Bull. Environ. Contam. Toxicol. (1993) 50:61–68

Environmental Contamination and Toxicology

Evaluation of Cadmium Levels in Fertilized Soils

T. Crisanto Herrero and L. F. Lorenzo Martín

Institute of Natural Resources and Agrobiology, CSIC, Ap. 257, 37071 Salamanca, Spain

Cadmium is a normal component of phosphate fertilizers; its concentrations in them may vary as a function of the origin of the mineral since the levels of the element range from 0.1 to 0.4 mg $Cd.Kg^{-1}$ if the mineral is from the Kola peninsula and between 70 and 90 mg $Cd.Kg^{-1}$ if it is from Senegal (Adriano,1986). In the case of Senegal phosphates, according to Godin (1983), it is possible to obtain phosphate fertilizers containing up to 150 mg-Cd by Kg of P_2O_5.

Contamination may be caused, therefore, by the long term continuous application of phosphate fertilizers, which has resulted in the accumulation of cadmium. The nature and intensity of the interaction between cadmium and soil components are the most important factors responsible for the existence of a cadmium fraction, originating in the fertilizers, that is able to move through the soil. The aim of the present work was to evaluate the state of this element in several soils and to relate the values found with the soil variables.

MATERIAL AND METHODS

As mentioned, the study concerned the supply of cadmium to soils through phosphate fertilizers; the starting material was the Ap horizon of 20 soils from irrigated zones of the province of Salamanca (Spain). The original material was Quaternary (soils 1-10), and Neogene, loams and lime-stone (soils 11-20), (IGME, 1970). These had been subjected to intensive treatment with fertilizers over 20 years, the mean dose being 150 units of P_2O_5 per hectare per year, which is approximately equivalent to a mean increase in the cadmium content from 1 to 4g of cadmium per hectare per year. The phosphate fertilizers were originating from Morocco rock phosphate.

The soils displayed highly variable pH, between 4.8 and 7.5, with a low organic matter content and low levels of phosphorus and calcium. Most of them were sandy, some of them containing a total of 80% of sand, as may be seen in their analysis (Table 1).

Sends reprints requests to Dra Crisanto at the above address.

Table 1. Soil Characteristics

Soil	pH	Ca mg Kg-1	O.M. %	c.sand %	f.sand %	silt %	clay %	CEC meq Kg^{-1}
1	6.4	1900	1.64	29.7	39.0	9.4	21.6	12.7
2	7.5	3200	1.67	30.2	36.0	16.8	16.6	11.7
3	5.6	600	1.12	44.0	33.0	9.9	12.8	7.1
4	7.2	2200	1.50	27.2	35.0	16.8	21.3	13.1
5	5.6	1100	1.02	39.4	28.0	16.1	17.1	9.2
6	5.9	1400	1.33	24.5	25.0	30.8	20.4	14.1
7	6.0	1500	0.90	21.4	33.0	22.4	23.3	13.1
8	5.4	900	0.90	53.0	26.0	7.4	13.5	5.3
9	7.4	2400	0.95	40.9	31.0	9.0	19.3	9.2
10	4.8	200	0.69	55.0	22.0	10.7	12.1	6.5
11	5.9	600	0.76	44.0	29.0	6.4	20.3	14.2
12	6.9	430	0.50	39.0	41.0	8.0	12.0	11.9
13	7.1	900	0.76	50.0	20.0	4.7	25.6	14.4
14	7.4	470	1.00	54.1	26.0	7.2	12.4	8.4
15	7.3	1010	1.23	45.3	27.0	5.0	22.3	18.9
16	7.1	850	0.80	42.5	24.0	8.4	24.9	14.9
17	6.8	10	0.70	48.7	24.0	7.2	20.2	13.9
18	7.3	370	0.70	43.9	32.0	9.3	14.8	15.8
19	7.2	1000	0.70	34.8	29.0	9.2	27.3	19.8
20	6.1	630	0.76	39.0	36.0	7.9	17.5	16.8

