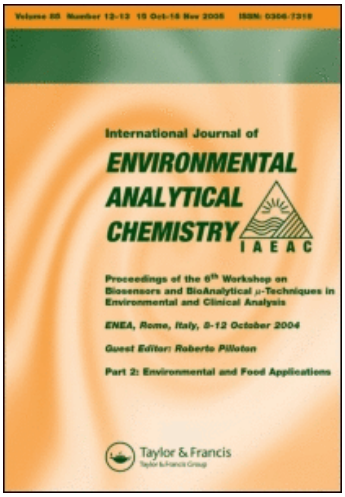

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ON-LINE HPLC MICRO EXTRACTION OF Zn(II) AND Cd(II) IN SOIL SLURRIES: A CHEMICAL SPECIATION METHOD

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An improved experimental method for the chemical speciation and study of metal ion reactions with soils and soil components is reported. The method that combines on-line HPLC micro extraction with off-line microfiltration can avoid the hysteresis problem, identify relevant free and bound chemical species, and produce mechanisms constants. The method is demonstrated with Zn(II) and Cd(II) reactions with a soil from a St. Lawrence River watershed.

KEY WORDS: Metals speciation, HPLC, Zn(II), Cd(II), soils.

INTRODUCTION

The deposition of transition metals onto St. Lawrence River watershed agricultural land raises related environmental and agricultural issues. One is the protection of the river from transported toxic metals. The other is the protection of crops from both nutritional deficiencies and toxic metal ion damage. Stable isotope analyses in the St. Lawrence River estuary have identified lead introduced upstream by human activities[1]. Comments by Streit *et al.*[2] are relevant to the second issue. They noted that a soil is a storage/controlled release system for metals that plants take up only from the solution phase. More exactly, Sposito[3] has pointed out that many positive correlations have been published of plant uptake of metal ions with their thermodynamic activities in soil solution. It is the same solution phase that might ultimately transport transition metals into the St. Lawrance River. Streit et al. regard metal ion transfer from soil to plant as poorly understood, with predictions by computer model being impossible. Instead of regarding such predictions as totally impossible, Eich *et al.*[4,5], Sposito[6], and Baes *et al.*[1] have suggested that predictive computer models must account for the physical chemistry processes. An important review by Sposito[6] reveals a large literature on the physical

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chemistry of metal ion reactions with soils, sediments, and their component materials. At least five types of samples have been investigated, including humic materials, metal oxides of Fe(II) and Al(III), clays, such carbonates as limestone and chalk, and a number of whole soils[4,5,15–25]. The reactions fall into the four broad categories in Table 1[4,5,15–24]. In addition to these direct reactions with soil components, precipitation of hydroxides or carbonates onto surfaces can take place in higher pH ranges[26,27]. The half lives reported for these categories of reaction range over as many as fifteen orders of magnitude[5,6]. From the point of view of risk assessment computer models, there are two groups of half lives. On group are fast compared to the rates of plant uptake and transport by flowing water. The second group includes those that are slow enough compared with plant uptake and hydrology transport rates to be rate determining under field conditions. Risk assessment computer models will therefore have to account for this distinction.

This means that a diverse set of experimental methods will be needed; methods already in use are listed in Table 2[7–14]. While techniques such as the pressure jump relaxation method are already giving valuable information about some of the faster reactions, there are also slow reactions such as the intraparticle diffusion identified by Leckie *et al.*, Bruemmer *et al.*, and Di Toro[17–22]. Since it is the slow reactions that will tend to control the rates of bioavailability and hydrology transport, experimental methods are also required for these classes. In addition, it is necessary to have methodology with which to determine separately labile surface sorption, and the kinetically slower intraparticle diffusion. Bar-Tal *et al.*[24] have made similar comments. The lack of such methodology has lead to many false reports of sorption—desorption hysteresis. This has been a long standing difficulty in the literature.

Table 1 Categories of metal ion reactions with soil components.

I	*Cation exchange reactions*
	– literature reports for humic materials and clays
	– kinetics mostly observable by relaxation methods
	– some cases with vermiculites slow enough to be monitored by methods other than relaxation kinetics (4, 5, 15, 16)
II	*Proton displacement reactions*
	– literature reports for humic materials, γ-Al_2O_3, goethite, limestone, chalk, & 38 Danish soils
	– cases with 1 mechanism step References: 15, 16
	– cases with 2 mechanism steps (17–23)
III	*Hydrolysis with subsequent chemisorption*
	– literature reports for goethite & synthetic zeolites
	– 2 mechanism steps
	– cases with 1 displaced proton 24
	– cases with 2 displaced protons
IV	*Intraparticle diffusion*
	– literature reports for goethite, $Al_2O_3.XH_2O$, & synthetic zeolites
	– 2 mechanism steps proposed (17, 22–24)

Table 2 Coventional experimental methods for metal ion reactions in soils systems[7-14].

Type of process	*Method*	*Phenomena monitored*	$T_{1/2}$ *range*
Complexing in solutions and colloidal sols	– Specific ion electrodes	Equilibria	
	– Ultrafiltration stirred cell	Equilibira	
	– competitive binding by ligands or cation exchangers	Kinetics	≈ ms
	– rotating disk electrode	Kinetics	≈ ms
Mass transfer between solutions and solids	– pressure jump relaxation	Kinetics	μs to ms
	– batch slurry methods with times contact and mechanical separation	Equilibria & kinetics	Tens of minutes to weeks
	– flow methods	Equilibria & kinetics	Tens of minutes to weeks

Table 3 Physical and chemical characteristics of the soil used.

