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A SINGLE EXTRACTION PROCEDURE OF SOIL FOR EVALUATION OF UPTAKE OF SOME HEAVY METALS BY PLANTS

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The usefulness of single extraction solutions for assessment of the bioavailability of some heavy metals to plants is discussed. Experimental data are given demonstrating the suitability of a single extraction with 0.01 mol/l CaCl₂. In a field study, a close relationship was found between the Cd content in vegetables and its concentration in the CaCl₂-extract. Furthermore the possibility of evaluating interelemental interaction during plant uptake by measuring different elements in the same extract is shown for Cd and Zn. The ability of the extract to reflect changes in metal binding on to the soil is shown for Ni in competition with Cu.

KEY WORDS: Heavy metals, Cd, Cu, Ni, Zn; soils; bioavailability; extraction.

INTRODUCTION

For the evaluation of the bioavailability of heavy metals quite a number of methods have been suggested. Table 1 lists four main groups of extractants with some examples from each group.

Synthetic chelating agents such as EDTA and DTPA, as their sodium or ammonium salts, are widely used as extractants, mainly because of their ability to form very stable, water-soluble and well-defined complexes with a wide range of polyvalent cations. This requires, of course, that the concentration be sufficiently high to react with all releasable bi- and trivalent cations. Unfortunately, the ability to dissolve solids, mainly carbonates and Fe- and Al-oxides, has been claimed for these extractants too. DTPA was designed to minimize dissolution of carbonates but uncertainty concerning the degree of dissolution of Fe and Al compounds remains. This obviously depends on concentration, pH, and relative stability of the complexes with respect to the binding in solid phase and dissolution kinetics of the solid phases. Interpretation of the results of these extraction systems is therefore rather complicated and mostly only a statistical relationship is given with respect to the bioavailability. Generalization of such results to other soil-plant systems always remains rather uncertain.

As can be seen in Table 2, containing data from the international proficiency study ISE¹⁵,

Table 1 Single extraction procedures for heavy metals in soil.

<i>Group</i>	<i>Type and solution strength</i>	<i>Reference</i>
Acid extractions	HNO ₃ (0.43 - 2 mol/l)	1, 2, 3, 4,
	Aqua Regia	5
	HCl (0.1 - 1 mol/l)	3, 6, 7, 8, 9, 10, 11, 34
Chelating agents	EDTA (0.01 - 0.05 mol/l)	12, 13, 14, 34
	DTPA (0.005 mol/l)	13, 16, 17, 18, 19, 20,
	(+TEA+CaCl ₂)	21, 22, 36
Buffered salt solutions	1 mol/l NH ₄ -acetate acetic acid buffer, pH=4.8	4
	1 mol/l NH ₄ -acetate, pH=7	3, 4
Unbuffered salt solutions	CaCl ₂ 0.1 mol/l	23
	CaCl ₂ 0.05 mol/l	24
	CaCl ₂ 0.01 mol/l	25, 26, 27, 36
	NaNO ₃ 0.1 mol/l	28
	NH ₄ NO ₃ 1 mol/l	29

the acid extractants are yielding practically equal amounts of Cd, Cu, Ni, Pb and Zn in the tested soils, regardless of the concentration of the acids used. The only exception is the andosol from Indonesia. Acid extractants are commonly used to identify soils responsive to Cu and Zn fertilizers and to evaluate the extent to which soils are contaminated. The almost total contents can only be related to plant uptake if additional parameters are taken into consideration. For instance it has been shown that the "total" Cd-content in soil should be evaluated together with pH and organic matter content of the soil^{32,35}. This again leads to more statistical than causal relationships.

Table 2 Heavy metal concentrations in soils as found by extraction with Aqua Regia (AR) and boiling 2 mol/l HNO₃ (H) (in mg/kg dry soil).

