a highly significant correlation ($p < 0.001$) between R_F values and pH, the sum of bases and the exchangeable Ca^{2+} and Mg^{2+} contents, as well as a significant negative correlation ($p < 0.05$) between R_F and the clay content and cation-exchange capacity of the soils. The results show the significance of soil properties to the mobility of cadmium wastes from industrial, mining and farming applications.

INTRODUCTION

The rapid expansion of farming, industrial and urban activities has raised serious environmental problems in relation to heavy metals in general and cadmium in particular. This element is considered to be the most hazardous of all heavy metals as it poses serious threats to human health even at very low concentrations in air, water or food [1]. This calls for the environmental control and monitoring of cadmium in order to avoid hazards, particularly in those places where it is bound to occur at high concentrations as a result of human activities [2–4].

Cadmium in soil may in principle be incorporated into the food cycle via vegetables or, alternatively, be washed towards surface or underground waters. In order to minimize environmentals hazards, one should investigate its soil mobility and how it is influenced by the soil properties.

Cadmium mobility in soils has so far usually been measured indirectly by batch adsorption techniques [5–7]. Other authors have used soil-packed columns [8] and, more recently, soil thin-layer chromatography (soil TLC) for this purpose [9]. This last technique, which was developed by Helling and Turner [10], has been widely used to study the mobility of pesticides in soils [11–17] on account of its simplicity, reproducibility and low cost. The soil TLC technique has also been used by Khan *et al.* [9] and by Singhal and Shing [18] to investigate the mobility of heavy metals and trace elements in soil, respectively; these studies did not consider the influence of soil characteristics on the metal mobility.

In this work we studied the influence of soil properties and constituents on the mobility of cadmium by soil TLC.

EXPERIMENTAL

Soil samples

We used 22 samples of natural, uncultivated soils that were collected from the soil surface horizon (0–20 cm deep) at different places in the province of Salamanca (Spain). The samples were sieved through 2-mm mesh, after which they were characterized chemically by using standard soil analysis

---

* Corresponding author.

TABLE I

SELECTED PROPERTIES OF 22 SOILS STUDIED

Soil	pH	Organic matter (%)	C/N	Clay (%)	Cation-exchange capacity (10^{-2} mol/kg)	Exchange cations (10^{-2} mol/kg)					Base saturation (%)
						Na^+	K^+	Mg^{2+}	Ca^{2+}	Σ	
1	6.9	6.90	11.1	19.3	23.07	0.41	0.39	3.64	10.42	14.86	64.41
2	6.3	0.60	4.9	59.2	26.90	0.19	0.13	3.87	13.27	17.46	64.90
3	6.0	5.22	12.0	17.7	24.72	0.58	0.23	1.42	11.02	13.25	53.60
4	5.0	8.90	15.3	13.9	18.50	0.08	0.10	0.37	1.38	1.93	10.43
5	5.3	5.95	15.3	11.6	15.25	0.51	0.01	0.20	1.82	2.54	16.65
6	6.7	6.68	11.9	16.8	16.95	0.17	0.43	1.14	5.20	6.94	40.94
7	4.9	5.29	22.7	14.8	12.20	0.17	0.07	0.57	2.24	3.05	25.00
8	5.1	5.52	15.8	22.4	11.95	0.14	0.19	0.69	2.28	3.90	32.63
9	4.9	4.24	20.8	17.8	9.00	0.29	0.14	0.82	2.22	3.47	38.55
10	5.0	6.10	22.6	22.0	14.20	0.26	0.21	0.48	1.03	1.98	13.94
11	5.2	7.28	21.1	19.3	19.30	0.11	0.53	0.84	2.10	3.60	18.65
12	5.6	3.44	13.5	11.8	13.45	0.23	0.19	0.72	1.40	2.54	18.88
13	5.1	4.66	17.3	14.2	13.00	0.61	0.21	0.19	0.67	1.68	12.92
14	5.3	1.13	8.6	8.7	4.50	0.56	0.00	0.31	1.03	1.90	42.22
15	5.4	0.36	6.8	8.9	5.25	0.10	0.06	0.30	0.81	1.27	24.19
16	5.5	1.78	9.2	14.1	9.65	0.25	0.23	1.25	2.90	4.63	47.97
17	6.1	1.15	12.0	10.6	6.60	0.25	0.08	0.79	2.85	3.97	60.15
18	5.7	4.33	14.4	7.0	7.00	0.18	0.08	1.25	2.66	4.17	59.57
19	6.9	1.75	7.9	20.8	13.70	0.30	0.62	1.51	7.46	9.89	72.18
20	5.9	1.55	14.7	14.9	17.40	0.10	0.53	0.82	6.29	7.74	44.48
21	4.8	1.92	16.8	27.1	8.20	0.58	0.21	1.15	2.51	4.45	54.26
22	5.4	5.16	20.0	20.3	12.30	0.09	0.13	1.18	4.25	5.65	45.93

methods [19], the organic matter content (%C × 1.72) and the carbon–nitrogen relationship (C/N) were calculated. The results obtained are shown in Table I.