Table 2. Cadmium content in Fertilizers

Fertilizer	Soluble Cd mg Kg^{-1}	Total Cd mg Kg^{-1}
1	2.84	8.29
2	4.85	11.41
3	5.75	12.55
4	3.87	8.78
5	4.43	9.37
maximum	5.75	12.55
average	4.34	10.08
minimum	2.84	8.29
St.er.(5 df)	0.204	0.430
LSD (5 %)	0.524	1.106

Soluble cadmium was extracted from the soils with M ammonium acetate (Soon and Bates, 1982) and total cadmium was extracted by digestion with a mixture of HF-$HClO_4$ (Tessier,1979) and dissolution of the residue with 2% hydrochloric acid. Two replications of every determination were made. In the resulting solutions cadmium was determined by atomic absorption spectrophotometry using a graphite chamber (Varian AA 1475), with standards from 5 to 50 ppb (soluble Cd), and 1 to 25 ppm (total Cd).

A study was also made of the possible movement of cadmium through the soil by the development of thin layer chromatography according to the technique of Helling (1968). Using the plate obtained with a soil suspension (<0.16 mm), once dry, a drop of $CdCl_2$ (0.1M) was added, thereafter developing the chromatogram with water until the water had risen 10 cm. Visualization of the run of the compound was carried out by spraying the plate with a 0.05% solution of dithizone in CCl_4 , thus permitting measurement of the characteristic Rf for each soil.

Finally, the cadmium contents of five fertilizers of different origin were analyzed, obtaining the values shown in Table 2 relative to existence of cadmium in the fertilizers.

RESULTS AND DISCUSSION

Evaluation of the supply of cadmium to the soils from the phosphate fertilizers (Table 2) revealed ranges between 2.80 and 5.75 mg Kg^{-1} of soluble cadmium and between 8.29 and 12.55 mg.Kg^{-1} of total cadmium, implying an increase of 0.008 to 0.030 mg.Kg^{-1} of soluble cadmium throughout the period considered. These values are lower than the 0.04 mg.Kg^{-1} reported by Bignoli (1986) in soils from the European Community for a similar period of time.

Once in the soil, cadmium is subject to several processes that may be listed as: A) specific adsorption onto the ions of the mineral interphase; B) precipitation of insoluble cadmium compounds, and C) formation of complexes or chelates as a result of interaction with the organic matter. The compounds found in the soil are $Cd_3(PO_4)_2$, $CdCO_3$ and $Cd(OH)_2$. The solubility curves of these, studied by Santillán and Medrano (1975), indicate that in such soils the solubility of cadmium decreases when pH rises, owing to the formation of some of the mentioned compounds.

The content of soluble cadmium in the whole set of soils studied in the present work (Table 3) ranged between 0.02 and 0.20 mg.Kg^{-1}; in the soils of pH < 7 this varied between 0.03 and 0.20, and in soils of pH>7 between 0.02 and 0.13. These values are higher than those reported by Williams (1976) for five unfertilized soils (0.013 to 0.130, mean 0,048). Also the mean value of soluble cadmium of the 20 soils was 0.073 mg.Kg^{-1}, 65% higher than the value of 0.044 found by Baerug (1987) in 125 unfertilized soils. In addition the total Cd values are higher than those recently described by Sánchez Camazano et al. (1990) in 22 natural soils from the province of Salamanca.

