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KINETIC STUDIES OF ALUMINUM AND COPPER
SPECIATION IN THE AQUATIC ENVIRONMENT

by

JULIA YANJIA LU, B. Sc., M. Sc.

A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfilment of the requirements for the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario

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**"KINETIC STUDIES OF ALUMINUM AND COPPER
SPECIATION IN THE AQUATIC ENVIRONMENT"**

submitted by

JULIA YANJIA LU, M. Sc.

in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

Chair, Department of Chemistry

Thesis Co-Supervisor

Thesis Co-Supervisor

External Examiner

1995, Carleton University

ABSTRACT

Bioavailability of metal ions to organisms, as well as their toxic effects strongly depends on the chemical speciation of the metal ions. Chemical species can be differentiated on the basis of their physical characteristics and chemical reactivity. A scheme for chemical speciation, which combines physical characterization by ultrafiltration of the dissolved metal species based on their molecular weights with chemical characterization of the dissolved metal species by their chemical reactivity, such as dissociation kinetics, has been developed and applied to samples of river surface waters, rain and snow. The kinetics of metal complex dissociation has been studied by ion-exchange by Chelex-100 cation-exchange resin using the Chelex batch technique. Assuming that in aqueous samples all of the metal complexes dissociate independently and simultaneously at their own rates and that all dissociation rates are slower than those of uptake rates of metal aquo ions by the Chelex resin in Chelex batch technique, a model for the dissociation kinetics of metal complexes has been developed and tested using samples of river surface water, rain and snow. Two analytical techniques of great sensitivity, graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS), have been tested for quantitation of metals and compared in terms of their usefulness for providing the kinetic data required for this work. It is concluded that ICP-MS has a greater potential for the resolution of labile complexes than GFAAS. The iterative deconvolution method, which uses a non-linear regression algorithm, has been applied to the analysis of kinetic data. The assumptions made in the kinetic model have been verified and the experimental conditions optimized

using model solutions containing metal ions and organic complexants. The Chelex batch technique, the kinetic model and the iterative deconvolution method have been validated using model systems, Cu-EDTA and Cu-NTA. Kinetic studies of chemical speciation have revealed that aluminum and copper are present in snow and rain waters, both as aquo ions and as simple inorganic complexes of organic ligands, and are bound to polyfunctional complexants or colloidal macromolecular materials in samples of Rideau River surface waters.

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CHAPTER 1 INTRODUCTION

1-1 *Chemical speciation*

A given element may be present in aqueous solutions in different chemical forms including molecules, anions or cations. For example, carbon may be present as carbonate in the forms of H_2CO_3 , HCO_3^- and CO_3^{2-} and nitrogen may be present as NH_4^+ , NO_2^- , NO_3^- . The term 'species' refers [1,2] to a specific molecule, ion or configuration in which an element may occur, or a distinct group of atoms consistently present in different compounds or matrices. Each species has its characteristic chemical reactivity and lifetime and it will react differently in different matrices or environments. Many species have groups that are strongly bound to a central atom and other groups that are only weakly bound. When the matrix changes the weakly bound groups may be replaced. The part of the species that remains unchanged through a matrix-generated transformation is called the "parent species", or "conceptional species". The species that actually exists in the environment is the "matrix species" or "functional species". This means that the term "chemical species" is actually an idealized concept. Analytical procedures generally convert the matrix species into a chemical form that is recognizable by the analytical instrument used for its quantification. The species which is quantified is called the "analyte species" and quite often is operationally defined. As long as an operational definition of the species is considered only as a first approach to species quantification, it is acceptable, but every effort must be made to identify and quantify the species. Only then can an understanding of the process under study be obtained.

Speciation may be loosely defined as the study of the occurrence and characterisation of various species of an element [3]. More specifically, speciation is:

- (1) the analysis of chemical species leading to their identification and quantification in a defined sample;
- (2) the description of the abundance (or numerical distribution) of species of an element in a defined sample;
- (3) the reactivity of a given species;
- (4) the transformation of one species into another.

Chemical species and their distributions depend on numerous physical, chemical, and biological factors. These factors include the general conditions such as ionic strength, temperature, pH, the concentrations and nature of inorganic ligands (e.g., HCO_3^- , CO_3^{2-} , F^- , Cl^- , SO_4^{2-}), organic ligands (e.g., humic materials, natural organic acids, peptides, polyaminocarboxylates) and particulate matters with surface sites available for metal binding. Also, kinetic conditions are important, since solutions are not necessarily at thermodynamic equilibrium and ligand exchange reactions can be quite slow. Rates depend on pH, polarizability, and the nature of ligands, including water. Redox reactions also can be slow and some are highly pH-dependent. Photoinduced redox reactions can maintain nonequilibrium conditions.

The total concentration of the element can be used to assess its environmental impact only if it is present in the environment as a single species. This condition is met only very rarely. The precise determination of the total amount of an element is not an easy task. Very few analytical methods measure the total amount of an element in all its

forms. Most analytical procedures actually measure only single species or groups of species, sometimes previously unrecognized.

The determination of species is a more complex task than the determination of total element concentrations. Analytical procedures of sufficient sensitivity and specificity are not available to determine the species of many environmentally significant elements, which frequently occur at very low concentrations. At present, most efforts in species determination are directed towards the identification and quantification of chemical species in isolated samples. Since, during sampling, storage, and analysis of the sample species, transformation may occur, appropriate action must be taken to ensure that the species to be determined does not change during the interval between sampling and analysis. Reliable methods for the preservation of the original distribution of the species do not yet exist, and the preservation of the original distribution of species during sample storage is most important. The ideal analytical method would determine species directly *in situ* and *in vivo*, noninvasively and nondestructively, and would allow the transformation of the species to be monitored over time.

In the natural aquatic environment, chemical species of a metal may include [4], for example, simple ionic species, inorganic complexes, organic complexes, lipid-soluble complexes, organometallic species, metals absorbed on colloidal particles, metals absorbed or assimilated by a living organism. The determination of the abundance and distribution of trace metals in the environment, their accumulation by organisms, their bioavailability, and their toxicity to terrestrial and aquatic organisms, including humans, can be understood only in terms of trace metal speciation.

1-2 *Chemical speciation, bioavailability and toxicity*

Living organisms may regulate metal concentration by uptake and/or by excretion. In polluted waters, however, living organisms may show a tendency to bioconcentrate metals. Lipophilic metal species (e.g., methylmercury) may bioconcentrate by a factor of 10^6 to 10^8 in fish [5]. Free and weakly complexed metals show a bioconcentration factor of 10^2 to 10^5 in biological cells [6-8]. Bioavailability is the ability of a chemical species of an element to meet the physiological requirement of an organism. It is influenced by the efficiency of intestinal absorption, by transport of species to sites of action, and by the utilization of active sites. Three groups of species have been identified as contributing to the bioavailable fraction: ionic metals [9-11], metals in weak complexes [12,13] and lipid-soluble metals [14]. Two mechanisms of assimilation of dissolved species by unicellular organisms have been proposed and are illustrated [15] in Figure 1:

- (1) direct transfer of the species (usually hydrophobic) through the cellular membrane;
- (2) dissociation of complexes (often hydrophilic or large species) prior to their uptake by the cellular membrane.

The latter mechanism depends on the chemical potential gradients between the external medium, the membrane surface, and the intracellular medium, the displacement of M tending towards the phase wherein its chemical potential is the lowest. The transfer is also controlled by the availability of the hydrated, 'free' form of metal ion M, which is limited by the type of complexing ligands, the concentrations of the complexing ligands, and the dissociation rates of the complexes in the external medium. These mechanisms

Figure 1 Schematic diagram of metal uptake through cell membrane. L_1 = external medium ligand; L_2 = 'transporter' ligand; L_3 = complexing sites on membrane; L_4 = complexing agent inside cell; P = membrane protein channel; M_s = metal ion M adsorbed on site eventually enabling its transport through the protein channel [15].

indicate that the uptake tendency of the dissolved species varies with the type of species present in the external medium.

When the capacity of a cell to detoxify accumulated metal is exceeded, damage to cytoplasmic constituents will occur. This is the toxic effect. Symptoms of intracellular toxicity may include ultrastructural deformities, reductions in cell division rate, respiration, photosynthesis, motility, electron transport activity and ATP production. Since only some forms of a given metal can penetrate the biomembrane to cause a toxic effect, metal toxicity to aquatic organisms cannot be gauged by measuring the total concentration. Studies of toxicity suggest that ionic or uncomplexed metal is the toxic form [16] and complexation with organic materials reduces metal toxicity in the oceans [17-19] and in rivers and lakes [20, 21]. Since molecules of different size may have different complexing ability and different kinetic properties, the size of chemical species is an important component of metal bioavailability. For example, Cd toxicity of *Simocephalus Serrulatus* decreases with increasing molecular size of natural organic material [22] and the highest molecular-weight fractions of soil humics lower the availability of Cu to wheat [23].

Two metals of great importance in the environment are aluminum and copper. Aluminum is a ubiquitous substance in the environment. Humans are exposed to aluminum from a variety of sources, including drinking water, food, ambient air, occupational settings and consumer products. The elevated total aluminum content in aquatic and marine plants near industrial and municipal waste outfalls [24,25] suggests that aluminum can be accumulated by living organisms. As pointed out by Hutchinson

[26] there is a long history of the role of aluminum in contribution to toxicity in aquatic and terrestrial organisms. The recent public concern about the toxicity of aluminum in the natural environment reinforces its importance in public health. The available evidence points to a strong correlation between aluminum and toxicity [27,28]. There is considerable evidence to show that cognitive impairment is related to aluminum in drinking water [29]. More importantly, the toxicity of aluminum depends on its speciation. For example, hydroxy species of aluminum are found to be the most toxic [30,31] and organic ligands reduce the toxicity of aluminum to fish [32]. Since the increased concentration of aluminum in the aquatic environment, due mainly to acid rain, may be linked to a rise in the frequency of cognitive disorders such as Alzheimer's disease [33], it is an urgent matter to understand the toxicity of the various aluminum species in the natural environment.

Copper is highly toxic to most species of aquatic plants [34], invertebrate species [35], fish [36] and humans [37]. Like aluminum, the toxicity of copper also strongly depends on the species of copper. Many studies have suggested that ionic copper (Cu^{2+}) and its hydroxides ($\text{Cu}_2(\text{OH})_2$, CuOH^+) are the most toxic [38] and that the presence of complexing ligands reduces copper toxicity [39-41].

Because the matrix of natural waters is complicated and aluminum and copper speciation are governed by inorganic and organic ligands, aluminum and copper speciation in the aquatic environment are still poorly understood. Further research on chemical speciation of these metals is necessary.

1-3 *Critical review of the techniques and the methods used for chemical speciation*

A variety of analytical techniques and methods have been used to determine metal speciation. On the one hand, some techniques may use direct detection and measurement of a particular metal species without previous separation. An example of this is ion-selective electrode potentiometry [42]. On the other hand, metal species may be separated by various methods and each fraction analyzed separately. Filtration [43], ultrafiltration [44], centrifugation [45], dialysis [46], gel filtration [47], ion exchange resin [48], solvent extraction [49], electrophoresis technique [50] and others are used to separate one of the species such as a free ion, an inorganic complex, or an organic complex. Mass spectrometry, atomic absorption spectrometry, electrochemical techniques such as anodic stripping voltammetry and other analytical techniques with high selectivity and sensitivity are then used to detect and measure the species separated. This approach is currently the most widely used method in speciation studies of natural waters.

Separation of metal species is based on differences in some physicochemical properties of the metal species, for examples, ionic charge, chemical reactivity or molecular size. Filtration and ultrafiltration are the most commonly used techniques for separating metal species according to their size. The principles of these technique are simple and straightforward. More details will be given on these techniques in Chapter 2.

There are two approaches for separating metal species according to their chemical properties: thermodynamic and kinetic. With the thermodynamic approach, it is assumed that all chemical reactions in the system have attained equilibria, governed by equilibrium

constants. In general, for any reaction between reactants and products at equilibrium, the equilibrium constant may be expressed as

$$K = \prod_j \phi_j^{v_j} \quad (1-1)$$

where the grand product $\prod$ involves both reactants and products; the stoichiometric coefficients v_j are positive for products and negative for reactants. The reactants and products in the system must satisfy not only the equilibrium constant in eq. (1-1) but also the mass balance conditions on the system. By solving the equilibrium constant equation and mass balance equations, one can obtain the concentration of each species in the system. In natural waters, however, there are many possible chemical reactions, and many of these reactions are coupled. Although some sophisticated computer programs [51,52] have been developed for computing equilibrium speciation of very complicated situations, modelling of natural water systems is still difficult because the number of reactions and the equilibrium constant for each reaction in such a system may not be known. Moreover, equilibrium models describe the chemistry at equilibrium, but not the rates by which the system reaches the equilibrium state.

The kinetic approach assumes that each species has its own chemical reactivity, which means its own formation and dissociation rate constants. If a kinetic model is constructed, and the formation and dissociation rate are measured, the rate equation and mass balance equations for the concentration of each species in the system may be solved. If the kinetics is measured over a sufficiently long time equilibrium conditions may be

achieved and the chemistry given by the kinetic model will be the same as chemistry given by the corresponding equilibrium model. For the idealized case in which the stoichiometric coefficients in a chemical reaction correspond to the kinetic reaction orders, the law of microscopic reversibility is obtained [53]. This law states that the equilibrium constant is equal to the quotient of the rate constants of the forward and the backward reaction

$$K = k_f/k_d \quad (1-2)$$

where K is the equilibrium constant and k_f and k_d are the rate constants for the forward and the backward reactions.

The most widely used techniques for kinetic studies of metal speciation are as follows:

- (1) the rate of reaction of metal ions with a selective complexing agent, such as pyrocatechol violet [54,55] or ferron [56];
- (2) the dissociation rate of a complex in the presence of a competing ligand, such as 4-(2-pyridylazo)resorcinol (PAR) [57,58].

Combinations of different approaches and methods form the basis of a number of more comprehensive schemes for resolving trace metal speciation in natural waters [59]. It has recently been recommended [60,61] that, in order to obtain the maximum amount of information on the speciation of a metal in a given sample of natural waters, speciation measurements should be made at different "analytical detection windows" because all analytical methods have limited detection windows. The analytical detection window corresponds to a limited range of a parameter value, such as stability constant,

dissociation constant or molecular weight, outside which compounds are not sensed by the detector. The analytical window may be varied by using the same analytical method but different analytical conditions, or by using different analytical methods having different analytical detection windows. Thus, one analytical approach may provide metal speciation information that cannot be obtained by another approach.

1-4 *Objectives*

The objectives of this research are:

- (1) to develop a comprehensive speciation scheme for speciation of trace metals in the aquatic environment;
- (2) to develop a technique for kinetic study of metal speciation which includes:
 - (i) development of a kinetic model;
 - (ii) evaluation of the analytical techniques for following the kinetics;
 - (iii) evaluation of the methods for the treatment of kinetic data;
- (3) to apply the scheme to aluminum and copper speciation in the aquatic environment: river surface water, rain and snow.

Filtration, ultrafiltration, anodic stripping voltammetry and the Chelex technique are included in this speciation scheme. Filtration is first used to divide the metal species into the particulate species and the dissolved species. Ultrafiltration is then used to further divide the dissolved metal species into different fractions. The dissolved metal species in each fraction are finally characterized according to their chemical reactivity at a hanging mercury drop electrode and at the Chelex cation-exchange resin. This thesis

focuses on the development and application of the Chelex batch technique for kinetic study of metal speciation in the aquatic environment.

CHAPTER 2 DEVELOPMENT OF THE SPECIATION SCHEME

The scheme used for aluminum and copper speciation is shown in Figure 2. This scheme combines physical speciation of metal species by size using filtration and ultrafiltration with chemical characterization using the chemical reactivity at a hanging mercury electrode and at chelex resin.

2-1 *Filtration and ultrafiltration*

2-1-1 *Filtration*

Filtration is a common method for separating particulate matters from fluids. The process of filtration involves passing the fluid mixture through a solid porous medium which can be a membrane filter or a packed column. In either case, particulate matters are retained on the surface of the medium or through its depth [62] by physical entrapment and chemical attachment [63]. Only membrane filters with physical entrapment are used in this research.

Membrane filters are made of different materials, for example, cellulose, including cellulose acetate, cellulose nitrate and cellulose esters and polycarbonate. The choice of membrane material depends on the requirements for the particular application such as the type of filtration, the nature and chemical composition of the sample, and the experimental conditions.

Clogging is a major problem in filtration [64-66] and can be partially solved by changing the filter when the filtration pressure exceeds up to 30 kPa [67]. Adsorptive

Figure 2 Speciation scheme. GFAAS: graphite furnace atomic spectrometry; ICP-MS: inductively coupled plasma mass spectrometry; ASV: anodic stripping voltammetry.

losses of analyte species can be minimized by preconditioning the filter. Particles retained by the membrane may increase adsorptive losses.

Filtration through a 0.45 μM membrane filter is used in this study to separate the dissolved species from the particulate forms [68]. This distinction is, of course, arbitrarily chosen, and the dissolved species include the colloidal and macromolecular matter, which may have metal species adsorbed, trapped, and complexed by the ligand groups on them. The dissolved metal species in the filtrate will be divided into fractions according to their size using the ultrafiltration technique described below.

2-1-2 Ultrafiltration

Ultrafiltration is a technique for discriminating the size continuum of dissolved species, on the basis of size at the molecular level. The technique involves the selective retention of solutes during convective solvent flow through molecular filters. Solute, colloids and species with dimensions larger than the specified filter pore size are retained while solutes smaller than the pore size of the filter pass with the solvent through the filter [69]. The filters for ultrafiltration generally consist of a thin organic polymeric hydrous gel film supported on porous polyethylene or cellulose ester bases.

Although the method is very simple in principle, a number of possible complications may affect the results. For examples, the molecular weight cut-off may not be precise if the pore size of the filter is not uniform or if solutes have a charge or irregular shape; breakthrough of solutes of larger molecular size may occur if the solvent volume in the ultrafiltration cell decreases to less than 10 % of the initial volume; interactions between the solutes and the filter materials may be important. The

differentiation of metal species by ultrafiltration is, therefore, by size, shape and charge characteristics rather than by molecular weight [70].

The purpose of ultrafiltration is to separate the dissolved metal species into convenient size groups. The metal species in each size group can then be characterized according to their chemical reactivity.

2-2 *Anodic stripping voltammetry*

The ASV technique generally uses a hanging mercury drop electrode (HMDE) and measures the concentration of free metal ions as well as easily reducible or labile metal complexes. Inert complexes are not detected [71]. In ASV, the electrodeposition step is characterized by the kinetic parameters of the dissociation of the metal complex, the thickness of the diffusion layer, and the concentration of the ligand [72]. A metal complex whose dissociation into electroactive species is fast compared to the rate of electrodeposition at a hanging mercury drop electrode in a particular experiment is called "ASV-labile" [69,70], or "very labile" [73]. In the ASV method, a water sample is mixed with an appropriate buffer solution and is then tested by the ASV technique using the potential that gives the maximum electrodeposition efficiency for the uncomplexed metal ion (least negative) as the electrodeposition potential [74]. The transient measurement time of ASV is of the order of 10^{-3} s [75], which limits ASV to measuring free metal ion or metal complexes which are removed at the HMDE during deposition [76]. The metals in natural waters which can be determined by anodic stripping voltammetry (DPASV) are copper, lead, cadmium and zinc all of which form soluble amalgams [70].

