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**METAL SPECIATION DYNAMICS IN FRESHWATERS:
A KINETIC EXPLORATION**

by

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M.Sc. (Garyounis University)

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

Department of Chemistry

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Ottawa, Ontario

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Dedicated to my loving parents

Abstract

In chemical and toxicological studies of metals in the freshwater environment, Cd, Cu, Ni, Pb and Zn have been found to be toxicants at the concentration levels they are in polluted freshwaters, whereas some of these metals are nutrients at lower levels of concentration. Metal speciation dynamics was investigated using several metal-speciation methods: Competing Ligand Exchange Method/Graphite Furnace Atomic Absorption Spectrometry (CLEM/GFAAS); Competing Ligand Exchange Method/Adsorptive Cathodic Stripping Voltammetry (CLEM/AdCSV); Anodic Stripping Voltammetry (ASV) with a Rotating Disk Electrode (RDE). CLEM/GFAAS and CLEM/AdCSV were used to determine dissociation rate coefficients of metal complexes in freshwaters. ASV was used to determine stability constants, dissociation rate coefficients and diffusion coefficients, of Cd, Cu, Pb, and Zn complexes in freshwaters, soil solutions (pore waters) and through-fall precipitation samples collected from the Rouyn-Noranda, (Abitibi, Quebec) and Sudbury (Ontario) areas. In the above samples of soil solutions (pore waters), the order of the lability of the metal complexes, $\text{Ni(II)} > \text{Cu(II)} < \text{Zn(II)}$, followed the reverse order of the Ligand Field Stabilization Energy (LFSE) with the exception of Cu(II); the position of Cu(II) was compounded of the LFSE and the Jahn-Teller effect. The slow coordination equilibrium of 3d-transition elements, especially of Ni(II) and Cu(II), in freshwaters suggests that the usual equilibrium assumption for freshwaters may not be valid. This study has demonstrated a direct relationship between the kinetic lability and the metal-to-Dissolved Organic Carbon (DOC) mole ratio. The

lability increased with decreasing size fraction, resulting in the labile fraction being small metal species e.g. aqua-complex or small inorganic metal complexes. It was found that in freshwaters, release of humic-substance-bound Ni(II) as Ni-aqua complex was dependent on the competition by Al(III) and Fe(III) with Ni(II) for binding sites of humic substances. Exposure of DOC in freshwaters to UV-B radiation (280-320 nm) resulted in photodegradation of the DOC, releasing the DOC-bound metals. The above results show that the freshwater systems are dynamic and often far removed from equilibrium. These kinetic speciation techniques therefore represent an important advance in our experimental ability to investigate lability of metal complexes in freshwaters, and soil solutions (pore waters).

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CHAPTER 1

INTRODUCTION

Statement of the Problem

“Because the hydrological cycle powers all others, and because life on earth is so intimately tied to water, aquatic chemistry is a central link between the cycles of elements at the surface of the earth and the working of biological systems. Life adapts to its environment and modifies it. It is well known that in aquatic environments the different chemical forms of a given element may assume very distinct roles, and that for their behaviour to be predicted, the forms must be distinguished from one another by some measurement. The composition of natural waters reflects both the geochemistry of the planet earth and the biochemical requirements of its inhabitants. These are delicately in tune, constantly modifying each other, linked by a few billion years of “co-evolution” and both ultimately responding to the same fundamental laws of chemistry” [1].

The biological effects and biogeochemical cycling of trace metals are profoundly influenced by their chemical speciation [2,3]. The above quotation emphasizes the importance of the hydrological cycle and brings out the need to study the biogeochemistry of elements. Many trace metals are nutrients at low levels. However, they may become toxicants at slightly elevated levels. Among the metals that have prominently featured in chemical and toxicological studies of the environment are Cd, Cu, Pb, Ni and Zn. Considerable quantities of these metals are emitted to the atmospheric environment from anthropogenic sources (e.g. coal burning, metallurgical and industrial

processes, and waste incineration), or are released into the aquatic environment as effluents from industrial and municipal sources [4]. A large fraction of total metal emissions reach the aquatic environment via different pathways. In all types of natural waters, metals are generally found in trace or even ultra-trace levels. Depending on the metal, the typical range may vary between several hundred $\mu\text{g/L}$ in highly polluted rivers and 0.001 $\mu\text{g/L}$ in unpolluted open ocean waters.

Chemical Speciation

In the aquatic environment, trace elements are distributed in a variety of physicochemical forms. The individual physicochemical forms may include particulate and dissolved forms, such as simple inorganic species, organic complexes, and metal ions adsorbed onto a variety of colloidal particles. These species can coexist and may or may not be in thermodynamic equilibrium with one another [5]. Change in the chemical speciation of an element may affect its bioavailability, its degree of adsorption on suspended matter, its rate of transfer to the sediment, and its overall mobility in a water system. Hence, measurement of total metal concentrations alone is not adequate for understanding the effects of toxic metals in the aquatic environment, except in the unlikely occurrence of the total metal concentration representing the bioavailable metal [6]. Metal speciation studies are therefore necessary for interpreting many biological (bioconcentration, bioavailability and toxicity) and geochemical (transport, adsorption and precipitation) processes. The chemical speciation of metals in natural waters is a critical parameter governing its toxicity to and assimilation by, aquatic microorganisms [7,8]. Dissolved metal may exist in freshwaters as free metal ion (really, metal-aqua complex), as

complexed with inorganic ligands e.g. carbonate complex, and complexed with organic ligands, e.g. humate or fulvate.

The notion of chemical speciation is central to equilibrium and kinetic aspects of aquatic chemistry [9]. In natural waters, only a small portion of the dissolved metal may be present as free metal ion (really, the metal aqua complex) because the metal ions form stable complexes with a large variety of inorganic and organic ligands [10], which influence the bioavailability, toxicity and mobility of the metal [11-13]. All the various types of metal species present in natural waters, such as free ions, dissolved inorganic complexes, dissolved organic complexes, metal species in the form of dispersed colloids and metals adsorbed on colloids or suspended matter should be taken into consideration.

Natural Organic Matter (NOM) and Dissolved Organic Carbon(DOC)

Natural Organic Matter (NOM) plays an important role in the speciation of trace metals in natural waters. DOC content in rivers, lakes and estuaries ranges from 1 to 10 mg/L (1 mg/L corresponding to 1-5 $\mu\text{mol/L}$ of complexing sites). However, interstitial waters of sediments, some estuarine waters and much polluted waters can have DOC levels of 100 mg/L or higher [14]. Dissolved Organic Carbon (DOC) is the predominant constituent of NOM. In aquatic systems humic substances (including the humic acid and fulvic acid) represent 70-90% of DOC in wetlands and 10-30% in seawater [15]. The major constituent of DOC is humic substance, which is ubiquitous in the aquatic and the terrestrial environment. Humic substances present polyfunctional, polyelectrostatic and conformational effects due to different functional groups, high charge density and

stereochemistry [16]. In natural waters with a high content of organic substances, humic substances have been recognised as playing a determinant role in the binding of metal ions. Since humic substances dominate metal-complexation in the natural environment, this thesis is primarily concerned with the metal-complexation properties of DOC.

The interactions of metal ions with humic substances can influence the transport and bioavailability of the metals, acid-base balance, and humic solubility in waters, sediments and soils. Much research effort has been focussed on the study of metal and proton binding by isolated humic substances, aimed both at elucidating mechanisms and providing quantitative information. Humic substances are a particularly important category of complexant because of their high concentrations, strong affinity for metals, and ubiquity in freshwaters, soil solutions (pore water), and through-fall precipitation samples. Freshwaters, soil solutions (pore water), and through-fall precipitation samples are a complex milieu and competitive binding of metals and protons is important. In studies of competitive binding of metals and protons it is important to consider competition between trace metals [17,18], proton competition [19,20], and competition with major cations Ca^{2+} and Mg^{2+} in freshwater [21].

Objectives

The objectives of this work are:

1. To investigate metal speciation in aqueous environmental samples that have been impacted by anthropogenic pollution.

2. To study the factors that influence chemical speciation of metals.

Contents of the Thesis

This thesis is divided into nine chapters. Chapter 1 gives statement of the problem, describing the driving force and objectives of this research, and presents an outline of the thesis. Chapter 2 describes the scientific background. Chapter 3 presents the various theories that underpin this research. Chapter 4 presents the applications of Competing Ligand Exchange Method/Adsorptive Cathodic stripping Voltammetry (CLEM/AdCSV) of Cu(II) and Ni(II) speciation in throughfall precipitation samples and soil solutions (pore waters). Chapter 5 presents the topics of chemical speciation and speciation parameters which are quantitative measures of the physico-chemical characteristics of the metal species present in lake water samples. Chapter 6 presents the ultrafiltration technique as a powerful tool for size fractionation and characterization of various size fractions: cascade ultrafiltration coupled with the kinetic speciation of the metal species in each molecular weight cut-off (MWCO) fraction has provided a more comprehensive picture and an insight into the physical and chemical characteristics of the metal species than either the ultrafiltration technique or the measurement of dissociation kinetics could do alone. Chapter 7 describes the experimental results of competition by aluminium and iron with nickel for binding sites on humic substances in laboratory model systems and in freshwaters, using the kinetic approach. Chapter 7 also presents and critically analyzes experimental results of dissociation kinetics of metal-fulvic-acid (FA) complexes in laboratory model systems, including a discussion on the importance of [metal]/[FA] mole ratio on the kinetic lability of the metal-FA complexes. Chapter 8 describes the influence

of UV-B (280-320 nm) irradiation on metal speciation in freshwaters. The exposure to UV-B radiation of the solar spectrum reduces the binding ability of Dissolved Organic Carbon (DOC) in freshwaters, resulting in release of trace metal bound to DOC. This loss in the binding ability of DOC is the result of photodegradation of organic matter and the wavelengths responsible for this effect seem to be restricted to the UV-B region (280-320 nm) of the solar spectrum. Chapter 9 summarizes the major findings and conclusions of this thesis.

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CHAPTER 2

SCIENTIFIC BACKGROUND

Current State of Knowledge

Complexation by Simple Ligands

For **simple ligands**, L, metal complexes can result from two types of interaction. *Outer-sphere complexes* result from purely electrostatic attraction between the ligand and the metal ion, both of which conserve their hydration sphere (for simplicity, only the coordinated aqua ligand of M is shown, that of the ligand L has been omitted):

where K_{os} is the stability constant of the *outer-sphere complex*.

Inner-sphere complexes result from formation of a covalent bond between the coordinating atom(s) and the metal ion, with partial or total dehydration:

Equilibrium Constant (Formation Constant) of Complexes

In the formation of the 1:1 complex between the cation M and a simple ligand, L, the corresponding thermodynamic equilibrium constant (formation constant) $ML\beta^{th}$, is defined by the law of mass action

$$ML\beta^{th} = \frac{\{ML\}}{\{M\}\{L\}} \quad (3)$$

The ‘th’ superscript denotes the thermodynamic constant, expressed as a function of activities ($\{\}$). Generally, only concentrations ($[]$) are analytically measurable and it is, therefore, useful to define

$$ML\beta = \frac{[ML]}{[M][L]} = ML\beta^{th} \frac{M_\gamma L_\gamma}{ML_\gamma} \quad (4)$$

where γ is the activity coefficient. In contrast to $ML\beta^{th}$, $ML\beta$ is a constant only if the term $\frac{M_\gamma L_\gamma}{ML_\gamma}$ is constant under the given experimental conditions. β^{th} is linked to the

corresponding standard-state free energy, ΔG^0 , by the expression:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln \beta^{th} \quad (5)$$

where $\Delta H^\circ, \Delta S^\circ, R$ and T are standard-state enthalpy change, standard-state entropy change, universal gas constant, and absolute temperature, respectively. In equation (3), $\{M\}$ and $\{L\}$ are the activities of the free hydrated cation and ligand, respectively; in particular, protonated forms of L are not included in $\{L\}$.

In the more general case of the combination of m cations M with l ligands L , the cumulative formation constant is given by:

$$ML\beta_{ml}^{th} = \frac{\{M_m L_l\}}{\{M\}^m \{L\}^l} \quad (6)$$

The complexes are **polynuclear** if $m > 1$ and **mononuclear** if $m = 1$.

Observed rates of complex formation are generally consistent with the Eigen mechanism in which formation of an outer-sphere complex between the metal and ligand, with the stability constant K_{os} , is followed by a rate-limiting loss of water from the inner coordination sphere of the metal [1,2], with the water loss coefficient k_w [3]. The rate of loss of the coordination water molecules by the ligand is extremely fast (on the order of 10^9 - 10^{10} per second) [4].

The first-order rate of loss of coordination water from $M(H_2O)_6$, for eqn (2) can be written as:

$$Rate = -\frac{d[M(H_2O)_6 L^{(2-n)^+}]}{dt} = k_{-w} [M(H_2O)_6 L^{(2-n)^+}] \quad (7)$$

$$K_{OS} = \frac{[M(H_2O)_6 L]^{(2-n)^+}}{[M(H_2O)_6^{2+}][L^{n-}]} \quad (8)$$

$$[M(H_2O)_6 L]^{(2-n)^+} = K_{OS} [M(H_2O)_6^{2+}] [L^{n-}] \quad (9)$$

Substituting eqn (9) in eqn (7),

$$Rate = -\frac{d[M(H_2O)_6 L^{(2-n)^+}]}{dt} = k_{-w} K_{OS} [M(H_2O)_6^{2+}] [L^{n-}] = k_f [M(H_2O)_6^{2+}] [L^{n-}]$$

where the formation rate coefficient $k_f = K_{OS} k_{-w}$, as shown below.

By the Principle of Microscopic Reversibility [5],

$$K_{OS} = \frac{k_f}{k_d} \quad (10)$$

$$k_f = k_d K_{OS} \quad (11)$$

$$\text{but } k_d = k_{-w}, \text{ therefore, } k_f = K_{OS} K_{-w} \quad (12)$$

where K_{os} is the stability constant for the outer-sphere complex and is primarily dependent on the charges of the reacting species and the ionic strength of the medium. The rate coefficient for water-loss, k_w , is characteristic of the reacting metal.

The rate of water loss by the metal ion can be significantly accelerated by metal hydrolysis; this effect is especially important for slow-reacting metals [6] such as Cr(III), Fe(III) and Al(III).