Table 3.	Cadmium content in soils		Cd mobility
Soil	Soluble Cd mg Kg^{-1}	Total Cd mg Kg^{-1}	Rf
1	0.07	0.32	0.83
2	0.13	0.24	0.47
3	0.06	0.20	0.63
4	0.11	0.29	0.46
5	0.15	0.34	0.58
6	0.13	0.26	0.56
7	0.20	0.26	0.69
8	0.09	0.21	0.96
9	0.02	0.21	0.19
10	0.05	0.17	0.46
11	0.05	0.21	0.26
12	0.05	0.24	0.32
13	0.06	0.26	0.45
14	0.03	0.29	0.29
15	0.04	0.29	0.17
16	0.04	0.39	0.24
17	0.03	0.31	0.33
18	0.03	0.21	0.50
19	0.09	0.19	0.26
20	0.04	0.23	0.56
av. (all soils)	0.074	0.256	0.46
St. er (19 df)	0.013	0.034	0.10
LSD (5 %)	0.009	0.072	0.21
av. (pH < 7)	0.084	0.250	0.56
av. (pH > 7)	0.061	0.263	0.34

With respect to total cadmium, this is also seen to be increased in the fertilized soils as compared with the unfertilized ones, the mean value being 0.26, which is similar to that obtained by Soon (1990) in 52 agricultural soils from Canada.

Upon grouping the soils according to whether their pH value was below or above 7, it is possible to observe the variation in the characteristic statistics of each group (Figure 1a). The highest values of soluble cadmium are consistently found in the group of 11 soils with a pH lower than 7, which agrees with the conclusions of several authors concerning the greater solubility of cadmium in acid soils (Santillán, 1975) (Cavallaro, 1978), this solubility being limited by the formation of cadmium phosphates and carbonates.

As a continuation of the foregoing, Figure 1b shows the statistics of the values of total cadmium in the groups of soils studied; the content in total cadmium is seen to be lower in the acid soils, positively corroborating the above assumption. The mean percentage of soluble cadmium with respect to total cadmium is 28%, a value similar to that estimated by Hickey (1984) in 4 contaminated soils. The simple correlation coefficients between soluble cadmium in the form of ions exchangeable with H^+, and other soils parameters were calculated. Significant values were obtained with the calcium content, $r=0.4602^*$ (p>95%) and with the percentage of the fine soil fraction, $r=0.7211^{***}$ (p>99,99%). Thus, in agreement with this latter result, the relationship between soluble cadmium and the percentage of coarse sand is significant and negative, $r=-0.6882^{***}$ (p>99,9%).

On considering assumptions A, B and C, postulated at the beginning of the discussion, it is seen that the evolution of cadmium in the soils studied depends on the following: A) adsorption onto the silt and clay components, as shown by the corresponding correlation coefficient, and B) to a lesser extent the degree of precipitation of cadmium compounds (Cavallaro, 1978); the third assumption cannot be considered here, since levels of organic matter in the soils were very low.

Concerning the first aspects, it is known that heavy metals participate in exchange reactions on the negatively charged surface of clay minerals. In acid soils, the reaction is reversible and at a pH of approximately 5.5 some heavy metals, essentially cadmium, do not compete with Ca^{2+} for adsorption; that is, they are free in the soil solution. However, when pH increases adsorption undergoes a strong increase and the reaction may become irreversible. It appears that the increase in adsorption coincides with the variation in pH by one unit, which in the case of cadmium is usually between 6.4 an 7.5 when the Metal(OH+) hydrolyzed form constitutes a significant fraction of the concentrations of aqueous metal ions (Forbes, Posner, 1976). In addition Street and others (1978) have observed that soluble cadmium decreases to 50% when pH increases. These results are confirmed in the soils studied here, where the amounts of total cadmium, which therefore includes the immobilized cadmium, were found to be higher in the soils with a pH higher than 7 (Figure 1b) and the mean amount of soluble cadmium is 27% less in the non-acid soils than in the acid ones.

Finally, the mobility of cadmium in the soils was studied. The cadmium present in the soil, originating from an external supply, remains in the surface layer, although some authors (Williams, 1987) have reported its presence at some 10 cm depth with respect to the zone of fertilizer application, although never below 30 cm. Mobility was studied by thin layer chromatography, determining the mean Rf value of two replications (run of compound/ run of solvent). Figure 1c shows a study of the statistics of this variable; mobility is seen to be greater in the acid soils, the mean Rf value of the non-acid soils being 61% of that of the mean Rf value of the acid soils.