The application of ASV to metal ion speciation is based on the following two assumptions: (1) the nonlablity of metal species is the property of that species only and is not due to an interfering species; (2) each stripping peak corresponds to a single species in solution. It can be shown, however, that both of these assumptions are invalid if surfactants are present in solution [70]. The problem of differentiating between a rapidly dissociating complex and one directly reduced at the electrode, inherent in the ASV technique, can be at least partially solved using the Chelex column technique described below.

2-3 The Chelex ion-exchange techniques

Chelex-100 resin is a co-polymer of styrene and divinylbenzene containing paired iminodiacetate ions which act as chelating groups in binding polyvalent metal ions, e.g., Cu^{2+} :

For simplicity, the charge signs on the species are omitted. The structure of chelex-100 resin, as well as the binding affinity, changes with pH as shown below [77]:

Kinetics of ion exchange is similar to the adsorption, including the following steps:

(1) transport of ions from bulk solution to surface; (2) "film" diffusion; (3) pore diffusion; (4) actual exchange process; (5) outward transport of the exchanged ions through pore and the film; (6) transport of the exchanged ions from the surface to bulk solution. For a stirred system, as will be described in this study, rate-determining step is either film or pore diffusion [78].

2-3-1 *The Chelex column technique*

In the Chelex column technique, Chelex-100 is used in a column as a cation-exchange resin. This technique can be regarded as a transient technique with a time scale of measurement of seconds to minutes, which can be changed by varying the flow rate or the column length. Thus, the chelex column-labile fraction is defined operationally as the fraction of the metal taken up by the resin in this time scale which is about 3-4 orders of magnitude longer than the time scale of measurement by ASV. Hence the Chelex column-labile fraction may well include some ASV-nonlabile metal species. Since the ASV and the Chelex-column techniques are performed on separate aliquots of the same size-fraction of the ultrafiltered sample, the Chelex column-labile fraction includes the ASV-labile fraction also. It should be noted that the two techniques define a labile species in different ways. In the Chelex technique a labile species is defined according to its chemical reactivity at the Chelex cation-exchange resin. In the ASV technique the

lability of a species depends not only on its chemical reactivity at the mercury electrode but also on the diffusional flux of the species from bulk solution to the surface of the electrode.

2-3-2 The Chelex batch technique

In the Chelex batch technique an appropriate amount of Chelex resin is added into the sample of one size fraction. The mixture is stirred by a magnetic stirring bar and the uptake of the metal by the Chelex resin is monitored as a function of time. The advantage of using Chelex resin for kinetic studies of metal speciation is that no other reagents are added and therefore perturbation of the system is small.

Chelex-labile (both the column and the batch technique) metal includes free metal ion, plus metal bound in complexes weaker than the Chelex-metal complex. In addition, metal complexes stronger than the Chelex-metal complex may appear as Chelex-labile if the Chelex resin is present in considerable excess relative to the concentration of the stronger ligand [76].

The Chelex column technique was initially used to obtain a shorter time scale, compared with the Chelex batch technique, when GFAAS is used to monitor the concentration of metal in the sample. It becomes not necessary when ICP-MS replaces GFAAS as the measuring instrument. The resolution of ICP-MS is of the order of ms, which is shorter than the time scale of the Chelex column technique.

These techniques characterize metal species into free metal ions (anodic stripping voltammetry (ASV) at controlled plating potential), metal complexes which are "very

labile" (ASV-labile), "moderately labile" (Chelex column-labile), "slowly labile" (Chelex batch-labile), and "inert" (the difference between the total dissolved metal and the sum of the above three types of labile species). When the Chelex batch technique is used for kinetic studies of aluminum and copper speciation, the metal species in each size fraction are identified according to their dissociation rate constants at the Chelex resin. In this case, the fastest component generally includes free metal ions and "very labile" species and the slowest component corresponds to "inert" species, if the measurements are continued for a long period. "Slowly labile" may include several kinetically distinguishable components in the kinetic studies of metal speciation. The ultrafiltration technique, when coupled with characterization of the metal species in each size fraction, thus provides a more comprehensive picture than either the ultrafiltration technique or the three techniques (ASV, Chelex column and Chelex batch technique) can do alone. It also gives an insight into the physical and the chemical characteristics of the metal species.

2-4 *Analytical techniques*

In Figure 2, the metal species in the dissolved phase after separation are determined by either graphite platform furnace atomic absorption spectrometry (GFAAS) or inductively coupled plasma mass spectrometry (ICP-MS). These two techniques have high selectivity and low detection limits and they can be used for direct determination of trace metal concentrations in the environmental water samples.

2-4-1 *Graphite furnace atomic absorption spectrometry (GFAAS)*

Figure 3 shows the principle of an atomic absorption spectrometer. The light

Figure 3 Schematic diagram illustrating operation of an atomic absorption spectrometer.

source emits the spectrum of the element to be determined and this emitted radiation is modulated before it passes through atomic vapour of the sample. The monochromator isolates a given line, usually the strongest resonance line, and this falls on to a photo-electric detector. The output from the latter is passed to an amplifier tuned to the same frequency as the light-source modulator, so that only the signal due to the radiation from the source is amplified; any radiation emitted by the atomized sample is not modulated and produces no signal at the output of the amplifier. Graphite platform furnace atomic absorption spectrometry has detection limits several orders of magnitude lower than those of ASV but, unlike ASV, can determine all metals. Because of its extremely high sensitivity and relative freedom from interferences, direct determination of all trace metals found in freshwaters is done routinely, rapidly and inexpensively without pre-concentration. This technique provides high accuracy and precision and is excellent for direct determination of trace metals in freshwaters.

2-4-2 Inductively-coupled plasma mass spectrometry (ICP-MS)

With its high sensitivity, low detection limits, simple spectra, wide dynamic range with almost complete coverage of the periodic table, and the capability of providing element isotopic composition, ICP-MS has recently become the most important analytical tool for multielement analysis. The detection limits of ICP-MS are comparable to or better than GFAAS. Moreover, its on-line monitoring capability gives real- or near real-time resolution. This feature allows fast kinetics of labile complexes to be readily studied.

Figure 4 shows a schematic diagram of ICP-MS. The sample solution is continuously delivered to the ICP plasma torch through a nebulizer by a peristaltic pump.

Figure 4 Schematic diagram of ICP-MS.

There the sample is dried, atomized and ionized. The ionic species are then analyzed by a quadrupole analyzer and detected by a channel electron multiplier. Through the nebulization, the sample can be continuously delivered into the plasma. This feature makes ICP-MS a very useful technique for kinetic study of metal speciation as will be described in the following chapters.

A limitation of the speciation scheme represented in this thesis is that the results it generates are operationally defined and are therefore difficult to interpret in terms of bioavailability. Nevertheless the rate of dissociation of a metal species is an important property which may be correlated with toxicity. For example, the toxicities to salmon of cadmium in river water and treated sewage effluents have been reported to correlate with Chelex batch-labile fraction of cadmium [79]. The Chelex batch technique may therefore provide results which have biological significance. For comparing one water body with another, it should be possible to make meaningful observations on the basis of the speciation data concerning differences in trace metal associations. The information provided by this scheme will be of particular value when assessing metal transport in the region of an effluent outfall [76].

CHAPTER 3 CHEMICAL SPECIATION OF ALUMINUM AND COPPER, AND THE PROPERTIES OF FULVIC ACID

Aluminum and copper are the elements under investigation in this study. Their basic physical and chemical properties, and their chemical forms in aquatic solutions, will be briefly reviewed in this chapter.

Humic substances are major organic constituents of soils and are among the most important complexing ligands of metal ions in the aquatic environment [80,81]. The presence of humic substances, therefore, will affect biochemical and geochemical cycling of aluminum and copper in the aquatic environment. On the basis of solubility, humic substances are usually divided into three major fractions: (i) humic acid (HA), which is soluble in dilute alkaline solution (e.g., 0.5 N NaOH) but is not soluble in acidic medium (pH 2); (ii) fulvic acid (FA), which is soluble in both acid and base; (iii) humin, which can not be extracted by dilute base or acid. Fulvic acid, which counts for more than 90 % of dissolved humic substances, is chosen as a laboratory model for organic ligand complexation in natural waters in this study. A brief review on the properties of fulvic acid is, therefore, also included in this chapter.

3-1 *Aluminum*

Aluminum is the third most abundant element in the earth's crust. It has an ionic radius in the crystal of 0.51 Å, which is considerably smaller than other commonly encountered trivalent metal ions and it has only one oxidation state of +3. Because of

its high ratio of charge to radius, Al(III) aquo ion is the "hardest" of the trivalent ions commonly found in the aquatic environment and in biological systems. As a result of this unique property, the chemistry of aluminum in natural waters is complex and influenced by pH and the presence of fluoride, sulfate, organic matter and other ligands.

Al(III) polarizes solvated water molecules very strongly in the absence of competing ligands, giving rise to several hydrolytic species including mono- and polynuclear species of aluminum. These hydroxo complexes and their equilibrium constants [82] are listed in Table 1. The distribution curves are presented in Figure 5 [83] for total concentrations 10^{-3} and 10^{-6} M of aluminum. Because the distribution curves in Figure 5 represent equilibrium conditions that include the solid phase Al(OH)_3 , some of the species listed in Table 1 that do not appear in Figures 5 are formed in solutions which are supersaturated with respect to Al(OH)_3 . It also can be seen from Figure 5 that the distribution diagram for the 10^{-3} M system, (a), is considerably different from that for the 10^{-6} M system, (b). For the 10^{-3} M system, Figure 5 (a), the predominant species at equilibrium between pH 4.3 and 11 is precipitated Al(OH)_3 ; only a small amount of Al(OH)^{2+} is present in the pH range 3-4.3. The Al(OH)_4^- complex begins to form at pH 10 and is predominant above pH 12. For the 10^{-6} M system, Figure 5 (b), the partially hydrolyzed mononuclear complexes, Al(OH)^{2+} and Al(OH)_2^+ , form in appreciable percentages between pH 3 and 6. Solid Al(OH)_3 begins to appear at pH 5 and is predominant in the pH range 5.2-8.8. The soluble Al(OH)_4^- complex begins to form at pH 7 and is the only species present above pH 10. Despite interest for over a century, the hydrolysis of Al^{3+} remains a controversial topic.

Table 1 **Overall formation constants [82] for hydroxo complexes of Al(III)**

Complex	Log β
Al(OH)^{2+}	9.0
Al(OH)_2^+	18.7
Al(OH)_3 (dissolved)	27.0
Al(OH)_3 (solid))	33.5
Al(OH)_4^-	33.0
$\text{Al}_3(\text{OH})_4^{5+}$	42.1
$\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$	33.0

Figure 5 Distribution of Al(III) hydroxy species [83] as a function of pH. a. $[Al(III)] = 10^{-3} M$; b. $[Al(III)] = 10^{-6} M$.

Al(III) also forms complexes with other ligands [84,85] such as F⁻, fulvic acid, sulfate, thiocyanate and hydrogen carbonate. Al(III) binds firmly with negatively charged organic functional groups in acidic and neutral solutions. Complexes of Al(III) with organic oxygen-containing ligands (phenolate O⁻, carboxylates) and nitrogen-containing ligands (amines) are usually very strong. Complexation reactions between Al(III) and humic substances, polycarboxylate, hydroxycarboxylate and polyaminocarboxylate are of special interest in the aqueous environment for the following reasons: (1) many of these ligands occur in natural waters and some of them exist in the human body. Citric acid is the main low-molecular-weight carrier of aluminum in plasma; (2) most of these complexes are water soluble.

Total concentrations of aluminum in natural waters range from a few $\mu\text{g L}^{-1}$ to g L^{-1} [86,87], depending upon weathering conditions, pH, type of ligands in the waters. The concentrations of dissolved aluminum are generally low in most natural waters due to the relatively low solubility of natural aluminum minerals, but increase with decreasing pH of the waters [88]. Dissolved aluminum occurs as aquo aluminum, hydroxide, fluoride, sulfate and organic complexes [89]. Organic aluminum levels are strongly correlated with total organic carbon concentration [90].

3-2 *Copper*

Copper ([Ar]3d¹⁰4s¹) has a relative abundance of 68 ppm in the earth's crust. It is mainly present as sulfide, oxide, or carbonate. Since a filled d shell is more easily disrupted than a filled p shell, the second and third ionization energies of Cu metal are

therefore lower than those of alkali metals. Copper is able to adopt oxidation states higher than +1, and it readily forms coordination complexes. The effective ionic radius is 0.77 Å for Cu(I), 0.73 Å for Cu(II) and 0.54 Å for Cu(III). The latter is not common and is easily reduced.

The equilibrium constant for the following reaction

is of the order of 10^6 , and therefore only small amounts of Cu^+ can exist in the environment unless it is stabilized by complexing or precipitating agents. For example, Cu_2S is very insoluble ($K_{\text{sp}} = 10^{-49}$) and will likely form in a reducing environment with sulfide present. The hydrolysis of Cu^+ is very slight since it resembles the hydrolysis of the alkali metal cations. The low solubility of Cu_2O leads to the important reaction

and this reaction limits the concentration of Cu^{2+} in aqueous solutions.

The hydroxo complexes of Cu(II) and their overall formation constants [91] are listed in Table 2. The distribution of hydroxy species [92] of Cu^{2+} as a function of pH is shown in Figure 6 for total concentrations of Cu^{2+} of 10^{-1} M, (a), and 10^{-5} M, (b). It can be seen from Figure 6 that the principal hydrolysis product is the dimer $\text{Cu}_2(\text{OH})_2^{2+}$. A series of mononuclear species, CuOH^+ to $\text{Cu}(\text{OH})_4^{2-}$, evidently are formed as well. The first three are important only in very dilute solution between pH 8 and 12 and the last only in more alkaline solutions.

Total concentrations of copper in most freshwaters are found to be low [93], generally $< 0.020 \text{ mg L}^{-1}$, but may occur at much higher levels in polluted water [94].

Table 2 Overall formation constants [91] for hydroxo complexes of Cu(II)

Complex	Log β
Cu(OH)^+	6.3
Cu(OH)_2	11.8
Cu(OH)_3^-	15.2
Cu(OH)_4^{2-}	16.4
$\text{Cu}_2(\text{OH})_2^{2+}$	17.7
$\text{Cu(OH)}_2 \text{ (s)}$	19.3

Figure 6 Distribution of Cu(II) hydroxy species [92] as a function of pH. (a), $[Cu(II)] = 10^{-1} M$; (b), $[Cu(II)] = 10^{-5} M$.

Copper shows a tendency to form complexes with inorganic and organic ligands. It therefore exists in a variety of dissolved and particulate chemical forms in natural waters. The dissolved forms can include the hydrated cations, Cu^{2+} complexes with inorganic ligands (e.g., CO_3^{2-} , OH^- , and Cl^-) and complexes with various naturally-occurring substances (e. g., phytoplankton metabolites or terrestrial humic substances) and anthropogenically-induced organic ligands (e.g., EDTA, NTA). In some freshwaters, more than 90 % of total Cu may be bound to humic substances [95]. Particulate forms which may bind copper range from colloids to large particles ejected from the bottom sediments by episodic events. Binding to colloids and particulates results in significant removal of copper from water body and may affect transport of copper downstream.

3-3 *Fulvic acid*

The concentration of dissolved organic carbon in natural water is typically 1-100 mg L^{-1} . Typical average values are 1 mg L^{-1} in rainwater and 2-10 mg L^{-1} in rivers [96]. Fulvic acid (FA) constitutes 90 % of the dissolved organic carbon in natural water, and, through complexation reaction with trace metals, has an important effect on trace metal concentration, on speciation, and on cycling of metal in the environment.

Fulvic acids are polydisperse hydrophilic polymers consisting of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O), with C and O being predominant. Elemental compositions of fulvic acids may vary with origins. For example, elemental analysis of isolated fulvic acids from five different origins gave compositions ranging from 49.4 to 57.9 % of C, 30.4 to 40.2 % of O, 3.4 to 5.9 % of H, 2.2 to 3.9 % of N, and

0.9 to 2.3 % of S [97]. Elemental compositions [98] of Laurentian fulvic acid, which is used in this study, are listed in Table 3.

Molecular weights ranging from a few hundred to several millions have been reported for humic substances. Molecular weights for fulvic acids are generally lower than those for humic acids. For the Laurentian fulvic acid that is used in this study, the range of the molecular weight and the distribution [99] are listed in Table 4. The results show that the higher the molecular weight fractions, the darker is the colour, suggesting either that the higher molecular weight fractions of Laurentian fulvic acid contain more conjugated chromophores than the lower molecular weight fractions or that intramolecular interactions contribute to a red-shift in absorbance. The increase in the pH of solutions made from lower molecular weight fractions to higher molecular weight fractions indicates that the highest molecular weight fraction has the lowest acidic group content per unit mass.

Although FA is chemically heterogeneous in nature and cannot be defined by a unique molecular structure, it can be described by a general model structure consisting of an extended network of aromatic nature with aliphatic, oxygen, nitrogen or sulphur bridges, bearing aliphatic, glucidic, peptidic and lipidic surface chains and chemically active functional groups of various nature, including carboxyls, phenolic and alcoholic hydroxyls, which confer on the macromolecule an acidic character [100,101]. Structural studies by FT-IR revealed that the major complexing groups in Laurentian fulvic acid are carboxylic groups (8.60 mmol g^{-1}), phenolic groups and alcoholic groups (3.03 mmol g^{-1}) [98,99]. Metal binding capacity of a given fulvic acid may be a function of the analytical

Table 3 **Element analysis and functional groups in the Laurentian fulvic [98]**

Element	Content (%)	Functional group	Content (mmol g ⁻¹)
C	45.1	Carboxylates A	5.11
O + S	49.7	Carboxylates B	3.49
H	4.1	Phenol	3.03
N	1.1		

Table 4 **Physical properties of the Laurentian fulvic acid fractions [99]**

MW range	Colour of the solid	%	pH (0.5 g L ⁻¹)	Colour of the solution (0.5 g L ⁻¹)
> 30000	Deep brown	37.0	3.00	Orange-yellow
10000-30000	Brown	2.8	2.95	Yellow
5000-10000	Brown	7.2	2.92	Yellow
1000-5000	Yellow-brown	15.5	2.87	Pale Yellow
< 1000	Yellow	37.5	2.84	Pale Yellow

technique used for the measurements. Because of chemical and steric differences in their neighbouring groups, the coordination sites on fulvic acids may well have a continuous range of affinities for metals as well as H^+ . Also, as a result of conformational changes due to electrostatic interactions among the various functional groups on a single molecule, the coordination properties of the molecule may depend on the extent of cation binding and on the ionic strength of the solution. Furthermore, electrostatic attraction and repulsion from neighbouring ionized groups may affect the metal affinity of a given group, thus making the free energy of complexation, and hence the complexation constant, dependent on the extent of cation complexation of the ligand, particularly its protonation.