<i>Soil Type</i>		<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Ni</i>	<i>Pb</i>	<i>Zn</i>
		<i>mg/kg</i>					
Garden soil (The Netherlands)	AR	2.20	46.7	120	25.9	315	715
	H	2.42	38.0	123	20.3	330	726
Sandy loam soil (Switzerland)	AR	1.30	72.3	84.0	18.8	995	1370
	H	1.49	68.5	82.8	16.4	1038	1440
Loess soil (Switzerland)	AR	1.32	64.5	121	45.0	36.4	373
	H	1.21	34.0	118	28.0	66.9	325
Marine clay (The Netherlands)	AR	0.10	20.0	5.34	13.1	8.90	34.9
	H	0.10	12.4	4.87	10.2	10.1	30.8
Sandy soil (The Netherlands)	AR	0.16	7.00	6.02	1.59	16.9	13.2
	H	0.14	5.62	5.93	1.03	18.9	12.0
Andosol (Indonesia)	AR	0.50	23.5	28.4	11.4	3.93	50.7
	H	0.04	5.90	10.3	1.29	6.30	9.70
Riverclay (The Netherlands)	AR	2.34	67.0	92.1	35.7	163	485
	H	2.53	55.5	89.0	31.9	169	526
Sandy soil (The Netherlands)	AR	0.10	4.56	3.74	1.30	26.0	9.64
	H	0.10	2.27	3.00	1.01	27.2	7.85

The best relation between the extractable amount and plant content of heavy metals independent of soil characteristics, seems until now to have been found when neutral unbuffered electrolyte solutions were used. Interesting results are reported by Häni and Gupta²⁸ for an extraction with 0.1 mol/l NaNO₃. Symeonides and McRae²⁹ published encouraging results using 1 mol/l NH₄NO₃ for extraction of Cd. In this case, however, very high additions of Cd salts were used, making their results less relevant for real situations.

Similarly it has been shown that extraction with CaCl₂ in various concentrations gives a good indication of the bioavailability of different heavy metals. Smilde et al.³⁰ recently published data showing that an extraction of soils with 0.1 mol/l CaCl₂ was sufficient to explain Cd and Zn contents in maize regardless of soil type. Our own experiments with green beans showed a very good relation of Zn concentration in a 0.01 mol/l CaCl₂ extract in a 1:10 (W/V) ratio with relative yield, again regardless of soil type and pH²⁶. Whitten and Ritchie²⁵, also using 0.01 mol/l CaCl₂ in a 1:5 (w/v) extraction ratio found a good relation between the Cd content in tops of subterranean clover and the Cd concentration in the extract on three different sites. Sauerbeck and Styperek²⁴, using a 0.05 mol/l CaCl₂ extraction, concluded that the CaCl₂ solution is a useful extractant in order to predict the availability of Cd in soils.

These electrolyte solutions extract the heavy metals present in the soil solution and part of the easily exchangeable forms. In this respect one should realize that the use of monovalent cations such as Na⁺ and NH₄⁺ would necessarily lead to lower values than the use of Ca²⁺. The reason for this is the fact that the monovalent cations are practically non-competitive for the adsorption sites on organic matter. Even for adsorption on the clay minerals and different sites on oxide surfaces, their competitiveness is limited. This is not the case when Ca²⁺ is being used and therefore we believe that a better picture of capacity and especially intensity parameters is obtained for availability of heavy metals. To demonstrate the differences in extractability, Table 3 presents some examples (source again ISE results¹⁵) of the amounts yielded by the extraction of some heavy metals using 0.1 mol/l NaNO₃ and 0.01 mol/l CaCl₂.

Among the different unbuffered electrolyte solutions we strongly prefer the 0.01 mol/l CaCl₂ solution because:

Table 3 Comparison of extraction efficiency of 0.1 mol/l NaNO₃ (1:2.5) and 0.01 mol/l CaCl₂ (1:10) solutions for some heavy metals in soils (µg/kg).

Soil type	Cd		Cu		Zn	
	NaNO ₃	CaCl ₂	NaNO ₃	CaCl ₂	NaNO ₃	CaCl ₂
Garden soil (The Netherlands)	3	10	310	394	390	1420
Sandy loam soil (Switzerland)	6	60	242	340	4888	23000
Loess soil (Switzerland)	36	133	220	500	8430	21715
Marine clay (The Netherlands)	1	1	27	112	36	180
Sandy soil (The Netherlands)	nd	nd	50	367	585	2347
Andosol (Indonesia)	nd	nd	31	160	883	1371
Riverclay (The Netherlands)	nd	nd	368	460	76	306
Sandy soil (The Netherlands)	nd	nd	34	175	2200	3005