Limitations of Thermodynamic Models

As with any thermodynamic calculation, the results cannot be taken as proof of the formation of a given compound. For aquatic media, the main limitations are as follows [10]:

1. The hypothesis that thermodynamic equilibrium is reached is often **not** justified.
2. Our ignorance of the nature and even the existence of certain complexes (e.g. mixed complexes). Mixed complexes are therefore not provided for in the model.
3. Our ignorance of the nature and properties of many homologous complexants.
4. The difficulty of correctly calculating activity coefficients for highly saline water or the gel phase of certain homologous complexants (humic substances).
5. Very few computer models include the secondary effects such as polyfunctional properties, conformational changes and polyelectrolyte properties, which are generally important in the case of homologous complexants (humic substances); a few models have, however, been developed to take into account the effects of

electric charge in cases involving adsorption on inorganic solids [7] and complexation by organic polyelectrolytes [8].

Naturally-Occurring, Organic Complexants in Freshwaters

Metal complexation by naturally-occurring, organic complexants in freshwaters controls the speciation of metals, and hence, the bioavailability and toxicity of metals. One such category of the above complexants is humic substances (e.g., humic and fulvic acids), which are produced by chemical and biological degradation of plants and other debris in aquatic systems and in soils. Trace metal complexation by humic substance plays an important role in solubilizing metals and in regulating transport, bioavailability and toxicity of metals in the aquatic environment.

Aquatic complexing agents can be divided into two categories: ‘simple’ ligands (e.g. Cl^- , CO_3^{2-} , amino-acids), and ‘homologous’ compound groups, from which this work will single out humic substances. Humic substances often contain a large number of complexing sites per molecule and the total molar concentration of these sites can be comparable to the concentrations of many simple ligands (Fig. 1).

In addition, as the stability of the corresponding complexes is often high, a rigorous interpretation of metal distribution in freshwaters should take into account the important role of homologous complexants (humic substances). Figure 2 shows that their main characteristics differ appreciably from those of the simple ligands, with the models of structures I—IV corresponding, overall, to particles of increasing size.

Homologous Complexants (Humic Substances) [10].

For the case of **homologous complexants** (humic substances), the reactions above can occur between M and each complexing site, but several secondary effects can influence the overall complexation process. These effects arise from the complexant's complicated structures and the fact that they often include a mixture of components, even after exhaustive fractionation. The coordinating sites (-S) will be distinguished from the complexing sites (-L). The -S sites denote only the groups of atoms (including carboxylic, phenolic, salicylic and nitrogen-bearing functional groups) which directly participate in bonding, forming either inner or outer-sphere complexes. The -L sites denote the entirety of the -S sites and their environments (steric, electric). Figure 3 presents a possible structure of humic substance [9] which is widely accepted.

Humic substances (humic and fulvic acids) which are ubiquitous in the aquatic and the terrestrial environment, are macromolecular, polydisperse systems, i.e., they contain a mixture of compounds of different molecular weights. Humic substances are physically and chemically heterogeneous, polyfunctional, organic complexants having numerous polar functional groups.

Their chemical heterogeneity arises from they having different functional groups in the complexants macromolecules and makes them unique in terms of their metal-complexation characteristics. Humic substances in water are water-swollen gels with functional groups both on their outside surface but also in the enormous cavernous

Figure 1. Concentrations of organic and inorganic compounds in three types of water [10].

Schematic structures	I	II	III	IV
	Simple ligand	Dissolved polyfunctional complexant	Monofunctional polyelectrolyte (permeable gel)	Monofunctional polyelectrolyte (surface reaction)

Examples	Cl^- CO_3^{2-} amino-acids citric acid	fulvic compounds PROM AROM	peptides proteins humic compounds polysaccharides cell walls	little hydrated Fe, Al, Mn oxides clays strongly hydrated metal hydroxides
		<div style="border: 1px solid black; padding: 5px; display: inline-block;"> metal oxides and clays covered by NOM </div>		
a polyfunctional character	weak often none	strong	intermediate	intermediate-weak
b change in conformation	weak or none	aggregation	gel formation spreading/coiling	coagulation
c polyelectrolyte character	weak or none	important	important	important

Figure 2. Characteristics of the main homologous complexing groups [10].

structures that develop inside the water-clogged colloidal humic substances. The geometric location of functional groups plays a significant role in their metal-binding properties. From the consideration of the geometric location, Zunion and Martin [11] have divided the functional groups, such as carboxylic acid, and phenolic hydroxyl groups into the following categories: (a) functional groups capable of forming chelate rings, with high bonding energy; (b) functional groups participating in open complex formation, with intermediate binding energy; and (c) functional groups, lying deeply buried within a macromolecule, with low binding energy. The general consensus is that the metal-binding humic substances can be classified as having both minor (~1-10%), strong binding sites, and major (~90-99%), weak binding sites [12].

Humic substances play an important role in water quality since they are the major constituents of Dissolved Organic Carbon (DOC). A detailed understanding of the metal binding properties of humic substances has particular importance for developing long-term solutions to the problems of waste storage, metal contaminations and remediation as well as the more fundamental characterization of metal ion transport and bioavailability. The metal ion complexation properties of humic and fulvic acids are complex.

Because of their heterogeneity and polyelectrolytic nature, humic substances possess the following unusual properties that make their metal-complexation reactions quite different from those that the metals undergo with simple, well-defined (homogeneous) ligands, such as salicylic acid and citric acid [10].

Figure 3. A tentative structure of humic acid [9].

(a) Polydispersity

Humic substances represent a variety of different molecules with a wide range of molecular masses.

(b) Polyfunctional properties

Each molecule contains a number of different functional groups. Fulvic and humic acids primarily have carboxylic or phenolic groups, but moieties bearing sulphur and nitrogen are also present.

(c) Polyelectrolyte properties

Each individual molecule has a large number of electric charges because of its polyfunctionality. Since most of the complexing sites have acid-base properties, they undergo dissociation at appropriate pH's, producing moieties with negative charge (anions). At a given temperature, the total charge depends on the pH and the degree of site occupation by metals, and on the ionic strength of the medium [10,13-17].

(d) Conformational properties

The electric charge and degree of hydration of the macromolecules also influences their conformational properties, and for steric reasons, this may also affect the stability of metal complexes. The conformation depends, in particular, on the hydration-dehydration process and formation of the hydrogen bonds or metallic bridges, which themselves depend on the degree of occupation of the complexing sites. Therefore, depending on experimental conditions, a given complexant can be present either as a simple solute or in

an aggregated gel form. In Figure 2, the complexants II-IV can vary with the chemical conditions in the medium, such as ionic strength, pH, the degree of occupation of the complexing sites [10,18]. Humic substances (which constitute about ~70-80% of the dissolved organic carbon in freshwaters) contain minor (~1-10%), strong binding sites, and major (~90-99%), weak binding sites [19, 12].

UV Radiation

The surface waters are exposed to UV-irradiation by the sunlight, the amount of which depends on the duration of the sunlight (a variable quantity, much dependent on the season and the climate). The exposure to UV light reduces the concentration of Dissolved Organic Carbon (DOC) in freshwaters [20], liberating trace metal bound to DOC. This loss is the result of photodegradation of organic matter and the wavelengths responsible for this effect seem to be restricted to the UV-B region (280-320 nm) of the solar spectrum [21]. The humic substances suffer photolytic decomposition by absorption of UV radiation generating smaller-size organic fractions [22]. The photodegradation of aquatic humic substances by UV light exposure has been verified *in situ* (rivers, open sea and lakes) and in the laboratory by Kieber et al. [21], De Haan [20] and Wetzel et al. [22], showing that the molecular size can decrease during photodegradation of humic substances. This effect has been observed for UV irradiation with wavelengths lower than 320 nm for at least 6 cm depth in the water column [20], even for short time periods.

Table 1. Photochemically produced reactive transient in surface water [23].

$^1\text{O}_2$	Singlet oxygen
H_2O_2	Hydrogen peroxide
O_2^-	Superoxide ion radical
$\cdot\text{OH}$	Hydroxyl radical
$\text{ROO}\cdot$	Peroxyl radical
Br_2^-	Dibromide radical

In natural waters, photochemical transformations can significantly affect the degradation of the dissolved organic matter (DOM) and the redox cycling of transition metals. DOM is often the chromophore in natural waters and acts as a sensitizer to produce reactive transients. The most common of these are singlet oxygen, peroxide, and the free radical species superoxide, hydroxyl radical, and organic peroxides, Table 1 [23].

Abundance of Aluminium and Iron in the Terrestrial Environment

Aluminium and iron are abundant and reactive elements in natural waters, with a variety of geochemical and chemical roles. In the dissolved and particulate phases of freshwaters, sediments and soils, they undergo significant interactions with Natural Organic Matter (NOM). In the case of Al, it has been shown that interactions with organic matter are central to the chemistry of the element in organic-rich soils [24,25], and consequently to its transfer to surface waters. They also play a crucial role in determining toxicity of aluminium [26]. Dissolved iron-organic complexes and iron oxide-humic colloids are important in the transport and fate of aluminium in rivers and estuaries [27].

Aluminium is the most abundant metal and the third most abundant element after oxygen and silicon. Comprising 8% of the earth's crust [28], aluminium is involved in many processes of increasing interest in both terrestrial and aquatic ecotoxicology and in soil and water quality assessments. Acid rain and acid mine drainage are two major causes of increased aluminium in freshwater systems. As acid water percolates through soil, pH decreases and aluminium dissolves. This process may increase aluminium concentrations to toxic levels (> 2 mg/L). The toxicity of aluminium in the natural environment is

believed to be directly related to the Al^{3+} concentration which is an important limiting factor for plant growth and root development in acid soils [29]. Complexation of Al^{3+} by Natural Organic Matter (NOM) changes the speciation of aluminium and influences its toxicity. Aluminium is toxic to both humans and aquatic organisms [30].

Iron is the second most abundant metal (after aluminium) and the fourth most abundant element in the Earth's crust. The essentiality of iron for the growth and well-being of almost all living organisms is well established in view of its involvement in a large number of biological systems. It is an almost ubiquitous component of ribonucleotide reductases. It is also involved in oxygen transport, activation and detoxification, in nitrogen fixation and in many reactions of photosynthesis [31].

Published literature dealing with the competition between metals for naturally-occurring, organic complexants in freshwaters are scarce. Mota et al. [32] have investigated the competition of aluminium, lead and cadmium for strong ligands in humic acid in natural waters using ion selective electrodes to measure free metal ion concentrations and have concluded that the release of lead and cadmium from metal-humic acid complexes upon addition of aluminium can increase the amount of lead and cadmium by a factor of 2 to 3, indicating that aluminium, lead and cadmium compete for strong binding sites of organic complexants. If, and as long as, organic complexants are present in large excess in freshwaters, metals do not compete with one other, because there are enough binding sites available on the organic complexants to satisfy all the metals present because of the large excess of the organic complexants over the metals [33].

Free Ion Activity Model (FIAM)

Major progress in our understanding of trace metal interactions with organisms in the aquatic environment over the past decade has come from a better appreciation of the importance of the chemical speciation of the metals in the natural environment and the ability to separate purely physiological effects from chemical ones. We can also distinguish two mechanisms of assimilation of dissolved species by unicellular organisms (e.g., plankton, bacteria). Fig. 4 presents a schematic diagram of complexing agents in the assimilation of metals (M) by aquatic organisms.

In Fig. 4, certain complexes, often hydrophobic, are capable of traversing the cellular membranes directly; on the other hand, for small hydrophobic complexes (e.g. alkyl complexes of mercury), which can directly traverse the biological membranes, it is above all the chemical nature of the complex which plays a predominant role in the assimilation of M [10]. As Fig. 4 shows schematically, whereas others must first dissociate, owing to their hydrophilicity or size, for these latter, labile complexes, the central role played by the activity of the hydrated, 'free' form of M, and the way in which the complexation reactions influence the principal assimilation steps are important determinants in the metals bioavailability. The Free-Ion Activity Model (FIAM) is the dominant model in this subject and is described below [34,35].

1. The activity of M in the external environment depends on the concentration of ligand L_1 , and on the stability of the complexes ML_1 ;

2. The activity of M at the surface of the membrane is a function of the ‘transporter’ ligand, L_2 , secreted to enable the hydrophilic cation to traverse the hydrophobic membrane [36] ; it also depends on the thermodynamic stability of ML_2 , when M is being transported, not by ‘transporter’ ligand, but within protein ‘channels’ [37], the size of M and its affinity for these protein structures will play roles analogous to the stability of the ML_2 complex;
3. Finally, the activity of M within the cell depends on the internal concentration of L_2 .

The direction of transport of M depends on its chemical potential gradients between the external medium, the membrane surface, and the intracellular medium, the displacement of M tending spontaneously towards the phase wherein its chemical potential is the lowest. On the other hand, the corresponding flux, i.e. the number of moles transported per unit time, depends on the rate of formation, dissociation, and the diffusion of all metal complexes. Therefore, for those labile ML_1 complexes which must dissociate in order for M to be assimilated, the direction of the flux (fixed by thermodynamic factors) and its magnitude (fixed by kinetic parameters) both depend directly on the complexation properties of M and L_1 .

However, FIAM does not imply that the hydrated metal (free metal ion) is the chemical species actually taken up by aquatic organisms. The free-metal ion activity simply reflects the chemical reactivity of the metals. It is this reactivity that determines the

extent of the metal's reaction with surface cellular sites, and hence, its 'bioavailability'. A number of key assumptions underlie the FIAM [35]:

1. The plasma membrane is the primary site for metal interactions with living organisms.
2. This interaction with the plasma membrane can be described as a surface complexation reaction, forming M-X-cell (charges on ligand not shown for simplicity).
3. Metal transport in solution, towards the membrane, and the subsequent surface complexation reaction occur rapidly, such that a pseudo-equilibrium is established between metal species in the bulk solution and those at the biological surface ('rapid', meaning faster than metal uptake, faster than the expression of the biological response). **This is the most important requirement for the FIAM to be applicable.**
4. The biological response, whether it is metal uptake, nutrition, or toxicity, is strictly dependent on the concentration of the M-X-cell surface complex, {M-X-cell}.
5. In the range of metal concentrations of toxicological interest, the concentration of free sites, {-X-cell}, remains virtually constant and variations in {M-X-cell} follow those of $[M^{z+}]$ in solution.

Figure 4. Schematic diagram of the role of complexing agents in the assimilation of metals (M) by aquatic organisms. Adapted from Campbell et al. [38].