CHAPTER 4 KINETIC STUDIES OF METAL SPECIATION USING THE CHELEX BATCH TECHNIQUE

It is well known now that the bioavailability of an element depends on both the chemical species in which the element is present in the environment and the rates of its biological uptake [102-105]. If the metal complexes in freshwaters are not sufficiently labile for the dissociation equilibria to be established in the time required for the measurements, then the dissociation kinetics of the metal complexes will determine the amount of the metal aquo ions available in the freshwater system. Since many metal complexes in freshwaters are not sufficiently labile, kinetic studies of such metal complexes are important for understanding the bioavailability of metals, metal speciation, and metal transport in the aquatic environment.

Kinetic methods were first used for analyzing multielement systems [106,107]. Later, the application of such methods has been expanded to chemical speciation [108-114]. All these studies were based on the measurement of the kinetics of components transferring from naturally-occurring forms to complexes with a probe ligand, and the concentration of either the product(s) or the reactant(s) was monitored as a function of time. In this study, the Chelex cation-ion-exchange resin was used as the probe ligand to study aluminum and copper speciation in the aquatic environment. The kinetic analysis of chemical speciation is based on the following kinetic model.

4-1 *The kinetic model*

The kinetic model was developed to study the dissociation kinetics of ML, where ML represents the metal ion bound to a ligand L or to various sites of L, which is a polyfunctional complexant. All of the ML complexes dissociate independently and simultaneously at a rate that depends on the nature of the ligand or the nature of the functional group, its position on the complexant, L, and the residual charge.

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

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 (4-1) 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 dissociation reaction as shown by equation (4-2):

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:

The model assumes that: 1) reaction (4-2) is first-order; 2) reaction (4-3) is much faster than reaction (4-2), so that reaction (4-2) becomes the rate-limiting step, and the rate of

loss of M from the solution then represents the kinetics of the dissociation of the metal complex, ML_i ; 3) that ML does not directly (i.e. without pre-dissociation) react with the Chelex resin. The direct reaction, represented as

is, however, a possibility if ML or its protonated form is a positively charged species at the pH 5.0 used for the kinetic measurements.

If these above assumptions are fulfilled, then the sum of the concentrations of all components remaining in the sample at time t can be described as

$$C(t) = \sum_{i=1}^n C_i^0 \exp(-k_i t) \quad (4-5)$$

where C_i^0 is the initial concentration of ML_i . The assumptions 1 and 2 have been experimentally verified and will be discussed in a later section. Assumption 3 could not be verified directly, but under the conditions that the Chelex resin is in large excess and that reaction (4-4) occurs independently and simultaneously for each ML_i , then the kinetics of uptake of ML_i by the Chelex can also be described by equation (4-5).

Compared with the kinetic models developed by Figura and McDuffie [75], which assumed that the rate-determining step was reaction (4-3), the model in this thesis assumes that reaction (4-3) is much faster than the dissociation reaction of metal complexes. A large excess of chelex resin is used in the experiments to satisfy this assumption and the results, as will be shown later in chapter 6, justify this assumption.

4-2 *Methods for analysis of data from kinetic studies*

Cabaniss [115] in his study of pH and ionic strength effects on Ni(II)-fulvic acid dissociation kinetics critically evaluated five data analysis methods: a Laplace transform technique [108,109] and four statistical approaches. He concluded that two of the methods, non-linear regression and non-linear regression with component stripping, produce a smaller number of parameter sets and are more useful for kinetic modelling than the other three methods. In their study of the deconvolution of photoluminescence data, McKinnon *et al.* [116] critically examined seven numerical deconvolution methods, including Laplace transform. They concluded the iterative deconvolution method was "the most successful and reliable of the deconvolution methods tested" and recommended its use. 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 rate constant and the initial concentration of each component.

Two methods will be used to illustrate the analysis of the data without any prior knowledge or assumption about the number of components or the rate constants for dissociation. First, a simple graphical method [117] and second, a direct non-linear regression analysis of equation (4-5) following the method outlined by McKinnon *et al.* [116] will be examined for the conditions under which the number of components may be determined and reliable values for the kinetic parameters may be obtained. Simulated data was used to illustrate the usefulness of the two methods. Data were simulated using a mixture of three components according to the following equation:

$$C(t) = C_1^0 \exp(-k_1 t) + C_2^0 \exp(-k_2 t) + C_3^0 \exp(-k_3 t) \quad (4-6)$$

The values for the rate constants, k_i , and the initial concentrations, C_i^0 , were arbitrarily chosen so that $k_1 / k_2 = k_2 / k_3 = 2$ or 3 . C_1^0 , C_2^0 and C_3^0 were varied by factors of 10 . Poisson noise was added to the simulated data. The computer program used in this study is a non-linear regression package [118] (an on-line interactive routine on the computer network at Carleton University) which uses the Levenberg-Marquardt method for computing parameter estimates.

4-2-1 *The graphical method*

If metal ions are lost from solution by first-order processes a plot of $\ln$ (concentration of metal ion) as a function of time will have curvature if dissociation of more than one metal complex contributes to the total loss of metal ion. The rate of dissociation of the complexes must be separated by a series of subtractions of the concentration of each component from the total concentration remaining, beginning with the component with the slowest rate. At sufficiently long times all but the slowest component will have decayed and a linear segment will be unambiguously observed from which its rate constant may be obtained. The initial concentration is obtained by extrapolation to zero time. The concentration of this species is then subtracted from the total concentration, leaving a clear linear segment corresponding to the second slowest component in the mixture. The procedure may be repeated as many times as required. The values of the rate constants obtained by this procedure may be further refined by non-linear regression analysis of equation (4-6).

The results of the analysis for the system containing equal concentrations of each component by the graphical method is illustrated in Figure 7. The first inset (curve b) shows the logarithmic curve for the decay for all three components, clearly showing curvature, and the second inset (curve c) shows the curve for the remaining two components after subtraction of the slowest. The curvature is much less, but discernible. Values for k_1 , k_2 and k_3 and C_1^0 , C_2^0 and C_3^0 were thus determined by the graphical method for each set of conditions. The actual values and the values obtained by this analysis are summarized in Table 5. This Table also contains the results obtained by the iterative deconvolution method described in the next section.

4-2-2 *The iterative deconvolution method*

The iterative deconvolution method is based on non-linear regression analysis of kinetic data. Equation (4-5) is fitted by non-linear regression assuming a number of components, starting with one and increasing until the sum of squares of the weighted residuals, defined as

$$\text{Sum of squares of weighted residuals} = \sum \left[\frac{C(t) - C_T(t)}{C(t)^{1/2}} \right]^2 \quad (4-7)$$

achieves a minimum value, where $C(t)$ is the experimental value and $C_T(t)$ is the calculated value using the parameters obtained from the iterative deconvolution method.

The plot of weighted residuals over the course of the reaction gives a visual indication of the adequacy of fitting for each point. With the correct number of components the plot of the weighted residuals should be randomly and uniformly distributed about zero throughout the course of the reaction. Non-uniform distribution of

Figure 7 Graphical method for the determination of the kinetic parameters for a simulated system with $k_1 / k_2 = k_2 / k_3 = 2$, $k_1 = 0.04$, $C_1 = C_2 = C_3 = 10$.
a, Plot of C as a function of time; b, plot of $\ln C$ as a function of time; c, plot of $\ln (C - C_3)$ as a function of time.

Table 5 Kinetic parameters determined for the simulated data ($k_1 / k_2 = k_2 / k_3 = 2$) by the graphical method and the iterative deconvolution method

System	Parameter	Values assigned	Values determined	
			Graphical method	Iterative deconvolution method
I	C_1	10.0	5.86	11.2
	C_2	10.0	13.3	8.66
	C_3	10.0	10.8	10.1
	k_1	0.0400	0.0475	0.0375
	k_2	0.0200	0.0231	0.0192
	k_3	0.0100	0.0102	0.0100
II	C_1	1.00	1.48	0.245
	C_2	10.0	10.5	10.4
	C_3	10.0	9.60	10.4
	k_1	0.0400	0.0536	0.0207
	k_2	0.0200	0.0185	0.0214
	k_3	0.0100	0.0100	0.0101
III	C_1	100	90.9	101
	C_2	10.0	19.9	9.13
	C_3	10.0	9.94	9.49
	k_1	0.0400	0.0423	0.0390
	k_2	0.0200	0.0226	0.0184
	k_3	0.0100	0.0100	0.00992
IV	C_1	10.0	10.7	10.6
	C_2	1.0		0.0845
	C_3	10.0	10.0	10.4
	k_1	0.0400	0.0365	0.0390
	k_2	0.0200		0.0394
	k_3	0.0100	0.0100	0.0100

Table 5 (cont'd) Kinetic parameters determined for the simulated data ($k_1 / k_2 = k_2 / k_3 = 2$) by the graphical method and the iterative deconvolution method

System	Parameter	Value assigned	Values determined	
			Graphical method	Iterative deconvolution method
V	C_1	10.0		9.09
	C_2	100	106	101
	C_3	10.0	13.9	10.1
	k_1	0.0400		0.0414
	k_2	0.0200	0.0211	0.0201
	k_3	0.0100	0.0106	0.0100
VI	C_1	10.0	7.24	10.4
	C_2	10.0	12.9	9.91
	C_3	1.00	1.02	0.690
	k_1	0.0400	0.049	0.0391
	k_2	0.0200	0.0215	0.0194
	k_3	0.0100	0.0100	0.00930
VII	C_1	10.0	14.8	2.24
	C_2	10.0		16.0
	C_3	100.0	105	102
	k_1	0.0400	0.0404	0.629
	k_2	0.0200		0.0278
	k_3	0.0100	0.0101	0.0100

residuals, observed as curvature, indicates missing terms in the model [119].

The iterative deconvolution method was tested by the same simulated data sets as used in testing the graphical method. The values of the sum of squares of the weighted residuals for the simulated data for equal concentration of all three components and for the cases when C_2 was reduced to one and increased to 100 are given in Table 6. In each system the sum of squares of the weighted residuals showed no change in increasing the number of components from 3 to 4 and three components only are kinetically distinguishable. The weighted residuals as a function of time for the simulated system where all components are of equal concentration are shown in Figure 8. The distribution of the residuals with 3 components is better than with 2 components. Increasing the number of components to four generally caused no significant change in the distribution of the weighted residuals. Analysis by non-linear regression using four components, however, gave unrealistic and in some cases negative kinetic parameters.

When the choice is made of the number of components non-linear regression yields the kinetic parameters. The values of the rate constants and initial concentrations obtained by the iterative deconvolution method are given in Table 5, where they may be compared with the values obtained by the graphical method. The values for the rate constants and initial concentrations determined by the iterative deconvolution method were usually better but sometimes worse than those obtained by the graphical method. In the graphical method a component was sometimes missed completely whereas the iterative deconvolution method always gave values for the rate constant and initial concentration of each component chosen.

Table 6 Sum of squares of the weighted residuals of iterative non-linear regression for the simulated 3-component systems. $k_1/k_2 = k_2/k_3 = 2$, $k_1 = 0.04$, $C_1 = C_2 = 10$

C_2	Number of components fitted	Sum of squares of the weighted residual
10.00	1	10.3
	2	0.0740
	3	0.0530
	4	0.0530
1.00	1	9.56
	2	0.0620
	3	0.0602
	4	0.0602
100.0	1	8.11
	2	0.133
	3	0.0646
	4	0.0646

Figure 8 Plots of the weighted residuals as a function of time for kinetic analysis of a simulated system with $k_1 / k_2 = k_2 / k_3 = 2$, $k_1 = 0.04$, $C_1 = C_2 = C_3 = 10$. Bottom trace, 2-component-fitting; top trace, 3-component-fitting.

The accuracy of the analyses varied considerably among the three components. In the graphical method, rate constants and initial concentrations of the third component (the slowest) were determined within a few percent of the assigned values, except when $C_2 / C_3 = 10$. The first component was the most poorly analyzed, the values having been obtained following two subtractions. Also, when the concentration of the component being subtracted was greater than that of the next slowest component by a factor of 10, the analysis for the latter was unreliable and sometimes indeterminate. As an example, analysis by the graphical method for the case where the concentration of C_2 was reduced by a factor of ten is shown in Figure 9. The second inset shows no curvature, indicating that the second component was effectively lost between the first and the third. Values for C_2 and k_2 were not obtained for this case by the graphical method. Although the values of the sum of squares of the weighted residuals for the same system, as shown in Table 6, decrease a bit when the number of components increases from 2 to 3, the distribution of the weighted residuals, as shown in Figure 10, show the fit with three components is not an improvement over that with two components. The iterative deconvolution method therefore does not necessarily provide a more reliable indication of the number of components than the graphical method, even though kinetic parameters were evaluated from the non-linear regression analysis with three components.

The limitations in the relative ratio of concentration of each species which may be resolved from the other components and for which kinetic parameters may be obtained are important in analysis of freshwaters because concentrations of complexes may vary widely. The greater the difference in the values of the rate constant the greater may be

Figure 9 Graphical method for the determination of the kinetic parameters for a simulated system with $k_1 / k_2 = k_2 / k_3 = 2$, $k_1 = 0.04$, $C_1 = C_3 = 10$, $C_2 =$

1. a. Plot of C as a function of time; b, plot of $\ln C$ as a function of time; c, plot of $\ln (C - C_3)$ as a function of time.

Figure 10 Plots of the weighted residuals as a function of time for kinetic analysis of a simulated system with $k_1 / k_2 = k_2 / k_3 = 2$, $k_1 = 0.04$, $C_1 = C_3 = 10$, $C_2 = 1$. Bottom trace: 2-component-fitting; top trace: 3-component-fitting.

the difference in the concentration of each species.

The resolution of the three components is significantly improved when the ratio of rate constants is increased to three. The values of the rate constants and initial concentrations obtained by both the graphical method and the iterative deconvolution method for the simulated data for equal concentration of all three components and for the cases when C_2 was reduced by a factor of 10 and increased by a factor of 10 are given in Table 7. The kinetic parameters for the system where all components are of equal concentration were obtained with errors less than 3 %. For the systems where the concentration of C_2 was altered, the iterative deconvolution method gave better results than the graphical method. When the concentration of one component was 10 time larger than the next faster component, the graphical method failed to detect the faster component.

These limitations to the analysis by the graphical method arise mainly from the difficulty in choosing the range of time over which the logarithmic function is linear. The degree of noise in the data clearly contributes to this difficulty. There is no objective method for this and success depends heavily on the judgment of the analyst. The iterative deconvolution method has the advantage of being entirely objective but its limitations are nevertheless apparent in the values of Table 5 and 7.

Table 7 Kinetic parameters determined for the simulated data ($k_1 / k_2 = k_2 / k_3 = 3$) by the graphical method and the iterative deconvolution method

System	Parameter	Value assigned	Values determined	
			Graphical method	Iterative deconvolution method
VIII	C_1	10.0	9.82	10.0
	C_2	10.0	10.2	9.94
	C_3	10.0	10.3	9.96
	k_1	0.0900	0.0918	0.0885
	k_2	0.0300	0.0302	0.0298
	k_3	0.0100	0.0101	0.00998
IX	C_1	10.0	10.5	8.96
	C_2	1.00		1.94
	C_3	10.0	10.1	10.1
	k_1	0.0900	0.0811	0.0948
	k_2	0.0300		0.0452
	k_3	0.0100	0.0100	0.0100
X	C_1	10.0		9.71
	C_2	100	108	100
	C_3	10.0	10.5	10.2
	k_1	0.0900		0.0902
	k_2	0.0300	0.0313	0.0301
	k_3	0.0100	0.0101	0.00100

5-1. *Materials and reagents*

Screw-capped polyethylene and Teflon bottles (500, 1000, 2000 and 5000 mL capacity) were used as reactors and sample storage containers. These bottles were pre-cleaned following the procedure described below. The reactors were equilibrated with the samples before the kinetic measurements.

A 0.45- μm membrane filter (CN-6 Metrice, 47 mm diameter, 150 μm thickness, Gelman Sciences, Inc.) was used to separate particulates from the dissolved species in this study. This filter is made of mixed cellulose esters and has the advantage of low background interference and excellent water flow rates (65 mL min⁻¹ cm⁻² at 520 mm Hg).

A stirred ultrafiltration cell (model 8200, Amicon) and disc membrane filters YM100, XM50, YM10, YM5, YM1 and YC05 (Amicon, 62 mm diameter) which have molecular weight cut-offs 100,000, 50,000, 10,000, 5,000, 1,000 and 500 with nominal pore size ranging from 5 to 1.1 nm, respectively, were used to divide the dissolved species in the water samples into size fractions.

Chelex-100 cation exchange resin (Bio-Rad, 50-100, 100-200 and 200-400 mesh, sodium form) was equilibrated with the NaOAc-HOAc buffer at the pH of the samples. This pre-treatment of the Chelex resin is used to minimize the change in pH of the sample during the kinetic measurements, because a buffer cannot be used for this purpose, as will be stated later. Because the dryness of the resin affected its properties, and hence

changed the pH of the sample during the kinetic measurements, the resin was isolated from the buffer solution immediately before the kinetic measurements. The NaOAc-HOAc buffer was prepared by adding 59.0 mL of concentrated pure acetic acid (A.C.S., Anachemia) to about 1 L of ultrapure water. The pH of this solution was adjusted to 5.0 by adding 6 N NaOH (reagent grade, Fisher Scientific) and the solution was diluted to 2 L with ultrapure water. Since the monitoring of the signal was started 18 seconds before the resin was added, any contamination of the resin from the pre-treatment would be indicated by a sudden increase in the signal. In case of any contamination, the experiment was terminated.

The Laurentian fulvic acid (FA), supplied by Dr. D.S. Gamble, Agriculture Canada, was prepared following known procedures [120,121] from a sample of a podzol collected from the Laurentian forest preserve of Laval University, Quebec, Canada. The properties of Laurentian fulvic acid are listed in Table 3 and 4. The phenol content was used for the calculation of the [FA]/[Metals] ratios. The stock solutions of FA were prepared by dissolving appropriate quantities of FA in ultrapure water.

The mixed-metal standard was the ICPMS-2 metal standard (Delta Scientific) containing Al, Zn, Cu, Cd, Ni, Pb and other metals ($10 \mu\text{g mL}^{-1}$ each). A stock solution containing only Cu ($1000 \mu\text{g mL}^{-1}$) was prepared by dissolving an appropriate quantity of copper metal (99.9 % pure) in nitric acid, heating, and diluting the solution to the appropriate volume with ultrapure water; the final solutions contained 1 % (v/v) ultrapure HNO_3 . A stock solution ($1000 \mu\text{g mL}^{-1}$) of aluminum was prepared by dissolving 0.5000 ± 0.0002 g aluminum powder (SPEX) in 20 mL 1 : 1 HCl (ULTREX-brand) : 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 M Ω -cm was obtained directly from an ultrapure water system, Milli-Q-Plus (Millipore Corporation).

5-2 *Cleaning procedure*

The following cleaning procedure was used. All containers used in this research project were sequentially soaked in 1 : 1 HCl : H₂O (HCl was AR grade) and 1 : 1 HNO₃ : H₂O (HNO₃ was AR grade) for one week at room temperature, followed by five rinses with ultrapure water. In order to leach out trace analytes, these containers were then soaked in 6 g l⁻¹ Na₂EDTA aqueous solution [122- 124] for 24 hours, followed by a rinse with ultrapure water. Finally, they were soaked in ultrapure water for two or more weeks until they were used. The containers used for the Chelex batch experiment and for the sample storage were pre-equilibrated with the water sample for 24 hours before use.