- a. it is a solution which has more or less the same salt concentration (0.01 mol/l) as the average soil solution;
- b. Ca^{2+} is the dominant cation on the adsorption complex of soils. Therefore the CaCl_2 solution is better able to extract other adsorbed cations, without appreciable changes in the final equilibrium solution compared with the extraction solutions containing other cations. In this situation it is possible to use heavy metal concentrations in the extract as sole intensity parameters. This enables an easier evaluation of interelemental interactions in uptake;
- c. various nutrients and metals are measured in a single extract, so that interpretation can also include concentration ratios between the elements;
- d. the divalent cation causes good coagulation in the suspension, making high concentrations unnecessary, as would be the case with salts of monovalent cations (Na^+ , NH_4^+);
- e. the relatively low salt and especially chloride concentration facilitates strongly the final determination of metals;
- f. the CaCl_2 extract allows determination of all the important nutrients (including N) besides the various heavy metals;
- g. measurements can be taken simultaneously, making automation an attractive option;
- h. the amount of chemicals used for extraction and the amount of waste from harmful solutions is minimal.

The following experiments demonstrate the capability of 0.01 mol/l CaCl_2 for assessing heavy metal availability.

EXPERIMENTAL

First experiment: Cd uptake by vegetable crops under field conditions

For the first experiment soil samples were used originally collected by the Institute for Soil Fertility Research (Haren, NL) for inventory purposes³⁵. These soil samples originated from 50 different locations situated near the river Meuse, being more or less frequently inundated, and thus affected to a varying extent by deposition of polluted sediments. Characteristics of these different locations are summarized in Table 4.

Two vegetable crops (lettuce and endive) were successively grown on the sampled locations and analyzed for their Cd content. Soil samples were extracted by 0.01 mol/l CaCl_2 solution in a 1:10 (w/v) ratio at 20 ± 1 °C and the extracts analyzed for Zn- and Cd-concentration and pH. Figure 1 gives the relation between the Cd content in lettuce and the concentration of Cd in the CaCl_2 extract. In Figure 2 the same relation is given for endive.

Table 4 Characteristics of soil samples from 50 different locations near the river Meuse.

	Org. matter %	CaCO_3 %	< 2 μm %	pH- CaCl_2	Cd-tot. mg/kg	Zn-tot. mg/kg
minimum	1.40	0.0	4.6	5.03	0.43	64
maximum	11.95	14.0	23.3	7.14	12.6	1474

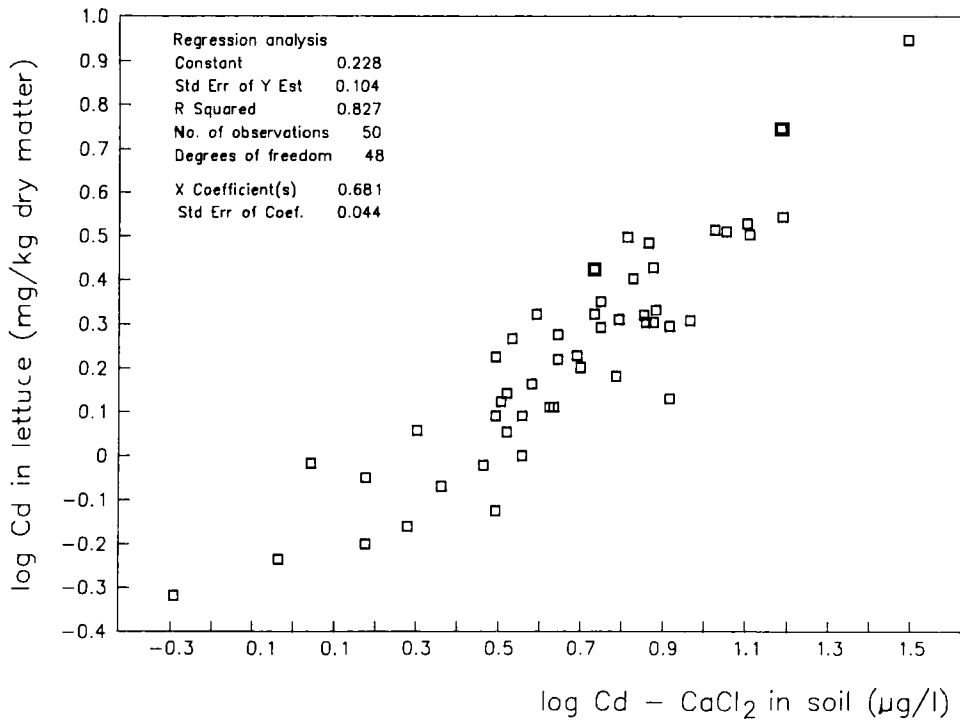


Figure 1 Double logarithmic plot of the relationship between the Cd content in lettuce and the Cd concentration in a 0.01 mol/l CaCl_2 extract of soil (exp.1).