6. During exposure to the metal of interest, the nature of the biological surface remains constant (i.e. the metal dose not induce any changes in the nature of the plasma membrane).

Deficiencies in our Current Knowledge

The dominant tool for the analysis of metal ion speciation has been the local equilibrium (or pseudo-equilibrium) approximation [39]; that is, complexation reactions are assumed to be fast relative to other processes. The equilibrium distribution among dissolved organic and inorganic species is assumed despite the fact that the total metal concentration may vary as a result of some controlling biogeochemical process. All reactions that are considered to take place in the system are also considered to have reached equilibrium. In many cases, complexation of metals by ligands is indeed rapid relative to other processes of interest, and equilibrium models then provide a good representation of complexation phenomena in natural waters [40]. However, natural systems are not equilibrium systems. They are dynamic and often far-removed from equilibrium [39,41-44]; hence, equilibrium speciation methods may not apply [45]. Heterogeneous ligand systems e.g. humic substances, which are colloidal, polyelectrolyte ligands, can depart considerably in kinetic behaviour from simple ligands and can result in systems that are dynamic and far removed from equilibrium [39]. In some instances, the rates of biogeochemical reactions may be influenced, or even controlled by the rates of metal complexation reactions [44].

Hypothesis

The hypothesis to be tested is that chemical speciation methodologies based on kinetics reflect more correctly the realities of freshwaters, soil solutions (pore water), and through-fall precipitation samples, in which metal release is often kinetically controlled.

Kinetic studies of metal speciation cannot only differentiate chemical species according to their kinetic parameters but can also give information on the distribution of the chemical species in the system at any time during biogeochemical processes (such as biological uptake) they may undergo. The operationally-defined nature of the metal species identified by the current approaches to the study of chemical speciation and metal bioavailability results from a failure to account for the analytical timescale of measurement. Hence, the results obtained from kinetic studies should be useful for estimating metal bioavailability if a kinetic model can be constructed to represent the process of biological uptake.

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CHAPTER 3

THEORY

Techniques for Chemical Speciation

A variety of analytical techniques have been used to measure metal speciation in natural waters, but few have been applied successfully in the complicated matrices encountered in freshwaters. Ion-Selective Electrode (ISE) potentiometry is the only technique capable of direct determination of free metal ion activity. However, it is of limited value because it lacks the necessary sensitivity and is subject to numerous interferences [1]. Most existing methods of chemical speciation give information on “operationally-defined” species. Sequential extractions for speciation of trace metals in soils [2] have been severely criticized by Nirel and Morel [3] who described the “operationally-defined” results of this procedure as: “what is measured is defined by what is measured”. Anodic stripping voltammetry has been reported to provide a measure of bioavailable metal but the results are known to be operationally-defined. Hence, novel chemical techniques and methods are required to characterize and quantify the bioavailable chemical species by speciation parameters which provide quantitative measures of the characteristics of the metal species [4-8]. The speciation parameters are: dissociation rate coefficient (a measure of the kinetic lability), diffusion coefficient (a measure of the mobility), and stability constant (a measure of the thermodynamic stability, and hence, of the equilibrium activity of free metal ion).

The Competing Ligand Exchange Method

Kinetic speciation by competing ligand exchange method (CLEM) employs a competing ligand which rapidly binds metals to form strong complexes [9-11]. The following kinetic model developed by Olson et al. [12,13] has been adapted to study the dissociation of ML, where M is a metal ion and L is a macromolecular, polyfunctional complexant, such as a humic substance, having binding sites of different chemical affinities (for simplicity, the charge on M and L have been omitted). In the complexant L, the metal M is bound to multiple sites, all of which dissociate independently and simultaneously at a rate that depends on the nature of the functional group, its position on the macromolecules, and the residual charge. The dissociation is first-order or pseudo-first-order. Consider an aqueous mixture of n components, in which each component, designated ML_i , exists in equilibrium with its dissociation products:

where k_1 and k_{-1} are the rate coefficients for the forward and the backward reaction, respectively.

The Kinetic Model uses chemical competition with Chelex-100 chelating resin (solid) as the competing ligand, which is added in sufficient excess [14]. Chelex reacts with M as follows:

The model assumes that:

1. reaction (14) is much faster than reaction (13) and
2. $[R] \gg [M]$.

Because $[R] \gg [M]$, reaction (14) is pseudo-first-order. Since k_2 is large, as has been determined by Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) [7,8,15] and with Chelex in sufficient excess, the condition $k_2 [R] \gg k_{-1} [L]$ holds, and the overall reaction (15) is irreversible.

Hence, the rate of formation of the M-R complex is determined by the rate of dissociation of ML in reaction (13), and the rate expression is simply:

$$\frac{d[M-R]}{dt} = -\frac{d[ML_i]}{dt} = k_1 [ML_i] \quad (16)$$

The two assumptions made above have been validated as follows: assumption No. 1, by our previous studies using ICP-MS [7,8,15-17], and assumption No. 2, by taking a

sufficient excess of the competing ligand, R, over the very low concentration of the trace metal ions present in the water samples.

If each complex, ML_i , undergoes, independently and simultaneously, a first-order or pseudo-first-order dissociation reaction, the sum of the concentrations of all components of the complex ML remaining undissociated at any time t , $[ML]_t$, can be described by equation (17). Simultaneous kinetic analysis of multicomponent systems is well established and has been widely used [18-20]. Kinetic analysis applied to metal speciation has been reported by several authors [12,13,16-18,21-24].

$$[ML]_t = \sum_{i=1}^n [ML_i]_0 \exp(-k_i t) \quad (17)$$

The $[ML]_t$ can be measured by Graphite Furnace Atomic Absorption Spectrometry (GFAAS) using Chelex 100 as the competing ligand. The metal concentration is measured over time and rate coefficients for the dissociation of metal complexes are obtained by non-linear regression analysis. Other workers [10] have used 4-(2-pyridylazo) resorcinol (PAR) as a competing ligand to form a water-soluble metal complex, and have measured the absorption of the metal-PAR complex at 500 nm. The PAR method [10] provides a large quantity of data points but suffers from poor analytical sensitivity, especially for nickel complexes at the mM concentration range which is relevant to unpolluted freshwaters. Chelex batch techniques, on the other hand, use a solid-phase cation-exchange resin as the competing ligand, in combination with

measurement by Inductively Coupled Plasma Mass Spectrometry (ICP-MS), and are highly sensitive and provide a large number of data points [8]. However, the ICP-MS measurement requires expensive equipment and is restricted to water samples having a low salt content.

Similarly, the free metal ion concentration $[M]_t$ at any time, t , can be described by an exponential rise function as shown in equation (18):

$$[M]_t = \sum_{i=1}^n [ML_i]_0 [1 - \exp(-k_i t)] = [MR]_t \quad (18)$$

Upon the addition of an appropriate competing ligand, the complex of the metal with the competing ligand, $[MR]_t$ (and hence, $[M]_t$), can be determined by Adsorptive Cathodic Stripping Voltammetry (AdCSV).

Adsorptive Cathodic Stripping Voltammetry (AdCSV)

Adsorptive Cathodic Stripping Voltammetry (AdCSV) involves complexation of the metal present in a solution with an added organic ligand. After passive adsorption of a fraction of this complex in the form of a thin film, onto a hanging mercury drop electrode the complexed metal is reduced during a cathodic scan and the resulting current increase is measured. There are two main advantages related to adsorptive deposition. First, any oxidation state can be used rather than only the metallic state. The second advantage is that the material is collected as a monomolecular layer on the electrode surface, so all the

material is instantaneously accessible to reduction (or oxidation); therefore, the reduction current is independent of diffusion of the reactive species and very fast potential scanning techniques can be employed, producing larger currents [25]. Adsorptive Cathodic Stripping Voltammetry (AdCSV) to metal complexes is complementary to Anodic Stripping Voltammetry (ASV). It makes possible the determination of about 40 elements in a great variety of matrices that are impossible to determine by ASV because of their insolubility in mercury [26].

In AdCSV, the metal complex formed, after the addition of a suitable competing ligand, is accumulated by adsorption on the electrode-solution interface. Wang [27] has described the steps involved in the AdCSV (accumulation-stripping) as follows. If in the sample solution, the metal ion M^{n+} forms with the added, competing ligand L the complex ML_n^{n+} having surface-active properties, then it can be accumulated on the electrode surface according to the following mechanism:

In the simplest case, the M^{n+} reacts with L according to reaction (19) that takes place in the solution and is the chemical stage of the process:

The complex formed is subsequently adsorbed on the electrode surface:

Figure 5. The preconcentration mechanism and the stripping scheme in AdCSV.

Adapted from Wang [27].

If the rates of the adsorption and chemical stages are comparable, then adsorption of the ligand and complexation will proceed at the electrode practically simultaneously, and it will be very difficult to distinguish them.

In the stripping phase electrode is usually polarized cathodically. In the majority of complexes the metal ion is reduced either partly or completely, but reduction of the ligand in the adsorbed complex is also possible [28]. Upon partial reduction of the metal ion, the number of ligands in the complex may be changed, but the new complex remains adsorbed at the electrode surface [29,30]

Competing Ligands used in AdCSV

Usually, the competing ligands used in AdCSV are surface-active compounds so that they are able to adsorb or chemisorb on the Hanging Mercury Drop Electrode (HMDE). It seems that the presence of π -electrons increases the adsorption process [28], whereas the presence of S donors helps the chemisorption. Sulfur-containing ligands are chemisorbed on mercury, while others are adsorbed mainly by π -electrons interactions with the electrode surface. In principle, the ligands are electrochemically inactive, but electroactive ligands may also be used if their electrode reactions do not interfere with the stripping reactions of metal ions [31]. The complex formed must be stable and show electrochemical activity. The kinetics of the complex formation should be fast to allow

quick adsorption or chemisorption on the electrode (Hg) surface, which is especially important in flow systems.

The use of a Hanging Mercury Drop Electrode (HMDE) is preferred for AdCSV because it offers the possibility of renewing the electrode surface (by renewing the Hg drop), and thus allowing repetitive measurements at fresh electrode surface. It is essential in AdCSV that a new electrode (Hg) surface is exposed since the electrode surface becomes saturated with the metal complex or the free ligand. The HMDE has the disadvantage of suffering from blockage of the glass capillary which, however, costs only a small amount of time/money to replace with a new glass capillary. Rotating disk electrode voltammetry/square wave voltammetry (RDEV/SWV) has also been used successfully in AdCSV [32].

Two illustrations of the applications of AdCSV to freshwaters are presented here as follows:

1. Adsorptive Cathodic Stripping Voltammetry of $\text{Cu}(\text{Oxine})_2$ complex.
2. Adsorptive Cathodic Stripping Voltammetry of $\text{Ni}(\text{DMG})_2$ complex.

Adsorptive Cathodic Stripping Voltammetry of $\text{Cu}(\text{Oxine})_2$ complex:

Oxine (8-hydroxy-quinoline) is a well-known complexing agent for the analytical determination of numerous metals. The ligand is involved in two acid-base equilibria

Figure 6. The structure of bis(8-hydroxyquinolinato)copper(II) used in CLEM/AdCSV.

with $pK_{a1} = 5.16$ and $pK_{a2} = 9.63$ [33], which define the relative concentrations of the cationic, neutral and anionic species of Oxine at a given pH. The Cu(II)-Oxine complexes have 1:1 and 1:2 stoichiometries, $\text{Cu}(\text{Ox})^+$, and $\text{Cu}(\text{Ox})_2$. Solis et al. [34] reported that 1:2 complex $[\text{Cu}(\text{Ox})_2]$ is the predominant species at $\text{pH} > 4$. The high stability constant for the square-planar bis(8-hydroxyquinolino)copper (II) ($\beta_{\text{Cu}(\text{Ox})_2} = 1.6 \times 10^{26}$) is indicative of the highly stable character of this complex [35], the structure of the complex is shown in Figure 6 [36].

Solis *et al.* [34] have reported that the $\text{Cu}(\text{Oxine})_2$ complex gives quasi-reversible waves involving adsorbed reactants and soluble products.

where k_{ad} and k_s are the adsorption and the charge transfer rate constant, respectively, of the electrochemical reaction. For simplicity, the charges of the ligand and complexes have been omitted.

Adsorptive Cathodic Stripping Voltammetry of $\text{Ni}(\text{DMG})_2$

The high selectivity of DMG for complexation and precipitation of Ni^{2+} results from the unusual structure of the solid $\text{Ni}(\text{DMG})_2$ complex. DMG forms a red, square-planar, strong chelate, $\text{Ni}(\text{DMG})_2$, with Ni(II). The square-planar bis(dimethylglyoximate)

Figure 7. The structure of bis(dimethylglyoximate)nickel(II) used in CLEM/AdCSV.

Ni(II) complex has two planar units stacked one on another so that the nickel “atoms” are bonded [37] with the following structure as presented in Figure 7 [38]. The reaction in the bulk solution in the presence of amino and dimethylglyoximato ligands involve the equilibria:

At 0.1M NH₃ and in the absence of DMG, the nickel-amino complex is expected to predominate [39]; in the presence of an excess of DMG, the Ni(DMG)₂ chelate should be formed almost exclusively (since the Ni(DMG)₂ chelate has high stability, a large excess of DMG is not required):

Under the experimental conditions (used in this work) of the DMG added in excess, the equilibrium represented by equation (23) lies far to the right, *i.e.* Ni(II) is converted quantitatively into the Ni(DMG)₂ chelate.

Ramirez et al. [40] have reported that adsorption of Ni(DMG)₂ on a mercury electrode shows a reversible behaviour.

where X represents a free “site” on the electrode surface, and $\text{Ni(DMG)}_2^{\text{ads}}$ represents the adsorbed bis(dimethylglyoximato) Ni(II) complex in the interface; k_{ads} and k_{des} represent the rate coefficients for adsorption and desorption, respectively; both dependent upon the electrical state of the system.