Based on the recommended procedures in the literature [125,126], the cleaning procedure of 0.45- μ m filters involved washing with 2M HNO₃ followed by ultrapure water, and before use, conditioning by passage of 250 mL of ultrapure water and 500 mL of sample.

In order to remove both heavy metal contaminants and organic wetting agents

which might interfere with subsequent analysis, the Amicon disc membrane filters for ultrafiltration were preconditioned [76] by successively soaking in dilute NaOH aqueous solution ($\text{pH} < 11$), 0.5 % ultrapure HNO_3 (ULTREX), and finally in ultrapure water. The ultrafilters were then stored in a 10 % ethanol in water solution until use.

5-3 *Samples*

Since both the distribution of metal species and the chemical affinity of the COOH functional group in the Chelex molecule depend on the pH, the pH for both the model solutions and the natural water samples must be maintained at a specific value so that the results obtained from different samples can be compared. Considering the cation-exchange affinity of the Chelex resin, common pH values of natural waters and aluminum and copper speciation, $\text{pH } 5.0 \pm 0.5$ was chosen throughout this work.

To test the usefulness of the Chelex batch technique for metal speciation, a series of model solutions was prepared. 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. The model solutions were prepared by spiking ultrapure water or the NaOAc-HOAc buffer solutions with appropriate volumes of standard solutions of metals and of the fulvic acid solution (0.1000 g L^{-1}). The pH (measured with a Fisher Scientific, Accumet 925 pH/ion meter) of the samples was made 5.0 using dilute HNO_3 or NaOH solutions, and the model solutions were left to stand overnight for equilibration. The pH was confirmed after the equilibration.

Surface water samples (5 L) from the Rideau River near Carleton University were

collected using a precleaned polyethylene water sampler. pH and conductivity (measured using a conductivity bridge, YSI, Model 31) were measured immediately after sample collection. To bring the concentration of the metal analyzed to appropriate levels for the kinetic study, some of the samples were spiked with standard solutions of Cu, Ni, Zn, Cd and Pb to contain a few $\mu\text{g L}^{-1}$ of each, and the pH of the sample was adjusted to 5.0 ± 0.5 . After leaving the sample to stand for two days for equilibration, the samples were filtered through a $0.45 \mu\text{m}$ filter to separate the particulate matter. The filtrate was collected and left to stand for one day for equilibration before making kinetic measurements. The pH was confirmed after the equilibration. Fluoride content in the samples of river waters was determined using an ion-selective electrode (Orion Research Inc. Model 94-09) at pH 5.5.

Samples of rain and snow were collected with a pre-cleaned 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 room temperature until the snow melted. The snow-melt was filtered through a $0.45 \mu\text{m}$ filter; the pH and the conductivity were measured before and after the filtration. The major ions in one of the snow samples were Na ($34 \mu\text{g L}^{-1}$), Ca ($383 \mu\text{g L}^{-1}$) and Mg ($26 \mu\text{g L}^{-1}$). To bring the concentration of the metals in the snow sample to appropriate levels for the kinetic study by ICP-MS, some of the snow samples were spiked with standard solutions of Al, Cu, Ni, Zn, Cd and Pb, bringing the concentration of metal ion to a few $\mu\text{g L}^{-1}$ of each metal. After leaving the spiked sample to stand for two days for equilibration, the samples were filtered through a $0.45 \mu\text{m}$ filter. The filtrate was collected and was equilibrated for one day before the

kinetic measurements were made.

5-4 *Measurement of dissolved organic carbon (DOC)*

A Total Organic Carbon Analyzer (SHIMADZU, Model TOC-5000) was used to determine the concentrations of total carbon (TC) and inorganic carbon (IC) in the samples of river surface water, rain and snow. The concentrations of DOC in the samples were calculated by subtracting the IC concentration from the TC concentration. For the TC determination, 25 μL of water sample was introduced into the analyzer and the TC components in the sample were combusted at 680 °C using the catalyst for regular sensitivity measurement (P/N 017-42801-01) to form CO_2 , which was determined by a non-dispersive infrared gas analyzer (NDIR). For the IC measurement, 50 μL of water sample was injected into the analyzer, and the IC components in the sample were decomposed by the IC reagent (a solution of phosphoric acid) to form CO_2 which was also detected by NDIR. Since the filtrates of 0.45 μm filter for all water samples, except one, were used for TC and IC determination, the differences between TC and IC were therefore DOC in the water samples.

5-5 *Aluminum and copper speciation*

5-5-1 *Determination of total concentrations in the unfiltered water sample.*

The total metal in the unfiltered water sample was determined by graphite platform furnace atomic absorption spectrometry using the following two methods: 1) atmospheric-pressure digestion; 2) high-pressure bomb acid digestion. The atmospheric-pressure

digestion was done following the procedures prescribed in the standard methods of analysis [127]. The high-pressure bomb digestion was carried out in 10 % HNO_3 solution in a Teflon-lined steel bomb by heating the steel bomb in an air oven at a temperature 150°C for four hours. The high pressure bomb digestion procedure yielded higher recoveries than the atmospheric-pressure digestion procedure and was therefore adopted for all further work.

The total metal was also measured separately in the dissolved and the particulate phases. The sum of these two values gave the total metal concentration in the water sample.

5-5-2 Determination of the total concentrations in the particulate phase

After 500 mL water sample had passed through a $0.45\ \mu\text{m}$ filter, the filtrate containing the retained particulate was transferred into a Teflon-lined bomb and digested with 20 mL of 10 % HNO_3 in an air oven at 150°C for four hours. The solution was then transferred into a 500-mL volumetric flask and diluted to the mark with ultrapure water containing 1 % HNO_3 . Aliquots of this 500 mL solution were analyzed for the metal content by graphite furnace atomic absorption spectrometry.

5-5-3 Speciation of metals in the dissolved phase

The filtrate from the $0.45\ \mu\text{m}$ filter was used for studies of the speciation of dissolved metals, employing ultrafiltration, the Chelex-100 column and the Chelex-100 batch technique.

5-5-3.1 Ultrafiltration. When filtering a sample, the first 10 % and the last 50 % of the ultrafiltrate were discarded, collecting only the middle fraction. The initial

volume might contain a reduced concentration of species in the ultrafiltrate because of dilution by water trapped in the filter [126] and the last 50 % of the ultrafiltrate often contained higher concentrations of organic carbon because of leakage of high-molecular-weight substances retained above the membrane [128].

5-5-3-2 The Chelex column technique. In the Chelex column technique, the water sample was passed through a Chelex-100 column, which contained 5 grams of Chelex-100 resin, at a flow rate of 2 mL min⁻¹. The effluent was collected for determination of the Chelex column-nonlabile metal species. Subtraction of the Chelex column-nonlabile species from the total dissolved metal gave the Chelex column-labile metal species.

5-5-3-3 The Chelex batch technique. Figure 11 shows the schematic diagram of the Chelex batch experiment. The reactor was designed to allow the clear sample solution to be withdrawn continuously through a filter made of nylon membrane, placed in front of the outlet tube, thus separating the solution from the Chelex resin. The pre-treated Chelex resin was added to a sample solution (400 ml) and the mixture was stirred with a Teflon-coated magnetic stirring bar. The time at which the Chelex resin first came in contact with the sample in the reactor was taken as the zero time. The sum of the concentrations of all the components of the metal remaining in the solution was monitored as a function of time using either ICP-MS or GFAAS. The temperature was controlled at 20 ± 0.5 °C. The pH of the sample was also monitored throughout the Chelex-100 batch experiment. Changes in the pH were found to be $< \pm 0.5$ for the unbuffered samples and $< \pm 0.02$ for the buffered samples.

Figure 11 Schematic diagram of the apparatus for the Chelex batch experiment.

5-6 *Measurement of metal concentrations*

5-6-1 *Graphite furnace atomic absorption spectrometry (GFAAS)*

For this analysis an atomic absorption spectrometer (Perkin Elmer, Zeeman, Model 5000 equipped with an autosampler), an HGA-500 graphite furnace, pyrolytically-coated graphite tubes and laboratory-made platforms fabricated from pyrolytic graphite were used. Aliquots of the test solutions (1 mL) were acidified with 10 μL of concentrated nitric acid in small plastic vials. 10-20 μL of this acidified test solution was injected into the graphite furnace and deposited at the same place on the graphite platform. The solution was dried, pyrolyzed and atomized. The atomic absorbance signal was measured 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 furnace at 300 mL min⁻¹. Figure 12 and 13 show the pyrolysis and atomization curves for AAS determinations of aluminum and copper. The profiles (not shown) of the atomization step were also monitored as a function of time for aluminum and copper. The experimental conditions are listed in Table 8. The temperature of 2400 °C, although not the optimum atomization temperature, was chosen as the atomization temperature for both aluminum and copper from consideration of the lifetime of graphite platform and tube. The analytical calibration curves for GFAAS determination of aluminum and copper are shown in

Figure 12 Pyrolysis (○) and atomization (•) curves for GFAAS determination of aluminum. $[\text{Al(III)}] = 50 \mu\text{g L}^{-1}$, sample size: $10 \mu\text{L}$.

Figure 13 Pyrolysis (○) and atomization (●) curves for GFAAS determination of copper. $[\text{Cu(II)}] = 50 \mu\text{g L}^{-1}$, sample size: $10 \mu\text{L}$.

Table 8 Analysis lines and instrumental conditions for the GFAAS
determination of aluminum and copper

Parameter	Aluminum	Copper
Analysis line, nm	309.2	324.8
Pyrolysis temperature, °C	1200	1100
Atomization temperature, °C	2400	2400
Atomization duration, s	7	5
Clean-up temperature, °C	2600	2600
Clean-up duration, s	3	3

Figure 14 and 15.

5-6-2 Inductively-coupled plasma spectrometry (ICP-MS)

In inductively-coupled plasma mass spectrometry (Perkin Elmer Elan 5000), a peristaltic pump continuously delivered the sample solution to the ICP torch through the nebulizer at a flow rate of 1 mL min^{-1} . The ionic species were analyzed according to their mass/charge ratio by the quadrupole mass analyzer, followed by signal detection with a channel electron multiplier. The signal was monitored as a function of time. Signals were detected at the mass corresponding to each element to be analyzed. A dwell time for collection of the signal for each element was chosen to give good resolution and low noise. A short dwell time more accurately captures a "snapshot" of the sample spectrum in time, which is especially useful in metal speciation for kinetic study of fast components, but may raise the uncertainty level of the measurement beyond acceptable limits. Therefore, a compromise was made by selecting a dwell time of 100-1000 ms. The interval between successive data points was determined by the dwell time. The experimental conditions and the data acquisition protocol for the ICP-MS determination are listed in Table 9. The resolution of ICP-MS determines how well the adjacent masses can be separated. Two resolution modes available on the ICP-MS spectrometer, the normal and the higher resolution modes, were tested using a snow sample, from masses in the ranges 25-29 and 62-65 to check for overlap from adjacent masses with aluminum (mass 27) and copper (mass 64). Figure 16 and 17 show that aluminum and copper are well separated from the adjacent masses at both modes. To ensure good separation, the high resolution mode was used in all measurements. Figure 18 shows the analytical

Figure 14 Analytical calibration curve for GFAAS determination of aluminum.

Figure 15 Analytical calibration curve for GFAAS determination of copper.

Table 9 Instrumental operating conditions and data acquisition protocol for the ICP-MS determination

<u>ICP Mass Spectrometer</u>	
RF power	1000 W
Coolant argon flow rate	15 L min ⁻¹
Auxiliary argon flow rate	850 mL min ⁻¹
Carrier argon flow rate	900 mL min ⁻¹
Sampler/Skimmer	Nickel
 <u>Data Acquisition</u>	
Dwell time	100-1000 ms
Scan mode	peak hop
Points/spectral peak	1

Figure 16 Mass spectrum (mass 24 - 30) at normal (bottom) and high (top) resolution modes.

Figure 17 Mass spectrum (mass 60 - 66) at normal (bottom) and high (top) resolution modes.

Figure 18 Analytical calibration curves for ICP-MS determination of aluminum ($\circ$) and copper ($\bullet$) in 5 mg L^{-1} FA solution.

calibration curves for ICP-MS determination of aluminum and copper. The effect of matrix on the ICP-MS signal was also examined and the results show (Figure 19) that the presence of acetate buffer significantly suppressed the ICP-MS signal of aluminum. The appropriate standard was therefore used for each measurement.

Figure 19 Effect of salt loading on the ICP-MS signal of aluminum. ○, in 1 % HNO_3 ; ●, in $[\text{NaOAc}] : [\text{HOAc}] = 0.32 : 0.18$ buffer

2 OF 2

PM-1 3 1/2" x 4" PHOTOGRAPHIC MICROCOPY TARGET
NBS 1010a ANSI/ISO #2 EQUIVALENT

PRECISIONSM RESOLUTION TARGETS

CHAPTER 6 RESULTS AND DISCUSSION

6-1 *pH, conductivity, fluoride concentrations and dissolved organic carbon (DOC)*

Table 10 shows the pH and the conductivity of the samples of Rideau River surface water, rain and snow. The pH and the conductivity are important parameters of water quality. The conductivity reflects the ionic concentrations of the dissolved solute. The pH of the samples of Rideau River waters was found to be higher than those of the rain and the snow-melt. The pH of Rideau River water was relatively constant (8.0 ± 0.1), whereas the pH of the rain and the snow-melt varied from day to day and ranged from 3.8 to 6.1. The conductivity averaged between 390 and 470 $\mu\text{S cm}^{-1}$ for the samples of Rideau River surface water, between 17.0 and 37.7 $\mu\text{S cm}^{-1}$ for the samples of rain, and between 8.10 and 11.0 $\mu\text{S cm}^{-1}$ for the samples of snow-melt. There was no significant difference in the pH and the conductivity between the samples unfiltered or filtered through a 0.45 μm filter.

Table 11 shows the fluoride ion concentrations in the samples of Rideau River surface waters. At pH 8, the equilibrium distribution of Al-species in aqueous solution is predominantly $\text{Al}(\text{OH})_4^-$; only at pH ~ 5 would there be a significant fraction of the Al present as AlF^{2+} [129]. Moreover, since the concentration of fluoride in the river surface water was much lower than what was used in the calculation [129], the effect of fluoride complexation of aluminum was not important in this study.

Table 12 shows the concentrations of dissolved organic carbon in the samples of Rideau River water, rain and snow-melt. The results show that about 87 % of the total

Table 10 pH and conductivity of the samples of Rideau River surface waters, rain and snow

Sample	Date of sampling	pH	Conductivity ($\mu\text{S cm}^{-1}$)
River water	December 24, 1991	8.0	400
River water	January 3, 1992	7.9	390
River water	January 28, 1992	8.0	470
River water	February 26, 1992	8.0	390
Rain water	September 15, 1991	3.8	23.7
Rain water	September 26, 1991	5.9	37.7
Rain water	November 24, 1991	6.1	26.9
Rain water	April 17, 1992	5.3	17.0
Snow-melt	December 3, 1991	5.7	8.10
Snow-melt	April 12, 1992	4.7	11.0

Table 11 Fluoride in the samples of Rideau River surface waters

Date of sampling	Fluoride concentration, $\mu\text{g L}^{-1}$
March 5, 1992	53.0
March 10, 1992	140

Table 12 Dissolved organic carbon in the samples of Rideau River surface waters, rain and snow

Sample	Date of sampling	DOC, mg L^{-1}
River surface water (unfiltered)	March 11, 1994	51.6
River surface water (filtered)	March 11, 1994	6.6
Rain	November 15, 1993	3.4
Rain	December 12, 1993	1.6
Snow-melt	February 24, 1994	1.0
Snow-melt	February 25, 1994	0.7
Snow-melt	March 10, 1994	1.1

organic carbon in the samples of river surface waters is present in the particulate phase and that the concentration of dissolved organic carbon is much higher in the river surface water than in the rain and snow.

6-2 *Filtration, ultrafiltration and the Chelex column technique*

6.2-1 *Aluminum*

Tables 13 and 14 show the aluminum species in the samples of Rideau River surface waters at pH 8.0. The total aluminum metal concentration in the samples of river surface waters averaged $100.5 \mu\text{g L}^{-1}$, of which $\sim 77 \%$ was in the particulate phase and $\sim 23 \%$ in the dissolved phase. Approximately $\sim 58 \%$ of the dissolved species of aluminum was Chelex column-labile, $> 20 \%$ was Chelex batch-labile, and $< 20 \%$ was inert; the last fraction was probably $\text{Al}(\text{OH})_4^-$ and aluminum species adsorbed on or trapped by colloidal matter. Only 11 % of the total dissolved aluminum species passed through the ultrafilter with a M.W. cut-off of 500; of this fraction about 77 % was Chelex column-nonlabile. Equilibrium calculations indicated that at pH 8 the predominant dissolved Al species in water was $\text{Al}(\text{OH})_4^-$ [129]. The $\text{Al}(\text{OH})_4^-$ species was probably small enough to pass through the ultrafilter with a M.W. cut-off of 500, and was Chelex column-nonlabile; possibly the fully ionized Chelex²⁻ repelled the negatively charged $\text{Al}(\text{OH})_4^-$.

Humic materials, which have relatively large molecular weights and a wide range of distribution of molecular weights, depending upon their sources, are abundant in natural waters. In natural waters, the multifunctional humic materials bind metal ions to

Table 13 Aluminum species in the samples of Rideau River surface waters, pH 8.0

	[Al(III)], $\mu\text{g L}^{-1}$		
	January 3, 1992 (pH 7.9)	January 28, 1992 (pH 8.0)	February 26, 1992 (pH 8.0)
Total [Al(III)]	97.7 ± 2.1	106 ± 8	97.3 ± 2.2
[Al(III)] in the particulate phase	71.9 ± 1.7	84.4 ± 6.5	76.6 ± 0.8
[Al(III)] in the dissolved phase	25.8 ± 0.4	22.0 ± 1.4	20.7 ± 1.4
Lability of the dissolved species			
Chelex column-labile	15.1 ± 1.8	13.4 ± 2.3	11.3 ± 1.8
Chelex batch-labile	6.7 ± 1.6	5.8 ± 2.7	5.8 ± 0.1
Inert	4.0 ± 0.2	2.8 ± 1.8	3.6 ± 0.5

The values shown after $\pm$ signs are standard deviations of 3 successive, replicate determinations by GFAAS.