Property	*Value*	*Notes*
pH	6.6 ± 0.1	Soil (in g)/Solvent (in mL) ratio—1:2
Cation exchange capacity	3.1 mequiv/100 g soil	
Organic carbon	10.94 ± 0.18 μg/mg	
Particle size distribution		
% Clay	2%	Particles < 2μm
% Silt	3%	Particles between 2 μm and 20 μm
% Sand	95%	Particles > 20 μm

Table 4 Experimental parameters for on-line HPLC micro extraction.

Parameter type	*Value*
Slurried soil solids	0.0800 g
Slurry solution	40.0 mL
Zn(II), initial concentration	1.75×10^{-5} M
Cd(II), initial concentration	1.75×10^{-5} M
Sample loop volume	20.0 μL
Mobile phase flow rate	1.0 mL/min
Solids on-line, each injection	40.0 μg
Integrator chart speed	5.07 mm/min

Freundlich isotherms have sometimes been used for empirical descriptions of sorption and even ion exchange. In chemical units, it may be written as Equation (1).

$$(q_l/w) = kN^n \quad (1)$$

q_l is the number of equivalents of labile surface bound metal ions, w is g of soil, N is the normality of the metal ion in solution, and k and n are empirical constants. Since this isotherm is intended to describe only equilibria, it then requires that q_l be experimentally determined. Usually the existing experimental methods yield only values of the total q_T =

$q_l + q_D$ instead, in which q_D is the number of equivalents of reagent trapped as a bound residue. This has led to a chronic problem of false hysteresis reports in the literature. The total sorbed, q_T, has frequently been used instead of the labile sorbed q_l, in isotherm calculations. In some cases, q_T was determined by sorption experiments and used in Freundlich isotherm calculations, and then q_l values obtained from desorption experiments were used for separate Freundlich calculations. q_D was usually not separately determined. The kinetics and thermodynamics are quite different. Neither of them is properly described when the calculations are carried out with q_T instead of q_l. Another difficulty is that false reports of binding dissociation hysteresis are produced this way. While it is proposed here that the law of mass action equilibrium constants should be used for chemical systems instead of the Freundlich isotherm[6], the same problems would exist for any type of equilibrium calculations.

An experimental method is therefore needed that will permit q_l and q_D to be separately determined, so that q_l can be used for the equilibrium calculations instead of q_T. It will subsequently be important to use q_D for a different part of any mechanism calculations. In the present case, q_l represents the amount of labile surface bound metal ion, and q_D is the amount trapped by slow or irreversible processes including intraparticle diffusion.

The objective of this work was to fill the methodology gap by developing and demonstrating an experimental method for distinguishing between labile surface binding and intraparticle diffusion of metal ions in whole soils, and for separately determining the stoichiometry, equilibria and kinetics behaviour of each. The use of high performance liquid chromatography (HPLC) for transition metal ion analyses is well established[28]. In addition, on-line microfiltration has been in use for several years for determining the chemical speciation and kinetics behaviour of organic chemicals in soils[29–34]. Labile surface sorption and intraparticle diffusion can be clearly distinguished from each other, and the present work was undertaken to adapt the method to the investigation of metal ion reactions with soil.

EXPRIMENTAL

Arrangement and operation of the HPLC system

A conventional HPLC system for metal ion analysis was adapted for on-line micro extraction. It consisted of a Varian Star 9010 solvent delivery system, a Dionex post column reactor and a Beckman Model 165 variable wavelength UV—visible detector. Figure 1 shows the injection system as modified for the micro extraction of soil solids on-line in the HPLC system[31,32], and the subsequent removal of the extracted solids by back flushing. The components include a Rheodyne 7725 injection valve equipped with a 20 μL sample loop, an Altech on-line microfilter containing 2.0 and 0.5 μm stainless steel frits in series, an Altech 100 HPLC pump for backflushing, and a Rheodyne 7000 switching valve. An Altech refillable guard column filled with Pellicular 10 μm C packing was used. The analytical column was a Supelcosil LC-18 reverse phase column, 75 × 4.6 mm.

The analytical column was prepared for use by flushing with running 100 mL of the mobile phase containing sodium octane sulfonate at 1.0 mL/min. The subsequent chromatography was performed with this same flow rate of mobile phase. Helium at 50 psi produced a PAR solution flow rate of 0.5 mL/min. into the post column reactor. The photometric absorbency of the Zn(II) and Cd(II) complexes was measured with a detector setting of 520 nm.