During adsorption, solvent molecules in the compact layer are replaced by molecules of the adsorbed surface-active substance (surfactant), resulting in a controlled interfacial accumulation of a monolayer of metal chelate at the electrode surface. The amount of adsorbate on a fully covered electrode surface (monolayer coverage) is typically $10^{-9} - 10^{-10} \text{ mol cm}^{-2}$ for low molecular weight adsorbates and $10^{-11} \text{ mol cm}^{-2}$ for high molecular weight adsorbates [27]. The extent of adsorption is often related to the solubility of the reactant in the solvent; low solubility tends to promote strong adsorption. At sufficiently strong positive or negative potentials, a strong electric field is generated, leading to the replacement of the less-polar particles of the surface-active substance by polar solvent molecules, and the surfactant is completely desorbed from the electrode. The response of the surface-confined species is directly related to the surface concentration. The relationship between the equilibrium surface concentration and the bulk concentration is described by an adsorption isotherm. Adsorption of Ni(DMG)_2 onto the electrode surface has been found to obey a Frumkin isotherm with the time required to reach equilibrium surface coverage ranging from 30 s to > 20 min. for nickel concentrations of 62.5 – 0.5

ng/mL [39]. Pihlar et al. [39] concluded that the adsorbed species at the polarized electrode is a neutral complex, that there is a negligible influence of deposition potential on the reaction rate and that the desorption reaction proceeds by two consecutive steps:

followed by reduction:

The desorption process proceeds simultaneously with reduction of the nickel(I) intermediate, leading to a pseudo-faradaic discharge across the electrical double layer, and a corresponding increase in the total current passed through the cell [39].

The mechanism for the reduction of adsorbed complexes is poorly understood. Vukomanovic et al. [41] have reported a 16-18 electron process, whereas Pihlar et al. [39] have reported a 2 electron process for the reduction of the $\text{Ni}(\text{DMG})_2$ complex pre-concentrated and adsorbed on a mercury electrode from a basic solution. As shown below in the Kinetic Model, the overall reaction in an aqueous solution of $\text{Ni}(\text{II})$ containing NH_3 and DMG ligand at typical experimental conditions ($[\text{Ni}(\text{II})] \leq 10^{-6} \text{ M}$, $[\text{NH}_3] \approx 0.1 \text{ M}$, $[\text{DMG}] \approx 10^{-3} \text{ M}$, *i.e.*, $[\text{DMG}] \gg [\text{Ni}(\text{II})]$) can be divided into three steps: (1) a homogeneous equilibrium between different nickel species in the solution, (2) an

adsorption process, and (3) reduction of the adsorbed complex by an irreversible charge transfer. Steps (2) and (3) are slow in the measurement time scale of the technique used and are both dependent on the electrode potential.

Anodic Stripping Voltammetry

The high analytical sensitivity of Square Wave Anodic Stripping Voltammetry (SWASV) with a Thin Mercury Film-Rotating Disk Electrode (TMF-RDE) allows for the determination of trace elements in natural waters with minimal sample treatment so that chemical equilibrium is not disturbed appreciably. “ASV labile” and “ASV non-labile” species [42] have sometimes been correlated with metal bioavailability and toxicity [43]. However, the term “lability” as applied to Anodic Stripping Voltammetry (ASV) has an operational definition related to the observed stripping current. Complexes that lie between the operational definitions of “labile” and “non-labile” complexes contribute to ASV currents to an extent that depends on their dissociation rate and concentration [42]. Hence, a theoretical framework is required to correctly interpret the analytical signals in ASV, and relate the results to natural processes in the environment. Van Leeuwen et al. [44] have presented a critical study of the role of the size of macromolecular ligands and dissociation kinetics of complexes in voltammetric techniques for complexation measurements in freshwater media.

Metal complexes, ML, are transported from the bulk solution to the electrode surface by convective-diffusion (Fig. 8). Transport of ML from the bulk solution to the Nernstian diffusion layer is by convection; however, within the diffusion layer mass transport is

controlled entirely by diffusion. A complex with a small diffusion coefficient will diffuse more slowly than a complex with a large diffusion coefficient, generating a lower current. Within the diffusion layer ML may undergo first-order dissociation, existing in equilibrium with the dissociation products, M and L (reaction 27). For simplicity, charges have been omitted.

As a first approximation, the association rate coefficient, k_a , and dissociation rate coefficient, k_d , are coupled by the stability constant, K .

$$K = \frac{C_{ML}}{C_M C_L} = \frac{k_a}{k_d} \quad (28)$$

where C_{ML} , C_M , and C_L are the concentration of ML, M, and L in the bulk solution, respectively.

If a sufficiently negative potential is applied to the electrode, M will be reduced to M^0 , driving reaction 27 to the left. The magnitude of the applied potential required to reduce M depends on the stability of ML. Lability is related to the kinetics of complex dissociation when M is consumed at the electrode surface [44]. Complexes are called labile if the association/dissociation process (kinetic flux) is fast compared with the

diffusion of ML to the electrode (diffusive flux). According to the Nernstian diffusion-layer concept, the concentration of ML decreases linearly from the boundary of the diffusion layer to the electrode surface; the extent of this concentration gradient depends on the lability of ML. The time scale of the electrochemical measurement defines the metal species that can be measured by placing constraints upon the kinetics of metal complex dissociation [42,44,45]. In ASV, the thickness of the diffusion layer defines the time scale of the electrochemical measurement [44,45]. Although an average diffusion layer thickness can be defined for a hanging mercury drop electrode [45], precise control over the thickness of the Nernstian diffusion layer requires a rotating disk electrode [46]. The application of a TMF-RDE and linear scan anodic stripping voltammetry to determine the dissociation kinetics of metal complexes in natural waters was reported by Shuman and Michael [47]. Shuman and Michael [42] reported a first-order dissociation rate coefficient $\approx 2 \text{ s}^{-1}$ for a copper complex in a spiked marine coastal water sample. A TMF-RDE with differential pulse anodic stripping voltammetry and square wave anodic stripping voltammetry was used to determine dissociation rate coefficients and diffusion coefficients of metal complexes in samples of a river surface water [5], model solutions and snow [4,48].

Rotating Disk Electrode Voltammetry

The general solution of the three-dimensional convective diffusion equation to describe the limiting flux, J , of a metal complex (ML) system at the electrode surface was derived by De Jong and van Leeuwen [49,50].

$$J(t) = D_M^{1/2} k_d^{1/2} c_T \frac{(\epsilon^{-1} + K')^{3/2}}{K'(1 + K')} \exp(\Lambda_{ss}^2 \delta^2) \operatorname{erfc}(\Lambda_{ss} \delta) \quad (29)$$

where $C_T = C_M + C_{ML}$ is the total metal concentration in the bulk solution, $K' = Kc_L$, $\epsilon = D_{ML} / D_M$ and Λ_{ss} is the lability parameter as defined by De Jong and van Leeuwen [49,50] and is given by:

$$\Lambda_{ss} = \frac{k_d^{1/2} (1 + \epsilon K')^{1/2}}{D_{ML}^{1/2} \epsilon K'} \quad (30)$$

where ϵ is the ratio of the diffusion coefficients of ML and M, respectively, hence, metal complexes that are labile at electrode surface obey the condition [49,50].

$$\Lambda_{ss} \delta \gg 1 \quad (31)$$

The limiting current is related to the flux by equation (32):

$$i_{lim} = nFAJ(t) \quad (32)$$

The limiting current at a rotating disk electrode is given by combining equations (29) and (32).

$$i_{lim} = nFAD_M^{1/2} k_d^{1/2} c_T \frac{(\epsilon^{-1} + K')^{3/2}}{K'(1 + K')} \exp(\Lambda_{ss}^2 \delta^2) \operatorname{erfc}(\Lambda_{ss} \delta) \quad (33)$$

De Jong and van Leeuwen [49,50] have shown that for a labile system, equation (33) can be simplified to equation (34). The theory for the determination of diffusion coefficients and dissociation rate coefficients at a rotating disk electrode has been described previously [48,51-53]. The limiting current, i_{lim} , is given by:

$$i_{\text{lim}} = nFAD \frac{C_T}{\delta} \quad (34)$$

where n is the number of electrons involved in the electrode reaction, C_T is the concentration of diffusing species in the bulk solution, D is the diffusion coefficient of the electroactive species, F is Faraday constant, A is the electrode surface area, and δ is the thickness of the diffusion layer.

The thickness of the diffusion layer, δ , at a rotating disk electrode is given by [46]:

$$\delta = 1.61D^{1/3}\nu^{1/6}\omega^{-1/2} \quad (35)$$

where ω is the angular velocity (rad s^{-1}) and ν is the kinematic viscosity (viscosity/density). A typical value of ν for an aqueous solution is $10^{-2} \text{ cm}^2 \text{ s}^{-1}$, which has been adopted for this work [4].

Combining equations 34 and 35 yields the Levich equation [46], which describes the relationship between the limiting current and the diffusion coefficient at a rotating disk electrode.

$$i_{\text{lim}} = \frac{nFAD^{2/3}C_T \omega^{1/2}}{1.61\nu^{1/6}} \quad (36)$$

Equation 36 shows that the diffusion coefficient, D , can be calculated from the dependence of i_{lim} on the angular velocity of the rotating disk electrode. For anodic

stripping voltammetry, it is more convenient to use the total charge, Q (in coulombs), required for the reduction of the free metal ion, M , where $Q = \int i dt$.

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CHAPTER 4

KINETIC SPECIATION IN ATMOSPHERIC PRECIPITATION SAMPLES COLLECTED FROM THE SUDBURY (ONTARIO) AREA

Adsorptive Cathodic Stripping Voltammetry (AdCSV)

An important advantage of AdCSV over traditional electrochemical techniques such as ASV is that AdCSV can be applied to virtually any element provided that a suitable ligand can be found for the element of interest. In the presence of a large excess of a competing ligand, such as DMG for the determination of Ni, eqn (18) can be rewritten as

$$[\text{Ni}^{2+}]_t = [\text{Ni}(\text{DMG})_2]_t = \sum_{i=1}^n [\text{NiL}_i]_0 [1 - \exp(-k_i t)] \quad (\text{a})$$

Similarly, in the presence of a large excess of Oxine as a competing ligand for the determination of Cu, eqn (18) can be rewritten as

$$[\text{Cu}^{2+}]_t = [\text{Cu}(\text{Ox})_2]_t = \sum_{i=1}^n [\text{CuL}_i]_0 [1 - \exp(-k_i t)] \quad (\text{b})$$

The concentration of “free” metal ion, $[M^{2+}]$, at any time, t , can be described by an exponential function that rises exponentially to a limiting value. For GFAAS using Chelex 100 as the competing ligand, eqn (17) can be applied directly.

Since the individual components in reactions (13) and (14) dissociate simultaneously and independently, the equations a, b, and 18 are summations of all the individual dissociation rate coefficients, $k_{d,i}$, that arise from the dissociation of the individual complexes, ML_i .

Experimental

Reagents

All solutions were prepared with ultrapure water of resistivity 18.2 M Ω -cm, which was obtained direct from an ultrapure water system, Milli-Q-Academic (Millipore Corporation, Bedford, MA, USA). Stock solutions of 1000 μ g/mL nickel and copper were prepared, separately, by dissolving pure nickel and copper powder (SPEX, 99.999%) in ultrapure nitric acid (Ultrex II, J.T. Baker Inc., Phillipsburg, NJ, USA), and diluting with ultrapure water containing 1 % (v/v) nitric acid. For Ni/AdCSV, a stock solution of 0.1M dimethylglyoxime (DMG) was prepared by dissolving an appropriate amount of the solid DMG (Fisher Scientific, certified) in ethanol (Spectro grade). The pH buffer solution was 2M sodium acetate (NaOAc). The 2M sodium acetate (NaOAc) stock solution was prepared by dissolving an appropriate quantity of sodium acetate trihydrate (ACS grade/BDH) in ultrapure water. Prior to its use, the sodium acetate solution was purified of metals by electrolysis at $-1.5V$ versus E_{SCE} for at least 72 h. A 2M stock

solution of acetic acid was prepared from 99% minimum sub-boiling acetic acid which was distilled in a quartz still (prepared by Seastar Chemicals Inc. Sydney B.C., Canada), by diluting with ultrapure water; 2M aqueous NaOH (ANACHEMIA) was added to it. All solutions were prepared by dilution of the stock solutions with ultrapure water immediately prior to determination unless otherwise specified.

For Cu/AdCSV, 0.01M stock solution of 8-hydroxyquinoline (Oxine) was prepared by dissolving an appropriate amount of the solid Oxine (Fisher Scientific, certified) in pure methanol (HPLC grade). The PIPES (Piperazine-N,N'-bis[2-ethane-sulfonic acid] and sodium hydroxide (ACS reagent grade, BDH) reagents were used to prepare the aqueous stock solutions of 0.5M PIPES and 1M NaOH, respectively. Variable amounts of HNO₃ (Ultrex II) and NaOH were used in order to adjust the pH to the desired value. The pH was checked before and after each experiment. Because the Oxine solutions can undergo photolytic decomposition, fresh solutions of Oxine were prepared weekly.

Laurentian Fulvic Acid (LFA)

A well-characterized FA extracted from Laurentian soil, was supplied by Fredriks Research Products (Amsterdam, The Netherlands). However, the term “well-characterized FA” requires some clarification. Titration of the FA revealed 3.03 and 3.49 mmol/g phenolic and carboxyl acid groups, respectively [1]. The bidentate complexing capacity was therefore approximately 3.26 mmol/g fulvic acid. It should be noted that for a naturally-occurring, heterogeneous complexant such as the FA, the molar mass is not directly accessible. Therefore, a molar concentration was calculated, based on the

bidentate complexing capacity, 3.26 mmol/g, of the Laurentian FA. A stock solution (1.0942 g/L) of the Laurentian FA was prepared by dissolving an appropriate amount of the freeze-dried Laurentian FA in ultrapure water. The stock solution was stored in the dark at 4 °C until use. The stock solution of the Laurentian FA 1.0942 g/L corresponded to 3.57×10^{-3} mol/L solution of the FA, calculated on the basis of the bidentate complexing capacity of the FA. Table 2 presents the results of NMR characterization of the Laurentian Fulvic Acid [2]

Apparatus

The voltammetric measurements for AdCSV were performed with an AUTOLAB (ECO-CHEMIE, Utrecht, Netherlands), equipped with a computer-controlled PGSTAT 30 potentiostat/galvanostat and equipped with a Metrohm 663 VA stand (Metrohm, Switzerland). A large Static Mercury Drop Electrode (SMDE) with a 0.52 mm^2 surface area was employed as the working electrode. The counter electrode was made of a platinum rod (Metrohm, Switzerland) and all potentials are referred to a $\text{Ag}_{(s)} | \text{AgCl}_{(s)} | \text{KCl}_{(aq)} (3\text{M})$ reference electrode, which was fitted with a porous Vycor tip. Analysis of voltammetric peaks was done using the General Purpose Electrochemical Software (GPES) v4.6 (ECO- CHEMIE, Utrecht, Netherlands). The data were transferred to a Pentium computer and saved for processing.