Table 14 Size fractionation of dissolved aluminum species, measured by GFAAS, in the sample of Rideau River surface water (Date of sampling: February 26, 1992. pH 8.0)

	[Al(III)], $\mu\text{g L}^{-1}$		
	Total	Chelex column-labile	Chelex column-nonlabile
[Al(III)] in the dissolved phase	20.7 ± 1.4	11.3 ± 1.8	9.4 ± 0.4
Ultrafiltration MW cut-off			
> 100 000	9.9 ± 1.6	3.4 ± 0.9	6.5 ± 0.8
100 000 - 3000	2.8 ± 0.6	1.7 ± 0.5	1.1 ± 0.6
3000 - 500	5.8 ± 0.6	5.7 ± 0.6	0.1 ± 0.0
< 500	2.2 ± 0.2	0.5 ± 0.2	1.7 ± 0.0

The values shown after $\pm$ signs are standard deviations of 3 successive, replicate determinations by GFAAS.

their functional groups. Because of its small ionic radius and high charge density, Al^{3+} ion is a very strong Lewis acid and can therefore easily form strong complexes with many ligands. Also, polymeric colloidal materials which abound in natural waters can adsorb and trap Al^{3+} ions. It is not surprising therefore that ~ 90 % of the dissolved aluminum species was retained by the ultrafilter with a M.W. cut-off of 500, and 48 % was retained by the ultrafilter with a M.W. cut-off 100,000. In other words, the dissolved aluminum species were predominantly large charged species, likely to be non-labile and non-bioavailable [27].

Table 15 shows Al species in rain water and snow. The total Al metal concentrations in the rain and the snow samples were $212 \mu\text{g L}^{-1}$ and $601 \mu\text{g L}^{-1}$, respectively, of which > 80 % of the aluminum species was in the particulate phase. At pH 5, > 50 % of the dissolved species of aluminum in snow-melt was Chelex column-labile, whereas > 80 % in rain water was Chelex column-labile.

Table 16 shows the results of size fractionation by ultrafiltration, and the lability of Al species in the samples of snow. For the sample collected on April 12, 1992, > 80 % of the aluminum species in the dissolved phase passed through the ultrafilter with M.W. cut-off 1000, of which 50 % was Chelex column-labile. Since the samples of snow contained relatively low levels of organic matter, the size and molecular weight of aluminum species in these samples were small. At pH < 6, the samples of snow had more aluminum species that were Chelex-labile compared to that in the Rideau River water at pH 8. The aluminum species in these samples were probably a mixture of $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^+$, $\text{Al}(\text{OH})_4^-$ and other small inorganic complexes of aluminum. Table

Table 15 Aluminum species, measured by GFAAS, in the samples of rain and snow

	[Al(III)], $\mu\text{g L}^{-1}$	
	April 12, 1992	April 17, 1992
	(Snow, pH 4.7)	(Rain, pH 5.3)
Total [Al(III)]	601 ± 18	212 ± 18
[Al(III)] in the particulate phase	594 ± 18	170 ± 19
[Al(III)] in the dissolved phase	7.0 ± 0.8	42.0 ± 1.4
Lability of the dissolved species		
Chelex column-labile	3.8 ± 1.0	35.6 ± 1.6
Chelex column-nonlabile	3.2 ± 0.2	6.4 ± 0.2

The values shown after $\pm$ signs are standard deviations of 3 successive, replicate determinations by GFAAS.

Table 16 Size fractionation of dissolved aluminum species in the samples of snow

		[Al(III)], $\mu\text{g L}^{-1}$ (%)	
		Sampling date:	Sampling date:
		April 12, 1992, pH 4.7	March 10, 1995, pH 5.3
		Chelex column- labile	Chelex column- nonlabile
		Total	Total
[Al(III)] in the dissolved phase		7.0 ± 0.8	3.2 ± 0.2
Ultrafiltration MW cut-off			
> 10,000		0.3 ± 0.1	0.3 ± 0.1
10,000 - 1000		0.8 ± 0.2	0.0
< 1000		5.9 ± 0.1	2.9 ± 0.3
			4.2 ± 0.2
			2.3 ± 0.1
			21.6 ± 2.0

The values shown after $\pm$ signs are standard deviations of 3 successive, replicate determinations by GFAAS.

16 also shows that the size distribution of aluminum species in the samples collected on different days is not significantly different from each other.

To test the effects of pH on metal species of different sizes in the same type of samples and to compare metal species in samples with different matrix, the pH of the samples of river surface water was changed to 5.0 ± 0.5 from their natural pH. A model solution containing metals and fulvic acid was also tested to obtain some qualitative information on metal speciation. Table 17 shows the results on size fractionation of dissolved aluminum species in the model solution and in the sample of Rideau River surface water. For the model solution, 13 % of dissolved aluminum species has a MW cut-off larger than 100,000, 47 % has MW cut-off of 3,000 - 10,000, and 40 % has a MW cut-off smaller than 3000. In Rideau River surface water, all aluminum species have MW cut-off $\leq 100,000$, with 75 % of them having MW cut-off < 3000 and the remainder having MW cut-off between 100,000 and 3000. The difference in size distribution of aluminum species in these samples shows the presence of organic substances with different molecular weight and function groups (different matrix components). Comparison of the results in Tables 14 and 17 suggests that a decrease in pH of river surface water shifts the distribution of aluminum to a lower molecular weight range. This is probably because some of the aluminum colloids break down with decreasing pH.

6-2-2 *Copper*

Table 18 shows Cu(II) species in the sample of Rideau River surface water. Up to 90 % of copper was in the dissolved phase and more than 55 % of these dissolved copper species was Chelex column-labile. Results from ultrafiltration showed that 27 %

Table 17 **Size fractionation of dissolved aluminum species in the model solution containing metals and fulvic acid and in the sample of Rideau River surface water, pH 5.0 ± 0.5 (Date of sampling: July 13, 1994)**

	[Al(III)], $\mu\text{g L}^{-1}$	
	Model solution*	River surface water
[Al(III)] in the dissolved phase	2.32	25.7
Ultrafiltration MW cut-off		
> 100,000	0.306	0
100,000 - 3000	1.09	6.42
< 3000	0.924	19.3

* [FA]/[M] = 0.92, [M] = {Al(III)} = 1.48 } + {[Cd(II)] = 0.089} = {[Cu(II)] = 0.16} + {[Ni(II)] = 0.17} + {[Pb(II)] = 0.048} + {[Zn(II)] = 0.15} = 2.1 μM .

Table 18 Size fractionation of dissolved copper species, measured by GFAAS, in the sample of Rideau River surface water (Date of sampling: February 26, 1992, pH 8.0)

	[Cu(II)], $\mu\text{g L}^{-1}$		
	Total	Chelex column-labile	Chelex column-nonlabile
Total Cu(II)	9.5 ± 1.4		
[Cu(II)] in the particulate phase	0.9 ± 0.0		
[Cu(II)] in the dissolved phase	8.6 ± 1.4	4.8 ± 1.8	3.7 ± 0.4
Ultrafiltration MW cut-off			
> 100 000	2.3 ± 0.9	1.7 ± 0.6	0.6 ± 0.2
100,000 - 10,000	2.7 ± 1.0	2.4 ± 1.0	0.3 ± 0.1
10,000 - 3000	1.7 ± 0.5	0	1.7 ± 0.2
< 3000	1.9 ± 0.1	1.0 ± 0.2	0.9 ± 0.0

The values shown after $\pm$ signs are standard deviations of 3 successive, replicate determinations by GFAAS.

and 22 % of the dissolved copper species had molecular weight $> 100,000$ and < 3000 , respectively. 74 % of the copper species having molecular weight $> 100,000$ was Chelex column-labile, whereas 53 % of the copper species having molecular weight < 3000 was Chelex column-labile.

Table 19 shows copper species in the samples of rain and snow. The total Cu was $24.6 \mu\text{g L}^{-1}$ in the snow (pH 4.7) and $30.3 \mu\text{g L}^{-1}$ in the rain water (pH 5.3), respectively. Most of the copper (98 %) was in the dissolved phase, and > 80 % of dissolved copper was Chelex column-labile in the sample of rain. Only ~ 20 % of copper in the sample of snow was in the dissolved phase. The atmospheric precipitation samples were affected by the weather conditions, and hence, the species of the same element in these samples varied from sample to sample. Since the pH of both the snow and the rain water was < 6 , the metal species in these samples were probably positively charged, and they were, therefore, exchangeable at Chelex-100 resin. Hence, most of copper species were found to be Chelex column-labile.

Table 20 shows the results of size fractionation by ultrafiltration, and the lability of Cu(II) species in the samples of snow. For the sample collected on April 12, 1992, all of the dissolved copper species had molecular weight cut-off $\leq 10,000$, compared with 42 % of the dissolved copper species in the sample of river surface water. 42 % of the dissolved copper in the sample of snow had molecular cut-off ≤ 500 . 83 % of the dissolved copper species in the sample of snow was Chelex labile. Compared to 56 % in the sample of river surface water. Thus different species of copper are present in these samples. The results for the sample collected on March 10, 1995 also show that large

Table 19 Copper species, measured by GFAAS, in the samples of rain and snow

	[Cu(II)], $\mu\text{g L}^{-1}$	
	April 12, 1992	April 17, 1992
	(Snow, pH 4.7)	(Rain, pH 5.3)
Total Cu(II)	24.6 ± 0.4	30.3 ± 3.4
Cu(II) in the particulate phase	19.8 ± 0.6	0.5 ± 0.05
Cu(II) in the dissolved phase	4.8 ± 0.2	29.8 ± 0.7
Lability of the dissolved species		
Chelex column-labile	4.0 ± 0.4	24.7 ± 1.0
Chelex column-nonlabile	0.8 ± 0.2	5.1 ± 0.3

The values shown after $\pm$ signs are standard deviations of 3 successive, replicate determinations by GFAAS.

Table 20 Size fractionation of dissolved copper species in the samples of snow

Date of sampling: April 12, 1992. pH 4.7. Measured by GFAAS.			
	[Cu(II)], $\mu\text{g L}^{-1}$		
	Total	Chelex column-labile	Chelex column-nonlabile
[Cu(II)] in the dissolved phase	4.8 ± 0.2	4.0 ± 0.4	0.8 ± 0.2
Ultrafiltration MW cut-off			
> 50,000	N.D.	N.D.	N.D.
50,000 - 10,000	N.D.	N.D.	N.D.
10,000 - 5,000	0.9 ± 0.4	0.9 ± 0.2	N.D.
5,000 - 1,000	0.9 ± 0.2	0.9 ± 0.2	N.D.
1,000 - 500	1.0 ± 0.3	1.0 ± 0.3	N.D.
< 500	2.0 ± 0.5	1.2 ± 0.6	0.8 ± 0.1
Date of sampling: March 10, 1995. pH 5.3. Measured by ICP-MS.			
[Cu(II)] in the dissolved phase	36.3		
Ultrafiltration MW cut-off			
> 10,000	5.00		
10,000 - 1000	0.000		
< 1000	31.3		

The values shown after $\pm$ signs are standard deviations of 3 successive, replicate determinations by GFAAS. N.D. = not detectable.

percentage of copper species has molecular weight cut-off < 1000 .

To test the effect of pH on the distribution of copper species in the same type of sample the pH of the samples of river surface water was adjusted to 5.0 ± 0.5 . A model solution containing metals and fulvic acid was also prepared and tested. Table 21 shows the size fractionation of dissolved copper species in the model solution and in the sample of Rideau River surface water. Different size distribution for these samples is a result of different matrices, especially different content of organic carbon. Comparing the results in Tables 18 and 21, one can see that a decrease in pH decreases the molecular weight of copper species in the sample of Rideau River surface water.

6-3 *Kinetic studies of metal speciation*

6-3-1 *Experimental conditions*

6-3-1-1 Evaluation of the analytical techniques for kinetic study of metal speciation. Freshwaters contain most, if not all, elements of the Periodic Table, plus a vast number of organic complexants. Innumerable interactions can occur in such systems, whereby an element is distributed in many different forms. The concentrations of trace elements are low, usually in the range of parts-per-billion (1 in 10^9) or even lower, in unpolluted freshwaters, and the concentration of each species of an element is even lower. These characteristics of freshwaters require that the analytical techniques used to determine the concentrations of elements in such systems be highly sensitive and also highly selective. Furthermore, the quantity and the quality of the experimental data are crucial for kinetic studies of chemical speciation because the number of kinetically

Table 21 **Size fractionation of dissolved copper species in the model solution containing metals and fulvic acid and in the sample of Rideau River: surface water, pH 5.0 ± 0.5 (Date of sampling: July 13, 1994)**

	[Cu(II)], $\mu\text{g L}^{-1}$	
	Model solution*	River surface water
[Cu(II)] in the dissolved phase	9.50	30.1
Ultrafiltration MW cut-off		
> 100,000	0.840	7.00
100,000 - 3000	1.43	5.40
< 3000	7.23	17.7

*[FA]/[M] = 0.92, [M] = {[Al(III)] = 1.48} + {[Cd(II)] = 0.089} + {[Cu(II)] = 0.16} + [Ni(II)] = 0.17} + {[Pb(II)] = 0.048} + {[Zn(II)] = 0.15} = 2.1 μM .

distinguishable components, the dissociation rate constant and the initial concentration of each kinetically distinguishable component must be obtained by curve-fitting of the experimental data.

Two analytical techniques of great sensitivity used for direct, quantitative determination of metal concentrations in freshwaters are compared in terms of their usefulness for following kinetics of metal-complex dissociation. These are graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS). GFAAS has excellent sensitivity and selectivity and has been shown to be an analytical technique applicable to direct determination of metals for kinetic studies of metal speciation in natural waters. The discrete sampling required by GFAAS, however, produces data points separated at least by the time for withdrawing sample, a few seconds, and hence limits the number of data points. Also, the transfer of the sample and the time required for determination by GFAAS introduces a risk of contamination and loss of analyte by adsorption on the wall of the plastic vials, resulting in scatter of data points and hence in lower precision of the results obtained. As well, the time required for analysis by GFAAS limits its application to the study of only those species having a half-life no shorter than seconds. In order to overcome these limitations, an inductively-coupled plasma mass spectrometer (ICP-MS) with solution nebulization mode of sample introduction using a peristaltic pump, was tested. ICP-MS is a simultaneous multielement analytical technique that is used for the determination of over 75 elements in a variety of matrices. The detection limits of ICP-MS are comparable to or better than GFAAS. Its on-line monitoring capability gives real- or near real-time

resolution. This feature allows fast kinetics of labile complexes to be readily studied. GFAAS, however, is a useful technique for cross-checking the reliability of ICP-MS and for detecting isobaric interferences in ICP-MS.

The two techniques are compared in Figure 20 which shows aluminum remaining in the model solution as a function of time in the Chelex batch technique. The major difference between the data sets obtained by the two techniques is the much larger number of experimental data points obtained by ICP-MS than by GFAAS. This is a crucial factor, particularly at the beginning of the kinetic measurements where ICP-MS has provided experimental data points but GFAAS has failed to do so. The result is that ICP-MS can reveal the presence of very labile complexes, whereas GFAAS cannot. Also with the data from ICP-MS complexes which are kinetically close to one another can be resolved. This was not possible with GFAAS.

Using the iterative deconvolution method, Table 22, two kinetically distinguishable components of aluminum are resolved from the data obtained by ICP-MS, but only one kinetically distinguishable component is resolved from the data obtained by GFAAS for the buffered model solutions. The standard error in the kinetic parameters is generally one order of magnitude higher when using the data set obtained by GFAAS. Since the iterative deconvolution method is based on fitting experimental data, a large number of data points is essential for obtaining reliable results. If the interval between the experimental data points is too large, as in the case of the GFAAS determination, some kinetically distinguishable components are lost. The larger error on the data set obtained using GFAAS is attributable both to the small number of experimental data points and

Figure 20 Comparison of GFAAS and ICP-MS for data collection in the Chelex batch technique, pH 5.0. [Chelex] = 1 % (w/w), [NaOAc]:[HOAc] = 0.32:0.18. •, ICP-MS, [Al(III)] = 3.7 μ M; ○, GFAAS, [Al(III)] = 3.1 μ M.

Table 22 Kinetic parameters for the uptake aluminum species by the Chelex resin from the buffered ([NaOAc]:[HOAc] = 0.32:0.18) model solutions as a function of the initial concentration of aluminum, pH = 5.00 ± 0.02

[Al(III)] _{total} , μM	GFAAS	ICP-MS	
	$k_1 \times 10^{-3}, \text{s}^{-1}$	$k_1 \times 10^{-3}, \text{s}^{-1}$	$k_2 \times 10^{-4}, \text{s}^{-1}$
4.7	6.4 ± 0.8	-	-
3.9	6.4 ± 0.1	-	-
3.8	-	5.4 ± 0.03	3.8 ± 0.1
1.2	5.6 ± 0.4	-	-

[Al(III)]_{total} = the total initial concentration of aluminum. Values after $\pm$ 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 for the values of the rate constants are justified.

to a higher degree of scatter in the data points. Delivery of discrete, sequential samples involving a sample transfer step, inherent in the current GFAAS, as opposed to direct, continuous delivery of samples in the ICP-MS solution nebulization technique, limits the number of experimental data points by GFAAS. The much larger number of data points and the smaller scatter in the data points observed in the ICP-MS determination is due to the direct insertion of the sample, which eliminates the sample transfer step and the attendant time of the sample transfer step. This reduces significantly the adsorption loss of the analyte and the sample contamination, both of which are functions of the time taken by the sample transfer step, and hence, occur in GFAAS, but are almost absent in ICP-MS. In fact with the dwell time of the order of 10 milliseconds for measurements with ICP-MS many more data points can be collected. In this aspect ICP-MS has excellent potential for kinetic analysis and will be used in subsequent measurements, except as otherwise indicated. Nevertheless, the excellent selectivity of GFAAS, together with its much lower cost per sample and fast, sequential multi-element capability make it a very powerful technique for kinetic studies, especially for cross-checking the reliability of ICP-MS results and for identifying any possible interferences by molecular species in ICP-MS. Table 22 indicates that the rate constant for the aluminum uptake by the Chelex resin determined by these two techniques is in good agreement.

6-3-1-2 Effects of the concentration of the Chelex resin on the kinetics of aluminum uptake. To ensure that the reaction (4-3) was first-order or pseudo-first-order and that reaction (4-3) was much faster than reaction (4-2), concentrations of the Chelex resin of 0.25, 0.50, 0.75 and 1.00 % (w/w) in the model solutions were examined

for the uptake of the aluminum ions. The results are shown in Figure 21, indicating that the rate of uptake of aluminum by the Chelex resin increased when the concentration of Chelex resin was increased from 0.25 to 0.50 %, but showed only a small increase with further increase in the concentration of the Chelex resin. The concentration of 1 %, which is equivalent to a Chelex : metal ratio of 100 or higher, depending on the concentrations of the metals in the sample was therefore used in further studies. Under this experimental condition, the effect of a change in the sample volume during the kinetic measurements was negligible.

6-3-1-3 Effects of the resin particle size on the kinetics of copper uptake. Since the surface area per gram and hence the surface energy per gram 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. Thus a Chelex resin with different particle size may yield a different number of kinetically distinguishable components with different associated rate constants. Figure 22 shows the percentages of the copper remaining in the sample after the uptake of Cu(II) by the Chelex resin of 50-100, 100-200 and 200-400 mesh. The curves in Figure 22 show the overall rate of uptake of Cu(II) decreases with increasing particle size of the Chelex resin, especially when the particle size is increased to 50-100 mesh. Figure 22 also shows that the precision was very good under the same experimental conditions (curves with symbols • and ○). The effect of initial concentration of copper can be seen by comparing the two curves, ◇ and ▲, in Figure 22; a decrease in the Cu(II) concentration by a factor of ~7 decreased the overall rate of uptake of Cu(II).