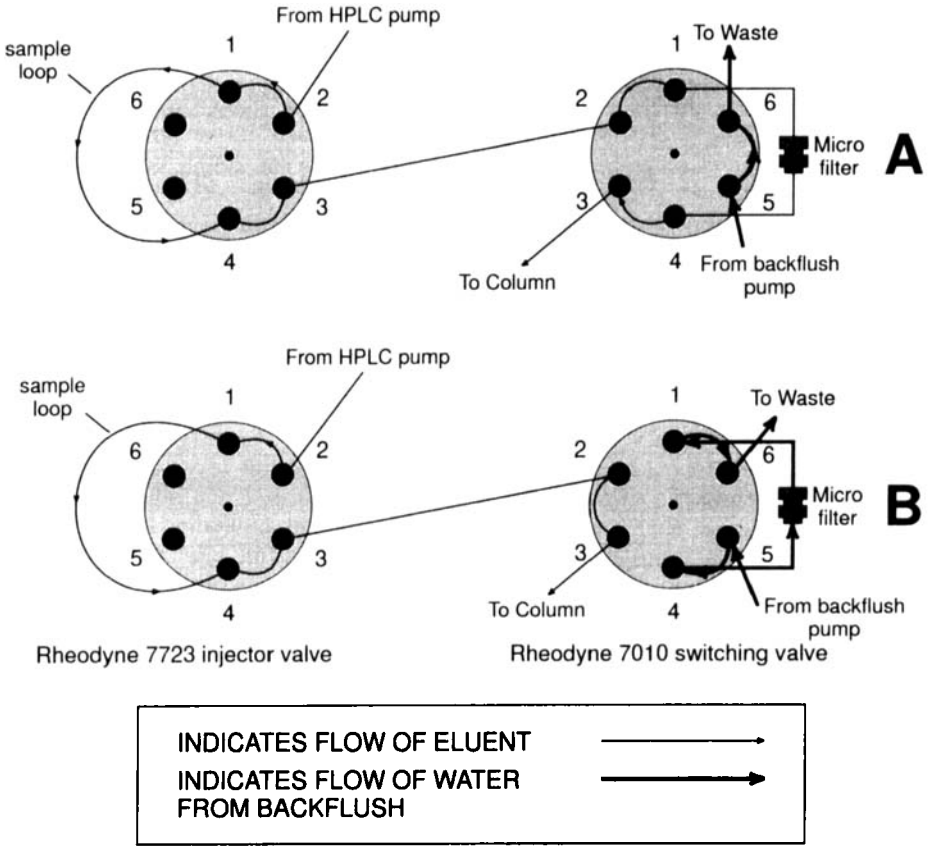

Figure 1 Injection – micro extraction system. A: injection valve in the "inject" position and the switching valve in the "run" position. B: injection valve as above, and the switching valve in the "bypass" position.

Reagents and materials

The soil used was collected from the top 15 cm of a cultivated field on the Raisin River watershed close to a branch of the Raisin River. The location is 30 km east of Cornwall, Ontario. It was air dried and passed through a 150 μm screen. The following standard analytical methods were used[33,34]. The pH was measured by the $CaCl_2$ method. The cation exchange capacity was measured by the ammonium acetate method. Organic carbon was determined by dry combustion. The particle size distribution was determined by the pipette method.

Stock solutions of two standards, Cd(II) and Zn(II), were prepared by dissolving solid sulfate salts (Aldrich, 99.999% purity) in ultrapure water, and acidifying them with nitric acid to 1% (v/v) nitric acid. Working standards, about 1×10^{-5} M, were prepared from these stock solutions by dropwise serial dilution just prior to use. These solutions were then standardized against certified atomic absorption standards (Fisher Scientific) by flame atomic absorption spectrometry (FAAS). The concentrations were also checked biweekly by flame AAS against certified atomic absorption spectrophotometric standard to ensure stability.

4-(2-pyridylazo) resorcinol (PAR), 98%, was obtained from Aldrich. Stock solutions

were prepared by first dissolving 0.5 g PAR in 400 mL of ultrapure water and 200 mL of reagent grade 30% ammonium hydroxide. Reagent grade glacial acetic (60 mL) acid was then carefully added to the solution. It was finally diluted to 1 L with ultrapure water, passed through a 0.22 μm filter, and degassed with helium. Only PAR solutions less than a week old were used.

The Mobile phase was prepared in two steps. HPLC Grade sodium octane sulfonate (0.94 g), and 15.0 g of reagent grade tartaric acid were first dissolved with 100 mL of HPLC grade methanol and 1800 mL of ultrapure water. The pH was adjusted to 3.5 ± 0.1 using reagent grade NaOH and HCl, and the solution was next diluted to 2 L with ultrapure water. Before use, the solution was passed through a 0.22 μm filter and degassed with high purity (99.995%) helium.

Procedures

a) Binding kinetics A blank experiment without slurried solids was run to test for the net effect of two possible experimental interferences, that is, i) the inner walls of the apparatus might add or subtract metal ions, ii) a small amount of binding sites might pass through the off-line microfilter, but not pass through the on-line microfilter. The blank sample was prepared by first collecting the off-line microfiltrate of an unspiked slurry, and then spiking this filtrate with the metal ions. This slurry had the same solid to water ratio as the experimental sample. Injections of the spiked filtrate showed no changes in metal ion concentrations outside the experimental errors. No corrections for such effects were therefore required.

The experimental sample was prepared by slurring a 0.0800 g aliquot of the soil in 30.00 mL of ultrapure water in a capped Pyrex reaction vessel at 25.00°C. During the two days allowed for wetting of the soil solids, the pH was monitored. The experiment was initiated by the addition of metal ion stock solution to give a total solution volume of 40.00 mL. The initial solution concentrations of Zn(II) and Cd(II) were each 3.50×10^{-5} N. A magnetic stirrer maintained a uniform distribution of the solids within the slurry.

Solution concentrations were measured as functions of time. For the measurement of solution concentrations, the Zn(II)—Cd(II) combined analytical chemical standard was first injected. 100 μL Hamilton HPLC syringes were used for injections. Each injection gave both Zn(II) and Cd(II) peaks. A 1 mL disposable tuberculin syringe was used to take up an aliquot of the whole slurry. Gravity tends to cause an uneven vertical distribution of particles in a slurry. This could cause aliquots taken for analysis to have ratios of solid to liquid that were not representative of the whole slurried sample. Large and erratic data scatter would then be manifest as large standard deviations. The procedure includes two actions taken together to avoid this. First, the stirring rate is adjusted to avoid possible gravitational settling. Secondly, the standard deviations are monitored. A filtrate was next produced off-line by using a disposable 0.22 μm Nylon 66 filter on the disposable syringe. The filtrate was taken up from the end of the filter holder into a 100 μL Hamilton HPLC syringe, for injection. The reaction times for kinetics measurements were determined by recording the dates and times of day at which aliquot filtering was done. These off-line measurements gave the data for the solution phase kinetics curve. The standard solution was injected again. In this way the solution measurements were bracketed with measurements of the standards, to minimize the effect of any drift in instrument response. Total recoveries from the whole slurry were also measured as a function of time, by micro extraction on-line in the HPLC system. This was done by first taking an aliquot of the slurry into a Hamilton Model 710SNR syringe, with 350 μm bore

needles. The sample stirring was again adjusted to give representative aliquots. The aliquot of the whole slurry was next injected, to fill the 20 μL sample loop. The solid particles of the injected slurry were trapped by the on-line microfilters. The mobile phase then became the extractant. The resulting chromatographic peak for each metal ion now represented the total of its solution concentration plus the concentration of it extracted from the solids trapped by the on-line microfilters. Each slurry injection was also bracketed by injections of the standard solution, and also measured both metal ions. After each slurry analysis, the back flush system in Figure 1 was used to remove the solids from the on-line microfilters. This avoided excess instrument pressures. The pH of the slurry was measured continuously during the first hour of the experiment, and then was measured daily for the remainder of the experiment.