Table 2. NMR Characterization of Laurentian Fulvic Acid [2].

Chemical shift assignments	Chemical shift regions (ppm)	% TOC	$T_1\rho^1\text{H}(\text{ms})$	$T_2^{13}\text{C}(\text{ms})$	Elemental analysis
Ketonic	220-190	8.8	8.8	11.9	C 43.2 %
Carboxylic	190-162	33.8	33.8	13.1	H 4.0 %
Phenolic	164-145	2.2	2.2	22.7	N 0.83 %
Aromatic	145-108	12.0	12.0	11.4	Na 0.27 %
O-C-O	108-96	3.5	3.5	10.4	Fe 0.013 %
Carbohydrate	96-50	17.8	17.8	12.3	Ash <1.0 %
Aliphatic	50-0	21.8	21.8	8.0	

Procedure for CLEM/AdCSV of Ni(DMG)₂

Every water sample was de-gassed with ultra pure nitrogen gas for 15 min. prior to measurements and for 10 s before each scan. A nitrogen atmosphere was maintained throughout the experiments. Each scan was performed with a separate mercury drop at room temperature. After extruding the mercury drop, a pre-concentration step under stirred conditions was applied during $t = 30$ s at the deposition potential -0.6 V. After a waiting period of 5 s in rest solution, the potential scan was started. The parameters in SWV experiment were the following: the stirring rate 2000 rpm, step potential 4.9 mV, deposition time 30 s, purge time 5 s, conditioning potential 0 V, equilibration time 5 s, frequency 50 Hz, modulation amplitude 20.0 mV, modulation time 50 ms, interval time 50 ms.

Procedure for CLEM/AdCSV of Cu(Oxine)₂

The same procedure as was followed for CLEM/AdCSV of Ni(DMG)₂ was adopted, except that the parameters in the SWV experiment were the following: the stirring rate 2000 rpm, deposition potential -0.1 V, step potential 4.9 mV, deposition time 30 s, purge time 5 s, conditioning potential 0 V, equilibration time 5 s, frequency 100 Hz, modulation amplitude 20.0 mV, modulation time 50 ms, interval time 50 ms. Each scan was done on a separate mercury drop at room temperature. After extruding the mercury drop, a pre-concentration step under stirred conditions was applied $t = 30$ s at the deposition potential -0.1 V.

Determination of Ni(II) by CLEM/AdCSV

A 50 mL model solution buffered to pH 5.2 with 2M NaOAc/HOAc was de-gassed with high-purity nitrogen (Extra-Dry, BOC Gases) for 15 min. prior to the measurements and for an additional 10 s before each scan. 250 μ L of 0.1M DMG was added to this model solution and the adsorption of Ni(DMG)₂ on the HMDE was done for 30 s using a potential of -0.6 V (vs. E_{Ag/AgCl}). After a 10 s quiescent period, the adsorbed Ni(DMG)₂ complex was stripped using square-wave voltammetry (SWV). The stripping conditions were as follows: scan increment 10 mV s⁻¹, frequency 50 Hz, modulation amplitude 20 mV. Previously, these conditions had been found to be satisfactory for sensitive and reproducible determination of Ni(II) with a film electrode and yielded a detection limit of 14 ng/L for Ni(II) using a 120 s preconcentration / adsorption time [3].

Determination of copper by CLEM/AdCSV

To a 25 mL freshwater sample that has been buffered to pH 8.0 with 0.5M PIPES, variable amounts of HNO₃ (Ultrex II) and NaOH were added in order to adjust the pH to the desired value. The sample was degassed with high-purity nitrogen (Extra-Dry, BOC Gases) for 15 min. prior to the measurements and for an additional 10 s before each scan. 250 μ L of 0.01M Oxine was added to the sample and the adsorption of Cu(Oxine)₂ on the HMDE was done for 30 s using a potential of -0.1 V (vs. E_{Ag/AgCl}). After a 5 s quiescent period, the adsorbed Cu(Oxine)₂ complex was stripped using square-wave voltammetry (SWV). The stripping conditions were as follows: scan increment 10 mV s⁻¹, frequency 75 Hz, modulation amplitude 20 mV. These conditions were observed previously to be

Table 3. Analysis lines and instrumental conditions for Zeeman Spectra 880Z (Varian) Graphite Furnace Atomic Absorption Spectrometry (GFAAS) for CLEM/GFAAS.

Element	Analysis line (nm)	Ashing temperature (°C)	Atomization parameters	
			Temperature (°C)	Duration of atomization (s)
Cu	324.7	1200	1900	5
Ni	232.0	1100	2300	5
Zn	213.9	400	1900	3

satisfactory for sensitive and reproducible determination of Cu(II) with a thin mercury film electrode.

Determination of dissociation Kinetics by CLEM/GFAAS

The dissociation kinetics of Ni(II), Cu(II), and Zn(II) complexes in field-samples were studied using Chelex 100 as the competing ligand and GFAAS. The instrument operating conditions of GFAAS are presented in Table 3. The kinetic model was described in the previous Chapter.

Containers and Cleaning Procedure

All containers, filters, and tubing used in this work for sample collection or storage were made of Teflon or polypropylene. All vessels that came into contact with the samples were pre-cleaned by soaking in 10% HNO₃ (AR grade) for one week at room temperature, followed by five successive washes with ultrapure water. Finally, they were stored in ultrapure water until they were used.

Study Area

The Sudbury Mining site, Copper Cliff, Ontario

Soil solutions (pore waters) samples were collected in June 2001 from the lysimeters installed at Sudbury mining area sites (Fig. 9), which were also the sites for collection of through-fall precipitation samples and rainwater samples. Soil solutions (pore waters), through-fall precipitation and rainwater samples were collected from transects that

Figure 9. Location of the sites for soil solutions (pore water), through-fall precipitation and rainwater samples around Sudbury Mining Area, Copper Cliff, Ontario.

radiated from the Sudbury stack in the direction of the prevailing wind. Samples were collected at distances of 10, 24, and 51 km, respectively, from the Sudbury stack.

QA/QC

Quality control for measurements of copper, nickel, and zinc included periodic analysis of a Certified Reference Material, NIST 1643d. A prior set of samples was re-run if the analyzed value differed from the certified value by $> 10\%$. The relative standard deviation of replicate determinations was typically $\leq 5\%$.

Results and Discussion

Method optimization

Effect of Oxine concentration

The effect of Oxine concentration on AdCSV/SWV peak height is shown in Fig. 10, which shows the results obtained by varying the concentration of Oxine in ultrapure water containing 0.01M PIPES (pH 7.5), 1 $\mu\text{g/L}$ Cu and 0.1M NaOH. The experimental conditions were the same as in Fig. 10. A current was observed when the Oxine concentration was 1.0×10^{-8} M. The peak height increased with increasing Oxine concentrations up to 1.0×10^{-4} M and decreased at Oxine concentrations higher than 1.0×10^{-4} M. An Oxine concentration of 1.0×10^{-4} M was therefore chosen as the optimum experimental condition for the determination of copper speciation in freshwaters.

It was found that the peak potential shifted in a negative direction with increasing Oxine concentrations. Jin et al. [4] suggested that the increase in peak current and the negative

Figure 10. Effect of Oxine concentration on the AdCSV/SWV peak height obtained in a sample of ultrapure water containing 0.01M PIPES (pH 7.5), 1.57×10^{-8} M Cu (II).

Figure 11. Effect of deposition potential on the AdCSV/SWV peak height obtained in a sample of ultrapure water containing 0.01M PIPES (pH 7.5), 1.57×10^{-8} M Cu(II), and 1×10^{-4} M Oxine.

shift in peak potential with increasing Oxine concentrations might be caused by increased stability of the adsorbed copper-Oxine complex, whereas the decrease in the peak current at Oxine concentrations higher than 1.0×10^{-4} M may be caused by competitive adsorption of Oxine onto the mercury surface.

Effect of deposition potential on copper accumulation

The potential applied on the HMDE affects the efficiency of the deposition during the deposition step as result of coulombic effects and competitive adsorption [5,6]. Hence, applied potential ranged between -0.1 and -1.0 V were tested to determine the optimum potential (Fig.11). The copper accumulation onto mercury drop was found to be optimum at a potential of -0.1 V. The decreasing reduction current with more negative deposition potentials may be due to the saturation of the drop surface by the adsorbed copper-Oxine complexes.

Effect of deposition time

Figure 12 shows the effect of increasing deposition time on the AdCSV/SWV peak height. It was found that the peak height increased linearly with time up to 30 s. longer deposition times caused saturation of the Hg drop surface; therefore, deposition times of 10-30 s were used depending on the metal concentrations in various water samples.

Figure 12. Effect of deposition time on the AdCSV/SWV peak height obtained for a sample of ultrapure water containing 0.01 M PIPES (pH 7.5), 1.57×10^{-8} M Cu(II), at a deposition potential of -0.1 V.

Figure 13. Effect of variation in the deposition potential on the AdCSV/SWV peak height obtained with a sample of ultrapure water containing 0.04 M HEPES (pH 7.5), 5.1×10^{-8} M Ni(II).

Effect of deposition potential on nickel accumulation

Figure 13 shows the effect of deposition potential on the AdCSV/ASV peak height. It was found that the peak height increased with increasing deposition potential up to -0.6 V, which was therefore selected as the deposition potential for optimum accumulation of Ni (DMG)₂ on HMDE.

Effect of DMG concentration

The effect of DMG concentration on the AdCSV/SWV peak height is shown in Fig. 14. The two lines in Fig. 14 show the results obtained by varying the concentration of DMG in the ultrapure water sample and the rainwater Site 2 sample from Sudbury area containing 0.04 M HEPES (pH 7.5), and 5.1×10^{-8} M Ni(II). A current was observed in ultrapure water sample even when the DMG concentration was only 1.0×10^{-6} M. In the rainwater Site 2 sample from Sudbury, the peak heights for 1.0×10^{-6} M and 5.0×10^{-6} M were higher than those for the ultrapure water sample containing the DMG. This may have been due to the enhancement of the peak signal by the adsorption of the natural organic matter on the HMDE. The same phenomenon was observed by Murimboh et al. [7] for the adsorption of Laurentian fulvic acid on to thin film mercury electrode. In both samples, the peak height increased with increasing DMG concentrations up to 1.0×10^{-4} M and became nearly constant at DMG concentration higher than 1.0×10^{-4} M. DMG concentration of 1.0×10^{-4} M was therefore used as the optimum experimental condition for determination of nickel speciation in freshwaters. Interestingly, it was found that the peak potential did not shift with variations in the DMG concentration.

Lability of Ni^{2+} -FA complex

The lability (i_p/i_o) of Ni^{2+} -FA complexes was studied in model solutions containing a well-characterized FA (Laurentian FA) [2]. The effects of varying concentrations of FA on the release of Ni(II), using the same model solutions and the same experimental conditions, were studied. Figure 15 presents the results; the bottom curve can be interpreted as that Ni(II) has occupied most of the strong sites of FA forming strong complexes, which are inert. With further decrease in the concentration of FA (the second and the top curve from bottom), all the strong sites of the FA are now completely filled, leaving the remaining nickel to bind to the weak binding sites of the FA, resulting in the formation of weak nickel-FA complexes, which are labile. The kinetic speciation parameters presented in Fig. 15 were obtained by non-linear regression analysis. The results of analysis are presented in Table 4, which shows that the Ni(II)-FA complex formed with the FA concentration 1.7×10^{-6} M has a larger dissociation rate coefficient ($k_1 = 2.20 \times 10^{-2} \text{ s}^{-1}$) than the Ni(II)-FA complex with the FA concentration 1.7×10^{-5} M ($k_1 = 1.58 \times 10^{-2} \text{ s}^{-1}$), and the Ni(II)-FA complex with the FA concentration 1.7×10^{-4} M ($k_1 = 0.57 \times 10^{-2} \text{ s}^{-1}$). The above results of increasing dissociation rate coefficients with increasing mole ratios of $[M]/[FA]$ agrees with the hypothesis that with the increasing mole ratios of $[M]/[FA]$, more metal ions bind to the weaker binding sites of the FA, resulting in weaker complexes that are more labile.

Figure 14. Effect of DMG concentration on the AdCSV/SWV peak height obtained with (○), ultrapure water; and (▲), rainwater Site 2 sample from Sudbury containing 0.04 M HEPES (pH 7.5), 5.1×10^{-8} M Ni(II).

Figure 15. The lability (i_p/i_o) of the Ni(II)-FA complexes in a model solution containing a well-characterized Laurentian fulvic acid, determined by CLEM/AdCSV. pH, 5.2 ± 0.2 ; ionic strength, 3.19×10^{-2} M. DMG was competing ligand. Concentration of nickel (II) is the same for all curves. (Δ), $[\text{Ni } 8.5 \times 10^{-7} \text{ M} + \text{FA } 1.7 \times 10^{-4} \text{ M}]$; (O), $[\text{Ni } 8.5 \times 10^{-7} \text{ M} + \text{FA } 1.7 \times 10^{-5} \text{ M}]$; ($\blacklozenge$), $[\text{Ni } 8.5 \times 10^{-7} \text{ M} + \text{FA } 1.7 \times 10^{-6} \text{ M}]$.

Table 4. Kinetically distinguishable components of nickel complexes in model solutions containing a constant concentration of Ni(II) and variable concentrations of the FA, determined by CLEM/AdCSV. pH 5.2 ± 0.2 ; ionic strength $\sim 3.19 \times 10^{-2}$ M.