Figure 21 Effect of the concentration of the Chelex resin on the kinetics of uptake of aluminum from the model solutions, pH 5.0. $[Al(III)] = 0.26 \mu M$. $\circ$, $[Chelex] = 0.25 \%$ (w/w); $\bullet$, $[Chelex] = 0.50 \%$ (w/w); $\diamond$, $[Chelex] = 0.75 \%$ (w/w); $\blacklozenge$, $[Chelex] = 1.00 \%$ (w/w).

Figure 22 Effect of resin particle size on the kinetics of uptake of copper from the model solutions, pH 5.0. [Chelex] = 1 % (w/w). $\diamond$, 50-100 mesh resin, [Cu(II)] = 2.1 μM ; $\blacktriangle$, 50-100 mesh resin, [Cu(II)] = 0.31 μM ; $\blacklozenge$, 100-200 mesh resin, [Cu(II)] = 2.1 μM ; $\bullet$ and $\circ$, 200-400 mesh resin, [Cu(II)] = 2.1 μM .

The results of the analysis of the curves by the iterative deconvolution method are listed in Table 23. Three kinetically distinguishable components of Cu(II) were resolved, but the percentage of the second (slower) component, C_2^0 , was much higher when the Chelex resin with the particle size of 50-100 mesh was used. 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 may be related to the following factors:

- (1) ratio of external/internal surface area. The smaller particle size has a larger ratio of external/internal surface area and thus has a faster rate of uptake of Cu(II) by the Chelex resin;
- (2) diffusion path lengths. The diffusion path lengths of the exchanging ions to and from the active sites are shorter with smaller particle size, so that exchange is more rapid;

Since the kinetic behaviour of Cu(II) with the Chelex resin of 100-200 mesh was only slightly different from that of the Chelex resin of 200-400 mesh, both of these Chelex resins were used for further studies. These results also suggested that any change in the surface area of the Chelex resin due to grinding of the resin by the magnetic stirring bar was not significant.

6-3-1-4 Examination of signal drift of ICP-MS and blanks. Since the kinetic experiments may last for a few hours, a drift in the signal must be checked and corrected for, if it is severe. A standard solution was measured every half hour for up to eight hours. The signal changes from the beginning to the end were $-540 \text{ counts s}^{-1}$

Table 23 Effect of the particle size of the Chelex resin on the kinetic parameters for the uptake of copper from model solutions containing Cu(II), pH 5.0 $\pm$ 0.5

Chelex resin, mesh	[Cu(II)] _{total} , μ 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 ⁻⁴ , s ⁻¹
50-100	0.31	12 $\pm$ 3	7.6 $\pm$ 2.5	80 $\pm$ 3	5.4 $\pm$ 0.06	8 $\pm$ 0.4	< 1.0 $\pm$ 0.1
	2.1	61 $\pm$ 1	5.4 $\pm$ 0.08	35 $\pm$ 0.5	2.9 $\pm$ 0.02	4 $\pm$ 0.2	< 7.0 $\pm$ 0.2
100-200	2.1	93 $\pm$ 2	2.1 $\pm$ 0.02	6 $\pm$ 0.7	5.0 $\pm$ 0.4	1 $\pm$ 0.05	< 1.9 $\pm$ 0.2
	2.1	95 $\pm$ 0.9	1.7 $\pm$ 0.01	4 $\pm$ 0.2	3.4 $\pm$ 0.2	1 $\pm$ 0.06	< 1.4 $\pm$ 0.3
200-400	0.31	82 $\pm$ 1	4.1 $\pm$ 0.04	11 $\pm$ 0.3	4.0 $\pm$ 0.1	7 $\pm$ 0.1	< 1.7 $\pm$ 0.04
	2.1	89 $\pm$ 0.9	3.4 $\pm$ 0.02	9 $\pm$ 0.2	5.3 $\pm$ 0.9	2 $\pm$ 0.04	< 3.1 $\pm$ 0.07
	2.1	90 $\pm$ 0.8	3.4 $\pm$ 0.2	8 $\pm$ 0.2	5.9 $\pm$ 0.1	2 $\pm$ 0.04	< 3.6 $\pm$ 0.09

[Cu(II)]_{total} = the total initial concentration of copper. C_i⁰ = the initial percentages of the *i*th kinetically distinguishable component. Values after $\pm$ 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 for the values of the rate constants are justified.

for copper measurement and 605 counts s^{-1} for aluminum measurement, with standard deviations of 414 (based on 10 measurements) for Al and 568 for Cu, respectively. Since most of the experiments were run less than three hours, the signal drifts for both aluminum and copper were considered not significant.

Three types of blanks were measured as a function of time:

- (1) ultrapure water without any addition. This blank was used to check whether the system was clean and how large was the background signal from the water solvent;
- (2) ultrapure water + the Chelex resin. This blank was used to check whether there was contamination of the resin during the pre-treatment with NaOAc-HOAc buffer and whether aluminum and copper might be leached from the resin during the kinetic experiments;
- (3) Rideau River water without any addition. The purpose of this blank was to correct for adsorption or desorption of aluminum and copper and for contamination from the walls of the reactor.

Figure 23 and 24 show the signals from these blanks as a function of time for aluminum and copper. The signal vs. time for ultrapure water (*) shows 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 (◇) in both figures for ultrapure water + the Chelex resin indicate that there is no significant contamination of aluminum and copper during the pre-treatment of the Chelex resin, nor leaching of these metals from the Chelex resin. The curves (○) in both Figures for the sample of river surface water without any additions to

Figure 23 Aluminum signal as a function of time. •, ultrapure water only; $\diamond$, ultrapure water + the Chelex resin; $\circ$, Rideau River water only.

Figure 24 Copper signal as a function of time. *, ultrapure water only; $\diamond$, ultrapure water + the Chelex resin; $\circ$, Rideau River water only.

it show that there is no measurable loss of aluminum and copper during the kinetic measurements by ICP-MS. The very slight increase in the blanks with time is probably due to leaching of the previously-adsorbed analytes from the walls of the reactor which had been pre-equilibrated with the sample before the kinetic measurements.

6-3-2 *Verification of assumptions made in the kinetic model*

Assumptions 1 and 2 made in the kinetic model have been verified using model solutions of aluminum with various initial concentrations of aluminum, with and without fulvic acid, using either inductively coupled plasma mass spectrometry (ICP-MS) or graphite furnace atomic absorption spectrometry (GFAAS) to monitor the concentration of aluminum left in the solution as a function of time.

6-3-2-1 Rate of uptake of aluminum by the Chelex resin as a function of the initial concentrations of aluminum in model solutions. The results, as shown earlier in Table 22, indicate that the dissociation rate constant, measured by both GFAAS and ICP-MS, was not changed by changes in the initial concentration of Al(III), indicate that the dissociation of the Al-complex was first-order. Because ICP-MS cannot tolerate sample solutions having high-salt content, such as the buffered solutions for more than a very short period of sample delivery, only one sample was analyzed with ICP-MS. The concentration of each of the kinetically distinguishable components of aluminum in the test solutions in the Chelex batch technique (as determined by ICP-MS) was observed to decrease exponentially as a function of time (Figure 20), indicating first- or pseudo-first order kinetics for the loss process. Also, the rate constants for the component with the fastest decay rate were within $\pm 9 \%$ of the average value when the initial concentrations

of aluminum were varied by a factor of 3 or 4, thus verifying the assumption made earlier that the kinetics of equation (4-3) was first-order or pseudo-first order.

6-3-2-2 Rate of uptake of aluminum by the Chelex resin from model solutions with and without fulvic acid. Figure 25 shows the results from model solutions of aluminum with and without fulvic acid, indicating that the reaction $\text{Chelex} + \text{Al} \rightarrow \text{Chelex-Al}$ (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. Similar results will be shown later for copper. Assumption 3 could not be verified, but the results presented in this work suggest that this is not an important factor at the pH used for the kinetic measurements.

6-3-3 *Validation of the Chelex batch technique for kinetic study of metal speciation*

These experiments with model systems were designed to test the applicability of the Chelex batch technique for metal speciation. EDTA and NTA are anthropogenic complexants forming stronger complexes than those formed from 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 analysis of Cu(II)-EDTA and Cu-NTA systems should reveal two kinetically distinguishable components for each, when $[\text{ligand}]/\text{Cu(II)} < 1$, where $[\text{ligand}] = [\text{EDTA}]$ or $[\text{NTA}]$, 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

Figure 25 Uptake of aluminum by the Chelex resin from the model solutions, pH 5.0. [Chelex] = 1 % (w/w). a, [FA] : [M] = 0.00, [Al(III)] = $1.3 \mu\text{M}$; b, [FA] : [M] = 3.9, [Al(III)] = $0.70 \mu\text{M}$; c, [FA] : [M] = 7.7, [Al(III)] = $0.83 \mu\text{M}$. [M] = [Al(III)] + [Cd(II)] + [Cu(II)] + [Ni(II)] + [Zn(II)] + [Pb(II)] = $2.1 \mu\text{M}$.

complex, should be observed when the ratio of $[\text{ligand}]/[\text{Cu(II)}] > 1$. The distribution of each component should be determined by the stability constants of the Cu-EDTA or the Cu-NTA complex at pH 5.0. The reason for choosing Cu(II) as the model metal ion for this test is that Cu(II) is well known for forming strong, well-characterized complexes with EDTA or NTA.

Figure 26 shows the percentage of Cu(II) remaining in the model solutions after the uptake of Cu(II) by the Chelex resin as a function of time for solutions with different $[\text{EDTA}]/[\text{Cu(II)}]$ ratios. The rate of uptake of copper decreases with increasing $[\text{EDTA}]/[\text{Cu(II)}]$ ratios because more Cu(II) becomes bound as the Cu-EDTA complex. The results of the data analysis by the iterative deconvolution method are listed in Table 24. Two kinetically distinguishable components of Cu(II) were resolved for the samples with $[\text{EDTA}]/[\text{Cu(II)}]$ ratios of 0.38 and 0.77, whereas only one kinetically distinguishable component was observed for the sample with $[\text{EDTA}]/[\text{Cu(II)}]$ ratio of 2.3. The distributions of copper aquo ions and Cu-EDTA complexes obtained by the analysis of the kinetic data agree within 8 % with those predicted from the equilibrium calculations. EDTA forms a 1:1 chelate complex with Cu(II), which has a high stability constant even at pH 5.0. In Figure 26, the curve for $[\text{EDTA}]/[\text{Cu(II)}] = 2.3$ reflects the fact that there is very little Cu(II) aquo ion available in the presence of excess EDTA.

Figure 27 shows the percentage of Cu(II) remaining in the model solutions after the uptake of Cu(II) by the Chelex resin as a function of time for the solutions with different $[\text{NTA}]/[\text{Cu(II)}]$ ratios. The rate of Cu(II) uptake decreases with increasing $[\text{NTA}]/[\text{Cu(II)}]$, but the decrease in the rate is less for the Cu-NTA complex than for the

Figure 26 Uptake of copper from the model solutions as a function of [EDTA]/[Cu(II)] ratio. pH 5.0. [Chelex] = 1 % (w/w). [Cu(II)]_{total} = 2.1 μ M. $\blacksquare$, [EDTA]/[Cu(II)] = 0; $\circ$, [EDTA]/[Cu(II)] = 0.38; $\blacklozenge$, [EDTA]/[Cu(II)] = 0.77; $\diamond$, [EDTA]/[Cu(II)] = 2.3.

Table 24 Kinetic parameters for the uptake of copper species by the Chelex resin from the model solutions as a function of the [EDTA]/[Cu(II)] and [NTA]/[Cu(II)] ratios, pH 5.0 $\pm$ 0.5

[EDTA]/[Cu(II)]	[Cu(II)] _{total} , μ 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 ⁻⁴ , s ⁻¹
0	2.1	89 $\pm$ 0.9	3.4 $\pm$ 0.02	9 $\pm$ 0.2	5.3 $\pm$ 0.9	2 $\pm$ 0.04	< 3.1 $\pm$ 0.07
0.38	2.1	58 $\pm$ 0.9	2.8 $\pm$ 0.03			42 $\pm$ 0.3	< 1.7 $\pm$ 0.007
0.77	2.1	31 $\pm$ 0.9	2.4 $\pm$ 0.08			69 $\pm$ 0.6	< 1.4 $\pm$ 0.006
2.3	2.1					96 $\pm$ 0.4	< 0.36 $\pm$ 0.006
[NTA]/[Cu(II)]							
0	0.31	82 $\pm$ 1	4.1 $\pm$ 0.04	11 $\pm$ 0.3	4.0 $\pm$ 0.1	7 $\pm$ 0.1	< 1.7 $\pm$ 0.04
0.36	0.31	68 $\pm$ 2	2.4 $\pm$ 0.05	17 $\pm$ 0.7	2.9 $\pm$ 0.1	15 $\pm$ 0.5	< 1.6 $\pm$ 0.07
0.71	0.31	33 $\pm$ 1	4.3 $\pm$ 0.1	57 $\pm$ 1	1.4 $\pm$ 0.01	10 $\pm$ 0.4	< 1.0 $\pm$ 0.09
1.1	0.31			100 $\pm$ 0.6	1.1 $\pm$ 0.004		
1.4	0.31			100 $\pm$ 0.7	1.0 $\pm$ 0.002		

[Cu(II)]_{total} = the total initial concentration of copper. C_i⁰ = the initial percentages of the *i*th kinetically distinguishable component. Values after $\pm$ 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 for the values of the rate constants are justified.

Figure 27 Uptake of copper from the model solutions as a function of $[\text{NTA}]/[\text{Cu(II)}]$ ratio, pH 5.0. $[\text{Chelex}] = 1\%$ (w/w). $[\text{Cu(II)}]_{\text{total}} = 0.31\ \mu\text{M}$. $\bullet$, $[\text{NTA}]/[\text{Cu(II)}] = 0$; $\blacklozenge$, $[\text{NTA}]/[\text{Cu(II)}] = 0.36$; $\circ$, $[\text{NTA}]/[\text{Cu(II)}] = 0.71$; $\diamond$, $[\text{NTA}]/[\text{Cu(II)}] = 1.1$; $\blacksquare$, $[\text{NTA}]/[\text{Cu(II)}] = 1.4$.

Cu-EDTA complex. Moreover, the percentage of Cu(II) remaining in the solutions after the uptake is complete is the same for the samples with different [NTA]/[Cu(II)] ratios, but increases with increasing [EDTA]/[Cu(II)] ratios (Figures 26 and 27). This is probably a reflection of the fact that the Cu-NTA complex is thermodynamically weaker than the Cu-EDTA complex.

The results of the analysis of the curves using the iterative deconvolution method are listed in Table 24. Three kinetically distinguishable components were resolved for the samples with the [NTA]/[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 samples with the [NTA]/[Cu(II)] > 1. This value agrees well with the value of $(2 \pm 1) \times 10^{-3} \text{ s}^{-1}$ obtained by Hering and Morel [130]. In the [NTA]/[Cu(II)] system, the component removed most quickly is Cu(II) aquo complex. The initial concentration of this ion obtained from the kinetic studies agrees well with that predicted from equilibrium calculations. Besides the 1:1 Cu-NTA complex, NTA also forms a 1:2 Cu-NTA complex. The slower components were probably 1:1 and 1:2 Cu-NTA complexes. These results show that the Chelex batch technique is applicable to metal speciation.

6-3-4 *Aluminum speciation*

6-3-4-1 **Effects of the presence of metal ions on the kinetics of uptake of aluminum by the Chelex resin.** Model solutions containing aluminum only and containing aluminum plus several metals (Cd, Cu, Ni, Pb and Zn) were compared in order to reveal competitions among the metal ions for binding sites in the Chelex resin, which may cause apparent multicomponent behaviour. Figure 28 shows that the effect of the

Figure 28 Effects of the presence of metal ions on the kinetics of uptake of aluminum species in the model solutions, pH 5.0. [Chelex] = 1 % (w/w). $\circ$, $[\text{Al(III)}] = 1.5 \mu\text{M}$. $\bullet$, $\{[\text{Al(III)}] = 1.5\} + \{[\text{Cu(II)}] = 0.16\} + \{[\text{Cd(II)}] = 0.089\} + \{[\text{Ni(II)}] = 0.17\} + \{[\text{Pb(II)}] = 0.048\} + \{[\text{Zn(II)}] = 0.15\} = 2.1 \mu\text{M}$.

presence of other metal ions on the kinetics of uptake of aluminum is not significant. The results also indicate that the number of binding sites in the Chelex resin is sufficient for the metal ions to be taken up simultaneously and independently.

6-3-4-2 Effects of the concentration of NaOAc-HOAc buffer. Since both the chemical affinity of the Chelex resin and metal speciation change with pH, the pH must be controlled through the whole process of the kinetic measurement. NaOAc-HOAc is a commonly-used buffer and was the first tested for controlling pH of the samples.

Figure 29 shows the uptake of the aluminum species by the Chelex resin as a function of time from the model solutions containing aluminum with different concentrations of the NaOAc-HOAc buffer. The measurements were made by GFAAS. Although for all of these samples more than 90 % of the aluminum species was taken up by the Chelex resin in a few hundred seconds, the time to reach the equilibrium was longer for the buffer of higher concentrations. The rate constants for the uptake of the aluminum by the Chelex resin obtained using the iterative deconvolution method, as shown in Table 25, decreased with increasing concentrations of the buffer, and a second kinetically distinguishable component appeared when the concentration of OAc^- was increased to 0.16 M. As pointed out by Pai *et al.* [131], the effect of the salt content on the metal uptake by the Chelex-100 is attributed to the competition between the cations of the salt and the metal ions of the sample for the exchange sites on the Chelex resin, as well as to the complexation reaction between the metal ions and the anions of the salt. A similar explanation would apply to the system with aluminum ions and the sodium acetate buffer. Since the cation, Na^+ , in the buffer was the same as that in the

Figure 22 Effects of the concentration of NaOAc-HOAc buffer on the kinetics of uptake of aluminum species in the model solutions, determined by GFAAS, pH 5.0. [Chelex] = 1 % (w/w). •, [NaOAc] : [HOAc] = 0.32 : 0.18, [Al(III)] = 3.1 μ M; ○, [NaOAc] : [HOAc] = 0.16 : 0.090, [Al(III)] = 2.6 μ M; ■, [NaOAc] : [HOAc] = 0.080 : 0.045, [Al(III)] = 2.3 μ M; ▼, [Buffer] = 0.00, [Al(III)] = 0.82 μ M.

Table 25 Effect of the concentration of NaOAc-HOAc buffer on the kinetics of uptake of aluminum species by the Chelex resin from model solutions, determined by GFAAS, (pH = 5.00 ± 0.02 for the buffered samples and 5.0 ± 0.5 for the unbuffered samples)

[NaOAc]:[HOAc]	[Al(III)] _{total} , μM	C_1^0 , %	$k_1 \times 10^{-3}$, s^{-1}	C_2^0 , %	$k_2 \times 10^{-4}$, s^{-1}
0 : 0	1.1	100	9.9 ± 1		
0 : 0	0.82	100	10 ± 2		
0.040 : 0.022	1.6	100	8.9 ± 0.4		
0.080 : 0.045	2.3	100	7.9 ± 0.4		
0.16 : 0.090	2.6	93	7.8 ± 0.4	7	$< 4.2 \pm 1$
0.32 : 0.18	3.1	90	6.2 ± 0.3	10	$< 6.0 \pm 0.8$

[Al(III)]_{total} = the total initial concentration of aluminum. C_i^0 = the initial percentages of the i th kinetically distinguishable component. Values after $\pm$ 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 for the values of the rate constants are justified.

