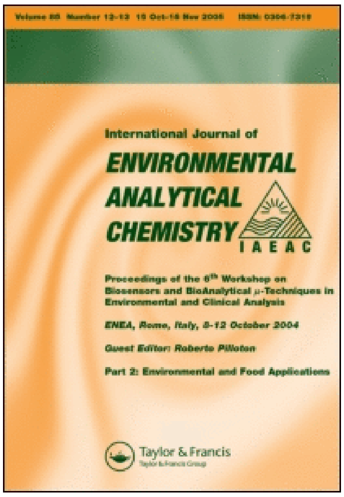

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# Kinetic Studies of Metal Speciation Using Inductively-Coupled Plasma Mass Spectrometry

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# KINETIC STUDIES OF METAL SPECIATION USING INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY

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Kinetic studies of uptake of metal ions by the Chelex batch technique were made to determine Cd, Cu and Pb speciation in model solutions, a snow sample and a river surface water sample. Inductively-coupled plasma mass spectrometry (ICP-MS) and graphite furnace atomic absorption spectrometry (GFAAS) were used for direct determination of these metals. ICP-MS with the solution nebulization technique minimized contamination and adsorption problems involved in the discrete sampling technique of GFAAS, and hence, gave more precise and accurate results. Also, ICP-MS allowed collection of many more data points than GFAAS and was able to resolve components with similar rates of dissociation, which could not always be resolved by GFAAS with its discrete sampling technique. ICP-MS was therefore preferable to GFAAS for kinetic studies of metal speciation. The kinetic data were analyzed by the iterative deconvolution method. The applicability of the Chelex batch technique to metal speciation was validated by analysis of model solutions containing these metal ions with or without EDTA, NTA and fulvic acid. Use of the Chelex batch technique for Cd, Cu and Pb speciation in snow and river surface water samples revealed a number of kinetically distinguishable components of these metals (as complexes) ranging from one to three, probably present as aquo ions or inorganic complexes in the snow sample, and bound to macromolecules/and or colloidal materials in the river surface water sample.

**KEY WORDS:** Metal speciation, kinetics, ICP-MS, GFAAS.

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## INTRODUCTION

Trace metals are natural components of the environment and their toxicity to living systems is well known[1-3]. In natural aquatic systems, trace metals exist in different chemical forms, and these different chemical forms play various roles in the geochemical and biological cycling of trace metals as has been demonstrated for the interactions of metals with the biota[4], solid surfaces[5,6], light[7], and reactive solutes[8].

Both metal speciation, bioavailability and toxicity are functions of the tendency of the metal to react, as quantified by the free metal ion activity, under pseudoequilibrium conditions[4,9,10]. For metals occurring as organic complexes, pseudoequilibrium conditions among dissolved species may be maintained only if the rates of metal complexation/dissociation reactions are fast compared with rates of metal uptake[11]. If, however, complex dissociation and ligand-exchange rates are slow compared to biological uptake, the rate of metal incorporation into the biota will be limited by abiotic chemical kinetics[4]. Kinetic speciation reveals differences in dissociation rate constants of not only metal complexes of mono-, multi-complexants, but also metal complexes of poly-functional complexants and mass transfer limitations on the accessibility of the binding sites; this is in contrast with equilibrium methods where a single binding constant and a homogeneous set of binding sites are an adequate model[12]. The use of kinetics thus reveals heterogeneity of binding sites not always revealed in equilibrium studies and may help to clarify lability as a factor in bioavailability[13].

Simultaneous kinetic analysis of multicomponent systems is well established[14-18] and extensively used[19-21]. Kinetic analysis applied to metal speciation has been reported by several authors[22-32]. Kinetic studies of metal speciation can not only differentiate chemical species according to their kinetic parameters but also give information on the distribution of the chemical species in the system at any time during the kinetic process. The results obtained can therefore be used to estimate the bioavailability of a metal, if the kinetic model can be constructed to represent the process of biological uptake. Because of the difficulties involved in using living organisms, for example, limited amount of sample available, poorly-characterized materials, and high cost, other well-characterized and commercially available materials have been used in this laboratory study. Chelex-100 cation exchange resin (to be henceforth called Chelex-100) which has been used by others[33-38] for metal speciation, has been used in this study. Also, the toxicity of cadmium to salmon and the Chelex-100 batch fraction of cadmium has been found to be well correlated[39].

The objective of this work was to compare the usefulness of ICP-MS and GFAAS for following kinetics of metal dissociation in the Chelex batch technique and to measure the kinetics of Cd(II), Cu(II) and Pb(II) speciation in river surface water and snow samples using the Chelex batch technique[26].

## KINETIC MODEL

Consider an aqueous mixture of n components in which each component, designated $ML_i$, exists in equilibrium with its dissociation products:

$$ML_i \rightleftharpoons M + L_i \qquad (1)$$

where M is the metal ion and $L_i$ is the i$^{th}$ mono- or multi-functional ligand, or i$^{th}$ M binding site on a polyfunctional complexant. For simplicity, the charge sign on the metal ion (M) is omitted. Equation 1 is a general statement of the reaction in which electrochemical neutrality is neglected since the charge on ML varies with the extent of metal binding. The model describes a system in which each complex, $ML_i$, undergoes independently and simultaneously, a first-order, or pseudo-first-order dissociation reaction as shown by equation 2:

$$ML_i \xrightarrow{k_i} M + L_i \qquad (2)$$

where $k_i$ is the rate constant for the dissociation of $ML_i$ species. Either reactant or product concentration can be monitored over time.

The reaction between the metal ion M and the Chelex resin is given by:

$$\text{Chelex} + M \rightleftharpoons \text{Chelex-M} \qquad (3)$$

Combining equations 1 and 3 one gets:

$$\text{Chelex} + ML_i \rightleftharpoons \text{Chelex-M} + L_i \qquad (4)$$

The model assumes that: 1) the reactions are first-order or pseudo-first-order; 2) reaction 3 is much faster than reaction 2, so that reaction 2 becomes the rate-limiting step, and the measured kinetics then represents the kinetics of the dissociation of the metal complex, $ML_i$; 3) that ML does not directly (i.e. without pre-dissociation) interact with the Chelex resin. Such a reaction is a possibility if ML or its protonated form is a positively charged species at the pH 5.0 ± 0.5 for the kinetic measurements. If these assumptions are fulfilled, then the sum of the concentrations of all components remaining in the sample at time t can be described as:

$$C(t) = \sum_{i=1}^{n} C_i^0 \exp(-k_i t) \qquad (5)$$

where $C_i^0$ is the initial concentration of $ML_i$. The assumptions 1 and 2 have been experimentally verified in a later section. Assumption 3 could not be verified directly, but the results presented in this paper suggest that this is not an important factor at the pH 5.0 ± 0.5 used for the kinetic measurements.

## EVALUATION OF DATA ANALYSIS METHODS

In his study of pH and ionic strength effects on Ni(II)-fulvic acid dissociation kinetics Cabaniss[40] critically examined five data analysis methods: a Laplace transform technique (a kinetic spectrum technique) and four statistical approaches. He concluded that two of the methods, non-linear regression and non-linear regression with component stripping, produce smaller parameter sets and are more useful for kinetic modelling than the other three methods. McKinnon *et al.*[41] in their study of the deconvolution of photoluminescence data critically evaluated five numerical methods, including Laplace transform, and concluded the iterative deconvolution method was "the most successful and reliable of the deconvolution methods tested" and recommended its use as the method of choice. We have earlier used the iterative deconvolution method[41] for analyzing the data for kinetic studies of metal speciation[22-24]. This method has the advantage of combining data analysis and result assessment together and has been found to be a reliable method for analyzing kinetic data to determine the number of components, the rate constant and the initial concentration of each component. In this paper, we have again used the iterative deconvolution method for analyzing kinetic data.

## MATERIALS AND METHODS

### *Materials*

Chelex resin (Bio-Rad, 100–200 and 200–400 mesh, sodium form) was equilibrated with NaOAc-HOAc buffer at pH 5.0. Because dryness of the resin affects the properties of the resin and changes the pH of the sample during kinetic measurements, the resin was kept in the buffer solution till the time of kinetic measurements, when it was separated from the buffer solution. The NaOAc-HOAc buffer was prepared as follows: 59.0 mL of pure concentrated acetic acid (A.C.S., Anachemia) was added to about 1 L of ultrapure water. The pH of this solution was adjusted to 5.0 using 6 N NaOH (reagent grade, Fisher Scientific) and the solution was diluted to 2 L with ultrapure water.

The Laurentian soil fulvic acid (FA), supplied by Dr. D. S. Gamble, Agriculture Canada, Ottawa, was prepared following known procedures[42-43] from a sample of a podzol collected from the Laurentian forest preserve of Laval University, Quebec, Canada. Ultrafiltration revealed that about 37% of the fulvic acid had molecular weight (MW) > 30,000, ~ 38% had MW < 1000, ~ 15% had MW 1000–5000, and the rest had MW 5000–30,000[44]. Titration of the fulvic acid revealed 3.03 and 3.49 m mol/g phenolic and carboxylic acid groups, respectively[45].

ICPMS-2 high pure metal standard (Delta Scientific), containing Al, Cd, Cu, Ni, Pb, Zn and other metals (10 mg/L each), was used. Stock solution of a single metal (1000 μg/mL), e.g. Cd, Cu and Pb was prepared by dissolving appropriate quantities of the following materials in nitric acid (ULTREX) with heating, and diluting the solutions to appropriate volumes with ultrapure water; the final solutions were made to contain 1% (v/v) nitric acid: CdO (Baker, Analyzed reagent) for cadmium, copper metal (99.9% pure) and $Pb(NO_3)_2$ (Fisher, A.C.S. reagent) for lead. Stock solution (1000 μg/mL) of aluminum was prepared by dissolving 0.5000 g aluminum powder (SPEX) in 20 mL 1:1 HCl (ULTREX):$H_2O$ with heating, and diluting the solution to 500 mL with ultrapure water.

Stock solutions of ethylenediaminetetraacetic acid (EDTA) (80.59 mM) and nitrilotriacetic acid (NTA) (1.12 mM) were prepared by dissolving appropriate quantities of EDTA (sodium salt, Fisher Scientific Company, Certified A.C.S.) and NTA (BHD Chemicals Ltd., 99%) in ultrapure water.

Water of resistivity 18.2 MΩ-cm was obtained direct from the ultrapure water system, Milli-Q-Plus (Millipore Corporation). Screw-cap polyethylene and Teflon bottles were used as reactors and sample or reagent storage containers, respectively. These bottles were precleaned following the procedure described in our previous paper[26]. The reactors were equilibrated with the samples before the kinetic measurements.

