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Plant and Soil

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https://doi.org/10.1007/BF00010280

Plant and Soil **171**: 263–266, 1995.

Uptake of soil cadmium by three field crops and its prediction by a pH-dependent Freundlich sorption model

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Received 30 June 1994. Accepted in revised form 3 October 1994

Key words: cadmium, distribution coefficient, Freundlich, plant availability, soil solution, sorption

Abstract

Crop contamination with cadmium is a function of soil contamination. Here we study the applicability of the soil solution bioavailability hypothesis to Cd: that is, whether uptake of Cd was more directly related to its concentration or activity in the soil solution than in the soil solid phase. Experimental data from past soil-crop surveys for Cd were used to test this hypothesis. It was also investigated whether pH-dependent desorption of cadmium would be an important mechanism in affecting cadmium activity and thus uptake. To do so we calculated the correlation between the Cd transfer factor (ratio between Cd level in plant dry material and Cd level in the topsoil) and either the soil pH, or the calculated soil solution Cd concentrations.

There was no correlation between the Cd contents of the soil and of the edible parts of leafy plants (endive, spinach and lettuce). There was a strong negative correlation between soil pH and the log transfer factor for Cd at pH 4.5–7. 2 and thus plant content. There also was a negative correlation between soil pH and calculated cadmium concentrations in the soil solution. For spinach grown on soils with pH > 7.2 the transfer factor increased, which is tentatively ascribed to cadmium mobilization by dissolved organic matter.

The soil solution hypothesis should be further tested by pot and field trials. Special attention should be paid to the role of pH and dissolved organic matter.

Introduction

In general, Cd concentrations in Dutch agricultural soils and crops are below permissible levels. At low soil Cd concentration solubility of Cd is believed to be controlled by sorption reactions rather than by precipitation. The distribution can be described by a Freundlich sorption equation, assuming binding site heterogeneity (Del Castilho and Bril, 1993). We can expect that a low coefficient of sorption for Cd, e.g. induced by a low pH, implies a high accumulation by crop plants. Gerritse et al. (1983) and Smilde et al. (1992) showed that Cd concentrations in soil solution extracts correlated well with Cd uptake by various crop plants.

The main purpose of the present study was to test the simple hypothesis that Cd concentration of the soil solution governs the cadmium levels in crops, with pH-dependent desorption of Cd being the main controlling mechanism. The hypothesis shares Sposito's (1983) viewpoint: that the metal ion activity in the soil solution governs metal content in crops. Cd activity and concentration in the solution are both likely to show correlation with plant levels, because dissolved Cd species showed rapid dissociation kinetics (Del Castilho et al., 1993a), in contrast with e.g. Cu. Because soil solution data from previous surveys for Cd were lacking, they were calculated using a pH-dependent Freundlich sorption model. The soil pH as such, and its effect on Cd concentrations, were used for the prediction of Cd transfer.