Reagents

The solutions used included 0.1 *M* cadmium chloride in methanol and 0.05% dithizone in carbon tetrachloride. The orange colour of cadmium–dithizone complex was readily observed on all the soil plates used.

Preparation of the soil plates

The soil samples were ground in a mortar and subsequently sieved through 160 μm mesh, after which 7.5 g of soil and 15 g of distilled water were used to prepare a slurry that was spread as a 0.5-mm-thick layer over each of the 20 × 5 cm plates used with the aid of a TLC soil applicator. The three central plates in each set of five used for each type of soil were chosen for the subsequent experiments. The selected plates were dried in a chamber at room temperature and a relative humidity of 70%.

Soil TLC procedure

The plates were marked with two horizontal lines at distances of 2 and 12 cm, from the base. One drop (*ca.* 5 μl) of the cadmium chloride solution was placed on the baseline of the three plates with the aid of a micropipette. The plates were then allowed to develop in closed individual glass chromatographic chambers that were 22 cm long and 3 cm wide by using distilled water as developer. Next, the plates were washed to a distance of 10 cm from the baseline and allowed to dry at room temperature. Finally, cadmium mobility was determined by spraying the plates with the dithizone solution.

Fig. 1 shows line sketches of some typical chromatograms obtained. All spots showed some tailing. Cadmium mobility was measured as R_F and R_b values by using the following relations:

$$R_F = R_L/10$$

$$R_b = R_t/10$$

where R_L and R_t denote the frontal distance travelled by the metal and the bottom of the spot, respectively.

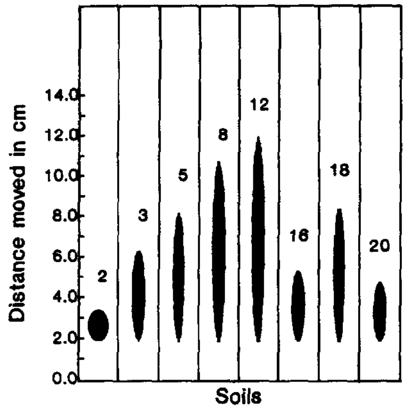

Fig. 1. Line sketches of some typical chromatograms.

RESULTS AND DISCUSSION

The results obtained in the determination of the mobility of cadmium in the 22 soils studied are shown in Table II as R_F values.

TABLE II

R_F OF CADMIUM FOR THE SOILS STUDIED

Soil No.	R_F (mean ± S.D., n = 3)
1	0.15 ± 0.01
2	0.14 ± 0.02
3	0.43 ± 0.01
4	0.85 ± 0.03
5	0.62 ± 0.01
6	0.19 ± 0.02
7	0.69 ± 0.03
8	0.87 ± 0.03
9	0.87 ± 0.02
10	0.93 ± 0.02
11	0.89 ± 0.03
12	1.00 ± 0.01
13	0.93 ± 0.02
14	1.00 ± 0.01
15	0.80 ± 0.01
16	0.34 ± 0.01
17	0.88 ± 0.03
18	0.66 ± 0.03
19	0.33 ± 0.02
20	0.27 ± 0.01
21	0.35 ± 0.01
22	0.80 ± 0.03
Range	0.14 ± 0.02–1.00 ± 001
Average	0.64 ± 0.02
Mode	0.87 ± 0.01

TABLE III

CADMIUM MOBILITY IN SOILS[a]

Class	R_F	Mobility	Soil No.	Soil (%)
1	0.00–0.09	Immobile	–	0
2	0.10–0.34	Slightly mobile	1, 2, 6, 16, 19, 20	27
3	0.35–0.64	Moderately mobile	3, 5, 21	14
4	0.65–0.89	Mobile	4, 7, 8, 9, 11, 15, 17, 18, 22	41
5	0.90–1.00	Very mobile	10, 12, 13, 14	18

[a] Classification according to Helling and Turner [10].

The R_F values for the soils varied from 0.14 to 1.00, which indicates that the mobility of cadmium in them was highly variable. The mean (0.64) and mode (0.87) of these values indicate that cadmium was highly mobile in many of the studied soils.

The R_b values were found to be 0.00 in all the chromatograms, so cadmium was not fully mobile in any soil.