b) Extraction tests A contaminated soil was prepared for tests with which on-line micro extraction could be used to assess the limitations of conventional batch extractions. A 4.00 g aliquot of the soil was slurried in 50.00 mL of a stock solution containing 1.0×10^{-3} M Zn(II) and 1.0×10^{-3} M Cd(II). After overnight stirring, the supernatant solution was decanted. This process was repeated three times over the course of a week. The contaminated soil was then washed with ultrapure water until no Zn(II) or Cd(II) could be detected in the washes by HPLC. It was air dried for 3 days and aggregates were gently broken up, in preparation for use.

A slurry was prepared with 0.0800 g of the contaminated soil in 40.00 mL of ultrapure water. Total metal ions recoverable were measured by injection of the whole slurry for on-line micro extraction at reaction times of 1, 24 and 72 hours.

A conventional off-line extraction was carried out. 0.0800 g of the contaminated soil was slurried in 40 mL of the mobile phase. Off-line microfiltrates were injected for conventional HPLC analyses at the same reaction times of 1, 24, and 72 hours.

Data processing

The two measurements of a standard solution that bracketed in-time the measurement of each sample aliquot were averaged. The bracketed sample concentration was then calculated from the average. This minimized analytical chemical errors from drifts in instrument response. Filtrate and slurry kinetics curves were calculated by the method of least squares. The calculations were accomplished using spreadsheets and a curve-fitting program.

RESULTS AND DISCUSSION

A comparison of the chromatographic peaks in Figure 2 shows that on-line micro extraction of the injected solids did not distort the peaks for Zn(II) and Cd(II). There were no changes in retention time, line broadening, asymmetry or tailing. This implies that the extraction of the labile bound metal ions was fast in comparison to the flow of the mobile phase. Three factors might have contributed to this. The first is the relatively large ratios of extractant to solid indicated in Table 5. The upper limit that would be possible is given by the peak retention times. The lack of peak distortions from on-line micro extractions suggests that the extractions might use extractant to solid ratios smaller than those corresponding to the peak widths at the baseline. Even these "peak width" extractant to solid ratios are an order of magnitude larger than those commonly used in

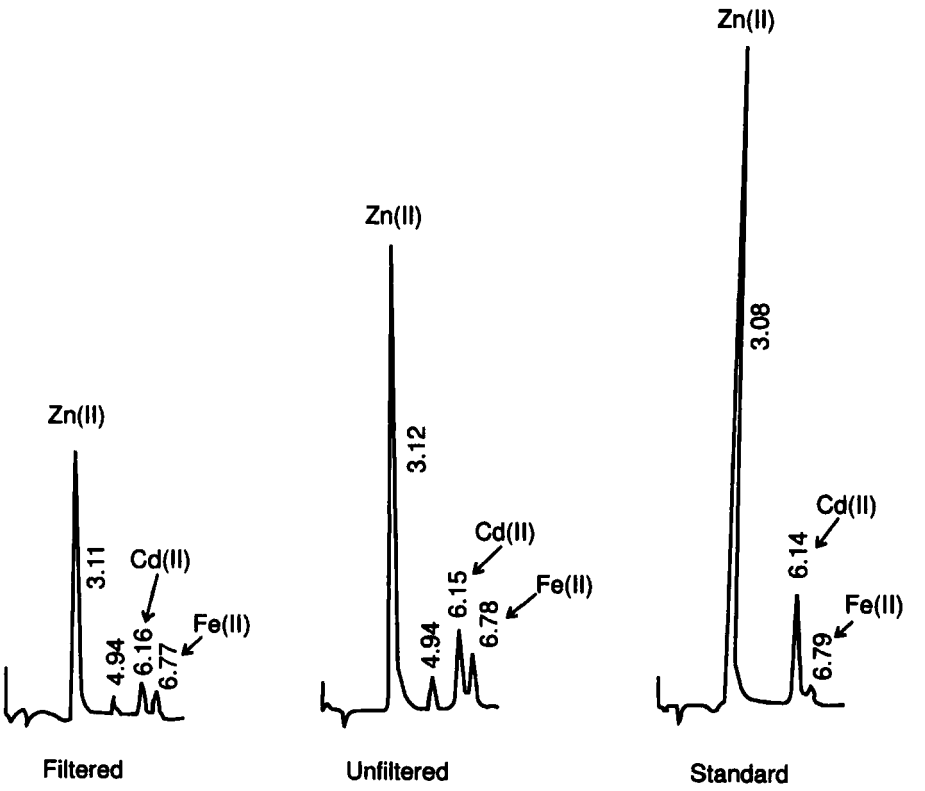

Figure 2 HPLC chromatographic peaks for Zn(II) and Cd(II). *Injection 1:* off-line filtrate, for solution phase analysis. *Injection 2:* whole slurry with on-line micro extraction, for totals recoverable from (solution + solids). *Injection 3*: analytical chemical standard.

Table 5 Ratios of mobile phase as extractant, to soil solids during on-line micro extraction ambient temperature.