In both figures log-transformed values are used for both parameters in order to suppress the influence of extreme values. From experiments with replicated treatments we know that error variance in Cd content increases with the value of the mean. Log-transformation stabilizes the error variance and makes it independent of the mean. Regression analysis demonstrates a very high degree of correlation, with $r^2=0.827$ in the case of lettuce and $r^2=0.645$ for endive. The addition of other regressors, namely pH and Zn concentration in the extract proved to be totally insignificant, although effects of both pH and Zn concentration on Cd uptake have been demonstrated in solution culture experiments. Especially the absence of an influence of the Zn concentration may appear surprising, but can be explained by the fact that the Zn concentration closely followed the Cd concentration as is shown in Figure 3. Inundation and ensuing sedimentation leads to heterogeneous pollution in the vertical direction and soil samples were taken only from the upper layer. In this situation lettuce, having much less rooting depth than endive, was expected to show a closer relationship.

The same experiment has been evaluated using acid extractable ("total") Cd in combination with pH and organic matter content. The explanatory value of multiple regression equations involving these factors remained far below that of the single regression equation with Cd- CaCl_2 (personal communication by W. van Driel, Institute for Soil Fertility Research, Haren, NL).

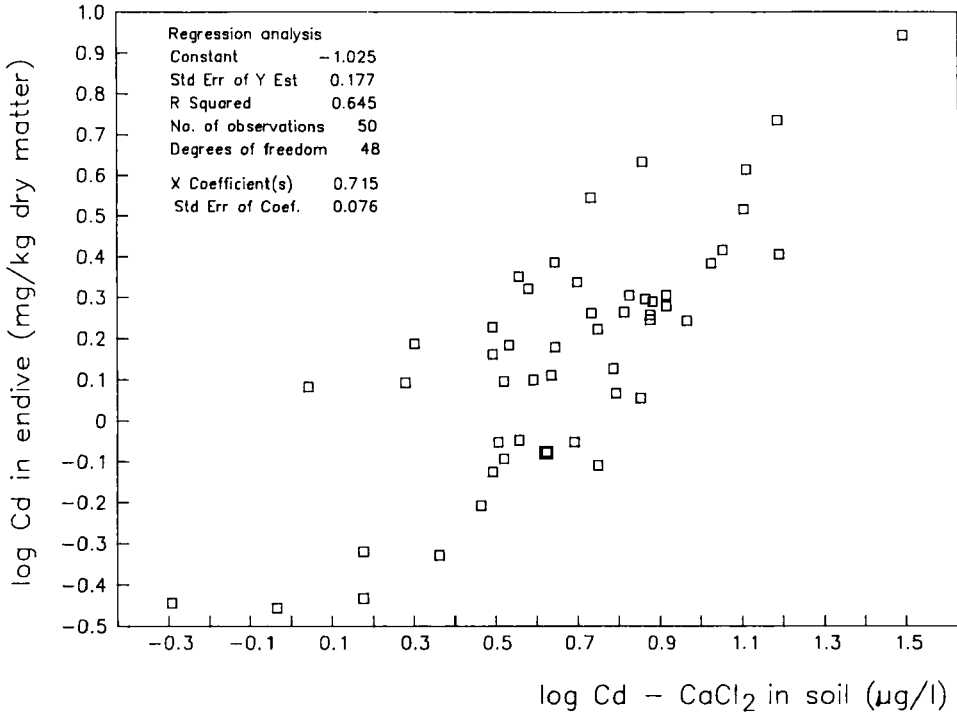


Figure 2 Double logarithmic plot of the relationship between the Cd content in endive and the Cd concentration in a 0.01 mol/l CaCl₂ extract of soil (exp.1).

Second experiment: Interelemental competition in Cd and Zn uptake (by spinach)

To demonstrate the possibility of the evaluation of interelemental interaction in uptake by plants, a factorial pot experiment was designed with variable Zn and Cd additions. Spinach was used as test crop on a calcareous loam soil with pH-CaCl₂ = 7.6, a limed sandy soil with pH-CaCl₂ = 6.4 and a sandy soil with pH-CaCl₂ = 5.4. Four different levels of Cd and four different levels of Zn were created by adding cadmium and zinc nitrate solutions. In Table 5 the added amounts of Zn and Cd, expressed in mg/kg soil, are given. The rates were adapted to the soil, aiming at comparable Cd contents in spinach for the different soils in the Cd-only treatments. The 1:100 Cd to Zn ratio corresponds to the mean ratio of these two metals in recent sediments (harbour dredgings)³¹.