### *Samples*

To test the usefulness of the Chelex batch technique for metal speciation[26], a series of synthetic, aqueous samples were prepared as follows. Some of the model solutions contained a mixture of the metals: Al(III), Cd(II), Cu(II), Ni(II), Zn(II) and Pb(II), whereas others contained a single metal only. Since both the distribution of metal species and the chemical affinity of the functional group in the Chelex molecule depend on the pH, the pH was maintained at 5.0 ± 0.5 for both the model solutions and the natural water samples. The model solutions were prepared by spiking ultrapure water or the buffer solution with an appropriate volume of the following solutions: the metal standard, the fulvic acid (0.1000 g/L), the EDTA, or the NTA solution. The pH (measured using a Fisher Scientific, Accumet 925 pH/ion meter) of all the samples was adjusted with dilute $HNO_3$ or dilute NaOH solutions, and the samples were equilibrated overnight. The pH was confirmed after the equilibration.

A 5 L sample of Rideau River surface water (initial pH 8.0 ± 0.3) was collected using a precleaned polyethylene water-sampler from a site at Carleton University. Since the concentration of the above metals in the unpolluted river surface water sample was too low for the kinetic study, the sample was spiked with standard solutions of Cu, Ni, Zn, Cd and Pb to make it contain a few µg/L of each metal, and the pH of the spiked sample was adjusted to 5.0 ± 0.1. After equilibrating for two days, the spiked samples were filtered through a 0.45 µm filter to separate the particulate matter. The filtrate was collected and left to stand for one day for equilibration before kinetic measurements were made. The pH was confirmed after the equilibration.

A sample of snow (initial pH 5.3 ± 0.2) was collected with a precleaned polyethylene sample-collector at a site on the roof top of the chemistry building at Carleton University. The sample was kept in the sample-collector at the room temperature until the snow melted. The snow-melt was filtered through a 0.45 filter; the pH of the filtrate was measured before and after the filtration. In order to bring the concentration of the metals in the snow sample to appropriate levels for the kinetic study the snow sample was spiked with standard solutions of Al, Cu, Ni, Zn, Cd and Pb, so as to make the sample contain a few µg/L of each metal, and the pH of the spiked sample was adjusted to 5.5 ± 0.1. The spiked sample was equilibrated overnight before the kinetic measurements were made.

### *Methods*

The performances of a graphite furnace atomic absorption spectrometer (Perkin-Elmer Zeeman, Model 5000, equipped with an autosampler) and an inductively-coupled plasma mass spectrometer (Perkin-Elmer Sciex Elan-5000) with the solution nebulization technique were evaluated for the determination of aluminum concentrations.

For graphite furnace atomic absorption spectrometry (GFAAS), an HGA-500 graphite furnace, pyrolytically-coated graphite tubes and laboratory-made platforms fabricated from pyrolytic graphite were used. Aliquots (1 mL) of the test solutions in small plastic vials were acidified with 10 µL of concentrated nitric acid. 10–20 µL of this acidified test solution was injected into the graphite furnace, the solution was dried at 120°C for 40 s, pyrolyzed at 1300°C for 35 s and atomized at 2400°C for 7 s for determination of aluminum. The atomic absorbance signal was measured at 309.2 nm in the peak area mode. The atomization cycle in GFAAS was followed by a 3-second clean-up step of the graphite tube at 2600°C. The argon gas flow was interrupted during the atomization cycle. During the drying, pyrolysis and clean-up cycles, argon gas was passed through the graphite furnace at a flow rate of 300 mL/min.

For inductively-coupled plasma mass spectrometry (ICP-MS), the sample solution was continuously delivered with a peristaltic pump at a flow rate of 1 mL/min; the sample solution was delivered through the solution-nebulizer to the ICP torch. The flow rates of coolant, auxiliary and carrier argon gas were 15, 850 and 900 mL/min, respectively. The metal species were analyzed according to their mass/charge ratio by a quadrupole mass analyzer, followed by signal detection with a channel electron multiplier. The signal (counts/s) was monitored as a function of time with a scan mode of peak hop, 1 point/spectral peak. The sampling rate, i.e. the time between two successive data points, is determined by the dwell time, which is the number of milliseconds that each mass is measured on a sweep; the longer the dwell time, the more precise is the measurement. A shorter dwell time, however, more accurately captures a "snapshot" of the sample spectrum in time, and hence, allows better resolution, which is especially useful for kinetic studies of fast components in metal speciation. A dwell time of 100–1000 ms was chosen based on the consideration of both quality and quantity of the experimental data. The instrumental operating conditions and data acquisition protocol for the ICP-MS determination were the same for all metals tested.

### *Kinetic study*

The kinetic measurements were made by the Chelex-batch technique[26]. The pretreated Chelex resin was added to a 400 mL sample solution in a cylindrical Teflon reactor (500 mL capacity), and the mixture was stirred with a Teflon-coated magnetic stirring bar. Samples for analysis were withdrawn through a nylon membrane filter, placed at the end of the outlet tube of the reactor, which filtered out the Chelex resin and gave a clear filtrate. The zero time for the kinetic measurement was taken as the time at which the resin first came in contact with the sample in the reactor. The sum of the concentrations of all of the kinetically distinguishable components of the metal remaining in the sample was monitored as a function of time using either ICP-MS or GFAAS. The pH of the sample was also monitored throughout the Chelex batch experiment. The changes in the pH between the beginning and the end of the experiment were found to be < ± 0.5. In order to ensure that reaction 3 was first- pseudo-first-order, various concentrations of Chelex resin, 0.25, 0.50, 0.75 and 1.00% (w/w), were tested for the uptake of aluminum from the model solutions. The uptake of aluminum by Chelex-100 greatly increased when the concentration of Chelex resin was increased from 0.25 to 0.50% (w/w), but increased only slightly with further increase in the concentration of the Chelex resin. The concentration of 1% (w/w) (equivalent to a Chelex: metal mole ratio of 100 or higher, depending on the concentrations of the metals in the sample) was therefore used in further studies. Under this condition, the effect of changes in the sample volume during the kinetic measurements was negligible.

## RESULTS

### *Comparison of GF-AAS and ICP-MS*

Figure 1 shows the uptake of aluminum by the Chelex resin from the synthetic buffered sample containing Al(III) measured by both of the above techniques. The major difference between these two curves is the much smaller number of experimental points

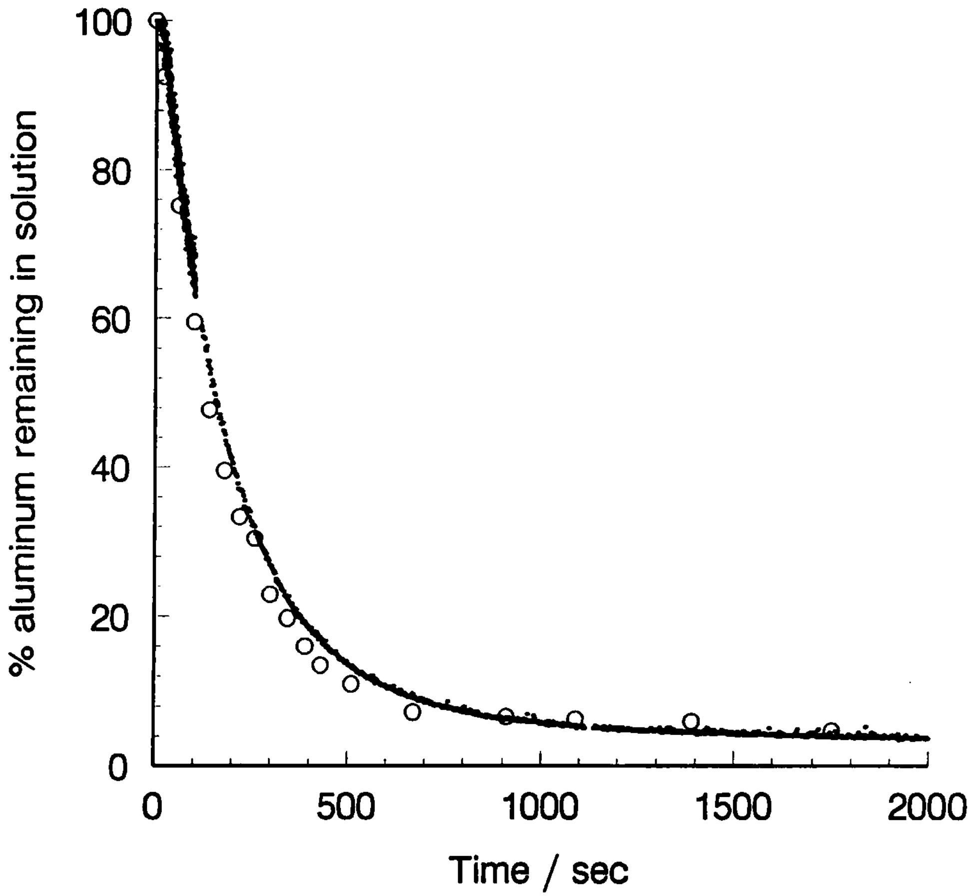

Figure 1 Aluminum remaining in the model solutions containing aluminum, as a function of time, after uptake of the aluminum by the Chelex resin of 100–200 mesh in the Chelex batch technique, pH 5.0. [Chelex] = 1% (w/w), [NaOAc] 0.32 M; [HOAc] 0.18 M. ●, ICP-MS, [Al(III)] = 3.7 μM; ○, GFAAS, [Al(III)] = 3.1 μM.

obtained by the GFAAS measurements compared to those obtained by the ICP-MS measurements. The data were analyzed by the iterative deconvolution method[24] and the results are listed in Table 1. Since ICP-MS could not tolerate sample solutions having high salt content, such as the buffered solutions, for more than a very short time, only a single sample was analyzed with ICP-MS, and hence, there is only a single value for ICP-MS against three values for GFAAS in Table 1. The results are summarized as follows:

1) the dissociation rate constant for the fastest component of aluminum determined by these two techniques agrees well;
2) for the buffered model solutions, two kinetically distinguishable components of aluminum were resolved by ICP-MS, but only one by GFAAS;
3) the standard error of the kinetic parameters, was generally one order of magnitude higher for the data set by GFAAS than that by ICP-MS. Sequential delivery of discrete samples involving a sample transfer step, inherent in the current GFAAS

**Table 1** Rate constants for the dissociation of aluminum species in the buffered, model solutions containing aluminum by Chelex resin, as a function of the initial aluminum concentration. pH = 5.00 ± 0.02. The buffer composition: [NaOAc] and [HOAc] are 0.32 M and 0.18 M, respectively.

| *Analytical technique* | $[Al(III)]_{total}$ | $k_1 \times 10^{-3}$, $s^{-1}$ | $k_2 \times 10^{-4}$, $s^{-1}$ |
|---|---|---|---|
| *GFAAS* | 4.7 | 6.4 ± 0.8 | |
| | 3.1 | 6.4 ± 0.1 | |
| | 1.2 | 5.6 ± 0.4 | |
| *ICP-MS* | 3.7 | 5.4 ± 0.03 | < 4.0 ± 0.2 |