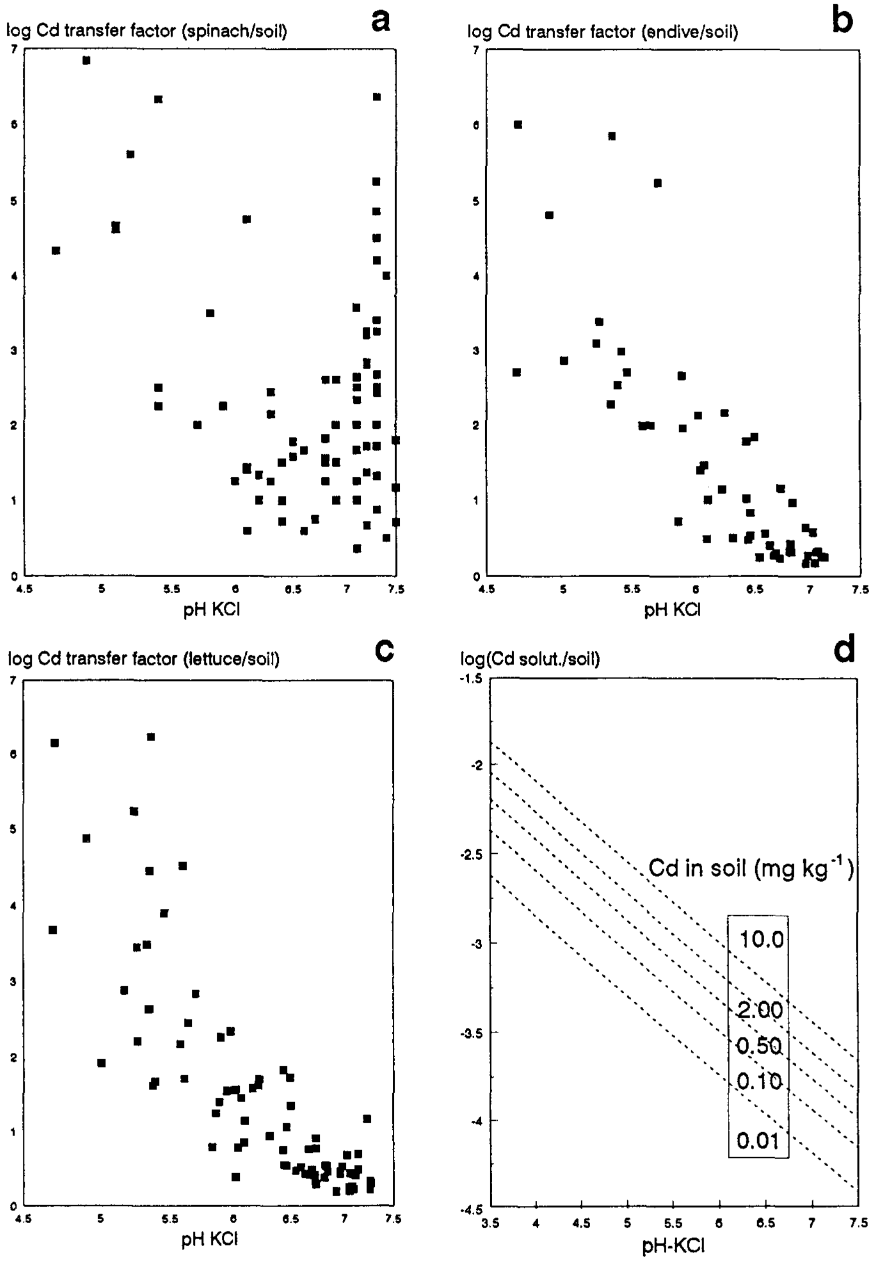

Fig. 1. Cd transfer factor of: spinach (**a**), endive (**b**) and lettuce (**c**); mg kg^{-1} dry material (plant, soil) vs. soil pH_{KCl}. Distribution of Cd between the soil solution ($\mu g\ L^{-1}$) and the soil (log [Cd solution]/[Cd soil]) as a function of pH (**d**).

Materials and methods

Crops

Agricultural soil surveys usually only present data (e.g. pH, heavy metal concentrations) for the topsoil layer, 0–30 cm. Crops like endive (*Cichorium endivia* L.), spinach (*Spinacia oleracea* L.) and lettuce (*Lactuca sativa* L.) form their roots almost exclusively in the topsoil. These crops are suited to test the soil solution hypothesis. Cadmium levels were measured using atomic absorption spectrometry (AAS) in rinsed plant material (normal domestic practice). Reference materials were used to monitor analytical quality.

Table 1. Soil characteristics of the fields where endive, lettuce or spinach were harvested. Results are expressed in % (w/w), except for Zn and Cd (mg kg^{-1}) and pH_{KCl}

	Endive soil			Lettuce soil			Spinach soil		
	Mean	Sdev[a]	Range	Mean	Sdev	Range	Mean	Sdev	Range
O.C.[b]	2.14	1.21	0.78–6.72	2.66	1.51	0.67–6.72	2.38	1.44	0.67–11.3
$CaCO_3$	0.88	2.05	<0.1–14	1.09	2.12	0.1–14	2.95	3.25	<0.1–13
Particles < 2 μm	14.4	4.17	4.6–23	14.3	5.96	4.4–28.6			
Particles < 16 μm	28.1	8.45	8.1–47.4	27.6	12.1	8.1–60.4	18.8	13.2	2–49
Soil pH_{KCl}	6.15	0.66	4.7–7.14	6.26	0.72	4.7–7.26	6.69	0.70	4.7–7.5
Soil Cd, mg kg^{-1}	2.01	1.89	0.43–12.6	2.72	2.97	0.33–12.6	0.45	0.17	0.19–1.1

[a] Sdev – standard deviation.
[b] O.C. – organic carbon.

Soils

Data from three previous surveys conducted at our Institute were used. One of these, a national survey executed in 1982, yielded data for Cd in soil and spinach (number of data pairs n, n = 82). Two other surveys in the region of the river Meuse floodplains, in 1988, yielded data for soils, lettuce (n = 77) and endive (n = 52). The topsoils in the surveys varied in clay, organic carbon and calcium carbonate concentrations, and in soil acidity; they showed large variations in soil Cd levels (0.2–12.6 mg kg^{-1}). The data are summarized in Table 1. Soil pH_{KCl} was determined in a settling suspension of overnight extracts of 5 g soil in 25 mL of a 1 *M* KCl solution. Cadmium was measured by AAS, using reference materials for quality control of the measurements. The percentage of particles < 2 μm or < 16 μm were determined with a pipet method (based on Stokes law). Size distribution was determined after removal of $CaCO_3$ (HCl addition), destructing the organic matter (hydrogen peroxide treatment), and the addition of a peptizing agent ($Na_4P_2O_7.10H_2O$).