[Ni(II)] M	[FA] M	C ₁ (%)	k ₁ , 10 ⁻² s ⁻¹	C ₂ (%)	k ₂ , 10 ⁻⁶ s ⁻¹	R ² of fitting
8.5×10^{-7}	1.7×10^{-4}	21.0±0.4	0.57±0.02	79.0±3.0	< 10 ⁻⁶	0.991
8.5×10^{-7}	1.7×10^{-5}	103.0±4.0	1.58±0.06	---	---	0.985
8.5×10^{-7}	1.7×10^{-6}	101.9±2.0	2.20±0.03	---	---	0.973

--- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

Nickel speciation in through-fall samples precipitation (TF) water samples collected from Sudbury mining area

Table 5 presents some characteristics of the through-fall precipitation (TF) samples collected from the Sudbury mining area in June 2001. The results in Figure 16 and Table 6 were obtained by AdCSV using DMG as the competing ligand. The experimental data were fitted to the kinetic model Eqn. 18 (Chapter 3) by non-linear regression analysis based on the Marquardt-Levenberg algorithm [8]. The results of regression analysis are presented in Table 6. The uncertainties represent the 95% confidence limits of the nonlinear regression analysis. In Figure 16, the quickly rising part at the beginning of each curve (component 1 in Table 6) was due to uptake of Ni-aqua complex, rapidly-dissociating inorganic complexes, and/or any other nickel labile species. The slowly-rising part of each curve (component 2 in Table 6) was probably due to the slow dissociation of strong nickel complexes or due to slowly labile nickel complexes (i.e. those bound to the strong sites). The limiting value at the top of the graph represents the signal that would be obtained for the reduction of the total nickel without any complexation. Therefore, the lability increases in the through-fall precipitation samples from Sudbury TF2 to Sudbury TF3 to Sudbury TF1. Unlike the situation for model solutions, the concentration of complexing sites in real samples is generally not known. However, a rough estimate can be obtained from the concentration of Dissolved Organic Carbon (DOC), which was roughly ~5 mg/L in each of the samples. Thus, the results suggest that the lability of the Ni(II)-complexes increases with increasing [Ni]/[DOC] ratio, as the strong binding sites were first occupied, and then the weak binding sites were

Table 5. Some characteristics of the through-fall precipitation (TF) water samples collected from Sudbury Mining area in June 2001. Samples were filtered through 0.45 µm filter (Gelman Material No. 63077).

	Sudbury TF1	Sudbury TF2	Sudbury TF3
pH	5.0	4.5	5.3
Conductivity (S/m)	0.0028	0.0016	0.0026
DOC (mg/L) †	2.4	5.0	1.4
Cd (µg/L)	2.0	0.3	0.6
Co (µg/L)*	3.3	0.2	0.3
Cu (µg/L) *	25	2.3	1.8
Pb (µg/L) *	2.0	0.8	0.5
Ni (µg/L) *	23	2.5	2.5
Zn (µg/L) *	140	41	27
Ca (mg/L) §	1.4	0.85	0.35
Mg (mg/L) §	0.87	0.23	0.062
Na (mg/L) §	0.21	0.08	0.11
K (mg/L) §	1.1	0.23	2.4
NH ₄ (mg/L) §	0.99	0.42	0.09

† determined by OI Analytical Model 1010 TOC Analyzer.

* determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

§ determined by Ion Chromatography (Dionex Autoion, system DX600)

Figure 16. The lability (i_p/i_o) of Ni(II)-DOC complexes in through-fall (TF) precipitation samples collected from Sudbury in June 2001, determined by CLEM/AdCSV, DMG was the competing ligand; (▲), Sudbury TF1, [Ni(II) 3.92×10^{-7} M] + [DOC 2.4 ± 0.1 mg/L], pH, 5.0 ± 0.1 ; ionic strength, $\sim 3.54 \times 10^{-4}$ M; (◆), Sudbury TF2, [Ni(II) 4.1×10^{-8} M] + [DOC 5.0 ± 0.2 mg/L], pH, 4.5 ± 0.1 ; ionic strength, $\sim 2.05 \times 10^{-4}$ M; (□), Sudbury TF3, [Ni(II) 4.1×10^{-8} M] + [DOC 1.4 ± 0.1 mg/L], pH, 5.4 ± 0.1 ; ionic strength, $\sim 3.31 \times 10^{-4}$ M.

Table 6. Kinetically distinguishable components of metal-complexes in through-fall precipitation (TF) samples collected from Sudbury in June 2001, determined by CLEM/AdCSV.

Sample	[Ni Total]†, µg/L	C ₁ (%)	k ₁ , (10 ⁻² s ⁻¹)	C ₂ (%)	k ₁ , (10 ⁻³ s ⁻¹)
Sudbury TF1	23	100 ± 4	4.3 ± 0.4	--	--
Sudbury TF2	2.5	67 ± 3	3.7 ± 0.5	33.0 ± 0.5	3.00 ± 0.04
Sudbury TF3	2.5	88 ± 4	3.2 ± 0.3	10 ± 1	3.00 ± 0.02

† Determined by GFAAS

-- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

occupied. The most labile Ni(II)-complexes were present in the sample from Sudbury TF1 because it had the highest nickel-to-DOC ratio ($[\text{Ni}]/[\text{DOC}] = 1.6 \times 10^{-4} \text{ mol/g}$). It was located close (about 10 km) to the Inco smelter at Copper Cliff (Sudbury), and hence, most likely received the highest amount of atmospheric deposition of nickel. The concentration of nickel at Sudbury TF1 is $3.9 \times 10^{-7} \text{ M}$. The Ni(II)-complexes in the sample from Sudbury TF2 was the least labile because of the relatively high DOC concentration ($5.0 \pm 0.1 \text{ mg/L}$) and of relatively low nickel concentration ($4.3 \times 10^{-8} \text{ M}$) as shown in Table 5, i.e. having the lowest [nickel] to [DOC] mole ratio ($[\text{Ni}]/[\text{DOC}] = 8.5 \times 10^{-6} \text{ mol/g}$) compared with the other Sudbury TF1 and Sudbury TF3 samples, resulting in its Ni(II)-complexes being the least labile in the samples from the three sites. Another possible explanation is competition of Ca^{2+} (a major cation) which forms weak complexes with humic substances; it is present in **large excess** relative to the concentrations of trace metals in the TF samples. The overwhelming amounts of Ca^{2+} in the sample from Sudbury TF1 probably resulted in the presence of a large amount of Ca^{2+} in the electrical double-layer and in the diffuse layer surrounding the negatively-charged DOC polyanions, screening the charge of the DOC polyanions and thereby significantly decreasing the total binding energy of the metal-DOC complexes [9]. The influence of major cations, such as Ca^{2+} and Mg^{2+} on metal speciation has been demonstrated by Mandal et al. [10], who have shown that overwhelming amounts of major cations (Ca^{2+} and Mg^{2+}) promote the release large fractions of DOC-bound Ni(II).

Lability of Cu(Oxine)₂ complex in rainwater sample

The lability (i_p/i_o) of Cu(II) complexes in model solutions and in freshwater sample rainwater Site 3 from Sudbury area was investigated. The model solution containing 1.0×10^{-4} M of Oxine was spiked with the same amount of Cu(II), 4.25×10^{-8} M, as was found in the sample rainwater Site 3 (i.e. simulating the concentration of Cu(II) in the sample rainwater Site 3), was investigated. Figure 17 presents the results of the above investigation. The rapidly-rising part at the beginning of each curve can be attributed to the presence of the copper aqua complex that was present in the original sample and/or organic copper complexes that were *labile*. This was probably due to the low DOC concentration (~ 1 mg/L) in the rainwater samples that make most of the copper complexes bind to weak binding sites on the DOC, resulting in formation of weak copper complexes that were *labile*. Figure 17 suggests the presence of one kinetically distinguishable component. The solid lines in Figure 17 represent data that were fitted to the Kinetic Model (equation 18) in Chapter 3 by non-linear regression analysis.

Figure 17 shows that approximately 100% of the copper complexes in sample rainwater Site 3 were labile with a dissociation rate coefficient of $k_d = 2.4 \times 10^{-2} \text{ s}^{-1}$. The results are probably due to low concentrations of Dissolved Organic Carbon (DOC) less than 1 mg/L in the rainwater sample. At low DOC concentrations (at relatively high [metal]/[DOC] mole ratios), the metal binding is dominated by the weak sites, resulting in the formation of weak Cu(II)-complexes, which are labile. Similar results were obtained by Mandal et al. [11] for the kinetic speciation of Cu(II) in model solutions of a

Figure 17. Lability (i_p/i_o) of Cu(II)-complexes in rainwater Site 3 sample from Sudbury, determined by CLEM/AdCSV. pH, 7.5 ± 0.2 ; ionic strength, 2.67×10^{-4} M; Oxine was competing ligand. ($\blacktriangle$), reference solution [Cu(II) 4.25×10^{-8} M]; ($\square$), rainwater Site 3 sample from Sudbury.

Figure 18. Dissociation kinetics of metal complexes in the Sudbury site 1 soil solution (pore water) sample, collected in June 2001, from the Sudbury area, determined by CLEM/GFAAS. pH 5.0 ± 0.1 ; ionic strength, 3.80×10^{-4} M; (●), [Cu(II) 4.2×10^{-7} M]; (O), [Ni(II) 6.3×10^{-7} M]; (▲), [Zn(II) 1.4×10^{-6} M].

Table 7. Dissociation kinetics of metal complexes in the Sudbury site 1 soil solution (pore water) sample, collected in June 2001, from the Sudbury area, determined by CLEM/GFAAS. pH 5.0 ± 0.1 , ionic strength 3.8×10^{-4} M.

d ⁿ	Metal	[M Total]†, µg/L	C ₁ (%)	k ₁ , (10 ⁻² s ⁻¹)	C ₂ (%)	k ₁ , (10 ⁻⁴ s ⁻¹)
d ⁸	Ni(II)	36.8	18.0±2.0	0.76±0.05	84.0±3.0	1.6±0.1
d ⁹	Cu(II)	26.6	--	--	101±9	0.54±0.04
d ¹⁰	Zn(II)	91.0	86.0±4.0	2.9±0.2	9.7±3.0	< 10 ⁻⁶

† Determined by ICP-MS

-- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

Table 8. Exchange rates for solvent water in hexaaqua complexes of selected 3d transition metal ions (weak field). Adapted from Butler and Harrod [12].

Metal	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)*
d^n	d^5	d^6	d^7	d^8	d^9	d^{10}
k_w, s^{-1}	3×10^7	3×10^6	1×10^6	3×10^4	8×10^9	7×10^7
LFSE (Dq)	0	4	8	12	6	0

* The data for Zn^{2+} are from other sources.

k_w – rate coefficient for water exchange

well-characterized fulvic acid using Chelex 100 as the competing ligand and Graphite Furnace Atomic Absorption Spectrometry to measure the dissociation kinetics.

Figure 18 and Table 7 show the following trend in the dissociation rates coefficients (lability) of the $3d$ transition metal complexes: $\text{Ni(II)} d^8 > \text{Cu(II)} d^9 < \text{Zn(II)} d^{10}$. This trend was observed in the soil solutions (pore water) samples which were collected from Sudbury mining area in November 2001. Also this trend was observed by Sekaly et al. [13] in the model solutions and freshwater samples. An opposite trend was reported for the stability constants of complexes of $3d$ transition metal ions with simple ligands [14], and with humic substances [15]. The reaction kinetics of Ni(II) is known to be slow relative to those of other first-row divalent transition metals because of the electron configuration of Ni(II) [16,17]. Slow Ni(II) ligand exchange kinetics between DOC and dimethylglyoxime (half-life: 5 – 95 h) was observed by Xue et al. [18] in an oligotrophic lake, and in a small river affected by inputs from sewage effluents and agriculture in Switzerland. Our results on the slow dissociation kinetics of Cu(II) complexes agree with those of Town and Filella [19], who found that Cu(II) -fulvic acid complexes are non-labile under anodic stripping voltammetry, and with that of a previous study by Sekaly et al. [20] using Chelex 100 as a competing ligand ($k_d \sim 10^{-3} - 10^{-6} \text{ s}^{-1}$), and also with that of Achterberg et al. [21], who reported that equilibrium between organically complexed Cu and suspended particulate matter was reached only after 4 – 15 h. Figure 18 and Table 7 show that the dissociation kinetics of Ni(II) -complexes and Cu(II) -complexes are slow relative to Zn(II) -complexes. This trend can be related to the effects of the effective nuclear charge and ionic radius [16]. Ligand-field Stabilization Energy (LFSE) [9] is

known to influence the rate of octahedral ligand substitution reactions of 3d transition metal complexes. The unfavourable changes in LFSE for some metals during complex formation [12] is illustrated by the data for one of the simplest substitution processes, the substitution of a coordinated water molecule in hexaaqua complexes of 3d transition metal ions with bulk solvent water in the absence of other ligands. With the exception of Cu(II), the rate coefficients of water exchange fall into the familiar order of LFSEs (weak field) as shown in Table 8, and indicate that inert complexes are those with large LFSEs. The enhanced stability of Cu-complexes is a result of the Jahn-Teller effect which shortens the equatorial bonds and lengthens the axial bonds of a tetragonally-distorted Cu(II)-L₆ complex [22]. However, the lability of the metal complexes of the soil pore water sample appears to follow the trend predicted by the LFSE.

Conclusions

In soil solution (pore water) samples collected from Sudbury area, the order of lability, Ni(II) > Cu(II) < Zn(II), can be related to the effects of the effective nuclear charge, ligand field stabilization energy and the enhanced stability of Cu(II)-complexes as a result of the Jahn-Teller effect. The slow complexation kinetics of both Ni(II) and Cu(II) suggest that the usual equilibrium assumption for freshwaters may be invalid.

Through-fall precipitation samples collected from Sudbury area, the samples Sudbury TF1 and Sudbury TF3 were the most labile Ni-complexes because they had the relatively highest Ni-to-DOC ratio, that make the Ni(II)-complexes are more labile, which are reported to be toxic. Natural complexants such as humic substances (humic acid and

fulvic acid) buffer metal concentrations over many orders of magnitude, resulting in chemostasis.

It appears that freshwaters are likely to contain a broad range of complexing ligands with various dissociation rate coefficients. Also, other organic complexants, i.e., other than humic substances such as amino acids, proteins and polysaccharides may compete for binding the trace metals including the target trace metals. All the above factors can have effects on the metal speciation parameters of freshwater systems. The application of AdCSV to natural waters may also cause further complications because of possible adsorption of surface-active organic substances on the surface of the HMDE [7,23]. Finally, the structure of chemically isolated humic and fulvic acids (used in this work) are normally different from those humic and fulvic acids present in freshwaters systems [24].