Metal ion	*Peak retention*		*Peak widths at baselines*					
			Δ Time, min			*(Extractant/Solid), L/g*		
	Time min.	*(Extractant solid), L/g*	*Filtrate*	*Flurry*	*Standard*	*Filtrate*	*Slurry*	*Standard*
Zn(II)	3.12	78.0	0.99	1.38	1.38	24.7	34.5	34.5
Cd(II)	6.15	153.8	0.59	0.59	0.61	14.8	14.8	15.3

the usual batch extractions. The next possible factor might be relatively fast release, by cation exchange, of the metal ions from surfaces into the stream of mobile phase extractant. The third possible factor is that there was a continuous flow of fresh extractant instead of a static batch operation. Static batch extractions attain equilibrium or pseudo equilibrium distributions of the metal ions between the surfaces and the solutions. Phase separation then leaves unrecovered, the portions of metal ions on the surfaces.

The chemical analysis of Zn(II) by on-line micro extraction of the injected slurry solids and by injection of the off-line micro filtrates gives the slurry and filtrate curves in Figure 3. Table 6 contains the least squares fit results of these curves. The anticipated initial fast reactions were observed, and could only be monitored by the stopped flow or pressure jump kinetics methods used by other authors[6]. During the first 30 s of the experiment, 2.0×10^{-5} (equiv/g) of metal ions were bound. This was the total for Zn(II) and Cd(II). During this same interval, 0.37×10^{-5} (equiv/g) of H^+ were released. Evidently about 18% of the metal ions being bound participated in a fast proton release mechanism. The other 82% were bound by some other category of fast reaction. Simple cation exchange is suspected.This implies that future applications of the method to mechanism studies will require measurements of eluted metal ions. Any or all of the Reaction Categories I and II in Table 1 might have contributed to the results observed in the first 30 s. The subsequent portions of the curves that have been monitored here represent the rate controlling steps under field conditions.

The fundamental importance of the two chemical analyses curves in Figure 3 lies in the unambiguous determination of the identities and kinetics behaviour of the three chemical species that are seen in Figure 4. The filtrate analysis curve in Figure 3 has simply been reproduced in Figure 4 as the solution phase curve. The curve in Figure 4 for labile bound Zn(II) has been calculated from the slurry and filtrate curves of Figure 3. The physical chemical meaning of the slurry curve in Figure 3 needs to be considered carefully. If no Zn(II) were lost by precipitation, chemical reactions, cation exchange, sorption, or intraparticle diffusion, then the slurry curve would simply be a straight line with zero slope and an intercept at the t = 0. concentration of Zn(II). The experimentally observed curve indicates losses of labile Zn(II) by at least two processes. First, there was

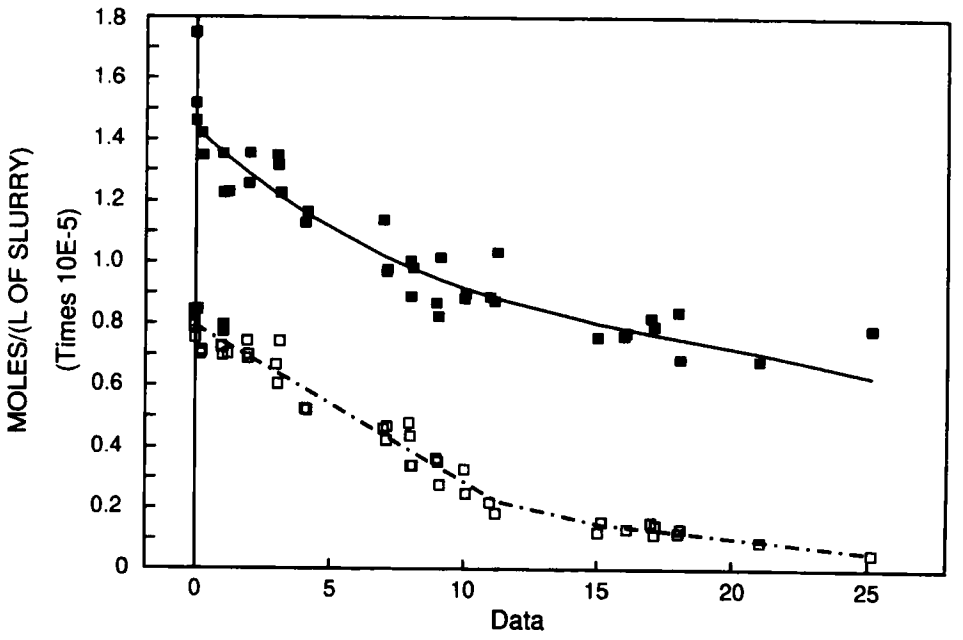

Figure 3 Zn(II) analyses in the sample spiked with Zn(II) and Cd(II). 25.0°C. Initial conditions: Zn(II) and Cd(II) each 1.75×10^{-5} M, pH = 6.3 ± 0.1. ■, Slurry analysis curve. ❑, Filtrate analysis curve. (See Table 6).