Because the soil TLC technique has only recently begun to be used for determining cation mobility in soils, and since few systematic studies involving large numbers of soils have been carried out so far, no mobility classification according to R_F values has yet been put forward. One the other hand, there is one such classification for pesticides in soils, which was proposed by Helling and Turner [10]. Table III shows the cadmium mobility in the studied soils according to such a classification.

In order to determine the influence of the soil properties on the mobility of cadmium, we determined the simple correlations between the R_F values and soil properties. The correlation coefficients obtained are included in Table IV. As can be seen, there was a highly significant negative correlation ($p < 0.001$) between R_F and pH, the Ca^{2+} and Mg^{2+} contents and the sum of bases. There is also a significant correlation at the 0.01–0.001 level between R_F and percentage base saturation, and another significant correlation at the 0.05-0.01 level between R_F and the cation-exchange capacity, clay and K^+ contents. On the other hand, there is no correlation between R_F and the organic matter content.

TABLE IV

SIMPLE CORRELATION COEFFICIENTS RELATING SOIL PROPERTIES TO R_F IN 22 SOILS

Soil property	Correlations coefficient (r)
pH	−0.66[a]
Organic matter content	0.16
Clay content	−0.45[b]
Cation-exchange capacity	−0.51[b]
Na^+ content	−0.06
K^+ content	−0.47[b]
Mg^{2+} content	−0.70[a]
Ca^{2+} content	−0.76[a]
Σ bases	−0.78[a]
Base saturation	−0.64[c]

[a] Significant at the < 0.001 level.
[b] Significant at the 0.05–0.01 level.
[c] Significant at the 0.01–0.001 level.

The variability in the cadmium mobility is mostly accounted for by the sum of bases ($R^2 = 0.61$), followed by the contents of the divalent cations Ca^{2+} ($R^2 = 0.58$) and Mg^{2+} ($R^2 = 0.49$). This is a result of the proven competition [20–23] between Cd^{2+} and exchangeable cations, divalent calcium and magnesium in particular. Milberg *et al.* [20] found cadmium to be adsorbed preferentially over calcium in soils. Also, McBride *et al.* [21] observed the cadmium retention capacity of soils to depend markedly on the exchangeable calcium content of the soil concerned: the retention capacity increased with increase in the calcium concentration. This author believes the calcium content of a soil is a reliable indicator of its cadmium retention capacity. Kinniburgh *et al.* [22] established a sequence of relative affinity of divalent cations for soil surfaces where the affinity of all alkaline earth elements is always lower than that of cadmium, and García-Miragaya and Page [23] found the competition of cadmium with exchangeable cations to decrease in the following order: Al < Ca < K < Na.

According to the above findings, the affinity for cadmium varies in the order Ca > Mg > K > Na, which is consistent with the variation of the correlation coefficients of R_F with the contents in these elements.

The pH of soil is considered by some researchers to be an important parameter on affecting the distribution and mobility of cadmium in soil [24,25]. Fuller [26] established a classification according to which cadmium should be fairly mobile in soils of pH 4.6–6.6 and moderately mobile in those of pH 6.7–7.8. The highly significant negative correlation between R_F and pH found in this work is consistent with this classification. Even though major generalizations are precluded by the large number of soil parameters that may influence cadmium mobility, we found high mobility (class 5) in soils whose pH values never exceed 5.6; on the other hand in soils whose pH values is $\geqslant$ 6.3 the mobility is slight (class 2).

We also observed a significant negative correlation between the R_F values and the cation-exchange capacity. Exchangeable cations are known to come from clay, the content in which was also significantly correlated with the cadmium mobility, and from organic matter. However, correlation with this last was insignificant and positive, so the increase in organic matter content should result in an increase in cadmium mobility. In fact, organic matter in soils may influence cadmium mobility by retaining the element through ion exchange, thereby reducing its mobility, and by favouring the formation of soluble complexes with the soluble humic fraction (fulvic acid), thus increasing the cadmium mobility [27]. Therefore cadmium eluviation in soils will be particularly marked in humic soils as the forests soils that possess high C/N ratios (*i.e.* they feature low degrees of organic matter humification and high fulvic acid contents). Soils 4, 9, 11, 12 and 13 were of this type. All of them yielded $R_F \geqslant 0.85$, so they allowed for a high cadmium mobility.

Complex-formation reactions between humic substances and heavy metals have aroused growing interest in the last few years [28–30]. The complex-forming ability of fulvic acids is ascribed to their possessing a number of oxygen-containing groups including–COOH, aromatic, alkyl and enol–OH, and –C=O functions of various types. The stability constant of the metal complex of cadmium with fulvic acid on the assumption of a 1:1 stoichiometry as determined by Mantoura *et al.* [31] varies between 4.57 and 4.95 (log *K*) depending on the acid concerned.