Values after ± signs are standard deviations of non-linear regression analysis. Since the total uncertainties of the analytical method, including that of the regression analysis, is greater than the values of the standard deviations shown above, only two significant figures in the values of the rate constants are justified.

technology (as opposed to direct, continuous delivery of samples by the solution nebulization technique of ICP-MS), limits the number of experimental data points in GFAAS. The much larger number of data points and the smaller scatter in the data points in ICP-MS is due to the direct delivery of the sample into the plasma torch. The larger error on the data by GFAAS was attributed to both the small number of experimental data points and to the large uncertainty in the data points. The GFAAS technique with the automated sampler uses small, plastic vials as sample containers, one vial for one datum point. Because of the ever-present contamination from the walls of even precleaned vials and from the ambient laboratory air (even in an air-conditioned laboratory environment), contamination of the analyte, and adsorptive loss on the vial wall are extremely serious problems in ultratrace analysis[46]. The GFAAS results showed variable levels of uncontrollable contamination (probably somewhat offset by adsorptive losses on the walls of the vials), and hence the results were less accurate; also, considerable scatter in the data points were observed and hence, the results were less precise than those of the ICP-MS measurements. Also, the fitting of the experimental data by the iterative deconvolution method requires a large number of data points for the best results. If the time gap between the experimental data points is large, as in the case of GFAAS, some kinetically distinguishable components may be lost. The ICP-MS uses a cylindrical Teflon reactor which combines both the functions of the separate vessel for the Chelex batch reactions and of the sample vial required for the automatic sampler of GFAAS, thereby eliminating the sources of contamination and adsorptive loss involved in the GFAAS technique. Since contamination and adsorptive loss strongly depends on time, the much shorter time involved in the ICP-MS determination gives results which are more precise and more accurate than those of GFAAS. Because of its ability to give a time resolution as small as 1 ms between the experimental data points, in principal ICP-MS allows resolution of chemical species having rate constants more than 1000 times larger than those that can be measured by GFAAS. However, with a competitive adsorption technique such as the present using Chelex, only rate constants much slower than the rate of uptake by Chelex can be measured. Nevertheless, the excellent sensitivity and selectivity of GFAAS, its much lower cost per sample, and fast, sequential multielement capability make it a very powerful technique for kinetic studies, especially for cross-checking the ICP-MS results and for identifying any possible interferences by molecular species in ICP-MS. ICP-MS was used for all further studies in this work.

### *Verification of assumptions 1 and 2 of the kinetic model*

The aqueous solution of aluminum described earlier was used in the Chelex batch technique[26], and the aluminum left in the solution as a function of time was monitored by either ICP-MS or GFAAS. Table 1 shows that the rate constant was not changed by changes in the initial concentration of Al(III), indicating that the dissociation of the Al-complex was first-order or pseudo-first-order. Figure 2 shows that the reaction Chelex + Al → Chelex-Al (curve a) was much faster than the dissociation of the Al-FA complexes (curves b and c). Hence, assumptions 1 and 2 of the kinetic model are satisfied for aluminum.

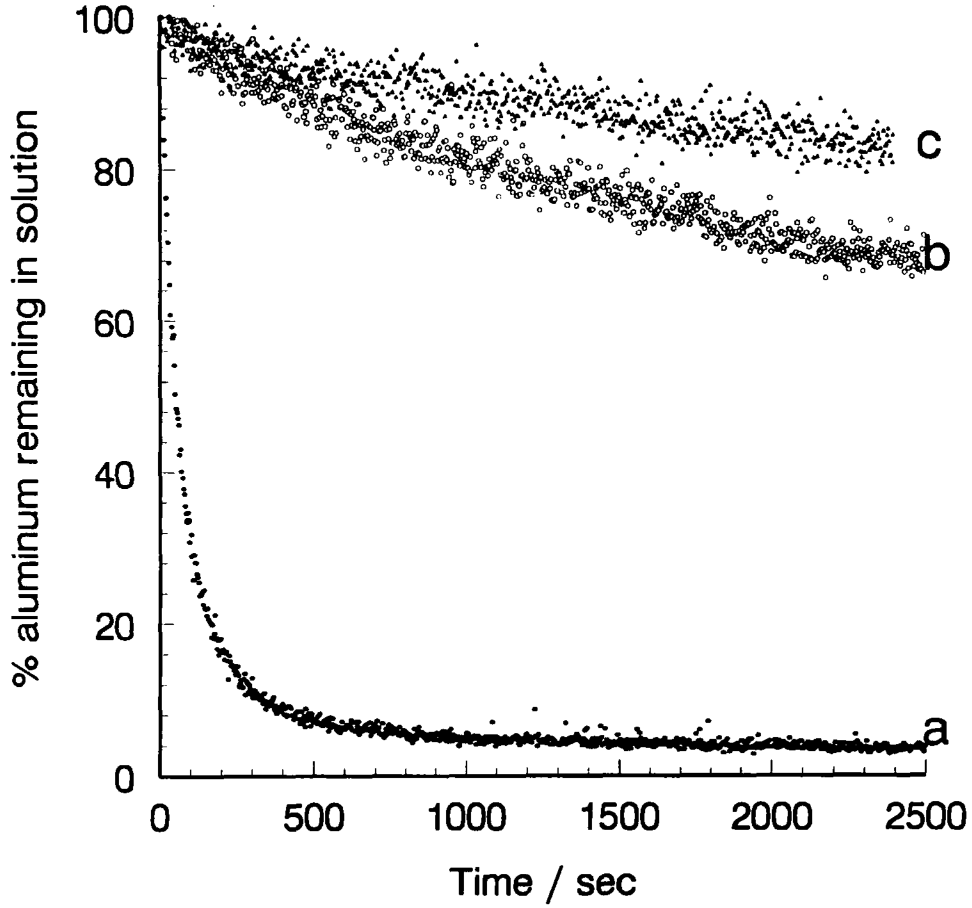

**Figure 2** Aluminum remaining in the unbuffered model solutions containing Al(III), Zn(II), Cd(II), Cu(II), Ni(II) and Pb(II), as a function of time, after uptake of the aluminum by the Chelex resin of 100–200 mesh in the Chelex batch technique, pH 5.0, determined by ICP-MS. [Chelex] = 1% (w/w). a, [FA] : [M] = 0.00, [Al(III)] = 1.3 μM; b, [FA] : [M] = 3.9, [Al(III)] = 0.70 μM; c, [FA] : [M] = 7.7, [Al(III)] = 0.83 μM. [M] = [Al(III)] + [Cd(II)] + [Cu(II)] + [Ni(II)] + [Zn(II)] + [Pb(II)] = 2.1 μM.

### *Validation of the Chelex batch technique for kinetic study of metal speciation*

Since the ratio of external/internal surface area and the surface energy of the Chelex resin are higher when the particle size is smaller, the particle size of the Chelex resin may affect the rate of uptake of metals in the Chelex batch technique, and the Chelex resin with different particle size may yield a different number of kinetically distinguishable components with different associated rate constants. Chelex resin of 50–100, 100–200 and 200–400 mesh was used to remove Cu(II) from model solutions[22] and the results showed a decreasing trend in the overall uptake rate of Cu(II) with increasing particle size of the Chelex resin, especially when the particle size is increased to 50–100 mesh. According to the manufacturer of the resin, the pore size of the Chelex resin of any given mesh is uniform. The difference in the kinetic behaviour of Cu(II) with the Chelex resin of different particle size must therefore be attributable to the different ratio of external/internal surface area and the different surface energy of the resin. The smaller particle size having a larger ratio of external/internal surface area and higher surface energy had a faster rate of uptake of Cu(II) by the Chelex resin. The results also showed when the particle size of the resin decreases to certain level, e.g., 100–200 mesh, further decrease in particle size (to 200–400 mesh) had no significant effect on the kinetic behaviour of Cu(II). The Chelex resin of 100–200 and 200–400 was therefore used in this study.

The applicability of the Chelex batch technique for metal speciation was tested using model systems: EDTA-Cu and NTA-Cu systems[22]. EDTA and NTA are anthropogenic complexants and are much stronger complexants than naturally-occurring complexants, such as humic materials. EDTA and NTA were chosen because they form simple, stable and well-characterized complexes with Cu(II), and can provide a limiting case of strong complexants. If the model proposed in this paper is valid, the kinetic study of Cu(II)-EDTA and Cu-NTA systems should reveal two kinetically distinguishable components for each, when $0 < [\text{ligand}]/[\text{Cu(II)}] < 1$, where [ligand] = [EDTA] or [NTA], one component corresponding to the Cu(II) aquo ion, the other to the Cu(II)-ligand complex. Only one component (corresponding to 1:1 Cu-EDTA or Cu-NTA complex) should be observed when the ratio of $[\text{ligand}]/[\text{Cu(II)}] > 1$. The distribution of each component should be given by equilibrium calculations using the initial concentrations of Cu(II) and the conditional stability constants of the Cu-EDTA or the Cu-NTA complex at pH 5.0.

The results of the data analysis by the iterative deconvolution method[24] are listed in Table 2. Two kinetically distinguishable components of Cu(II) were resolved for the solutions with [EDTA]/[Cu(II)] ratios of 0.38 and 0.77, whereas only one kinetically distinguishable component was predominant in the sample with [EDTA]/[Cu(II)] ratio of 2.3. The distributions of copper aquo ions and Cu-EDTA complex obtained by the analysis of the kinetic data agree within 8% with those predicted from equilibrium calculations.

The results obtained for these model solutions, using the iterative deconvolution method,[24] are also listed in Table 2. Three kinetically distinguishable components were resolved for the solutions with the $[\text{NTA}]/[\text{Cu(II)}] < 1$, whereas only one kinetically distinguishable component with dissociation rate constant of $1.1 \times 10^{-3}\ \text{s}^{-1}$ was observed for the solutions with the $[\text{NTA}]/[\text{Cu(II)}] > 1$. In the three-component [NTA]/[Cu(II)] system, the component dissociating the fastest is the Cu(II) aquo complex. The distributions of this component obtained from the kinetic studies agree well with those predicted from equilibrium calculations. As mentioned above, besides the 1:1 Cu-NTA complex, NTA also forms a 2:1 Cu-NTA complex, especially when $[\text{Cu(II)}] > [\text{NTA}]$. The slower components were probably 1:1 and 2:1 Cu-NTA complexes.