Table 6 Time dependence of metal ion analyses in raisin river soil slurry at 25.0°C
$Y = C_o + C_1 t + C_2 t^1$
Standard deviations

Metal ion	*Chemical analysis curve*	*Time interval, days*	*No. of data points*	*Error in Y* σ	*Polynomial Constants**		
					C_o	C_1	C_2
Zn(II)	Filtrate Section 1	0.–11.	37	0.483×10^{-6}	$(7.99 \pm 0.11) \times 10^{-6}$	$-(5.06 \pm 0.20) \times 10^{-7}$	—
	Section 2	11.–25.	10	0.159×10^{-6}	$(2.92 \pm 0.32) \times 10^{-6}$	$-(9.2 \pm 1.7) \times 10^{-8}$	—
	Slurry	0.–25.	36	0.724×10^{-6}	$(1.42 \pm 0.026) \times 10^{-5}$	$-(6.72 \pm 0.67) \times 10^{-7}$	$(1.68 \pm 0.35) \times 10^{-8}$
Cd(II)	Filtrate Section 1	0.–0.28	9	0.423×10^{-7}	$(5.46 \pm 0.38) \times 10^{-6}$	0.	—
	Section 2	0.28 – 25	40	0.414×10^{-6}	$(5.63 \pm 0.11) \times 10^{-6}$	$-(2.07 \pm 0.10) \times 10^{-7}$	—
	Slurry	0.–25.	39	0.142×10^{-5}	$(1.41 \pm 0.14) \times 10^{-5}$	$-(1.41 \pm 0.14) \times 10^{-5}$	—

Y = labile metal ion concentration, (moles/L)
t = reaction time, days
* = extra digits have been recorded to reduce computer truncation and round off errors, during future calculations

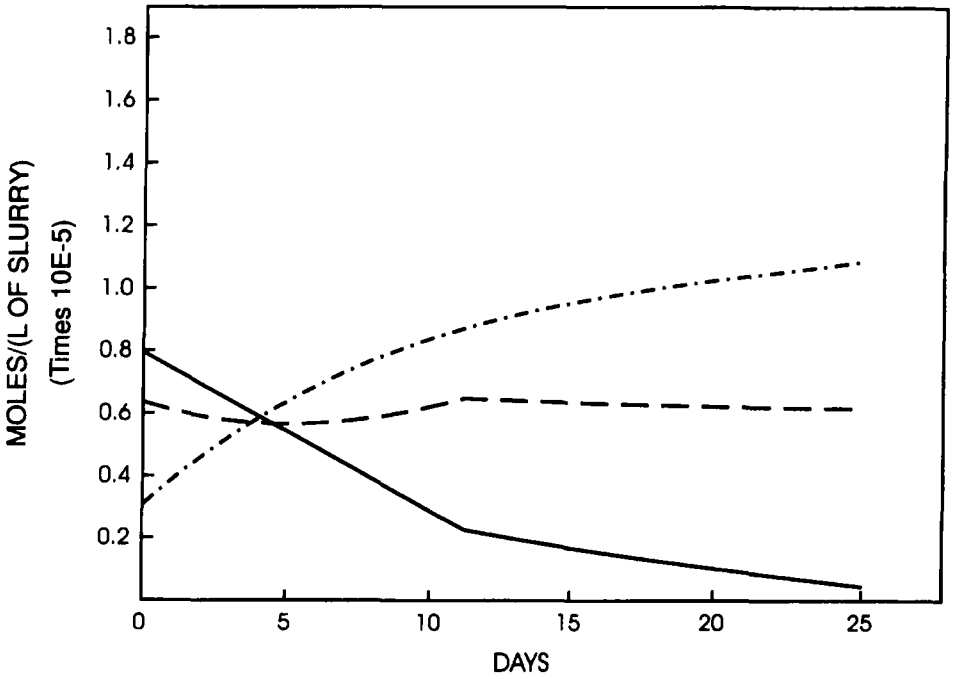

Figure 4 Zn(II) chemical species in the slurry of the Raisin River Soil, – In solution, - - - Labile bound., –·–·– Bound residue.

a fast initial process just as the literature would predict. Negative slopes in the remainder of the curve reflect one or more of the loss mechanisms listed above. Subtraction of the slurry curve from the t = 0. concentration of Zn(II) therefore gives its mirror image, the "bound residue" curve in Figure 4. Future research will be needed to determine the combination of "bound residue" mechanisms. The type of information in Figure 4 will be essential to such investigations, because the reports of false hysteresis produced by conventional sorption methods cause serious confusion. Likewise, the use of conventional batch extractions instead of the on-line micro extraction with its continuous flow of extractant can give an unresolved total of labile metal ion, including the portions in the solution and on the surfaces of the solids. Unless the three categories of chemical species are quantitatively resolved as in Figure 4, correct kinetics and equilibrium calculations cannot be carried out. This in turn would seriously hinder effective mechanism studies.

For the particular case of Zn(II) beyond 12 days in Figure 4, the bound residue processes removed Zn(II) from the labile pool that consists of (solution phase + labile surface sorbed) Zn(II). Since the kinetics of mass transfer between the solution and labile surface sites are fast compared to the bound residue processes, the former are not rate determining after the first 12 days. A shifting surface binding equilibrium is therefore being maintained. If it can be determined whether the labile binding has been caused by cation exchange or by physical sorption, then the measurement of the relevant type of binding capacity should permit the estimation of a surface-solution equilibrium constant at 25 days.

The Cd(II) reactions in the slurry were simultaneous with those of Zn(II), and were measured and calculated in the same way. The resulting slurry and filtrate analyses

curves for Cd(II) are presented in Figure 5. After the initial fast process, the slurry curve evidently underwent no further change. Within the limits of the standard deviation, it has a zero slope. On the other hand, the Cd(II) filtrate curve showed no decrease in its negative slope during about 21 days. The Cd(II) chemical species curves are shown in Figure 6. After the initial fast process, no further increase in the bound residue could be seen outside the standard deviation. The constant rate of loss from solution appears to be caused by a labile surface binding reaction. The nature of this reaction at the surface is not yet known for this particular case. A possibility is that Cd(II) might be replacing on the surface sites, some Zn(II) that has been lost from the labile pool by bound residue formation.

For some applications of the on-line micro extraction method, a pie chart such as Figure 7 could be useful. Not only do Zn(II) and Cd(II) have quite different biological properties, but also the three categories of chemical species represent quite different biological availabilities. The relative amounts of the six metal ion species are quickly visible for toxicology studies or for regulatory work.