After one month of incubation spinach was sown. It was harvested after a growing period of 35 days. Soils were extracted by 0.01 mol/l CaCl₂ under the conditions given above and in the extracts the Cd and Zn concentrations were measured. The results of analysis of both CaCl₂-extracts and plant materials are given in Table 5.

Clearly Zn influenced strongly the uptake of Cd from the soils with considerable differences between the soils. Especially in the calcareous soil this effect was very strong. To evaluate the whole experiment an approach as described by Braakhekke³³ has been used.

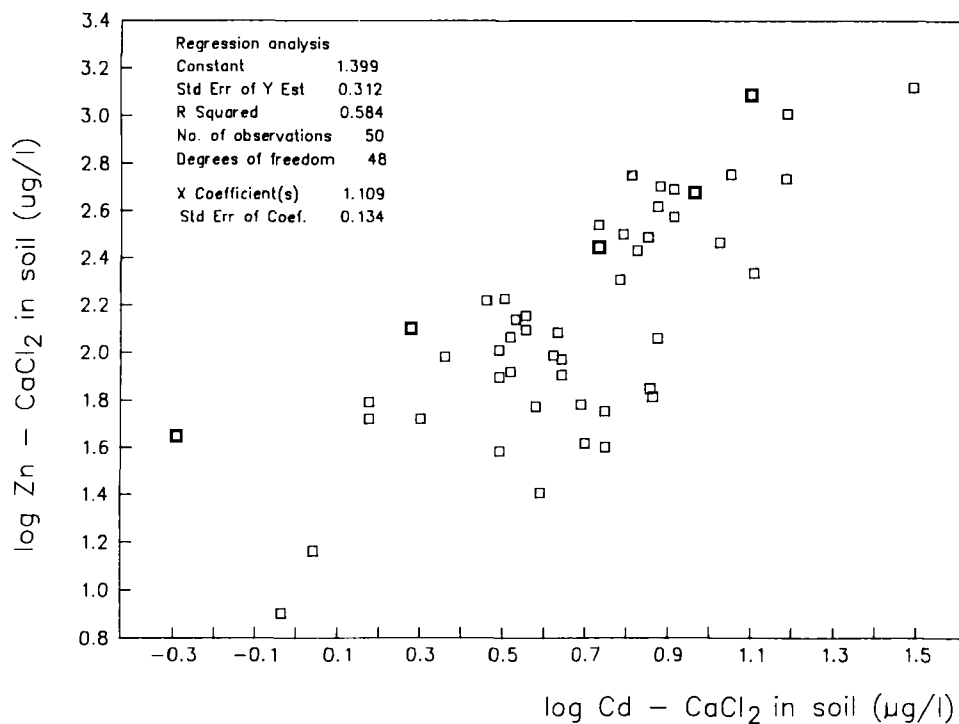


Figure 3 Double logarithmic plot of the relation between Cd and Zn concentrations in a 0.01 mol/l CaCl_2 extracts of soils (exp.1).

According to this model the interelemental interactions in uptake by plant species are best described by using the ratio of element concentrations in the plant as a function of these ratios in the substrate, expressed as logarithms. The observation should be on the 1:1 line in the case of no preference. Any deviation from this line indicates a preference in uptake for one or the other element. In Figure 5 such relationships are given using the data from this experiment.

Three lines are obtained with practically the same slope. The differences in intercept can possibly be related to differences in pH and its effect on Cd and Zn transport and uptake. Clearly the extraction of the soils with 0.01 mol/l CaCl_2 proves useful for the evaluation of interelemental competition.

Third experiment: Interelemental competition between Ni and Cu for binding onto soil sorption sites

The ability of 0.01 mol/l CaCl_2 extraction to reflect changes in binding of heavy metals onto the soil has been tested with Cu and Ni. Nutrient solution experiments did not reveal a significant effect of Cu on Ni uptake, but in soil these elements are competing for similar binding sites on the organic matter. A pot experiment with maize was conducted in 5-fold

Table 5 Concentrations of Zn and Cd in soil and plant at different levels of Zn and Cd.