**Table 2** Kinetic parameters for the dissociation of copper complexes in model solutions measured using Chelex resin of 200–400 mesh as a function of the [EDTA]/[Cu(II)] and [NTA]/[Cu(II)] ratios. pH 5.0 ± 0.5.

| | $[Cu(II)]_{total}$, µM | $C_1^0$, % | $k_1 \times 10^{-2}$, $s^{-1}$ | $C_2^0$, % | $k_2 \times 10^{-3}$, $s^{-1}$ | $C_3^0$, % | $k_3 \times 10^{-4}$, $s^{-1}$ |
|---|---|---|---|---|---|---|---|
| [EDTA]/[Cu(II)] | | | | | | | |
| 0.38 | 2.1 | 58 | 2.8 ± 0.03 | – | – | 42 | < 1.7 ± 0.007 |
| 0.77 | 2.1 | 31 | 2.4 ± 0.08 | – | – | 69 | < 1.4 ± 0.006 |
| 2.3 | 2.1 | – | – | – | – | 96 | < 0.36 ± 0.006 |
| [NTA]/[Cu(II)] | | | | | | | |
| 0.36 | 0.31 | 68 | 2.4 ± 0.05 | 17 | 2.9 ± 0.1 | 15 | < 1.6 ± 0.07 |
| 0.71 | 0.31 | 33 | 4.3 ± 0.1 | 57 | 1.4 ± 0.01 | 10 | < 1.0 ± 0.09 |
| 1.1 | 0.31 | – | – | 100 | 1.1 ± 0.004 | – | – |
| 1.4 | 0.31 | – | – | 100 | 1.0 ± 0.002 | – | – |

$C_1^0$, $C_2^0$ and $C_3^0$ = the initial percentages of the first (the fastest), the second (the next fastest) and the third (the slowest) kinetically distinguishable component, respectively. Values after ± signs are standard deviations of non-linear regression analysis. Since the total uncertainties of the analytical method, including that of the regression analysis, are greater than the values of the standard deviations shown above, only two significant figures in the values of the rate constants are justified.

The results in Table 2 show that the Chelex batch technique is applicable to metal speciation.

### *Effect of fulvic acid on the kinetics of Cd(II), Cu(II) and Pb(II) removal by Chelex resin (200–400 mesh) from model solutions containing [M], where [M] = [Al(III)] + [Cd(II)] + [Cu(II)] + [Ni(II)] + [Zn(II)] + [Pb(II)] = 2.1 µM*

#### *Cadmium*

Figure 3 shows the uptake of Cd(II) by the Chelex resin from the model solutions, with and without fulvic acid, as a function of time. The effect of fulvic acid on the kinetics of the Cd(II) components in the samples is not significant. The results obtained using the iterative deconvolution method[24] are listed in Table 3, along with the results for the model solutions of different concentrations of fulvic acid from reference 22. Two kinetically distinguishable components of cadmium were resolved in all of the samples tested. However, since the slower component, as shown in Table 3, accounted for only a few percent of the total and the standard deviations of non-linear regression analysis on this component was generally one order of magnitude greater than those of the faster component, the analysis of the slower component was not reliable. Therefore, only one kinetically distinguishable component may be reasonably identified in these model solutions. This is in agreement with the equilibrium calculations[47] which indicate only one cadmium species, Cd aquo ion, present in the aqueous samples at pH 5.0. The dissociation rate constant for the faster component decreased, as shown in Table 3, with increasing concentrations of fulvic acid, probably as a result of some of the Cd(II) ions being bound to fulvic acid. This point will be further discussed later. The slower component in all these samples accounted for only a few percent of the total, indicating that the Cd-FA was not a thermodynamically strong complex, and hence, most of Cd(II) species were present as Cd(II) aquo ions (the fastest component).

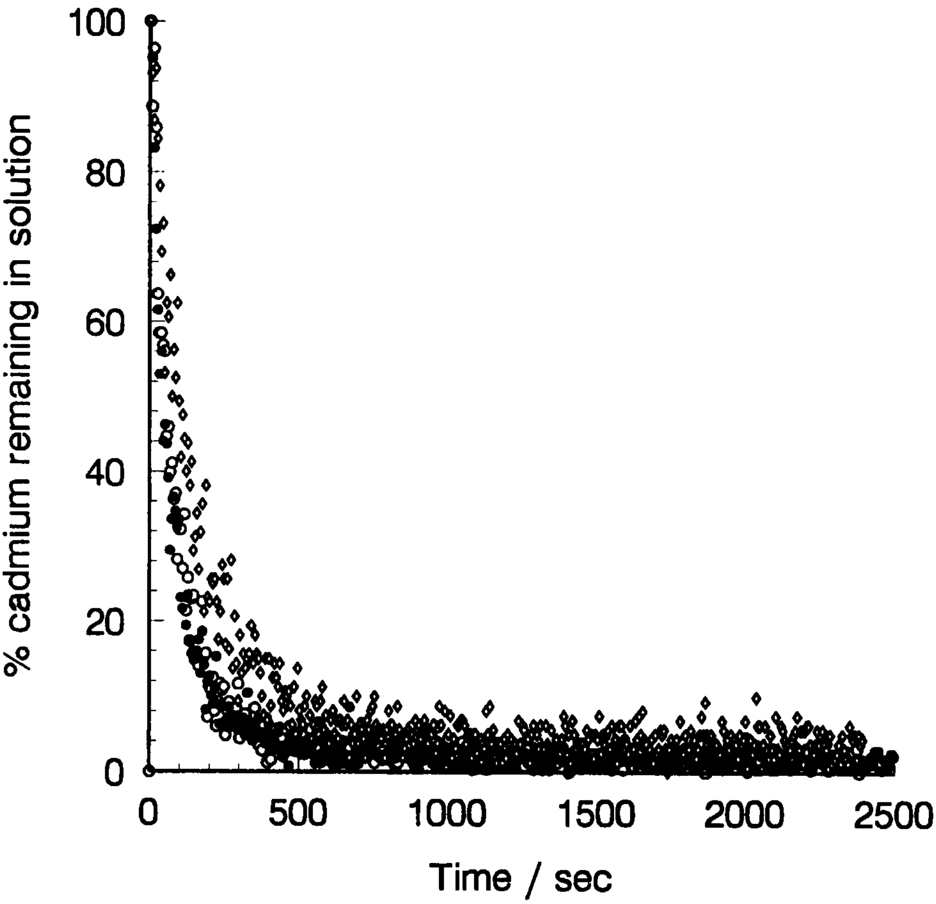

**Figure 3** Cadmium remaining in the model solutions, as a function of time, after uptake of cadmium by the Chelex resin of 200–400 mesh in the Chelex batch technique, pH 5.0. [Chelex] = 1% (w/w), [Cd(II)] = 2.2 × $10^{-2}$ µM. ○, [FA] : [M] = 0.0; ●, [FA] : [M] = 3.8; ◇, [FA] : [M] = 7.7. [M] = [Al(III)] + [Cd(II)] + [Cu(II)] +[Ni(II)] + [Zn(II)] + [Pb(II)] = 2.1 µM.

**Table 3** Kinetic parameters for the dissociation of cadmium complexes in model solutions containing Al(III), Cd(II), Cu(II), Ni(II), Zn(II) and Pb(II) by Chelex resin of 200–400 mesh as a function of the concentration of fulvic acid. pH = 5.0 ± 0.5.

| *[FA]:[M]* | *[Cd(II)], total* × $10^{-2}$, *µM* | $C_1^0$ % | $k_1 \times 10^{-2}$, $s^{-1}$ | $C_2^0$ % | $k_2 \times 10^{-3}$, $s^{-1}$ |
|---|---|---|---|---|---|
| 0 | 8.9 | 99 | 2.7 ± 0.03 | 1 | < 5.6 ± 0.3 |
| 0.29 | 8.9 | 98 | 2.7 ± 0.03 | 2 | < 2.4 ± 1 |
| 0.58 | 8.9 | 97 | 2.4 ± 0.04 | 3 | < 3.0 ± 0.4 |
| 0.87 | 8.9 | 98 | 2.2 ± 0.03 | 2 | < 1.4 ± 0.1 |
| 1.2 | 8.9 | 97 | 1.7 ± 0.02 | 3 | < 1.6 ± 0.01 |
| 3.8 | 2.2 | 97 | 1.1 ± 0.02 | 3 | < 0.4 ± 0.03 |
| 7.7 | 2.2 | 95 | 0.7 ± 0.02 | 5 | < 0.2 ± 0.05 |

$C_1^0$ and $C_2^0$ = the initial percentages of the faster and the slower kinetically distinguishable component, respectively; [M] = {[Al(III)] = 1.5 µM} + {[Cd(II)] = 0.089 µM} + {[Cu(II)] = 0.16 µM} + {[Ni(II)] = 0.17 µM} +{[Pb(II)] = 0.048 µM} + {[Zn(II)] = 0.15 µM} = 2.1 µM. Values after ± signs are standard deviations of non-linear regression analysis. Since the total uncertainties of the analytical method, including that of the regression analysis, is greater than the values of the standard deviations shown above, only two significant figures in the values of the rate constants are justified.

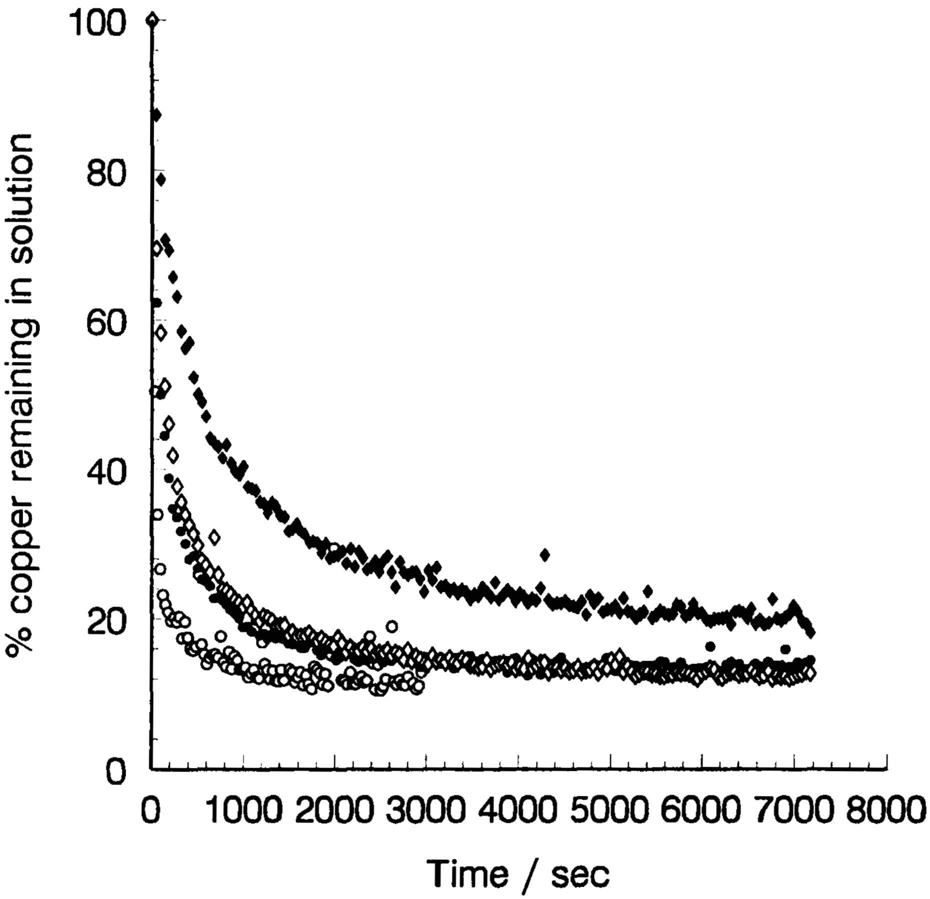

**Figure 4** Copper remaining in the model solutions, as a function of time, after uptake of copper by the Chelex resin of 200–400 mesh in the Chelex batch technique, pH 5.0. [Chelex] = 1% (w/w), [Cu(II)] = $1.6 \times 10^{-1}$ µM; ○, [FA] : [M] = 0.0; ●, [FA] : [M] = 0.58; ◇, [FA] : [M] = 0.87; ◆, [FA] : [M] = 1.2. [M] = [Al(III)] + [Cd(II)] + [Cu(II)] + [Ni(II)] + [Zn(II)] + [Pb(II)] = 2.1 µM.