A previously mentioned limitation of the conventional batch extraction is demonstrated by Figure 8 and 9. Chemical analyses of the extractant measure only those portions of the metal ions found in the solution phase, instead of the totals that are labile. It should be noted that the apparent trends in Figure 9 are hardly outside the estimated experimental error.

It is concluded that the on-line HPLC micro extraction method clearly distinguishes among, and quantitatively determines, metal ion chemical species that have quite different biological effects and leaching characteristics. Kinetics data produced with it should be able to support the mechanisms studies that are needed for risk assessment computer models.

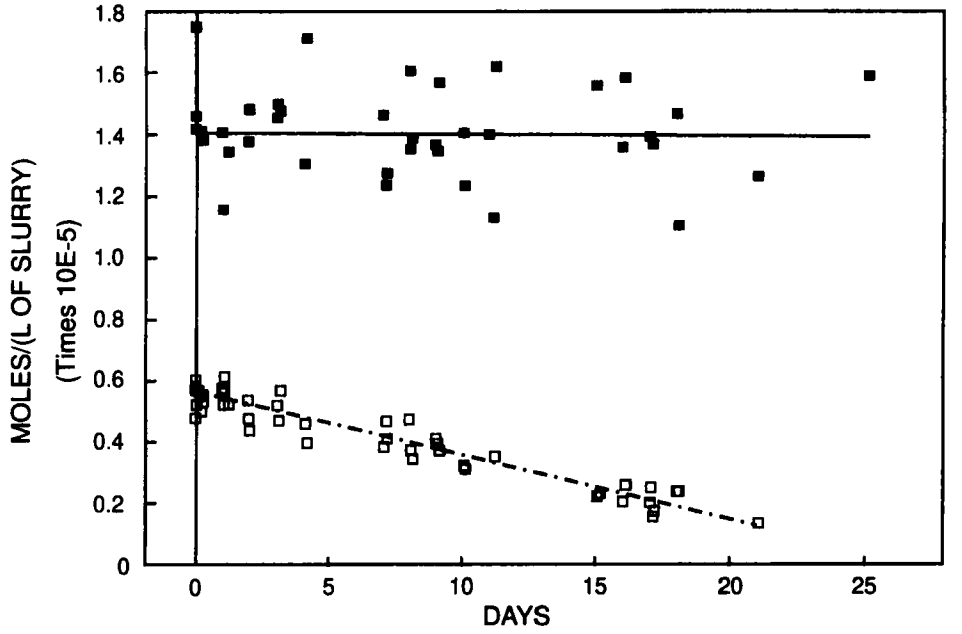

Figure 5 Cd(II) analyses in the sample spiked with Zn(II) and Cd(II). 25.0°C. Initial conditions: Zn(II) and Cd(II) each 1.75×10^{-5} M, pH = 6.3 ± 0.1. ■, Slurry analysis curve. ❑, Filtrate analysis curve. (See Table 6).

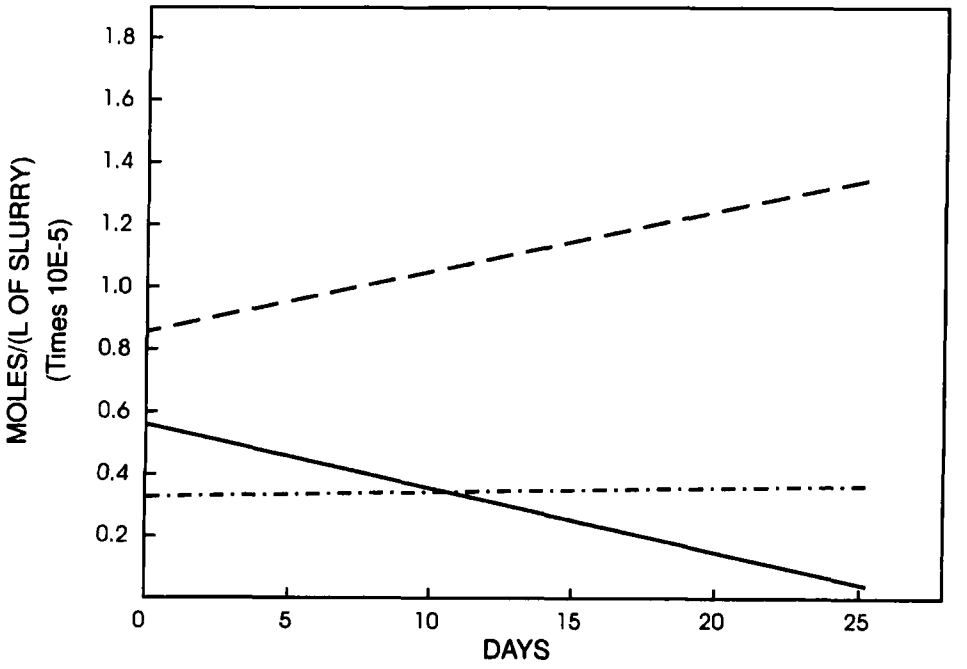

Figure 6 Cd(II) chemical species in the slurry of the Raisin River Soil, – In solution, – – – Labile bound., –·–·– Bound residue.