Addition rate in mg/kg		conc. in 0.01 mol/l CaCl ₂ (µg/l)		conc. in spinach (mg/kg DM)	
<i>a. Calcareous loam soil</i>					
<i>Cd</i>	<i>Zn</i>	<i>Cd</i>	<i>Zn</i>	<i>Cd</i>	<i>Zn</i>
0	0	0.09	ND	1.65	138
0	133	0.08	40	0.47	249
0	267	0.18	90	0.36	301
0	400	0.22	180	0.34	365
1.33	0	0.81	ND	10.3	147
1.33	133	1.55	30	2.84	251
1.33	267	2.20	100	1.88	291
1.33	400	2.63	190	1.76	357
2.67	0	1.75	ND	19.7	146
2.67	133	3.12	40	5.05	248
2.67	267	4.33	100	3.74	308
2.67	400	5.07	200	3.45	369
4.00	0	3.57	ND	29.8	150
4.00	133	6.52	50	6.62	249
4.00	267	7.28	110	4.94	298
4.00	400	8.78	210	5.13	374
<i>b. Limed sandy soil</i>					
<i>Cd</i>	<i>Zn</i>	<i>Cd</i>	<i>Zn</i>	<i>Cd</i>	<i>Zn</i>
0	0	0.25	ND	1.70	93.4
0	67	0.50	160	0.81	281
0	133	0.68	460	0.80	390
0	200	1.34	1440	0.88	461
0.67	0	3.55	ND	10.3	114
0.67	67	4.97	180	4.08	292
0.67	133	5.55	450	3.69	384
0.67	200	6.64	900	3.64	431
1.33	0	4.72	ND	18.6	97.8
1.33	67	8.31	180	7.07	276
1.33	133	10.4	620	6.88	412
1.33	200	11.7	1110	6.39	468
2.00	0	8.91	ND	25.5	108
2.00	67	12.4	170	10.8	297
2.00	133	13.4	450	9.24	383
2.00	200	16.7	950	9.55	475
<i>c. Sandy soil</i>					
<i>Cd</i>	<i>Zn</i>	<i>Cd</i>	<i>Zn</i>	<i>Cd</i>	<i>Zn</i>
0	0	2.51	90	3.27	218
0	33	3.33	1010	2.57	498
0	67	3.65	1810	2.76	696
0	100	3.80	3060	2.19	759
0.33	0	9.32	80	10.0	197
0.33	33	9.86	980	7.83	509
0.33	67	11.7	1930	8.61	680
0.33	100	12.5	3230	9.26	827
0.67	0	16.3	90	24.1	228
0.67	33	20.1	970	14.7	511
0.67	67	23.8	2080	20.4	904
0.67	100	23.1	3250	17.0	841
1.00	0	20.6	70	29.9	202
1.00	33	28.0	940	21.6	516
1.00	67	36.6	2260	28.1	901
1.00	100	36.3	3220	25.4	1034