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CHAPTER 5

METAL SPECIATION IN LAKE WATERS FROM THE ROUYN-NORANDA AREA

Experimental

Reagents

Chelex-100 chelating resin (Bio-Rad, 100-200 mesh, sodium form) was pre-treated for the experiment by washing it with ultrapure water. The wet capacity of Chelex-100 resin was 0.61 mequiv/g [1]. ICP Standards (SCP Science) containing Cu, Ni and Pb and other metals (10 mg L⁻¹ each), were used. Ultrapure nitric acid (Ultrex II, J.T. Baker Inc., Phillipsburg, NJ, USA), 10% (v/v), was used to wash the filter membranes. Ultrapure water of resistivity 18.2 MΩ cm was obtained direct from an ultrapure water system, Milli-Q-Academic (Millipore Corporation, Bedford, MA, USA). The stock solution of 0.1M dimethylglyoxime (DMG) was prepared by dissolving an appropriate amount of the solid DMG (Fisher Scientific, certified) in methanol (Spectro grade). For AdCSV, the pH buffer solution was 2M sodium acetate (NaOAc). The 2M sodium acetate (NaOAc) stock solution was prepared by dissolving an appropriate quantity of sodium acetate trihydrate (ACS grade/BDH) in ultrapure water. The sodium acetate solution was purified to be free of metals by mercury-cathode electrolysis at -1.5V versus E_{SCE} for at least 72 h. A 2M stock solution of acetic acid was prepared from 99% minimum sub-boiling acetic acid, distilled in a quartz still (Seastar Chemicals Inc., Sydney, BC, Canada), and by diluting

with ultrapure water; 2M aqueous NaOH (ANACHEMIA) was added to it. All solutions were prepared by dilution of the stock solutions with ultrapure water immediately prior to determination unless otherwise specified.

CLEM/AdCSV

For the kinetic study by CLEM/AdCSV, an Autolab PGSTAT 30 (Eco Chemie) controlled by a personal computer, equipped with a Metrohm 663 VA stand (Metrohm), was used. The working electrode for the voltammetric apparatus was a hanging mercury drop electrode (HMDE). The reference electrode was an Ag/AgCl electrode in a glass tube filled with 3M KCl, and the counter electrode was a Pt wire (Metrohm). All test solutions were purged for 10 minutes with ultra high purity nitrogen gas prior to analysis. Just before the stirring of the test solution was initiated, enough DMG was added to ensure a large excess (at least 500 fold excess) over Ni^{2+} . A potential of -0.6V was immediately applied to the HMDE to start a 30 s accumulation step by adsorption. The stirrer was then stopped and a 5 s quiescent time was allowed. The voltammogram was recorded by scanning from -0.6 V to -1.3 V using a square wave at 50 Hz with a step potential of 5 mV/s and an amplitude of 20 mV. The peaks occurred at approximately -1.0 mV . The signal was measured in the peak height mode.

Ultrafiltration

Ultrafiltration was carried out using an Amicon (Lexington, MA, USA) ultrafiltration stirred cell, model 8200, equipped with Amicon disc membrane filter (diameter of 62 mm).

Apparatus

Screw-capped Teflon cylindrical bottles (500 mL capacity) were machined to fabricate the Reactors (Fig. 19) for kinetic studies of the sample solutions using Graphite Furnace Atomic Absorption Spectrometry (GFAAS) [2]. For the GFAAS, Varian Zeeman atomic absorption spectrophotometer, model SpectrAA 880, equipped with an autosampler, and pyrolytically-coated graphite tubes (Varian), was used. The instrumental parameters used in the GFAAS determination of metals Cu(II), and Zn(II) are shown in Table 9. For the determination of metals concentration, 20 μ L of the sample solution was injected into the graphite furnace, where it was dried, ashed and atomized. The signal was measured in the peak area mode. Each completed determination was followed by a 3-s clean-up cycle of the graphite furnace at 2500 $^{\circ}$ C. During the drying, ashing and clean-up cycles, the internal argon gas was passed through the graphite furnace. The internal argon gas flow was interrupted during the atomization cycle, but was restored for the clean-up cycle. A Horiba D-24 pH/mV/conductivity meter (Canadawide Scientific) was used for the pH and conductivity determinations.

Teflon bottles of 1 L and 2.2 L capacity were used for collecting and storing of water samples and reagents. These bottles were pre-cleaned following the procedure described by Chakrabarti et al. [2]. The Teflon Reactor was pre-equilibrated with the water samples prior to using it for kinetic runs.

Figure 19. Experimental set-up for CLEM/GFAAS experiments.

Containers and their Cleaning Procedure

All containers, filters, and tubing used in this work for sample collection, handling, or storage were made of Teflon or polypropylene. All vessels that came into contact with the samples were pre-cleaned by soaking in 10% HNO₃ (AR grade) for one week at room temperature, followed by a five successive rinses with ultrapure water. Finally, they were stored in ultrapure water until they were used.

Dissolved Organic Carbon

The Dissolved Organic Carbon (DOC) in the water samples was measured using OI Analytical Model 1010 TOC Analyzer.

Study Area

The Rouyn-Noranda site, Abitibi, Quebec

Sampling was conducted in the mining region of Rouyn-Noranda (Abitibi, northwestern Québec) (48° 00' N, 79 ° 00' W) in June 2001. A large copper smelter has been operating near the site since 1927 and there were many lakes in the surrounding area which had been impacted with heavy metals such as Cd, Cu, Ni, Pb and Zn from atmospheric emission from the smelter and from effluents-runoff from mining and refining operations, resulting in a metal contamination gradient at the sample collection areas [3]. Of the four lakes sampled (Fig. 20), Lake Opasatica, situated upwind from the smelter and protected from atmospheric fallout, was used as Reference Lake. The two most contaminated lakes (Dufault and Osisko) both receive atmospheric fallout from the Rouyn-Noranda smelter

based on data from previous studies. One of them, Lake Osisko, also received liquid effluents from the adjoining smelter during many years in the past.

Determination of dissociation kinetic by CLEM/GFAAS

The dissociation kinetics of Ni(II) and Cu(II), complexes in field-samples was studied using Chelex-100 as the competing ligand and GFAAS. The instrument operating parameters of GFAAS are presented in Table 9. Three grams (one per cent, w/v) of Chelex 100 was added to the sample solution in a cylindrical Teflon Reactor (500 mL volume) and the sample solution was stirred continuously with a Teflon-coated magnetic, stirring bar. The initial time (time zero) for the kinetic measurement was taken as the time at which the Chelex-100 resin first came in contact with the water sample in the Teflon Reactor so that any contamination of the resin from its pre-treatment would be indicated by a sudden increase in the signal. In the case of any contamination, the experiment was terminated, and a fresh aliquot of test solution was substituted. The sample solution was filtered with an online 0.45 μm GN-6 membrane filter (Pall) to filter the Chelex-100 resin before introducing the filtrate into the graphite furnace using a peristaltic pump at a flow rate of 1 mL/min.

QA/QC

Quality control for measurements of copper, nickel, and zinc included periodic analysis of a Certified Reference Material, NIST 1643d. A prior set of samples was re-run if the analyzed value differed from the certified value by $> 10\%$. The relative standard deviation of replicate determinations was typically $\leq 5\%$.

Figure 20. Location of the sites for water samples from lakes around Rouyn-Noranda, Abitibi, Québec.

Table 9. Analysis lines and instrumental conditions for Zeeman Spectra 880Z (Varian) Graphite Furnace Atomic Absorption Spectrometry (GFAAS) for CLEM/GFAAS.

Element	Analysis line (nm)	Ashing temperature (°C)	Atomization parameters	
			Temperature (°C)	Duration of atomization (s)
Cu	324.7	1200	1900	5
Zn	213.9	400	1900	3

Results and Discussion

Tables 10 and 11 present some characteristics of the freshwater samples. Kinetic data for the dissociation of Ni(II) complexes in Rouyn-Noranda samples (collected in June 2001) determined by CLEM/AdCSV using dimethylglyoxime (DMG) as the competing ligand is shown in Figure 21. The experimental data were fitted to the kinetic model (equation 18, chapter 3) with a non-linear regression analysis based on the Marquardt-Levenberg algorithm [4]. The results of regression analysis are presented in Table 12. The uncertainties represent the 95% confidence limits of the nonlinear regression analysis. In some cases (Lake Osisko), a slowly-rising kinetically-distinguishable component ($k_d \sim 10^{-4} \text{ s}^{-1}$) was not observed from the nonlinear regression analysis. Two kinetically distinguishable components were observed in the Lake Opasatica sample and the Lake Vaudray sample.

Since it is not possible to define the individual binding sites of heterogeneous complexants, such as Natural Organic Matter (NOM), the problem in applying equation (18) in chapter 3 lies in attempting to fit the kinetic data to a set of rate coefficient, k_i , and concentration $C_{\text{NiL},i}^{\circ}$ parameters without any *a priori* knowledge about the total number of binding sites. Since equation (18) (Chapter 3) is non-linear, this is a difficult task. Furthermore, the avidity with which the individual binding sites might best be represented be a nearly continuous distribution [5]. The data for each experiment were fitted to equation (18) (Chapter 3) using kinetic models with one, two, three, and four kinetically distinguishable components. The model chosen was the one that provided the “best fit”. Hence, the measured dissociation rate coefficients do not necessarily imply the

presence of only one or two discrete metal complexes. They only represent the **minimum** number of components required to model the metal-complex systems. Sekaly et al. [6,7] have shown that the binding sites of humic substances probably exist as distributions of sites, but they can be separated into recognizable groups which may be approximated by a small collection of rate coefficients.

Up to two kinetically distinguishable components were identified in the freshwater samples. The rate constant of 0.28 s^{-1} for the sample from Lake Osisko is probably attributable to one or several of the following species: the metal aqua complex, quickly dissociating inorganic complexes and quickly dissociating organic complexes of the metal. The freshwater sample from Lake Osisko was the most labile because the Lake had a high nickel to DOC ratio (i.e., the conc. of Ni was high and the conc. of DOC was low). As shown in Fig. 20, the lake Osisko was located directly downwind and close to the smelter, and also had received liquid effluents from the smelting operations during many years in the past. The freshwater sample from Lake Vaudray was the most non-labile because the Lake had a low metal to DOC ratio (i.e., the conc. of Ni was low and the conc. of DOC was high) and was located away from the smelter and protected from atmospheric fallout. These results agree with those reported by Sekaly et al. [8] for the kinetic speciation of Ni(II), Pb(II), Cu(II) and Cd(II) in model solutions of Armadale fulvic acid, and Mandal et al. [9] for the kinetic speciation and toxicity of Ni(II) in freshwaters from the Sudbury (Canada) area. The importance of the metal-to-DOC ratio on metal speciation reflects the essential role of DOM in buffering free metal ion

Table 10. Some characteristics of the Lake water samples collected from Rouyn-Noranda, Quebec in July 2001. All samples were filtered through 0.45 µm filter (Gelman Material No. 63077).

Sample	Lake Opasatica	Lake Vaudray	Lake Osisko	Lake Dufault
pH	7.1	6.2	9.0	7.08
Conductivity µS/cm	90.3	30.4	33.3	14.7
Temperature °C	23.7	23.2	23.0	25.3
DOC† (mg/L)	8.4	10.0	3.4	6.9
Cu (µg/L)*	2.4	2.4	6.1	13.3
Fe (µg/L)*	31	69	30	160
Al (µg/L)*	63	78	10	7
Mg (µg/L)§	2900	970	5200	3200
Ca (µg/L)§	9800	3600	25000	17000
Na (µg/L)§	3300	870	29000	4100
K (µg/L)§	1100	400	1500	740
Cd (µg/L)*	0.1	0.1	0.2	0.9
Co (µg/L)*	0.06	-	0.07	0.16
Ni (µg/L)*	1.5	1	1.6	1.2
Pb (µg/L)*	0.11	0.13	0.1	0.58
Zn (µg/L)*	3	4	17	82

- Below the detection limit of ICP-MS

* determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

§ determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

† determined by OI Analytical Model 1010 TOC Analyzer

Table 11. Some characteristics of the lake water samples collected from Rouyn-Noranda, Quebec in July 2001, determined by Ion Chromatography (Dionex Auto ion, system DX600).

Sample*	Lake Opasatica	Lake Vaudray	Lake Osisko	Lake Dufault
F ⁻ (µg/L)	38	35	137	55.4
Cl ⁻ (µg/L)	3459	194	56948	4743
SO ₄ (µg/L)	8898	533	47830	45750
Br ⁻ (µg/L)	0	0	291	0
NO ₃ (µg/L)	171	348	145	331
NO ₂ (µg/L)	0	0	0	0
PO ₄ (µg/L)	0	0	0	0

* All water samples were filtered through 0.45 µm filter (Gelman Material No. 63077).

Figure 21. The lability (i_p/i_o) of Ni(II)-NOM complexes freshwater samples collected from Rouyn-Noranda in July 2001, determined by CLEM/AdCSV, DMG was the competing ligand; (○), Lake Osisko sample, $[\text{Ni(II)}] 2.7 \times 10^{-8} \text{ M}$ + $[\text{DOC } 3.4 \pm 0.2 \text{ mg/L}]$, pH, 8.2 ± 0.1 ; ionic strength, $\sim 1.33 \times 10^{-2} \text{ M}$; (▲), Lake Opasatica sample , $[\text{Ni(II)}] 2.6 \times 10^{-8} \text{ M}$ + $[\text{DOC } 9.4 \pm 0.4 \text{ mg/L}]$, pH, 7.6 ± 0.1 ; ionic strength, $\sim 1.37 \times 10^{-2} \text{ M}$; (□), Lake Vaudray sample, $[\text{Ni(II)}] 1.7 \times 10^{-8} \text{ M}$ + $[\text{DOC } 10.0 \pm 0.5 \text{ mg/L}]$, pH, 7.7 ± 0.1 ; ionic strength, $\sim 1.34 \times 10^{-2} \text{ M}$.

Table 12. Kinetically distinguishable components of Ni(II)-NOM complexes in freshwater samples collected from Rouyn-Noranda in July 2001, determined by CLEM/AdCSV.

Sample	[Ni]/[DOC] mol/g	C ₁ (%)	k ₁ , s ⁻¹	C ₂ (%)	k ₂ , s ⁻¹
Lake Opasatica	3.0 X 10 ⁻⁶	97±8	0.092±0.002	2.9±0.1	< 10 ⁻⁶
Lake Osisko	8.0 X 10 ⁻⁶	100±6	0.28±0.01	--	--
Lake Vaudray	1.7 X 10 ⁻⁶	64.0±3.2	0.018±0.003	34.0±1.8	0.0002

-- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

concentrations [9,10] in the aquatic environment, and suggest that the strong binding sites became saturated as the metal loading of the system increased and the system became progressively dominated by the weak sites (which are labile) at high nickel-to-DOC ratios.