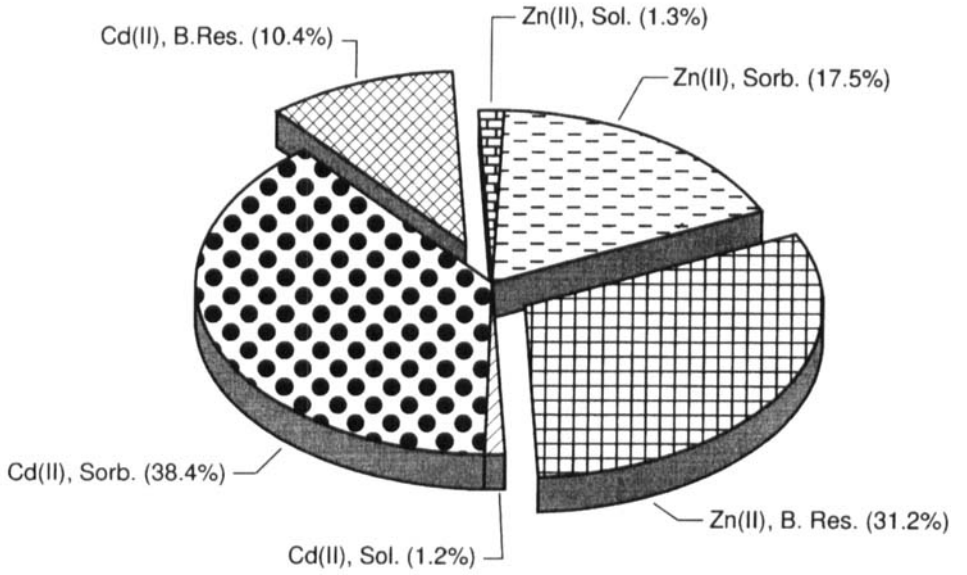

Figure 7 Comparison of Zn(II) and Cd(II) chemical species in the slurry at 25.00°C after 25. days. Legends: Sol., solution phase; Sorb., labile bound; B. Residue, bound residue. Percentages calculated for total of two metal ions.

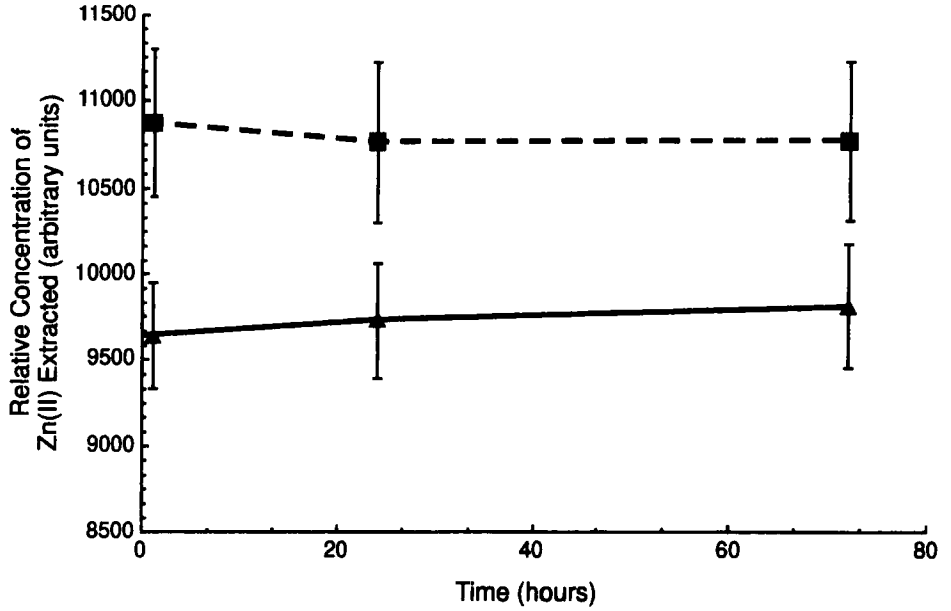

Figure 8 Zn(II) extraction from a model contaminated soil. A comparison of a conventional extraction with the on-line micro extraction. Standard deviation error bars from three replicates. ■, On-line micro extraction. ▲, Batch extraction.

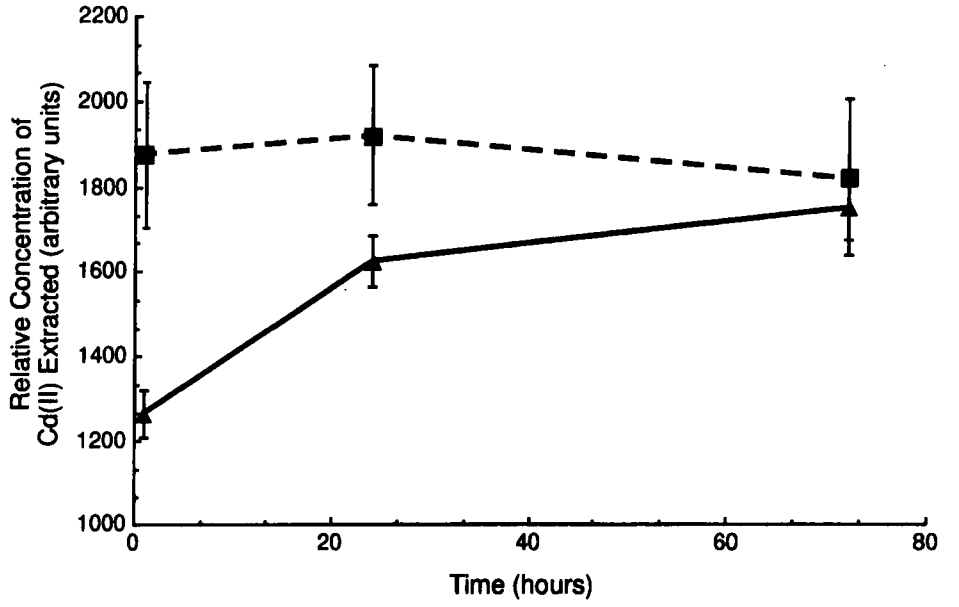

Figure 9 Cd(II) extraction from a model contaminated soil. A comparison of a conventional extraction with the on-line micro extraction. Standard deviation error bars from three replicates. ■, On-line micro extraction. ▲, Batch extraction.

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