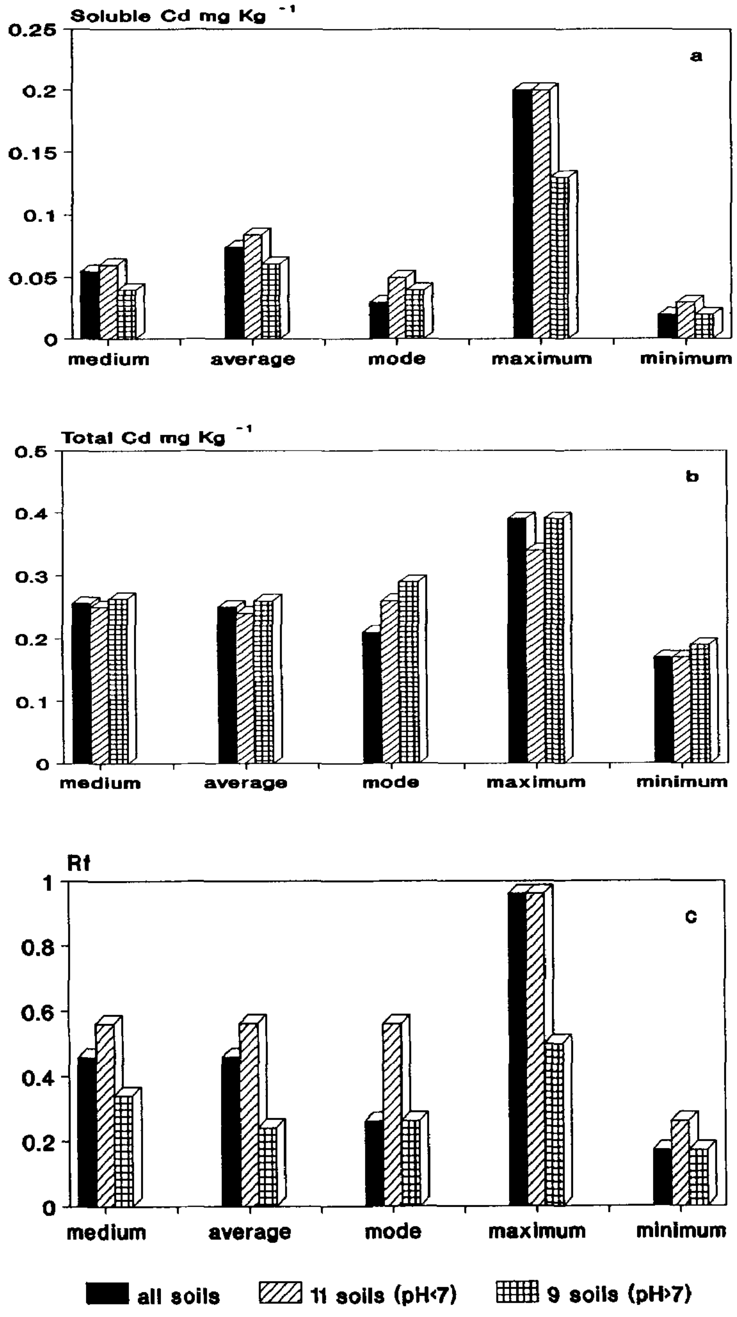

Figure 1. Evaluation of soluble Cd, total Cd and Cd mobility of soils, grouped according pH

The Rf value shows a significant and negative correlation, r=-0.5778** (p>99%) with the pH of the soils, thus confirming the notion that mobility is greater in acid soils as indicated by Page (1979), who states that the pH is the most important property of the soil with respect to the mobility of cadmium; this author therefore recommends that pH be kept above 6.5 when the soils are to receive large amounts of cadmium. The relationship between these two variables is also in agreement with that reported by Sánchez Martín (1990) in studies of the mobility of cadmium in 22 soils from the province of Salamanca (Spain).