*Copper*

Figure 4 shows the uptake of Cu(II) by the Chelex resin from the model solutions, with and without fulvic acid, as a function of time. The rate of Cu(II) uptake decreased with increasing concentrations of fulvic acid because of formation of the Cu-fulvic complex, which dissociates slowly to generate Cu(II) aquo ions which were taken up by the Chelex resin. The results obtained using the iterative deconvolution method[24] are listed in Table 4. Since fulvic acid is a polyfunctional complexant the dissociation kinetics of its Cu(II) complexes is different from that of chelating agent, EDTA or NTA, with Cu(II). The component $C_1$ which reflects the rate of its uptake by Chelex was not reduced to zero, suggesting that fulvic acid forms a complex with Cu(II) which dissociates at a rate not very different from the rate of its uptake by Chelex and cannot be resolved from the latter. The formation of this Cu(II)-FA complex causes the measured rate constant to decrease as the concentration of fulvic acid increases. The analysis indicates the existence of two Cu(II)-FA complexes which have slow dissociation rates. The rate

**Table 4** Kinetic parameters for the dissociation of copper complexes in model solutions containing Al(III), Cd(II), Cu(II), Ni(II), Zn(II) and Pb(II) measured using Chelex resin of 200–400 mesh as a function of the concentration of fulvic acid. pH = 5.0 ± 0.5.

| $[FA]:[M]$ | $[Cu(II)]_{total} \times 10^{-1}\ \mu M$ | $C_1^0$ % | $k_1 \times 10^{-2}\ s^{-1}$ | $C_2^0$ % | $k_2 \times 10^{-3}\ s^{-1}$ | $C_3^0$ % | $k_3 \times 10^{-5}\ s^{-1}$ |
|---|---|---|---|---|---|---|---|
| 0 | 1.6 | 75 | 3.3 ± 0.2 | 12 | 2.5 ± 0.3 | 13 | < 2.8 ± 1.0 |
| 0.29 | 1.6 | 55 | 3.0 ± 0.2 | 24 | 2.1 ± 0.1 | 21 | < 2.7 ± 0.9 |
| 0.58 | 1.6 | 56 | 1.6 ± 0.06 | 29 | 1.6 ± 0.04 | 15 | < 1.1 ± 0.2 |
| 0.87 | 1.6 | 51 | 1.2 ± 0.04 | 32 | 1.5 ± 0.03 | 17 | < 4.0 ± 0.2 |
| 1.2 | 1.6 | 35 | 0.5 ± 0.4 | 38 | 1.0 ± 0.1 | 27 | < 3.9 ± 0.3 |

$C_1^0$, $C_2^0$, $C_3^0$ and $C_4^0$ = the initial percentages of the first (the fastest), the second (the next fastest), the third (the next fastest) and the fourth (the slowest) kinetically distinguishable component, respectively; [M] = {[Al(III)] = 1.5 μM} + {[Cd(II)] = 0.089 μM} + {[Cu(II)] = 0.16 μM} + {[Ni(II)] = 0.17 μM} + {[Pb(II)] = 0.048 μM} + {[Zn(II)] = 0.15 μM} = 2.1 μM. Values after ± signs are standard deviations of non-linear regression analysis. Since the total uncertainties of the analytical method, including that of the regression analysis, is greater than the values of the standard deviations shown above, only two significant figures in the values of the rate constants are justified.

constant for the dissociation of component $C_2$ decreases as the concentration of fulvic acid increases. This is probably because the decreasing ratio of Cu(II)/FA causes occupation of stronger binding sites on fulvic acids, leading to a lower weighted average rate constant for dissociation[49]. The rate constant for dissociation of the slowest component has considerable uncertainty but it is clearly present.

According to the equilibrium calculations of Huang *et al*[47], there is only one species of copper in aqueous solutions at pH 5. The kinetic analysis of copper speciation in this study (Table 4), however, showed the existence of several long-lived components. This can be seen in Figure 4 where the signal for the Cu(II) aquo ion persists at a level significantly above the signal/noise ratio. Tests showed that this amount of Cu was not leached from the containing vessels. A possible explanation is the existence of an equilibrium between the Cu(II) ion and the Chelex resin, the equilibrium position corresponding to a small concentration of Cu, ~ 0.2 μM, in the solution. Since, however, Cu(II) aquo ion binds strongly to Chelex it seems unlikely that these amounts of Cu(II) ion could be released to the solution. On the other hand, Cu(II) ion could be retained in the solution by a "foreign" ligand (unpolymerized components from the Chelex resin manufacturing process) which was slowly released from the resin. There is also a possibility that these long-lived components are due to mass transfer limitations on diffusion of Cu(II) ions released from binding sites in the interior of gel-like structures of water-logged Chelex particles. It is also conceivable that copper may have been used (e.g., as a catalyst) in the manufacture of the Chelex-100 resin or its synthetic precursor (monomers) and may have been leached out into the model solutions during our experiments. This, of course, can be tested experimentally. At present, our results do not allow a clear distinction between these possibilities.

### *Lead*

Figure 5 shows the uptake of Pb(II) from the model solutions containing Pb(II), Al(III), Cu(II), Cd(II), Ni(II) and Zn(II), with and without fulvic acid, as a function of time. In the absence of fulvic acid, more than 96% Pb(II) aquo ions was taken up by the Chelex resin in 400 seconds, but the time to reach the same percentage of Pb(II) uptake increased with increasing concentrations of fulvic acid. The results of the analysis of experimental data by the iterative deconvolution method[24] are listed in Table 5, along

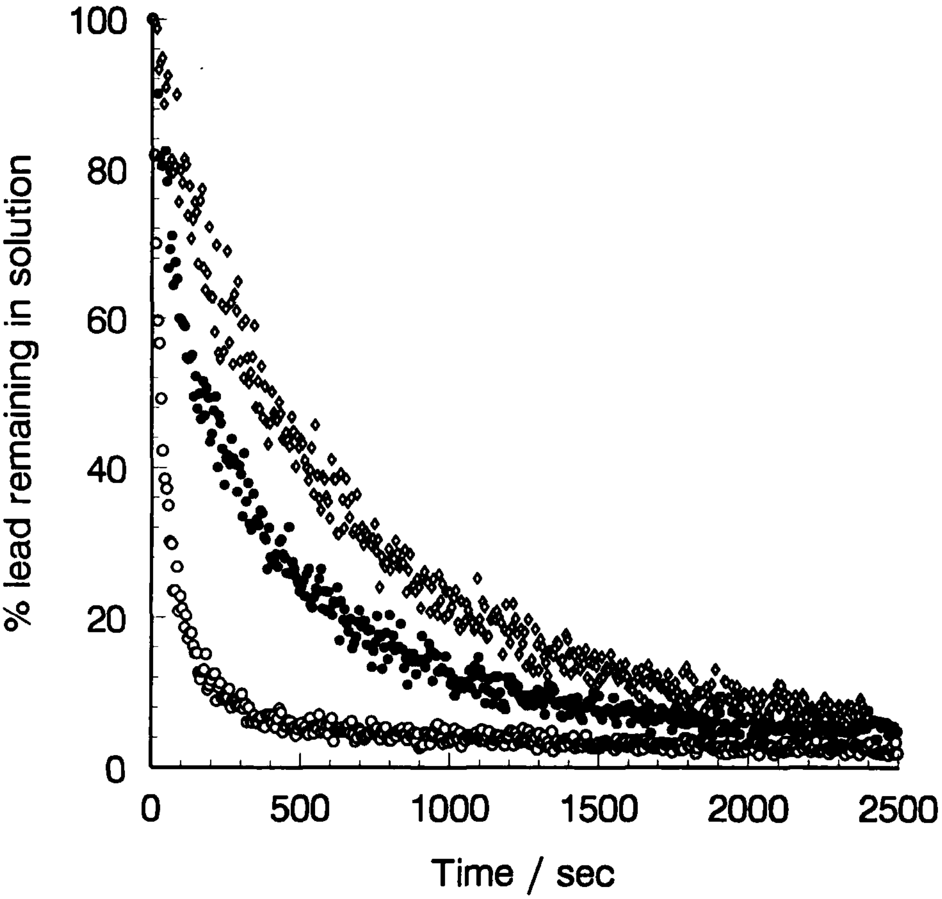

Figure 5 Lead remaining in the model solutions, as a function of time, after uptake of lead by the Chelex resin of 200–400 mesh in the Chelex batch technique, pH 5.0. [Chelex] = 1% (w/w), [Pb(II)] = $1.2 \times 10^{-2}$ µM; ○, [FA] : [M] = 0.0; ●, [FA] : [M] = 3.8; ◇, [FA] : [M] = 7.7. [M] = [Al(III)] + [Cd(II)] + [Cu(II)] + [Ni(II)] + [Zn(II)] + [Pb(II)] = 2.1 µM.

with the results for the model solutions of different concentrations of fulvic acid from reference 22. Three kinetically distinguishable components were resolved in the aqueous solution and four in the solutions containing fulvic acid. For the two major components, the percentages of the faster component decreased, whereas the percentages of the slower component increased with increasing ratios of [FA]/[M]. Note that for the experiment with ratio of [FA]/[M] of 3.8 the trend appears to be reversed. Actually this probably represents a scatter in the absolute value of the concentration because the final two experiments in Table 5 represent a set of experiments done at a different time. The dissociation rate constants for each of the two components decreased with increasing concentrations of fulvic acid. Further increase in the concentrations of fulvic acid increases the percentage of slower Pb(II) component because more Pb(II) ions are bound to the stronger sites in fulvic acid. This is observed in Table 5 where, with the two highest ratios of [FA]/[M], the third component has apparently disappeared and a corresponding increase in the quantity of the component with the slowest rate of dissociation was observed.