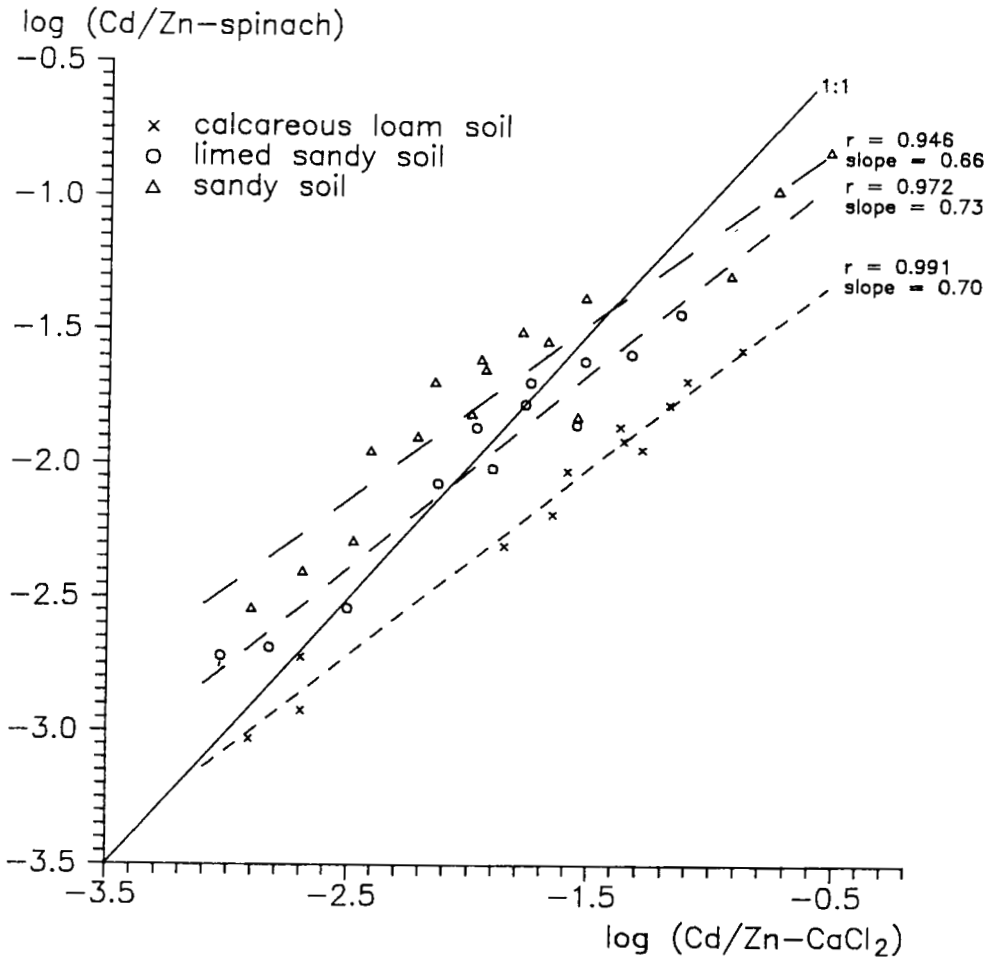


Figure 4 Double logarithmic plot of the mass ratio Cd/Zn in spinach as a function of the mass ratio Cd/Zn in CaCl₂ extracts of soils (exp.2).

with variable Cu and Ni additions (see Table 6) to investigate the Cu × Ni interaction in a plant-soil system.

The soil used was a sandy soil containing 2.0% of organic matter and having a CEC of 3.6 cmol+/kg. Cu and Ni were added as solutions of copper sulphate and nickel nitrate. After an incubation period of 3 weeks, maize was sown and two pots per treatment were harvested 43 days later. The rest of the experiment was harvested 62 days after sowing. In 0.01 mol/l CaCl₂ extracts of the different treatments the pH and the Ni concentration were determined. In this case a 1:2.5 (W/V) extraction ratio was used instead of the 1:10 (w/v) ratio adopted later. Furthermore extraction with 0.43 mol/l HNO₃ was performed and Ni concentrations were determined in this extract. Harvested plant material was analyzed for both total Cu and Ni. All analytical results are given in Table 6.