The results obtained in this work show the significance of soil properties to the behaviour of cadmium from industrial, mining and farming activities in soil. In addition, they prompt the need to determine some soil paramaters to be used as critical indicators in controlling the cadmium load of soils.

ACKNOWLEDGEMENT

This work was supported by the "Junta de Castilla y León" (Spain) under Project No. 0611/90.

REFERENCES

1 A. L. Page and F. T. Bingham, *Res. Rev.*, 48 (1973) 1.
2 T. Crisanto and L. F. Lorenzo, *Bull. Environ. Contam. Toxicol.*, 50 (1993) 61.
3 M. J. Sánchez-Martín and M. Sánchez-Camazano, *J. Environ. Qual.*, (1992) in press.
4 M. Sánchez-Camazano, M. J. Sánchez-Martín and L. F. Lorenzo, *Sci. Total Environ.*, (1992) in press.
5 M. Fic and M. Isenbeck-Schröter, *J. Contam. Hydrol.*, 4 (1989) 69.
6 P. R. Anderson and T. H. Christensen, *J. Soil. Sci.*, 39 (1988) 15.
7 S. C. Jarvis and L. H. P. Jones, *J. Soil Sci.*, 31 (1980) 469.
8 M. Lodenius and S. Autio, *Arch. Environ. Contam. Toxicol.*, 18 (1989) 261.
9 S. Khan, D. Nandan and N. N. Khan, *Environ. Pollut.*, 4 (1982) 119.
10 C. S. Helling and B. C. Turner, *Science*, 162 (1968) 562.
11 C. S. Helling, *Soil Sci. Soc. Am. Proc.*, 35 (1971) 732.
12 C. S. Helling, *Soil Sci. Soc. Am. Proc.*, 35 (1971) 738.
13 C. S. Helling, *Soil Sci. Soc. Am. Proc.*, 35 (1971) 743.
14 P. Jamet and J. C. Thoisy-Dur, *Bull. Environ. Contam. Toxicol.*, 41 (1988) 135.
15 S. Khan and N. N. Khan, *Soil Sci.*, 142 (1986) 214.
16 S. R. Sharma, R. P. Singh, S. K. Saxena and S. R. Ahmed, *J. Liq. Chromatogr.*, 8 (1985) 1327.
17 D. C. Peek and A. P. Appleby, *Weed Sci.*, 37 (1989) 419.
18 J. P. Singhal and R. P. Singh, *Colloid Polymer. Sci.*, 255 (1977) 488.
19 C. A. Black, *Methods of Soil Analysis*, American Society of Agronomy, Madison, WI, 1965.
20 R. P. Milberg, D. L. Brower and J. V. Lagerwerff, *Soil Sci. Soc. Am. J.*, 42 (1978) 892.
21 M. B. McBride, L. D. Tyler and D. A. Hovde, *Soil Sci. Soc. Am. J.*, 45 (1981) 739.

22 D. G. Kinniburg, M. L. Jackson and J. K. Syers, *Soil Sci. Soc. Am. J.*, 40 (1976) 796.
23 J. Garcia-Miragaya and A. L. Page, *Soil Sci. Soc. Am. J.*, 4, (1977) 718.
24 Council for Agricultural Science and Technology (CAST), *Effect of Sewage Sludge on the Cadmium and Zinc Content of Crops*, CAST Rep. No. 83, Ames, IA, 1980, p. 77.
25 A. L. Page, A. C. Chang and F. T. Bingham, in N. W. Leep (Editor), *Management and Controls of Heavy Metals in the Environment*, CEP Consultants, Edinburgh, 1979, p. 525.
26 W. H. Fuller, *Movement of Selected Metals, Asbestos and Cyanide in Soil: Application to Waste Disposal Problem*, EPA-600/2-77-020, Solid and Hazardous Waste Research Division, US Environmental Protection Agency, Cincinnati, OH, 1977.
27 F. J. Stevenson and A. Fitch, in P. M,. Huang and M. Schnitzer (Editors), *Interactions of Soil Minerals with Natural Organics and Microbes*, Soil Science Society of America, Madison, WI, 1986, p. 29.
28 R. H. Neal and G. Sposito, *Soil Sci.*, 142 (1986) 164.
29 R. G. Chubin and J. J. Street, *J. Environ. Qual.*, 10 (1981) 225.
30 H. A. Elliot and C. M. Denneny, *J. Environ. Qual.*, 11 (1982) 658.
31 R. F. C. Mantoura, A. Dickson and J. P. Riley, *Estuarine Coastal Mar. Sci.*, 6 (1978) 387.