From all the foregoing, it may be inferred that the soluble and total cadmium content of the soils studied is greater than the values figuring in the literature for uncultivated soils, including the 22 soils from the province of Salamanca. This would point to the presence of cadmium in the zone from anthropogenic sources. The mean content of soluble cadmium in the group of acid soils is 14% higher than the mean of all the soils, while the mean value of the non-acid soils shows a decrease of 17% with respect to these mean values.

In addition, the level of soluble cadmium in soils depends on the silt+clay percentage, and the mobility of cadmium (represented by the Rf values) is positively related to the pH of the soils, thus confirming the possibility of the presence in acid soils of soluble cadmium at concentrations higher than those to be found in non-acid soils.

Acknowledgments. This project was supported by the Junta de Castilla y León. Spain.

REFERENCES

Adriano DC (1986) Trace elements in the terrestrial environment. Springer Verlag, New York.

Baerung R (1987) Influence of commercial fertilizers on cadmium in soils and plants. Commercial fertilizers and geochemical problems. J Lag, Norwegian Univ. Press, Oslo. 101-109

Bignoli GM, Sabbioni E, Goetz L (1986) Environmental assessment of trace metals released from phosphatic fertilizers: Cadmium impact on groundwater quality and human exposure. 7th European conference on environmental pollution (Madeira) Portugal. 21 pgs

Cavallaro N, McBride MB (1978) Copper and cadmium adsorption characteristics of selected acid and calcareous soils. Soil Sci Soc Am J 42. 550-556

Forbes EA, Posner AM, Quirk VP (1976) The specific adsorption of divalente Cd, Co, Cu, Pb and Zn on goethite. J Soil Sci 27. 154-156

Godin P (1983) Les sources de pollution des sols: Essai de quantification des risques dus aux éléments traces. Sci du Sol 5. 73-87

Helling CS, Turner BC (1968) Pesticide mobility: Determination by soil thin-layer chromatography. Science 162. 562-563

Hickey MG, Kittrick JA (1984) Chemical partitioning of Cd, Cu, Ni and Zn in soils and sediments containing high levels of heavy metals. J Environ Qual 13. 372-376

I.G.M.E. (1970) Mapa geológico de España, escala 1:200.000 (Salamanca), hoja 37, Madrid

Page AL, Chang AC, Bingham FT (1979) Management and controls of heavy metals in the environment. CEP Consultants Ltd Edimburgh, UK. 525-28

Santillán-Medrano J, Jurinak JJ (1975) The chemistry of Lead and cadmium in soil: Solid phase formation. Soil Sci Soc Amer Proc 39. 851-856

Sánchez-Camazano M, Sánchez-Martín MJ, Lorenzo-Martín LF (1990) Distribución y contenido en cadmio en suelos naturales (in press)

Sánchez-Martín MJ, Sánchez-Camazano M (1990) Influencia de las características del suelo en la adsorción y movilidad del cadmio (in press)

Soon YK, Abboud S (1990) Trace elements in agricultural soils of Northwestern Alberta. Can J Soil Sci 70. 277-288

Soon YK, Bates TE (1982) Chemicals pools of cadmium, nickel and zinc in polluted soils and some preliminary indications of their availability to plants. J Soil Sci 33. 477-488

Street JJ, Sabey BR, Lindsay WL (1978) The influence of pH levels, Cd, sewage and incubation times on the solubility and absorption of Cd by plants. J Environ Qual 7. 286-290

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chemistry 51. 844-851

Williams CH, David DJ (1976) The accumulation in soil of cadmium residues from phosphate fertilizers and their effect on the cadmium content of plants. Soil Sci 121. 86-93

Williams DE, Vlamis J, Pukite AH, Corey JE (1987) Metal movement in sludge-amended Soils: A nine years study. Soil Sci 142. 124-131

Received April 15, 1992; accepted June 30, 1992.