Model calculation

The partition of Cd between the soil solid phase and the liquid phase was calculated using a pH-dependent Freundlich sorption model (Chardon, 1984) developed for Cd in Dutch soils. The basic model was the Freundlich Equation [1].

$$Cd_{SORBED} = K\, Cd_{SOLUT}{}^{1/n} \qquad (1)$$

where Cd_{SORBED} denotes sorbed soil Cd (mg kg^{-1}), Cd_{SOLUT} is dissolved Cd (μg L^{-1}), and n and K are soil-specific constants. Particularly at higher Cd levels, Cd_{SORBED} can be assumed to equal the soil Cd content. For 11 Dutch soils, described by De Haan et al. (1987), adsorption isotherms were determined at an ionic strength of 0.007 Eq L^{-1}. The average 1/n value derived from these experiments was 0.82 and showed little variation. Multiple regression analysis with soil parameters showed that K was strongly correlated with pH_{SOIL}

$$K = -0.3281 + 0.0528(10^{0.2598\, pHSOIL}) \qquad (2)$$

The calculated value of K was used to solve the mass-balance equation for a certain volume of soil:

$$T = S.Cd_{SOIL} + V.Cd_{SOLUT} = S.K.Cd_{SOLUT}{}^{1/n} + V.Cd_{SOLUT} \qquad (3)$$

where, for the volume of soil considered, T denotes the total amount of Cd (μg), S denotes the weight of soil material (g), and V denotes the volume of soil solution (L). When the total amount of Cd in the soil (T) is measured, Equation [3] can now be solved for dissolved Cd (Cd_{SOLUT}), using Newton-Raphson iteration, for a given combination of S and V. For a pH range of 4 to 7 a value of Cd_{SOLUT} was calculated using 1/n = 0.8, S = 1000 g and V = 0.3 L; using Cd_{SOLUT} and T, the distribution coefficient may be calculated.

Results and discussion

No direct correlations were found between Cd concentrations in leafy parts of lettuce, spinach or endive and soil Cd. For soil Cd, and endive, spinach or lettuce Cd the r^2 values were close to zero.

In the pH-range from 4.5 to 7.2, there was a negative correlation (for endive and lettuce $r^2 > 0.72$) between soil pH and Cd transfer factors in crops (Figs. 1a, b, c). For all crops there was about a tenfold decrease in transfer factor between pH 5 and pH 7.2 for each drop in pH unit.

At pH values > 7.2 some elevated transfer factors were found for spinach (Fig. 1a); these might be caused by increased solubility of Cd by complexation with dissolved organic matter at elevated pH (Herms and Brümmer, 1984).

Correlations between transfer factor (Figs. 1a/c) or distribution coefficient (Fig. 1d) and pH strongly suggest that a pH rise up to 7.2 is strongly governing sorption of cadmium to soil, and lowering the soil solution concentration, which in turn affects the availability.

It seems that pH (range 4.5–7.2) predicts the transfer of Cd quite well (Figs. 1a, b, c). However, other soil factors might also affect Cd uptake. Taking other parameters into account may diminish the bias, but may not increase the predicting power because of the natural variation of these parameters. Thus, the desired overall increase in accuracy might not be achieved. Dissolved organic carbon (DOC) is probably one of the important model parameters in addition to pH, clay and organic matter content, (Del Castilho et al., 1993a,b; Hesterberg et al., 1993). The effect of including DOC in a sorption model for bioavailability is not clear at present.

The soil solution hypothesis remains quite attractive. The distribution of Cd over plant (or soil solution) and soil depends to a large extent on soil pH. Direct measurement of soil solution Cd, however, seems needed to eliminate the errors in estimating this concentration, and to validate the hypothesis. Possibly more parameters, e.g. DOC, should be measured. The present paper confirms that there is no direct correlation between plant and soil Cd levels. Soil pH correlated negatively with the Cd transfer factor (concentration in plant/concentration in soil) for lettuce, endive and spinach. Also the estimated Cd distribution factor (model-calculated concentration in the soil solution/concentration in the soil) correlated negatively with pH. This supports the soil solution-bioavailability hypothesis for Cd. For further studies into the soil solution bioavailability hypothesis it is recommended to include measurement of Cd in the soil solution. Apart from pH, at least DOC data should be collected because, especially at more elevated soil-pH values, DOC might increase the availability of Cd to crops by promoting its desorption from soil increasing the soil solution Cd concentrations. This is especially to be expected at lower soil organic matter and clay levels.

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Section editor: A C Borstlap