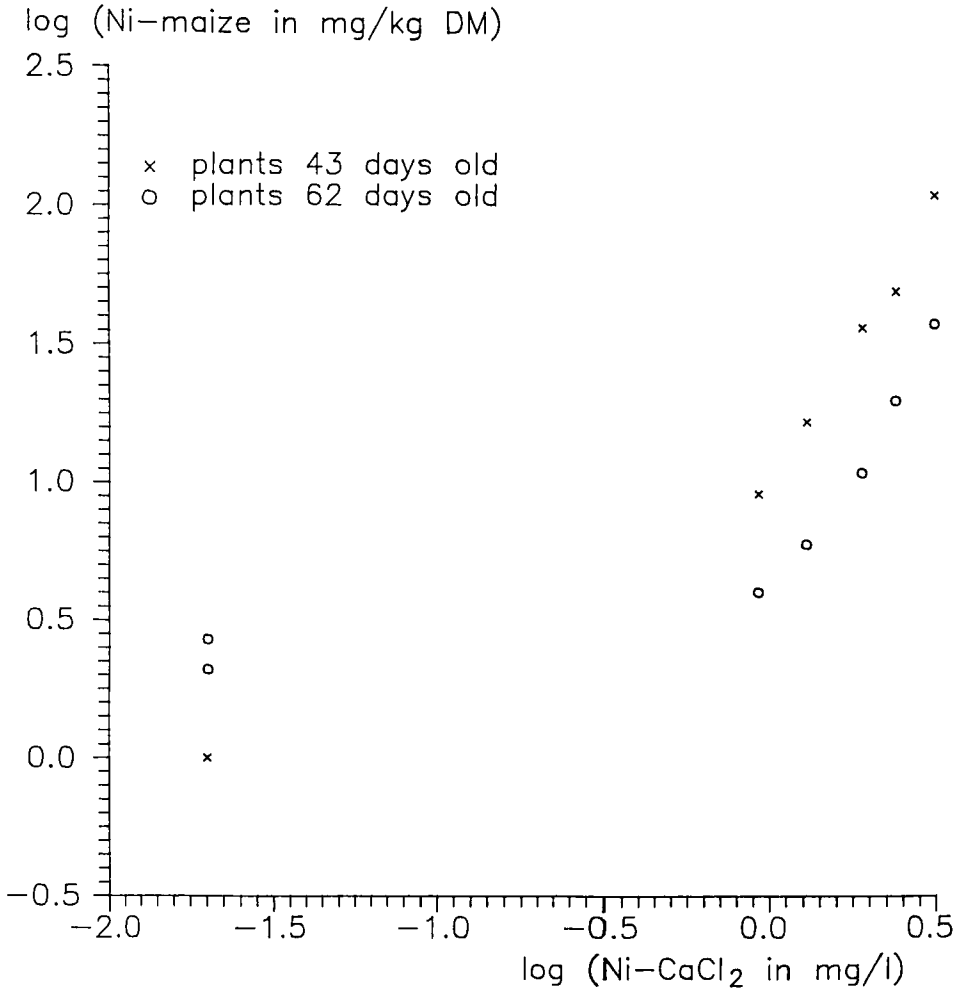


Figure 5 Double logarithmic plot of the relationship between the Ni content in maize and the Ni concentration in a 0.01 mol/l CaCl₂ extract of soil (exp.3).

It can be clearly seen that an extraction with 0.43 mol/l HNO₃ recovers practically all Ni added in the different treatments and that no relation whatsoever exists with respect to the Ni concentration in maize. On the other hand it can be seen that, while Ni recovered by the extraction with 0.01 mol/l CaCl₂ forms only a fraction of the added amount, this extractable amount increases with increasing Cu addition rates. The relationship between Ni concentration in CaCl₂ and Ni content in plant material is fair, as demonstrated in Figure 5. Interpretation of concentrations in plant material becomes rather difficult when there are strong effects on yield. Therefore, in this figure only data are used where the effects of added amounts of Cu and/or Ni on yield are restricted to about 15%. Apparently the

Table 6 Soil and plant parameters for an experiment with different levels of Cu and Ni in soil.

Added in mg/kg soil		0.43 mol/l HNO ₃ extr.	CaCl ₂ extr.	Concentration in maize (mg/kg DM)				Yield in g/pot		
Cu	Ni	Ni (mg/kg)	pH	Ni (mg/l)	43 days old		62 days old		43 days old	62 days old
					Ni	Cu	Ni	Cu		
0	0	0.6	4.67	0.02	1	11.2	2.7	5.9	9.20	82.72
40	0	1.1	4.72	0.02	1	18.1	2.1	10.3	9.81	81.72
80	0	1.1	4.81	0.02	1.4	16.0	2.7	13.8	2.06	36.96
120	0	0.9	4.76	0.02	-	58	2.3	19.7	0.77	4.29
0	10	10.3	4.64	0.92	9.1	12.0	4.0	5.5	10.34	81.99
40	10	9.8	4.67	1.28	16.7	17.6	6.0	10.1	8.17	78.45
80	10	10.5	4.69	1.50	66	30.0	25.7	16.6	1.42	15.19
120	10	10.6	4.82	1.45	127	57	41.3	26.2	0.79	1.06
0	20	20.1	4.74	1.88	36.5	12.5	10.9	5.8	8.47	78.53
40	20	19.9	4.79	2.36	49.5	18.7	20.0	11.6	5.67	69.65
80	20	19.5	4.73	2.81	191	47	74	20.5	1.03	1.98
120	20	19.3	4.79	2.88	-	-	366	86	0.46	0.43
0	30	29.4	4.81	3.09	110	12.2	37.9	6.4	6.75	71.63
40	30	33.0	4.79	3.99	126	18.6	61	13.5	3.94	51.14
80	30	31.1	4.80	4.23	157	168	99	22.0	0.46	2.95
120	30	27.3	4.79	4.74	-	-	-	-	0.34	0.30

Remark: The missing values in some of the treatments in this table are due to insufficient dry matter production at higher Cu and Ni levels.

CaCl₂ extraction is able to follow the changes in Ni status of the soil relevant for the concentration in the plant dry matter.

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