**Table 5** Kinetic parameters for the dissociation of lead complexes in model solutions containing Al(III), Cd(II), Cu(II), Ni(II), Zn(II) and Pb(II) measured using Chelex resin of 200–400 mesh as a function of the concentration of fulvic acid. pH = 5.0 ± 0.5.

| [FA]:[M] | $[Pb(II)]_{total}$ $\times 10^{-2}$, μM | $C_1^0$ % | $k_1$ $\times 10^{-2}$, $s^{-1}$ | $C_2^0$ % | $k_2$ $\times 10^{-3}$, $s^{-1}$ | $C_3^0$ % | $k_3$ $\times 10^{-3}$, $s^{-1}$ | $C_4^0$ % | $k_4$ $\times 10^{-4}$, $s^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|
| 0 | 4.8 | 95 | 3.0 ± 0.06 | 4 | 3.3 ± 0.5 | – | – | 1 | < 2.7 ± 0.4 |
| 0.29 | 4.8 | 65 | 3.7 ± 0.3 | 21 | 10 ± 3 | 10 | 2.8 ± 0.5 | 4 | < 3.2 ± 0.2 |
| 0.58 | 4.8 | 44 | 4.0 ± 0.3 | 44 | 7.8 ± 0.4 | 9 | 2.1 ± 0.1 | 3 | < 1.7 ± 0.1 |
| 0.87 | 4.8 | 32 | 3.5 ± 0.3 | 57 | 6.7 ± 0.2 | 10 | 1.6 ± 0.06 | 1 | < 1.2 ± 0.04 |
| 1.2 | 4.8 | 20 | 3.7 ± 0.4 | 62 | 4.9 ± 0.1 | 16 | 1.4 ± 0.04 | 2 | < 1.2 ± 0.05 |
| 3.8 | 1.2 | 35 | 1.9 ± 0.2 | 54 | 2.6 ± 0.1 | – | – | 12 | < 4.0 ± 0.3 |
| 7.7 | 1.2 | 12 | 2.0 ± 0.7 | 75 | 1.8 ± 0.1 | – | – | 13 | < 3.3 ± 0.1 |

$C_1^0$, $C_2^0$, $C_3^0$ and $C_4^0$ = the initial percentages of the first (the fastest), the second (the next fastest), the third (the next fastest) and the fourth (the slowest) kinetically distinguishable component, respectively; [M] = {[Al(III)] = 1.5 μM} + {[Cd(II)] = 0.089 μM} + {[Cu(II)] = 0.16 μM} + {[Ni(II)] = 0.17 μM} + {[Pb(II)] = 0.048 μM} + {[Zn(II)] = 0.15 μM} = 2.1 μM. Values after ± signs are standard deviations of non-linear regression analysis. Since the total uncertainties of the analytical method, including that of the regression analysis, is greater than the values of the standard deviations shown above, only two significant figures in the values of the rate constants are justified.

Fulvic acid is a polyfunctional complexant[50] and the major complexing sites for a metal in fulvic acid are oxygen-containing functional groups[51]. Although carboxyl groups are reported to play a predominant role in the binding of metal ions, mixed complexes[52–54], and complexes with ligands belonging to two fulvic acid molecules[55] probably are also formed. Furthermore, the nature of the complexing site changes with the metal/ligand ratio[49]. When metal ions are introduced into a fulvic acid solution, metal-fulvic complexes having different dissociation rate constants are therefore formed; slow dissociation rates may result from a chemical mechanism operating at the heterogeneous binding sites of fulvic acid and from secondary effects, such as slow diffusion of the metal ion into or out of the fulvic acid gel[56]. Since the properties of these heterogeneous binding sites are very similar, the differences in the dissociation rate constants are so small that an analytical method cannot discriminate between all fulvic acid-metal complexes; only an average rate constant for a group of binding sites is measured[49]. The ranges in the dissociation rate constants for both Cu(II) and Pb(II), in

**Table 6** Kinetically distinguishable components of cadmium, copper and lead species in the snow sample. pH 5.5.

| | $[M(II)]_{total}$, μM | $C_1^0$, % | $k_1 \times 10^{-2}$, $s^{-1}$ | $C_2^0$,% | $k_2 \times 10^{-3}$, $s^{-1}$ | $C_3^0$, % | $k_3 \times 10^{-5}$, $s^{-1}$ |
|---|---|---|---|---|---|---|---|
| Cd | $8.2 \times 10^{-2}$ | 99 ± 3 | 2.7 ± 0.03 | 1 ± 0.1 | < 2.0 ± 0.3 | – | – |
| Cu | $1.0 \times 10^{-1}$ | 77 ± 4 | 3.5 ± 0.1 | 13 ± 0.8 | 2.6 ± 0.2 | 10 ± 0.5 | < 3.0 ± 1 |
| Pb | $3.6 \times 10^{-2}$ | 94 ± 3 | 3.0 ± 0.05 | 6 ± 0.2 | < 1.6 ± 0.05 | – | – |

$C_i^0$ = the initial percentage of the $i$th kinetically distinguishable component. Values after ± signs are standard deviations of non-linear regression analysis. Since the total uncertainties of the analytical method, including that of the regression analysis, is greater than the values of the standard deviations shown above, only two significant figures in the values of the rate constants are justified.

**Table 7** Kinetically distinguishable components of cadmium, copper and lead species in the Rideau River surface water sample. pH 5.0.

| | $[M(II)]_{total}$, μM | $C_1^0$, % | $k_1 \times 10^{-2}$, $s^{-1}$ | $C_2^0$,% | $k_2 \times 10^{-3}$, $s^{-1}$ | $C_3^0$, % | $k_3 \times 10^{-5}$, $s^{-1}$ |
|---|---|---|---|---|---|---|---|
| Cd | $2.5 \times 10^{-2}$ | – | – | 96 ± 1 | 5.2 ± 0.06 | 4 ± 0.2 | < 6.1 ± 0.9 |
| Cu | $7.8 \times 10^{-2}$ | – | – | 51 ± 5 | 0.6 ± 0.04 | 49 ± 5 | < 2.1 ± 0.8 |
| Pb | $1.5 \times 10^{-2}$ | – | – | 89 ± 0.5 | 2.1 ± 0.01 | 11 ± 0.2 | < 14 ± 3 |

$C_i^0$ = the initial percentage of the $^i$th kinetically distinguishable component. Values after ± signs are standard deviations of non-linear regression analysis. Since the total uncertainties of the analytical method, including that of the regression analysis, is greater than the values of the standard deviations shown above, only two significant figures in the values of the rate constants are justified.

Tables 6 and 7, are due to the polyfunctionality of fulvic acid; they also reflect the effect of [metal]/[ligand] ratio on the nature of the complexing site occupied by the metal[49].

The results show that the dissociation rate constants for the kinetically distinguishable components of Cd(II), Cu(II) and Pb(II) in the model solutions decrease with increasing concentrations of fulvic acid, probably because the method used here determines an average value of a group of closely-related dissociation rate constants associated with heterogeneous binding sites of fulvic acid. With increasing [FA]/[metal ion] ratios, more metal ions are bound to stronger sites, leading to a smaller average value of dissociation rate constants[11,48–49].

### *Results of kinetic analysis of Cd, Cu and Pb speciation in a snow sample, (pH 5.0)*

### *Cadmium*

Figure 6 shows the uptake of Cd(II) by the Chelex resin (200–400 mesh) from the snow sample. Almost all of the Cd(II) species were taken up by the Chelex resin in 200 seconds, which was the same as the time required for the uptake of the Cd(II) species from the model solution of Cd(II) without fulvic acid (Figure 3). Although the log plot may indicate more than one kinetically distinguishable component, the amount of the slow component is within the uncertainty of the measurement. The data analysis by the iterative deconvolution method[24] (Table 6) shows that up to 99% of the Cd(II) species has a dissociation rate constant of $2.5 \times 10^{-2}$ $s^{-1}$. Comparison of Tables 3 and 6 suggests that the Cd(II) species was probably present in the snow sample as aquo ions or as simple inorganic complexes of Cd(II).

### *Copper*

Figure 7 shows the uptake of Cu(II) by the Chelex resin (200–400 mesh) from the snow sample. The plot of [Cu(II)] versus time is similar to that for the model solution of Cu(II) without fulvic acid (Figure 4, bottom curve). The logarithmic plot, Figure 7b, indicates

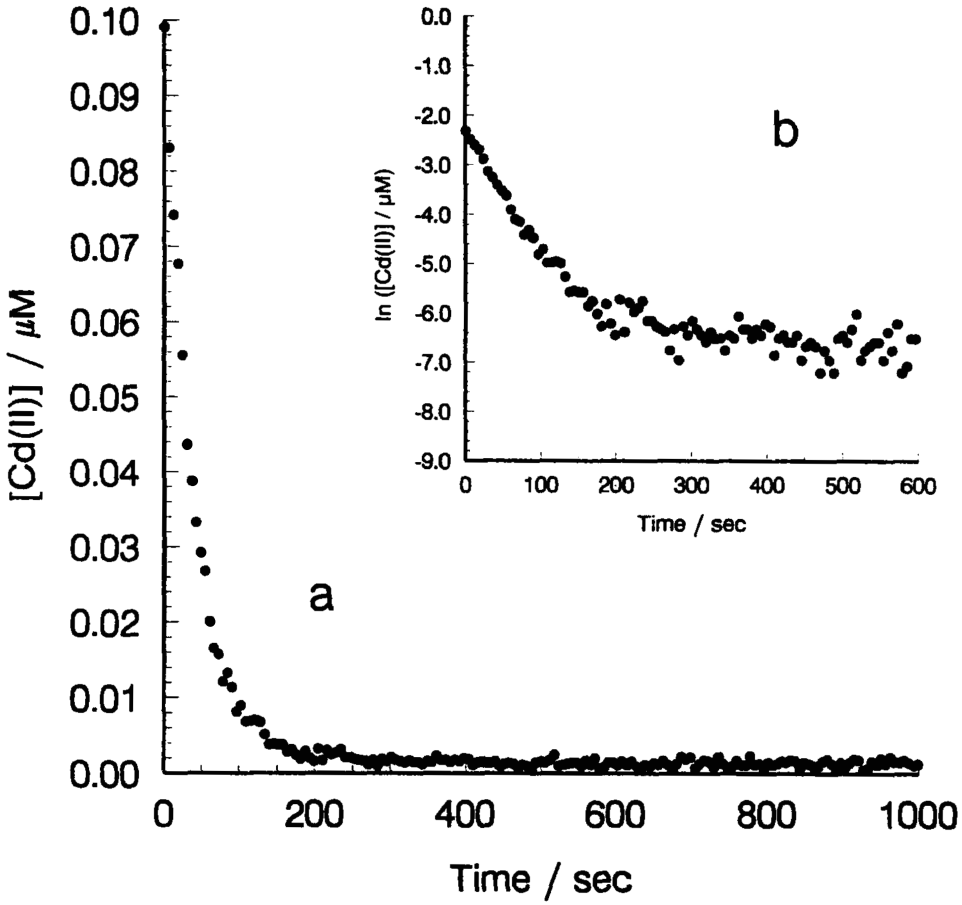

**Figure 6** Cadmium remaining in the snow sample, as a function of time, after uptake of cadmium by the Chelex resin of 200–400 mesh in the Chelex batch technique, pH 5.5. [Chelex] = 1% (w/w). (b) is the logarithmic plot of (a).

more than one kinetically distinguishable component of Cu(II) present in the snow sample. The data analysis by the iterative deconvolution method[24] (Table 6) gives three kinetically distinguishable components of Cu(II) having dissociation rate constants of $2.7 \times 10^{-2}$, $3.6 \times 10^{-3}$ and $< 1.2 \times 10^{-4}$ $s^{-1}$. Comparison of Tables 4 and 6 shows that the distribution of the kinetically distinguishable components of Cu(II) and their corresponding dissociation rate constants in the snow sample are similar to those of the model solution of Cu(II) without fulvic acid, and suggests that the Cu(II) species in the snow sample were probably Cu(II) aquo ions or simple inorganic complexes of Cu(II).