Chelex resin, the competition for the exchange sites in the Chelex resin was minimized. The decreased rate constants for the uptake of the aluminum are therefore attributed to the formation of Al-acetate complexes. The appearance of the second kinetically distinguishable component of aluminum at the high concentration of OAc^- was probably due to the formation of more than one Al-acetate complex [132].

6-3-4-3 Effects of the presence of the complexant, fulvic acid. Figure 30 shows the uptake of aluminum by the Chelex resin from unbuffered model solutions containing Al(III), Zn(II), Cd(II), Cu(II), Ni(II) and Pb(II), with or without fulvic acid. The pH changes during the uptake by the Chelex were < 0.5 pH unit. More than 96 % of the aluminum was taken up within 500 seconds by the Chelex resin from the solution without fulvic acid, whereas approximately 28 %, 32 % and 45 % of the aluminum in the solutions having the ratio of $[\text{FA}] : [\text{M}]$ of 0.58, 0.87 and 1.2, respectively, still remained in the solutions after 7000 seconds (where $[\text{M}] = [\text{Al(III)}] + [\text{Cd(II)}] + [\text{Cu(II)}] + [\text{Ni(II)}] + [\text{Pb(II)}] + [\text{Zn(II)}]$). This indicates that the aluminum species associated with the fulvic acid are taken up by the Chelex resin much more slowly than the aqueous Al ion. This agrees with the results reported by Campbell, *et al.* [133]. Figure 30 also validates the assumption made earlier that the rate of reaction (4-3) is much greater than that of reaction (4-2), making the latter reaction the rate-limiting step of the overall reaction.

The rate constants of the aluminum uptake by the Chelex resin obtained from the analysis by the iterative deconvolution method are listed in Table 26. In the absence of both the buffer and the fulvic acid, the aluminum aquo complex has three kinetically distinguishable components. The fastest component, which comprises a mean value of

Figure 30 Effects of the concentration of fulvic acid on the kinetics of uptake of aluminum species in the model solutions, pH 5.0. [Chelex] = 1 % (w/w). □, [FA] : [M] = 0.00; ○, [FA] : [M] = 0.29; ◆, [FA] : [M] = 0.58; ◇, [FA] : [M] = 0.87; ●, [FA] : [M] = 1.2. [M] = {[Al(III)] = 1.5} + {[Cu(II)] = 0.16} + {[Cd(II)] = 0.089} + {[Ni(II)] = 0.17} + {[Pb(II)] = 0.048} + {[Zn(II)] = 0.15} = 2.1 μ M.

Table 26 Effect of the concentration of fulvic acid on the kinetics of uptake of aluminum species by the Chelex resin from model solutions (pH = 5.00 $\pm$ 0.02 for the buffered samples, 5.0 $\pm$ 0.5 for the unbuffered samples)

[FA]:[M]*	[Al(III)] _{total} μM	C ₁ ⁰ %	k ₁ $\times 10^{-2}, \text{s}^{-1}$	C ₂ ⁰ %	k ₂ $\times 10^{-3}, \text{s}^{-1}$	C ₃ ⁰ %	k ₃ $\times 10^{-4}, \text{s}^{-1}$	C ₄ ⁰ %	k ₄ $\times 10^{-5}, \text{s}^{-1}$
UNBUFFERED SAMPLES									
0*	1.5	84	2.7 $\pm$ 0.05	14	4.3 $\pm$ 0.4	2	< 1.8 $\pm$ 0.2		
0	1.5	92	2.9 $\pm$ 0.09	5	4.5 $\pm$ 0.07	3	< 2.1 $\pm$ 0.3		
0.29	1.5	31	1.9 $\pm$ 0.1	27	2.6 $\pm$ 0.1	42	< 1.6 $\pm$ 0.02		
0.58	1.5			18	5.5 $\pm$ 0.3	33	8.4 $\pm$ 0.3	49	< 8.8 $\pm$ 0.2
0.87	1.5					30	9.2 $\pm$ 0.2	70	< 10 $\pm$ 0.1
1.2	1.5					23	5.0 $\pm$ 0.3	77	< 7.7 $\pm$ 0.2
BUFFERED SAMPLES									
0*	3.9			92	5.3 $\pm$ 0.3	8	4.0 $\pm$ 0.2		
4.1*	4.0			23	7.1 $\pm$ 0.2	40	17 $\pm$ 1	37	< 4.9 $\pm$ 0.06

[M]* = {[Al(III)] = 1.5} + {[Cd(II)] = 0.099} + {[Cu(II)] = 0.16} + {[Ni(II)] = 0.17} + {[Pb(II)] = 0.048} + {[Zn(II)] = 0.15} = 2.1 μM ; [Al(III)]_{total} = the total initial concentration of aluminum. *The samples contain aluminum only. C_i⁰ = the initial percentages of the ith kinetically distinguishable component. Values after $\pm$ 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 for the values of the rate constants are justified.

about 90 % of the $[\text{Al(III)}]_{\text{total}}$), has a rate constant of $2.8 \times 10^{-2} \text{ s}^{-1}$. The two slower components have rate constants of $4.4 \times 10^{-3} \text{ s}^{-1}$ and $2.0 \times 10^{-4} \text{ s}^{-1}$, respectively. The presence of the slower components of Al(III) when the total concentration of Al(III) is low (10^{-5} M) and the increase in the amount of these slower components of Al(III) with decreasing total concentration of Al(III) were also observed by Langford and Mak [134]. These slower components are probably polynuclear hydroxo species of Al(III) such as the Al_{13} tridecamer [135]. In the presence of the buffer (but in the absence of the FA), the fastest of the former three kinetically distinguishable components of aluminum disappears completely, and the two slower components of aluminum now have the rate constants: $5.3 \times 10^{-3} \text{ s}^{-1}$ (92 % of the $[\text{Al(III)}]_{\text{total}}$) and $\leq 4.0 \times 10^{-4} \text{ s}^{-1}$ (8 % of the $[\text{Al(III)}]_{\text{total}}$). This change is probably due to formation of aluminum monoacetate complexes, which have been studied by Hiraishi *et al.* [132]. The presence of Zn(II), Cd(II), Cu(II), Ni(II) and Pb(II) had no significant effect on the number of kinetically distinguishable components of aluminum present and on the rate constants.

In the presence of fulvic acid, two or three kinetically distinguishable components of Al(III), with dissociation rate constants ranging from 10^{-2} to 10^{-5} s^{-1} , were observed. These results agree well with those obtained by Langford and Mak [134]. With increasing ratio of $[\text{FA}]/[\text{M}]$, the initial fraction of the faster component decreased, whereas that for the slower component increased, probably reflecting the fact that most of the aluminum was bound to fulvic acid and the Al-fulvic acid was the slowest component. These results indicate either that the rate of uptake of the aluminum aquo ions by the Chelex resin is much faster than the rate of dissociation of the Al-fulvic

complexes (if the dissociation of aluminum complex produces the aluminum ions before their uptake by the Chelex resin), or that the rate of uptake of the aluminum aquo ions by the Chelex resin is much faster than the direct uptake of the Al-fulvic complexes by the Chelex resin. The variations in the dissociation rate constants measured for each component of Al-fulvic acid complex suggests the polyfunctionality of fulvic acid. The dissociation rate constants measured here are probably an average value of a group of closely-related rate constants. With changing ratios of $[FA]/[M]$, the distribution of aluminum species changed, leading to the change in the dissociation rate constant. By comparison, the results from the buffered solution showed only two kinetically distinguishable components. The rate constant of the major component of the aluminum in the buffered solution without fulvic acid was smaller than that in the unbuffered solution, probably because of formation of Al-acetate complexes.

Figure 31 shows the kinetics of uptake of aluminum species by the Chelex resin from different size fractions of a model solution containing Al(III), Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) and fulvic acid. The overall rate of uptake of aluminum species increased with decreasing MW. This behaviour can result from (1) different concentration distribution of the same components in different size fractions; (2) different components in different size fractions. Results from data analysis by the iterative deconvolution method are listed in Table 27. Three kinetically distinguishable components of aluminum were resolved from all three size fractions. The concentration of the fastest component obtained from the kinetic analysis was constant $((1.4 \pm 0.2) \times 10^{-2} \text{ M})$ in each size fraction, whereas the concentration of the slowest component decreased with decreasing

Figure 31 Uptake of aluminum by the Chelex resin from different size fractions of the model solution, pH 5.0. [Chelex] = 1 % (w/w). [Al(III)] = $1.5 \mu\text{M}$, [FA] : [M] = 1.2, [M] = {[Al(III)] = 1.5 } + {[Cu(II)] = 0.16 } + {[Cd(II)] = 0.089 } + {[Ni(II)] = 0.17 } + {[Pb(II)] = 0.048 } + {[Zn(II)] = 0.15 } = $2.1 \mu\text{M}$. ○, MW cut-off < 3,000; ●, MW cut-off < 100,000; ◊, the filtrate of $0.45 \mu\text{m}$ filter.

Table 27 Kinetically distinguishable components of aluminum in different size fractions of the model solution^a containing metal ions and fulvic acid, pH 5.0

Sample type	[Al(III)] _{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}
0.45 μm filtrate	8.6×10^{-2}	16 ± 35	1.5 ± 0.6	18 ± 27	2.7 ± 0.8	66 ± 11	$< 1.3 \pm 0.1$
YM10 filtrate	7.5×10^{-2}	22 ± 36	1.0 ± 0.3	28 ± 46	1.2 ± 0.6	49 ± 41	$< 0.5 \pm 0.5$
(MW cut-off < 100,000)							
YM1 filtrate	3.4×10^{-2}	36 ± 26	2.7 ± 0.7	28 ± 27	4.1 ± 0.8	36 ± 14	$< 1.3 \pm 0.2$
(MW cut-off < 3,000)							

^a[M] = {[Al(III)] = 1.5} + {[Cd(II)] = 0.099} + {[Cu(II)] = 0.16} + {[Ni(II)] = 0.17} + {[Pb(II)] = 0.048} + {[Zn(II)] = 0.15} = 2.1 μM ; [FA]/[M] = 1.2. [Al(III)]_{total} = the total initial concentration of aluminum. $1C_i^0$ = the initial percentage of the *i*th kinetically distinguishable component. Values after $\pm$ 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.

MW of the Al(III) species. The dissociation rate constant for each kinetic component in each size fraction is relatively constant. These results suggest that differences in the rate of uptake of Al(III) species from different size fraction result from different concentration distribution and that the larger Al(III) species dissociates slower than the smaller Al(III) species. High standard deviations of non-linear regression analysis were due to high noise levels of the experimental data.

Comparison of the results in this work with those obtained by Langford *et. al.*[58], who used PAR instead of Chelex resin as a probe ligand, reveals that k_1 measured in this work is generally one order of magnitude lower. The slowest component of aluminum revealed in this study may correspond to the unrecovered portion in their study.

6-3-4-4 Aluminum species in river surface water and snow. Figure 32 shows the uptake of aluminum from different size fractions of a sample of Rideau River surface water at pH 5.0 using the Chelex batch technique. The results indicate that the uptake of aluminum species by the Chelex resin was slightly slower when the molecular weight was larger. This is in agreement with the results obtained from measurements on different size fractions of a model solution, which have been presented before. The results obtained by the iterative deconvolution method are listed in Table 28. Only one kinetically distinguishable component of aluminum was resolved for both fractions of molecular weight cut-off 100,000 and 3,000. This is not surprising because the concentrations of DOC (6.6 ppm), fluoride (as shown in Table 11) and other inorganic ligands in Rideau River surface water is high compared with that of aluminum (ppb level). All aluminum ions are expected to be present as organic and inorganic complexes.

Figure 32 Uptake of aluminum by the Chelex resin from the sample of Rideau River surface water, pH 5.0. [Chelex] = 1 % (w/w). ○, MW cut-off < 3,000; •, MW cut-off < 100,000.

Table 28 Kinetically distinguishable components of aluminum species in the sample of Rideau River surface water, pH 5.0 ± 0.5 (Date of sampling: July 13, 1994)

Sample type	$[\text{Al(III)}]_{\text{total}}, \mu\text{M}$	$k_1 \times 10^{-5}, \text{s}^{-1}$
0.45 μm filtrate	9.5×10^{-1}	
YM100 filtrate (MW cut-off 100,000)	9.5×10^{-1}	4.2 ± 0.03
YM3 filtrate (MW cut-off 3,000)	7.1×10^{-1}	6.4 ± 0.03

$[\text{Al(III)}]_{\text{total}}$ = the total initial concentration of aluminum. Values after $\pm$ 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.

Comparison of the results in Table 26, 27 and 28 reveals that all these aluminum species were probably bound to macromolecular, polyfunctional complexants such as humic material, or polymeric colloidal material such as iron oxyhydroxide, all of which tend to give low rates of dissociation for aluminum species in freshwaters. The very closely related dissociation rate constants of aluminum species in different size fractions probably suggest that aluminum is bound predominantly to one type of site in the humic substances.

The kinetic study of Al(III) speciation for a sample of Rideau River surface water at pH 8.0 reveals three kinetically distinguishable components, but all components had dissociation rate constants $\leq 10^{-4} \text{ s}^{-1}$, suggesting no positively charged Al(III) aquo ions were present at this pH.

Figure 33 shows the uptake of aluminum from different size fractions of the snow-melt (pH 5.0). The iterative deconvolution method applied to these three sets of data reveals two kinetically distinguishable components of aluminum as shown in Table 29. The dissociation rate constants for each kinetically distinguishable component in all size fractions of snow sample are relatively constant, indicating the same type of binding sites for each aluminum component in each size fractions. In the snow sample, the faster component of aluminum had a rate constant of similar order of magnitude to that in the model solution of aluminum without the buffer and FA (Table 26), and was probably a similar aquo complex of aluminum; the slower component of aluminum was probably an aluminum complex of simple inorganic ligands, such as carbonate, sulphate, or fluoride.

Figure 33 Uptake of aluminum by the Chelex resin from the sample of snow, pH 5.6.
 [Chelex] = 1 % (w/w). ◇, MW cut-off < 1,000; •, MW cut-off < 10,000;
 ○, the filtrate of 0.45 μm filter.

Table 29 Kinetically distinguishable components of aluminum in the samples of snow, pH 5.0 ± 0.5

Date of sampling	Sample type	$[\text{Al(III)}]_{\text{total}}, \mu\text{M}$	$C_1^0, \%$	$k_1 \times 10^{-2}, \text{s}^{-1}$	$C_2^0, \%$	$k_2 \times 10^{-5}, \text{s}^{-1}$
April 1, 1993	0.45 μm filtrate	4.5×10^{-1}	31 ± 4	1.1 ± 0.1	69 ± 5	$< 54 \pm 7$
March 10, 1994	0.45 μm filtrate	1.0	43 ± 5	1.7 ± 0.08	57 ± 2	$< 7.2 \pm 0.2$
	YM10 filtrate	8.8×10^{-1}	66 ± 6	1.7 ± 0.07	34 ± 3	$< 9.5 \pm 0.4$
	(MW cut-off 10,000)					
	YM1 filtrate	8.0×10^{-1}	54 ± 7	2.1 ± 0.1	46 ± 3	$< 12 \pm 0.4$
	(MW cut-off 1,000)					

$[\text{Al(III)}]_{\text{total}}$ = the total initial concentration of aluminum. C_1^0 = the initial percentage of the 'th kinetically distinguishable component. Values after $\pm$ 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.

6-3-5 *Copper speciation*

6-3-5-1 Effects of the presence of metal ions on the kinetics of uptake of copper by the Chelex resin. Figure 34 shows the effects of the presence of metal ions on the kinetics of uptake of copper from model solutions. Results from analysis by the iterative deconvolution method are listed in Table 30. The dissociation rate constants of copper species are relatively unchanged in the presence of the metal ions indicating that there is no significant effect from the metal ions on the kinetics of uptake of copper. Variation in the percentage of the slowest component is a result of different initial concentrations of $[\text{Cu(II)}]_{\text{total}}$. As observed from the results for analysis of aluminum, as shown in Table 22, the dissociation rate constants for copper species in model solutions, Table 30, were not changed by changing the initial concentration of Cu(II), suggesting that for copper equation (4-3) was first order or pseudo-first order.

6-3-5-2 Effects of addition of the complexant, fulvic acid. Figure 35 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 Cu-fulvic complexes, which dissociate slowly to generate Cu(II) aquo ions which are taken up by the Chelex resin. These rates were analyzed using the iterative deconvolution method and the results are listed in Table 31. Since fulvic acid is a polyfunctional complexant the dissociation kinetics of its Cu(II) complexes is different from those of the chelating agents, EDTA or NTA. In the presence of fulvic acid the component C_1 was not reduced to zero as it was in the presence of EDTA and NTA. This suggests that fulvic acid forms a complex with

Figure 34 Effects of the presence of metal ions on the kinetics of uptake of copper by the Chelex resin, pH 5.0 ± 0.5 . [Chelex] = 1 % (w/w). ○, [Cu(II)] = $2.1 \mu\text{M}$; •, [M] = {[Al(III)] = 1.5} + {[Cu(II)] = 0.16} + {[Cd(II)] = 0.089} + {[Ni(II)] = 0.17} + {[Pb(II)] = 0.048} + {[Zn(II)] = 0.15} = $2.1 \mu\text{M}$.

Table 30 Effects of the presence of metal ions and the initial concentration of copper on the kinetics of uptake of copper species by the Chelex resin from model solutions, pH 5.0 ± 0.5

$[\text{Cu(II)}]_{\text{total}}, \mu\text{M}$	$C_1^0, \%$	$k_1 \times 10^{-2}, \text{s}^{-1}$	$C_2^0, \%$	$k_2 \times 10^{-3}, \text{s}^{-1}$	$C_3^0, \%$	$k_3 \times 10^{-4}, \text{s}^{-1}$
2.1 ^a	89 ± 0.9	3.4 ± 0.02	9 ± 0.2	5.3 ± 0.9	2 ± 0.04	$< 3.1 \pm 0.07$
0.31 ^a	82 ± 1	4.1 ± 0.04	11 ± 0.3	4.0 ± 0.1	7 ± 0.1	$< 1.7 \pm 0.04$
0.16 ^b	75 ± 5	3.3 ± 0.2	12 ± 1	2.5 ± 0.3	13 ± 1	$< 2.8 \pm 1.0$

$[\text{Cu(II)}]_{\text{total}}$ = the total initial concentration of copper. C_i^0 = the initial percentage of the i th kinetically distinguishable component.

^aSolutions contain copper only. $^b[\text{M}] = \{[\text{Al(III)}] = 1.5\} + \{[\text{Cu(II)}] = 0.16\} + \{[\text{Cd(II)}] = 0.089\} + \{[\text{Ni(II)}] = 0.17\} + \{[\text{Pb(II)}] = 0.048\} + \{[\text{Zn(II)}] = 0.15\} = 2.1 \mu\text{M}$. Values after $\pm$ 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.