*Lead*

Figure 8 shows the uptake of Pb(II) by the Chelex resin (200–400 mesh) from the snow sample. The logarithmic plot, Figure 8b, indicates more than one kinetically

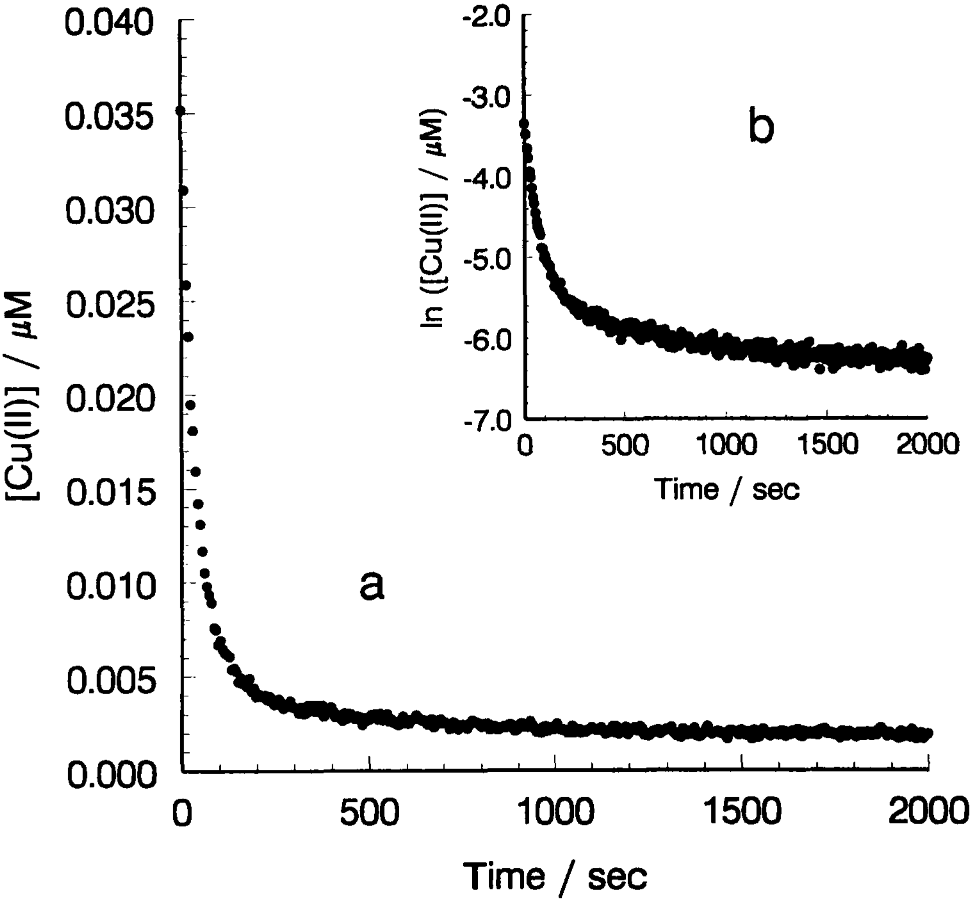

**Figure 7** Copper remaining in the snow sample, as a function of time, after uptake of copper by the Chelex resin of 200–400 mesh in the Chelex batch technique, pH 5.5. [Chelex] = 1% (w/w). (b) is the logarithmic plot of (a).

distinguishable component of Pb(II) present in the snow sample. The data analysis by the iterative deconvolution method[24] (Table 6) shows three kinetically distinguishable components of Pb(II) having dissociation rate constants of $3.1 \times 10^{-2}$ and $3.8 \times 10^{-3}$ $s^{-1}$ and $2.8 \times 10^{-4}$ $s^{-1}$, respectively. The kinetically distinguishable components of Pb(II) and their corresponding dissociation rate constants in the snow sample (Table 6) agree well to those of the model solution of Pb(II) (Table 5), suggesting that the Pb(II) species in the snow sample was probably present as aquo ions or as simple inorganic complexes of Pb(II).

The dissociation rate constants of Cd(II) components in the snow sample are in good agreement with those reported in our previous publication[22,26]. The difference in the dissociation rate constants of Cu(II) and Pb(II) components indicates different chemical species of Cu(II) and Pb(II) in these snow samples.

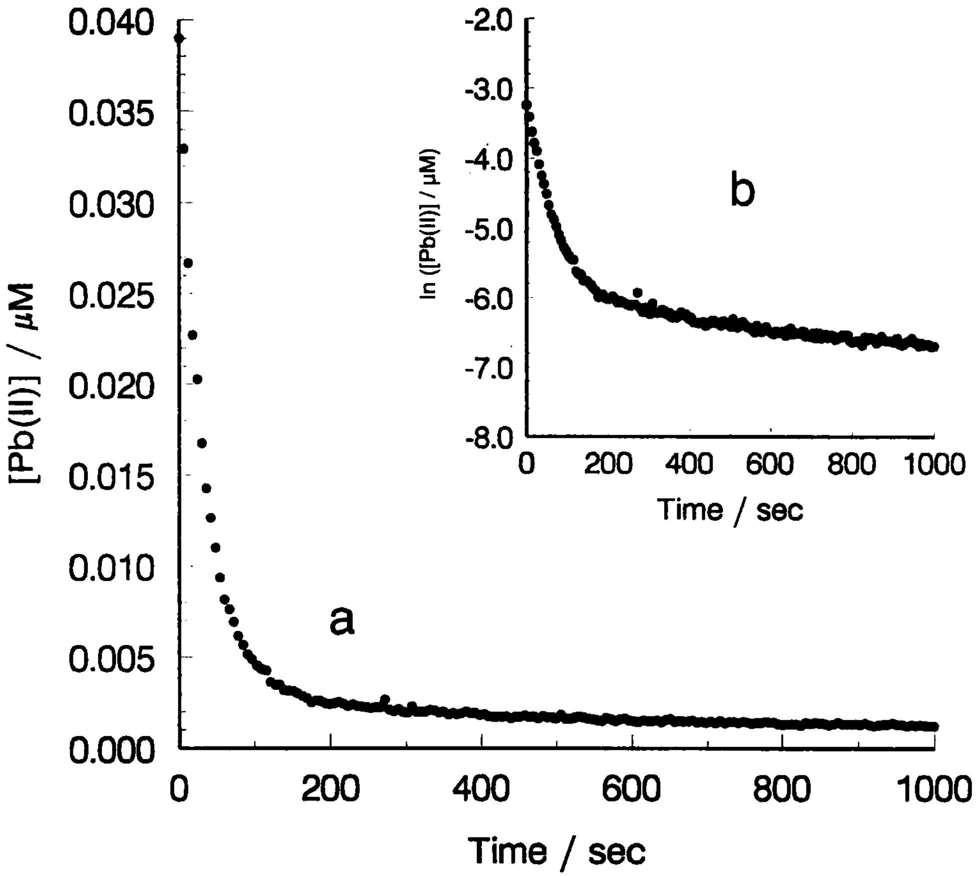

**Figure 8** Lead remaining in the snow sample, as a function of time, after uptake of lead by the Chelex resin of 200–400 mesh in the Chelex batch technique, pH 5.5. [Chelex] = 1% (w/w). (b) is the logarithmic plot of (a).

### *Results of kinetic analysis of Cd, Cu and Pb speciation in a Rideau River surface water sample, (pH 5.0)*

Figures 9–11 show the uptake of Cd(II), Cu(II) and Pb(II) by the Chelex resin (100–200 mesh) from a sample of Rideau River surface water at pH 5.0 in the Chelex batch technique. The curves a in all Figures are the signal vs. time for ultrapure water and serve as blanks, and show that the noise level for both metals is low and stable, indicating that the whole analytical system including the ICP-MS is performing well. The curves c in all Figures are the plots of signal vs. time for the sample of river surface water without any additions to it and serve as blanks. The purpose of the blank is to correct for adsorption or desorption of the analyte and for contamination from the walls of the reactor. The results show that there is no measurable loss of cadmium, copper and lead during the kinetic measurements by ICP-MS. The very slight increase in the blanks with time (Figures 9–11, curves c) was probably due to either leaching of the previously-adsorbed analytes from the walls of the reactor which had been pre-equilibrated with the sample before the kinetic measurements, or drifting of the signals after a relatively long time of collection of data. The curves b in Figures 9–11 show the uptake of Cd(II), Cu(II) and Pb(II), respectively, by the Chelex resin from the sample of the river surface water.