Figure 35 Effects of the concentration of fulvic acid on the kinetics of uptake of copper species in the model solutions, pH 5.0. [Chelex] = 1 % (w/w), [Cu(II)] = $8.9 \times 10^{-2} \mu\text{M}$. □ [FA] : [M] = 0.0; •, [FA] : [M] = 0.29; ○, [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)] = $2.1 \mu\text{M}$.

Table 31 Effect of the concentration of fulvic acid on the kinetics of uptake of copper species by the Chelex resin from model solutions containing Al(III), Cd(II), Cu(II), Ni(II), Zn(II) and Pb(II), pH = 5.0 ± 0.5

[FA]:[M] [*]	[Cu(II)] _{total} × 10 ⁻⁴ μM	C ₁ ⁰ %	k ₁ × 10 ⁻² s ⁻¹	C ₂ ⁰ %	k ₂ × 10 ⁻³ s ⁻¹	C ₃ ⁰ %	k ₃ × 10 ⁻⁵ s ⁻¹
0	1.6	75 ± 5	3.3 ± 0.2	12 ± 1	2.5 ± 0.3	13 ± 1	< 2.8 ± 1.0
0.29	1.6	55 ± 4	3.0 ± 0.2	24 ± 2	2.1 ± 0.1	21 ± 1	< 2.7 ± 0.9
0.58	1.6	56 ± 2	1.6 ± 0.06	29 ± 1	1.6 ± 0.04	15 ± 0.4	< 1.1 ± 0.2
0.87	1.6	51 ± 2	1.2 ± 0.04	32 ± 1	1.5 ± 0.03	17 ± 0.4	< 4.0 ± 0.2
1.2	1.6	35 ± 3	0.5 ± 0.04	38 ± 3	1.0 ± 0.1	27 ± 2	< 3.9 ± 0.3

[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. [Cu(II)]_{total} = the total initial concentration of copper. C_i⁰ = 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, are greater than the values of the standard deviations shown above, only two significant figures in the values of the rate constants are justified.

Cu(II) which dissociates at a rate not very different from the rate of its uptake by Chelex and thus 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 constant for the dissociation of component C_2 decreases as the concentration of fulvic acid increases. This is probably because decreasing the ratio of Cu(II)/FA causes occupation of stronger binding sites on fulvic acids, leading to a lower weighted average rate constant for dissociation [136]. 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.*[137], there is only one species of copper in aqueous solutions at pH 5. The kinetic analysis of copper speciation in this study (Table 30), however, consistently showed the existence of more than one kinetically distinguishable component and the signal for the slowest component of Cu(II) persists at a level significantly above the signal/noise ratio. Tests showed that this amount of Cu was not leached from the containing vessels, nor from the Chelex cation-exchange resin. 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, $\sim 0.02 \mu\text{M}$, in the solution. Since, however, Cu(II) aquo ion binds strongly to Chelex it seems unlikely that this amount 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 released from the resin, for example, an unpolymerized component from

the Chelex resin manufacturing process, which is a stronger complexing ligand than the Chelex resin. A test of this possibility is difficult because of the very low concentration of copper left in the solution.

Figure 36 shows the kinetics of uptake of copper species by the Chelex resin from different size fractions of a model solution containing Al(III), Cd(II), Cu(II), Ni(II), Pb(II) and Zn(II) and fulvic acid. The results from analysis using the iterative deconvolution method are listed in Table 32. Since almost all copper species in this model solution have molecular weight cut-off $< 3,000$, as shown in Table 32, it is not surprising that the kinetic curves for the three size fractions tested are the same, within the experimental uncertainty. Comparison of the results in Table 30 and 32 suggest that about 80 % of copper in this model solution is Cu(II) aquo ions.

6-3-5-3 Copper species in river surface water and snow. Figure 37 shows the uptake of Cu(II) by the Chelex resin from different size fractions of a sample of river surface water. The overall uptake rate is faster for copper species in the larger size fraction. The initial concentrations of the components and the dissociation rate constants obtained by the iterative deconvolution method are listed in Table 33. The distribution of three kinetically distinguishable components, C_1 , C_2 and C_3 , are similar in both size fractions. The dissociation rate constants for each component are higher in the YM100 filtrate, leading to a faster overall uptake of Cu(II) from the larger size fraction. This differs from that observed for Al(III) in Rideau River surface water and indicates that Cu(II) species are different in the two size fractions and that the larger species of Cu(II) dissociates faster than the smaller ones. This unusual result may suggest that the

Figure 36 Uptake of copper by the Chelex resin from different size fractions of the model solution, pH 5.0. $[\text{Chelex}] = 1\%$ (w/w). $[\text{M}] = \{[\text{Al(III)}] = 1.5\} + \{[\text{Cu(II)}] = 0.16\} + \{[\text{Cd(II)}] = 0.089\} + \{[\text{Ni(II)}] = 0.17\} + \{[\text{Pb(II)}] = 0.048\} + \{[\text{Zn(II)}] = 0.15\} = 2.1\ \mu\text{M}$. $[\text{FA}] / [\text{M}] = 1.2$. $\circ$, MW cut-off $< 3,000$; $\bullet$, MW cut-off $< 100,000$; $\diamond$, the filtrate of $0.45\ \mu\text{m}$ filter.

Table 32 Kinetically distinguishable components of copper in different size fractions of the model solution*, pH 5.0

Sample type	[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 , %	$k_3 \times 10^{-5}$, s^{-1}
0.45 μm filtrate	1.5×10^{-1}	67 ± 5	1.8 ± 0.06	16 ± 11	3.6 ± 0.3	17 ± 4	$< 5.4 \pm 0.7$
YM100 filtrate (MW cut-off 100,000)	1.4×10^{-1}	67 ± 5	2.2 ± 0.1	16 ± 11	3.5 ± 0.4	17 ± 5	$< 2.5 \pm 0.8$
YM1 filtrate (MW cut-off 3,000)	1.1×10^{-1}	68 ± 4	2.1 ± 0.07	14 ± 9	3.3 ± 0.3	18 ± 4	$< 1.4 \pm 0.8$

* $[\text{M}] = \{[\text{Al(III)}] = 1.5\} + \{[\text{Cu(II)}] = 0.16\} + \{[\text{Cd(II)}] = 0.089\} + \{[\text{Ni(II)}] = 0.17\} + \{[\text{Pb(II)}] = 0.048\} + \{[\text{Zn(II)}] = 0.15\} = 2.1 \mu\text{M}$; $[\text{FA}] / [\text{M}] = 1.2$. $[\text{Cu(II)}]_{\text{total}} =$ the total initial concentration of copper. $C_i^0 =$ the initial percentage of the 'th kinetically distinguishable component. Values after $\pm$ 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.

Figure 37 Uptake of copper by the Chelex resin from the sample of Rideau River surface water, pH 5.0. [Chelex] = 1 % (w/w). •, MW cut-off < 3,000; ○, MW cut-off < 100,000.

Table 33 Kinetically distinguishable components of copper in the sample of Rideau River surface water, pH 5.0 (Date of sampling: July 13, 1994)

Sample type	$[\text{Cu(II)}]_{\text{total}}, \mu\text{M}$	$C_1^0, \%$	$k_1 \times 10^3, \text{s}^{-1}$	$C_2^0, \%$	$k_2 \times 10^4, \text{s}^{-1}$	$C_3^0, \%$	$k_3 \times 10^5, \text{s}^{-1}$
YM100 filtrate (MW cut-off 100,000)	3.7×10^{-1}	44 ± 3	4.2 ± 0.1	34 ± 3	7.8 ± 0.2	22 ± 3	$< 5.4 \pm 0.2$
YM3 filtrate (MW cut-off 3,000)	2.9×10^{-1}	46 ± 5	2.7 ± 0.1	29 ± 6	5.9 ± 0.3	25 ± 6	$< 4.5 \pm 0.3$

$[\text{Cu(II)}]_{\text{total}}$ = the total initial concentration of copper. C_i^0 = the initial percentage of the i th kinetically distinguishable component. Values after $\pm$ 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.

rate of removal of copper may not be the rate of dissociation of the CuL_i complex, reaction (4-2), but may be the rate of removal of CuL_i by direct reaction with the Chelex, reaction (4-4). A large species may contain several ions of copper, bound to several different sites. If the large species is removed by reaction (4-4), several ions of copper are removed in one process and the rate of removal of copper will appear unusually fast. Thus, it will appear that the larger species is removed faster than the smaller species.

Comparison of the results in Table 32 and 33 shows that the rate constants for C_1 , C_2 and C_3 are smaller for the sample of river surface water of the same size fraction than those for the model solutions with the ratio of $[\text{FA}]/[\text{M}]$ of 1.2. Two of the dissociation rate constants for the Cu(II) components in the sample of river surface water are of the same order of magnitude as those for the two slowest components in the model solution of Cu(II) with fulvic acid, suggesting that the Cu(II) in the sample of river surface water was probably bound to humic materials or other polyfunctional complexants. Comparison of the results obtained by Olson and Shuman [109] reveals that k_1 measured in this study is lower. The slowest kinetic component resolved in this study may correspond to the unrecovered portion in their study.

Figure 38 shows the uptake of Cu(II) species by the Chelex resin from different size fractions of a snow sample. The results from analysis by the iterative deconvolution method, as shown in Table 34, reveals two and three kinetically distinguishable components of Cu(II) for the snow samples collected on April 1, 1993 and March 10, 1994, respectively. Comparison of these results with those in Tables 31 and 34 shows that the distribution of the kinetically distinguishable components of Cu(II) and their

Figure 38 Uptake of copper by the Chelex resin from the sample of snow, pH 5.6.
[Chelex] = 1 % (w/w). $\diamond$, MW cut-off < 1,000; $\bullet$, MW cut-off < 10,000;
 $\circ$, the filtrate of 0.45 μm filter.

Table 34 Kinetically distinguishable components of copper in the samples of snow, pH 5.0

Date of sampling	Sample type	$[\text{Cu(II)}]_{\text{total}}$ 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}
April 1, 1993	0.45 μm filtrate	1.0×10^{-1}	77 ± 4	3.5 ± 0.1	13 ± 0.8	2.6 ± 0.2		
March 10, 1994	0.45 μm filtrate	7.6×10^{-2}	83 ± 2	2.7 ± 0.1	10 ± 7	3.6 ± 0.2	7 ± 4	$< 1.2 \pm 0.1$
	YM10 filtrate	6.0×10^{-2}	72 ± 7	2.4 ± 0.1	18 ± 11	3.7 ± 0.3	10 ± 6	$< 1.1 \pm 0.1$
	(MW cut-off 10,000)							
	YM1 filtrate	6.0×10^{-2}	82 ± 7	2.6 ± 0.1	10 ± 26	6.6 ± 1	8 ± 6	$< 1.0 \pm 0.6$
	(MW cut-off 1,000)							

$[\text{Cu(II)}]_{\text{total}}$ = the total initial concentration of copper. C_i^0 = the initial percentage of the i th kinetically distinguishable component. Values after $\pm$ 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.

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 and/or simple inorganic complexes of Cu(II) such as sulphate/sulfite, nitrate/nitrite, chloride, etc.

CHAPTER 7 SUMMARY AND CONCLUSIONS

The scheme of metal speciation developed in this thesis has been successfully applied to samples of river surface waters and atmospheric precipitation. This speciation scheme addresses the whole size continuum of metal species and correlates the metal complexes separated into fractions based on their size with their dissociation kinetics. It thus provides a comprehensive scheme for characterization of metal species in the aquatic environment. Addressing the whole size continuum of metal species is of particular value in view of the growing recognition that a major proportion of metals in natural waters can be associated with colloidal matter. Kinetic studies of metal speciation described in this scheme cover a time scale of measurement from ~ 2 ms to several hours or days for the Chelex batch technique. This scheme provides a means of classifying dissolved trace metal species into "very labile", "moderately labile", "slowly labile" and "inert" categories with estimates for rate constants for dissociation of metal complexes for the various fractions of ultrafiltration. A decided advantage of this scheme is that the extremely high absolute sensitivity and excellent precision of the graphite platform furnace atomic absorption spectrometry and ICP-MS allow DIRECT determination of trace metals in natural waters to be done routinely and rapidly with excellent precision.

Application of the speciation scheme to the samples of river surface waters and atmospheric precipitation has shown that the distribution of metal species in the dissolved phase varies from sample to sample. The distribution of the metal species in aqueous media is pH-dependent. In the samples of Rideau River waters at pH 8, most of the Al

species are in the particulate phase, and have large molecular weight $> 100,000$ in the dissolved phase. They are most probably bonded by macromolecular ligands, e.g., humic materials, or adsorbed or occluded by polymeric colloidal materials, e.g., hydrous oxides. Most of Al(III) species in the smallest size-fraction (molecular weight < 500) are Chelex column-nonlabile, and are probably $\text{Al}(\text{OH})_4^-$. At pH 5.0, the distribution of the aluminum species in the sample of Rideau River surface waters shifted to lower molecular weight, probably because of the break down of the aluminum colloids. In the samples of rain and snow, most of the dissolved species of Al(III) have relative low molecular weight and are Chelex column-labile, probably as a result of low pH (< 6.0) and low content of organic substances. On the other hand, in the sample of Rideau River surface waters at pH 8.0, most of the Cu(II) species are in the dissolved phase. A large percentage of the dissolved species of Cu(II) have molecular weight $> 3,000$, indicating that Cu(II) is associated with humic substances or colloidal materials. Decrease in the pH also causes break down of the larger species of Cu(II). In the samples of rain water and snow, most of the Cu species are Chelex column-labile and are present in small size fractions (molecular weight < 1000).

Kinetic studies of metal speciation can provide information on the number of kinetically distinguishable components, the initial concentration for each component and the concentration of each component at any specific time during the kinetic run. This information is very important for understanding bioavailability of an element.

The advantages of using Chelex cation-exchange resin for kinetic studies of metal speciation are as follows:

- (1) chelex provides a wide scope for study as a result of its strong chelating property. According to the kinetic model developed in this work, all metal complexes of metals that are weaker than the metal-chelex complex can be measured with Chelex cation-exchange resin;

- (2) perturbation of the system is small because no other reagents are added.

If a proper anion-exchange resin is used to replace the Chelex cation-exchange resin in the batch technique, the kinetic model and the batch technique developed in this study can, then, be used to differentiate those negatively charged metal species, which appear as "inert" components in the Chelex batch technique. More complete information on metal speciation in the aquatic environment can be obtained.

Compared with GFAAS, ICP-MS has the following advantages:

- (1) Because of its better time resolution ICP-MS has capability to resolve labile complexes, not resolvable by GFAAS;
- (2) ICP-MS has excellent sensitivity. The limits of detection for some elements can be as low as 10^{-15} g;
- (3) ICP-MS is a true multi-element analytical technique.

GFAAS has some limitations when applied to kinetic studies; for example, the GFAAS results have more systematic errors and a larger scatter of data points. Also, GFAAS has lesser time resolution than ICP-MS. In spite of all these limitations, GFAAS also is an extremely useful technique for kinetic studies and can provide an independent check on the ICP-MS results.

The iterative deconvolution method with the nonlinear least-squares algorithm has

been found to be satisfactory for the analysis of kinetic data generated by the Chelex batch technique using ICP-MS. This work confirms the conclusions of McMinnon *et al.* [116] that the iterative deconvolution method is more effective than any other methods in terms of accuracy of results and resilience to noisy data. The iterative deconvolution method does not rely on subjective parameters, but is still limited in the power to resolve kinetic components whose rate constants are close.

Application of the Chelex batch technique to kinetic studies of aluminum and copper speciation in the model solutions and in the samples of river surface waters and snow has yielded valuable information about the dissociation rate constants of the aluminum and the copper species in these samples. The results reveal the importance of $[FA]/[metal\ ion]$ ratio, and hence, of 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 have 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.

Application of the Chelex batch technique for kinetic studies of Al and Cu speciation in the samples of Rideau River surface waters and snow has revealed a number of kinetically distinguishable components of these metals. One kinetically distinguishable

component of aluminum having dissociation rate $\sim 10^{-5} \text{ s}^{-1}$ and two kinetically distinguishable components of aluminum having dissociation rate constants of $\sim 10^{-2}$ and $\sim 10^{-5} \text{ s}^{-1}$ have been observed in the samples of river surface waters and snow, respectively. Three kinetically distinguishable components of copper having dissociation rate constants of $\sim 10^{-3}$, $\sim 10^{-4}$ and $\sim 10^{-5} \text{ s}^{-1}$, and three kinetically distinguishable components of copper having dissociation rate constants of $\sim 10^{-2}$, $\sim 10^{-3}$ and $\sim 10^{-4} \text{ s}^{-1}$, have been observed in the samples of river surface waters and snow, respectively. These results suggest that aluminum and copper are present both as an aquo ion and as simple complexes of inorganic ligands in snow, but probably bound to macromolecule complexants and colloidal substances in the Rideau River surface waters.

The major limitations of this work are as follows:

- (1) although metal species can be differentiated according to their physical and chemical properties using the techniques and methods developed in this work, they are still operationally defined. Identification of the ligands forming the metal complexes is only qualitative;
- (2) the use of Chelex as a complexant limits observation of the rate of dissociation reaction by the time taken for the reaction-formation of the Chelex-M complex. To estimate this rate, as a first approximation, we may assume that there is only one kinetically distinguishable component of aluminum present in the model solutions without any complexing ligands or the buffer solution. In fact, as shown in Table 26, one kinetically distinguishable component accounts for about 90 % of the aluminum. The half-life of 49 s for the uptake of aluminum (Figure 30)

corresponds to a formation rate constant for the Chelex-M complexes of $1.4 \times 10^{-2} \text{ s}^{-1}$. Only complexes of the metal ions whose rate constants for dissociation are approximately 10 times lower than this will be detected by the Chelex batch technique;

- (3) the kinetic model developed in this study has been validated experimentally using well-characterized systems, Cu-NTA and Cu-EDTA. The results for Al(III) and Cu(II) speciation, however, may predict possibility of partial failure of the kinetic model in more complicated systems. For example, direct uptake of positively charged complexes by the Chelex resin may occur instead of pre-dissociation of the metal complexes, as suggested in the kinetic model. More studies need to be done on the mechanism of metal uptake by the Chelex cation-exchange resin.

To solve problems (1) and (3) listed above, anodic stripping voltammetry (ASV) with controlled plating potential may be used to replace ICP-MS to follow the Chelex batch procedure. Controlled plating potential means that only a specific species of metal is monitored. The results will give information not only on mechanism but also on identity of the metal species. The problem of using ASV is that it is only applicable to the study of copper, because aluminum cannot be directly determined at a mercury electrode. Also, the time intervals between data points may be too large and some kinetic information may be lost. A similar limitation was observed when GFAAS was used to follow the kinetics.

For solving problem (2), application of other cation-exchange resins, such as activated alumina, may be examined in order to measure faster-dissociating components

of metals in the aquatic environment.

To determine if a polyfunctional complexant such as fulvic acid has a continuous range of affinities for cations and a continuum of binding sites with associated continuous range of dissociation rate constants, a study combining the measurement of thermodynamic and kinetic properties of metal-fulvic complexes will be necessary.

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