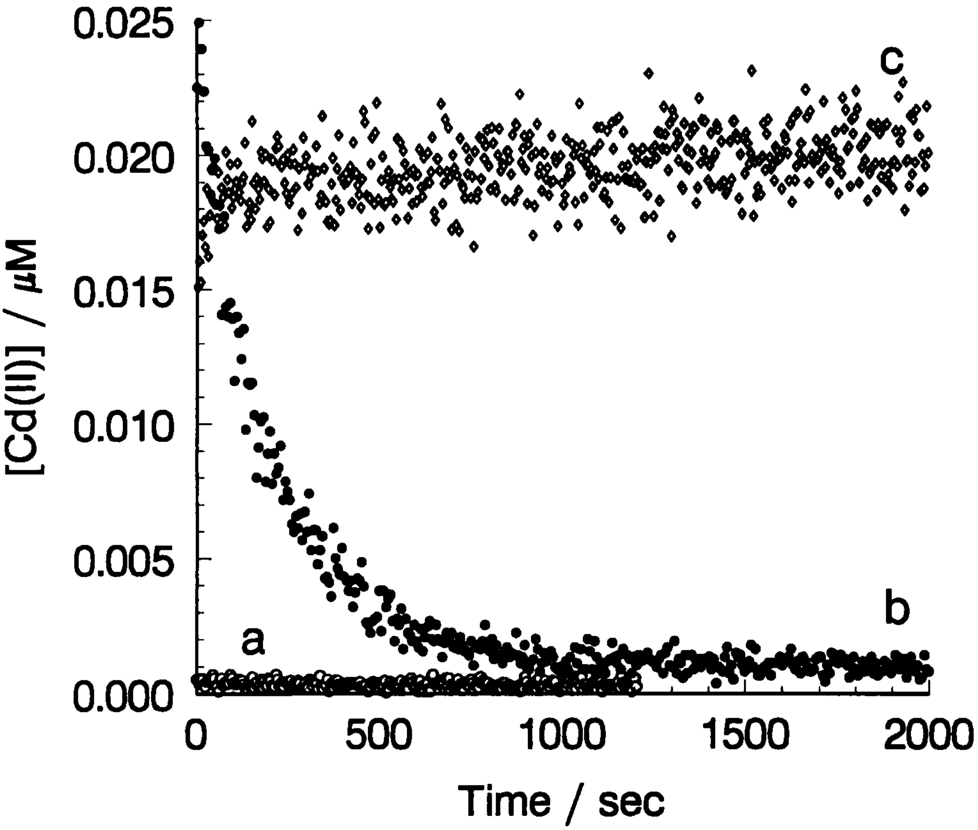

**Figure 9** Cadmium remaining in the sample of Rideau River surface water, as a function of time after uptake of cadmium by the Chelex-100 resin of 100–200 mesh in the Chelex batch technique, determined by ICP-MS. pH 5.0. a, ultrapure water without the Chelex resin; b, [Chelex] = 1% (w/w); c, the sample without Chelex resin.

### *Cadmium*

The results obtained by the iterative deconvolution method[24] (Table 7) show one kinetically distinguishable component of Cd(II) predominants in the river water sample. The dissociation rate constant for the predominant component of Cd(II) in the river water sample is about an order of magnitude smaller than that in the model solution of Cd(II) with fulvic acid (Table 3), suggesting that the Cd(II) in the river water sample was probably bound to humic materials, or colloidal hydrous oxides. These humic materials have properties different from fulvic acid and are present in higher concentration in the river water sample than fulvic acid in the model solution.

### *Copper*

The uptake rate of the total Cu(II) from the Rideau River surface water sample is slower than that from the model solutions of Cu(II), even with the ratio of [FA]/[M] of 1.2, as shown in Figures 4 and 10. Data analysis by the iterative deconvolution method[24]

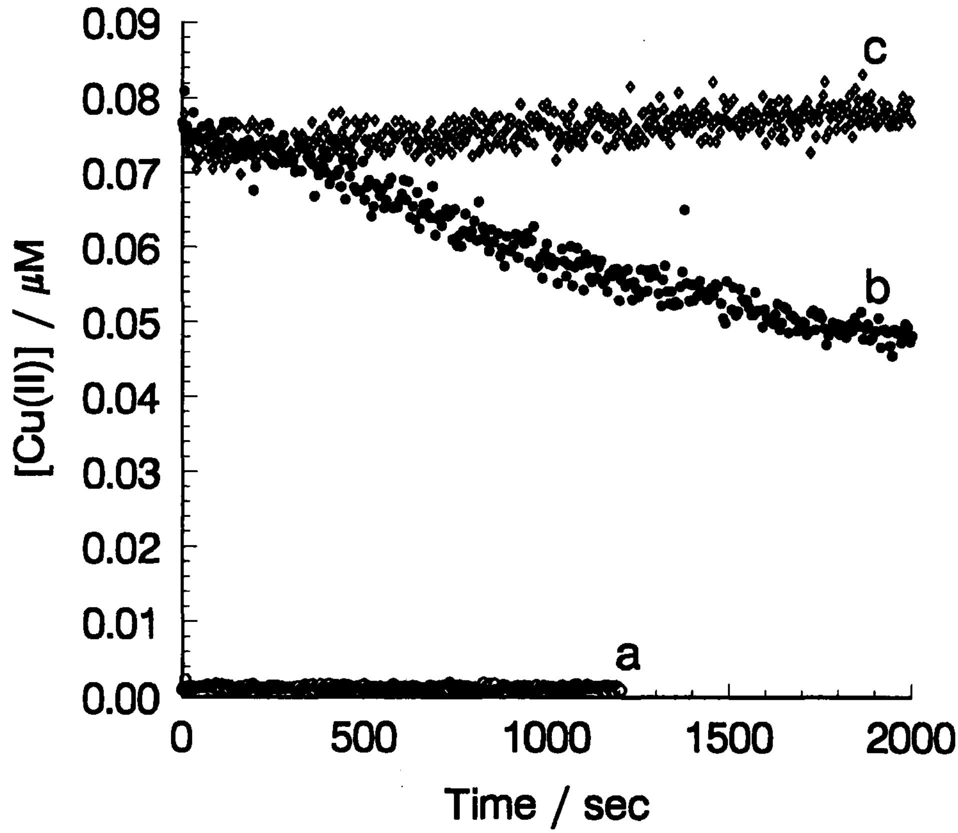

**Figure 10** Copper remaining in the sample of Rideau River surface water, as a function of time after uptake of copper by the Chelex-100 resin of 100–200 mesh in the Chelex batch technique, determined by ICP-MS. pH 5.0. a, ultrapure water without the Chelex resin; b, [Chelex] = 1% (w/w); c, the sample without Chelex resin.

revealed two kinetically distinguishable components of Cu(II), as shown in Table 7. The faster component, which accounted for 51% of the total Cu(II), had a dissociation rate constant of $6.2 \times 10^{-4}$ $s^{-1}$, and the slower component had a dissociation rate constant of < $2.1 \times 10^{-5}$ $s^{-1}$. Comparison with Table 4 suggests that Cu(II) in the river water sample was probably bound to humic materials or other polyfunctional ligands.

### *Lead*

More than 90% of the Pb(II) species was taken up by the Chelex resin in 2000 seconds, and the Pb(II) components left after this time were taken up very slowly, as shown in Figure 11. Data analysis by the iterative deconvolution method[24] revealed two kinetically distinguishable components of Pb(II). The distribution of the kinetic components of Pb(II) and their dissociation rate constants are listed in Table 7. The faster component, which accounted for 89% of the total Pb(II), had a dissociation rate constant of $2.1 \times 10^{-3}$ $s^{-1}$, and the slower component had a dissociation rate constant of < $1.4 \times 10^{-4}$ $s^{-1}$. Comparison with Table 5 suggests that Pb(II) in the river water sample was probably bound to humic materials or other polyfunctional ligands.

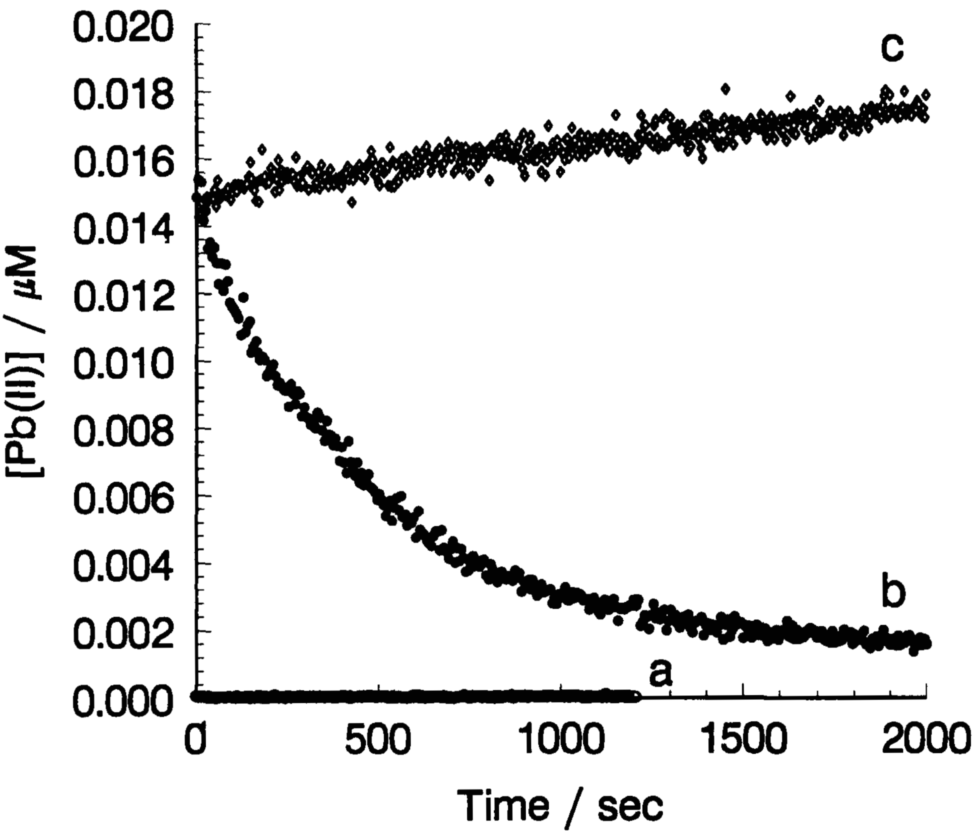

**Figure 11** Lead remaining in the sample of Rideau River surface water, as a function of time after uptake of lead by the Chelex-100 resin of 100–200 mesh in the Chelex batch technique, determined by ICP-MS. pH 5.0. a, ultrapure water without the Chelex resin; b, [Chelex] = 1% (w/w); c, the sample without Chelex resin.

## CONCLUSIONS

Inductively-coupled plasma mass spectrometry, combined with the Chelex batch technique, was found to be a useful technique for kinetic study of metal speciation in aqueous samples.

The iterative deconvolution method with the nonlinear least-squares algorithm was found to be satisfactory for the analysis of kinetic data generated by the Chelex batch technique using ICP-MS with the solution nebulization technique. This paper together with our previous paper[24] confirm the conclusions of McKinnon *et al.*[41] that the iterative deconvolution method is more effective than any other methods in terms of accuracy of results and resilience to noisy data.

The results reveal the importance of [FA]/[metal ion] ratio, and hence, the extent of occupation of heterogeneous binding sites in fulvic acid (a polyfunctional complexant) on the lability of the metal-fulvic acid complexes; the measured dissociation rate constants are weighted average values measured by the analytical window of the method. Although the analysis of the data indicated discrete sets of rate constants and hence heterogeneous binding sites in fulvic acid distinguishable by their rates of dissociation, the possibility remains that a polyfunctional complexant such as fulvic acid may have a continuous range of affinities for cations and a continuum of binding sites with associated continuous range of dissociation rate constants.

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