The results of Fig. 21 suggest that complexes with dissociation rate coefficients $> 10^{-1} \text{ s}^{-1}$ cannot be experimentally distinguished from the metal aqua complex using this technique. In the context of metal speciation, the lifetime (first-order dissociation) of the metal complex, ML, is inversely related to its dissociation rate coefficient ($\tau_{\text{ML}} = 1/k_d$). On a timescale much larger than the lifetimes of M and ML (i.e. $k_f t$ and $k_d t \gg 1$, where t is the timescale of measurement), the metal frequently interconverts (i.e. flip flops) between M and ML, and the system is in **dynamic** equilibrium. The other limiting case is when the lifetimes are much larger than the analytical timescale of measurement (i.e. $k_f t$ and $k_d t \ll 1$). In this case, the system is **static** and the complexes are defined as **inert** because both M and ML are essentially frozen in time [11]. The slowly rising sections of each curve are probably due to the slow dissociation of strong metal complexes. The fraction of metal complexes remaining at the end of each experiment represents the fraction of complexes that did not dissociate within the duration of the experiment. The dissociation rate coefficients for these complexes are estimated to be $< 10^{-6} \text{ s}^{-1}$, which represents the lower limit of rate coefficients that can be measured under the experimental conditions used (i.e. analytical window of 2 h).

Table 13. WHAM Model predictions of the speciation of nickel in the Lake water samples, compared with the experimental results collected in June 2001 from Rouyn-Noranda, Quebec.

	Free Metal Ion [Ni ²⁺]		
	Total [Ni(II)] by ICP-MS	WHAM	Experimental results by CLEM/AdCSV
Lake Opasatica	2.56×10^{-8}	1.89×10^{-8}	2.48×10^{-8}
Lake Osisko	2.73×10^{-8}	2.73×10^{-8}	2.72×10^{-8}
Lake Vaudray	1.70×10^{-8}	1.01×10^{-8}	1.02×10^{-8}

The Predictions by WHAM Model V

The Windermere Humic Aqueous Model (WHAM), a chemical equilibrium model and a computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion binding by humic substance [12], was used to predict the nickel binding by DOC in the water samples and to compare its prediction with the above experimental results. As suggested by Tipping [13], the originator of WHAM, in the WHAM calculation only 50% of the DOC was assumed to be “active” fulvic acid. The WHAM predictions presented in Table 13 agree reasonably well with the experimental results, even though the Model V (unlike the Model VI [14]) is not optimized for the competition of major ions, Ca(II) and/or Mg(II), and the ionic strength effects.

Table 14 presents the distribution of Cu species in lake water samples collected from the Rouyn-Noranda area. The unfiltered fraction contains all the Cu species, including particulate, colloidal, dissolved and the Cu-aqua complex. Traditionally, the filtrate that passes through filters with a pore size of 0.45 μm are **operationally-defined** as the “dissolved” phase, although this choice is arbitrary, since size distribution of aquatic components extend as a continuum, from tenths of nanometers to hundreds of micrometers [15]. The filtrate that passed through the 1000 Molecular Weight Cut-Off (MWCO) membrane probably contained Cu species that were present as small, inorganic complexes [e.g. $\text{Cu}(\text{OH})_2$ and $\text{Cu}(\text{Cl})_2$] and Cu-aqua complex. The concentration of Cu species in the 1000 MWCO fraction in Lake Osisko and Lake Dufault was found to be 5.0 $\mu\text{g/L}$ and 6.0 $\mu\text{g/L}$, respectively. However, no Cu species were observed in the 1000 MWCO fraction in the samples from Lake Opasatica and Lake Vaudray, suggesting the

all the copper was bound to the strong sites of the natural organic matter, forming inert complexes. The concentration of copper in Lake Dufault and Lake Osisko were relatively high because they were located close to the Horne smelter at Rouyn-Noranda (Québec), and hence, most likely received the highest amount of copper through atmospheric deposition. The results can be related to the copper-to-DOC ratio which was found to be relatively high for the Lake Osisko and Lake Default water samples as shown in Table 14.

Table 15 shows the concentrations of Zn(II) species in the various size fractions of the sample: 0.4, 5.2 and 0.7 µg/L of the Zn(II) species in particulate, dissolved, and Zn-aqua complex respectively. The concentrations of Zn species in the MWCO fraction in Lake Dufault was found to be about eight times higher than other lakes samples, suggesting that the zinc complexes were bound to the weak sites of the natural organic matter, forming labile complexes that were present as small, inorganic complexes [e.g. $\text{Zn}(\text{OH})_2$ and $\text{Zn}(\text{Cl})_2$] and Zn-aqua complex. For Zn as well as for Cu, the concentrations decreased with increasing distance from the smelter, the concentration of zinc in Lake Dufault and Lake Osisko were found to be high because they were located close to the smelter, and hence, most likely received the highest amount of zinc through atmospheric deposition. The results can be related to the Zn-to-DOC ratio which was found to be relatively high for the Lake Osisko and Lake Default water samples as shown in Table 15.

Table 14. Determination of Cu-complexes (including free metals ions), in freshwater samples collected from Rouyn-Noranda in July 2001, determined by filtration, ultrafiltration and GFAAS.

Sample	Lake Opasatica (µg/L)	Lake Vaudray (µg/L)	Lake Osisko (µg/L)	Lake Dufault (µg/L)
Unfiltered	4.0 ± 0.1	7.0 ± 0.5	12.0 ± 0.6	15.0 ± 0.1
Particulate	1.32 ± 0.02	3.6 ± 0.4	1.2 ± 0.1	1.60 ± 0.04
0.45 µm	2.4 ± 0.1	2.4 ± 0.1	6.1 ± 0.1	13.0 ± 0.5
1000 D MWCO	*	*	5.0 ± 0.1	6.0 ± 0.3
[Cu]/[DOC] mol/g	4.2×10^{-6}	3.7×10^{-6}	2.4×10^{-5}	2.9×10^{-5}

* Below the detection limit of GFAAS

Table 15. Determination of Zn-complexes (including free metals ions), in freshwater samples collected from Rouyn-Noranda in July 2001, determined by filtration, ultrafiltration and GFAAS.

Sample	Lake Opasatica (µg/L)	Lake Vaudray (µg/L)	Lake Osisko (µg/L)	Lake Dufault (µg/L)
Unfiltered	6.9 ± 1.0	9.0 ± 1.3	12.0 ± 1.9	95.1 ± 3.1
Particulate	0.40 ± 0.03	0.40 ± 0.01	0.51 ± 0.04	0.70 ± 0.05
0.45 µm	5.2 ± 0.5	7.3 ± 0.7	10.0 ± 1.4	80.0 ± 1.9
1000 D MWCO	0.7 ± 0.1	0.6 ± 0.1	1.1 ± 0.1	9.4 ± 0.4
[Zn]/[DOC] mol/g	5.5 × 10 ⁻⁶	6.1 × 10 ⁻⁶	7.7 × 10 ⁻⁵	1.5 × 10 ⁻⁴

Conclusions

Total metal concentration was found to be inversely related to the distance from the smelter, suggesting atmospheric fallout as a source of these metals found in these aqueous samples. In the freshwater samples collected from lakes around Rouyn-Noranda area, the most labile Ni-complexes and Cu(II)-complexes were found to be in Lake Osisko because of the relatively high [metal]/[DOC] mole ratio, and competition by major cations such as Ca^{2+} and Mg^{2+} .

The most significant finding of this research is that metals, such as Cu, Ni, and Zn, at the low [metal]/[DOC] mole ratio present in polluted freshwaters, form relatively inert complexes with humic substances, as a result of the strong (high-affinity) humate binding sites binding the metal ions and at the high [metal]/[DOC] mole ratio, form relatively labile complexes with humic substances, as a result of the weak (low-affinity) humate binding sites binding the metal ions.

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CHAPTER 6

FRACTIONATION OF METAL SPECIES BY ULTRAFILTRATION AND THEIR CHARACTERIZATION BY CLEM/GFAAS AND CLEM/AdCSV

EXPERIMENTAL

Apparatus

A Zeeman Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS), Perkin-Elmer, model 4100 ZL, AS-71 auto samplers, an HGA-600 graphite furnace, and pyrolytically-coated graphite tube (Perkin-Elmer B0504033) with integrated platforms were used for kinetic speciation by CLEM/GFAAS. For determination of metal concentrations by GFAAS, 20 μL of the solution was injected into the graphite furnace, where it was dried, ashed and atomized. The signal was measured in the peak area mode.

Water samples

Grab samples (15 L) of Rideau River surface water (Ottawa, Canada) ($\text{pH } 8.2 \pm 0.1$), Onaping River surface water (Sudbury, Canada) ($\text{pH } 7.2 \pm 0.1$), and Copper Cliff Creek surface water (Sudbury, Canada) ($\text{pH } 6.8 \pm 0.1$) were collected in pre-cleaned Teflon bottles. Immediately after collection, the samples were filtered through 0.45 μm membrane filters (Gelman, Ann Arbor, MI, USA). The filtrates were further subjected to fractionation by cascade (sequential) ultrafiltration.

Treatment of the Water samples

Rideau River surface water samples, Onaping River surface water, and Copper Cliff Creek surface water, were filtered using 0.45 μm Gelman filters in the laboratory within 24 h of the sample collection to separate the particulate phase from the dissolved phase. These filters, made of mixed cellulose esters, had the advantage of providing low blanks for the metals. Each 0.45 μm filter was able to filter $\sim 1\text{L}$ water sample without clogging. A sub-sample (250 mL) of the filtered sample was acidified with HNO_3 (Ultrex II, J.T. Baker Inc., Phillipsburg, NJ, USA) to $\text{pH} \sim 1.0$. The acidified sample was used to determine the total concentrations of Al(III) , Fe(III) and Ni(II) , using GFAAS. The filtered samples were collected in pre-cleaned Teflon bottles and stored in the dark at 4°C until cascade ultrafiltration was performed. The pH and electrical conductivity (EC) of the water samples were measured on subsamples immediately after samples were filtered through 0.45 μm Gelman filters. The ionic strength (IS) was calculated from EC using an empirical relationship (eqn. 37) [1]:

$$\text{IS} = 0.014 \times \text{EC} - 4 \times 10^{-4} \quad (37)$$

where units for IS and EC are mol L^{-1} and mS cm^{-1} , respectively. Calculated ionic strengths using eqn. 37 were in good agreement with those determined from full elemental analysis.

Dissolved Organic Carbon

The Dissolved Organic Carbon (DOC) in the water samples was measured using an OI Analytical Model 1010 TOC Analyzer. The DOC in the surface water samples of Rideau River, Onaping River and Copper Cliff Creek was 5.8 ± 0.1 mg of C/L, 5.9 ± 0.1 mg of C/L and 7.5 ± 0.1 mg of C/L, respectively.

Ultrafiltration

An Amicon model 8200 (Lexington, MA, USA) ultrafiltration stirred cell (Fig. 22) was used together with an Amicon Diaflo or a Millipore disc membrane (diameter 62 mm), YM1, YM10, YM100, which had Molecular Weight Cut-Offs (MWCO) of 1000, 10,000 and 100,000, respectively. The membranes had been pre-cleaned using 10% (v/v) ultrapure nitric acid (Ultrex II, JT Baker Inc., Phillipsburg, NJ, USA) to remove heavy metal contaminants and organic wetting agents that might interfere with the procedures for metal speciation [2]. Each membrane was rinsed by floating it skin (glossy) side down in a beaker of distilled water for at least one hour, changing water at least three times. The first 10% and the last 50% of the filtrate were discarded [2,3].

The water samples were placed directly into the stirred cell under nitrogen (pure) pressure and ultrafiltration was carried out until a previously determined filtrate volume was attained. Fluxes were adjusted to maintain a low retentate volume. The ultrafiltered fractions of the water samples were placed in a Teflon bottle and introduced into the GFAAS by means of a peristaltic pump. Some characteristics of the ultrafilter membranes used are summarized in Table 16.

Kinetic Speciation of Rideau River Surface Water Samples by Competing Ligand Exchange Method (CLEM) / GFAAS

Appropriate amounts (excess) of Chelex-100 cation-exchange resin (1% w/v) were added to the filtered, or the ultrafiltered water samples. The mixture was stirred with a Teflon-coated magnetic stirring bar. The kinetics of metal complex dissociation was determined by CLEM/GFAAS. For GFAAS, the analysis line and instrumental conditions shown in Table 17 were used. For CLEM, the procedure summarized below was used—the details of the procedure can be found in earlier papers [4,5] from this laboratory.

The pH of the sample was also monitored before and after the addition of pre-treated Chelex 100 resin to the sample solution (i.e. the pH of the sample before the Chelex was added and the pH at the end of the kinetic run). Changes in the pH were found to be $< \pm 0.5$ for the unbuffered samples and $< \pm 0.05$ units for the buffered samples. The ionic strength of the sample was measured before the sample was placed in the Teflon reactor. Y. Lu et al. [4] reported that any change in the surface area of Chelex resin due to grinding of the resin by the magnetic stirring bar was not significant. The procedure for Competing Ligand Exchange Method by Graphite Furnace Atomic Absorption Spectrometry (CLEM/GFAAS) has been described in Chapter 4.

Table 16. Characteristics of Amicon Ultrafiltration membranes.

Molecular Weight Cut-Off (MWCO)	100,000	10,000	1,000
Membrane type	generating cellulose	generating cellulose	generating cellulose
Surface area (mm²)	62	62	62
Volume Filtered (mL)	800	800	800
Filtration Time (hr)	1	5	48

Figure 22. Amicon ultrafiltration stirred cell.

Table 17. Analysis lines and instrumental conditions for Zeeman 4100ZL Graphite Furnace Atomic Absorption Spectrometry (GFAAS) for CLEM/GFAAS.

Element	Analysis line (nm)	Ashing temperature (°C)	Atomization parameters	
			Temperature (°C)	Duration (s)
Al	309.3	1200	2300	3
Fe	248.3	1400	2100	3
Ni	232.0	1100	2300	5

QA/QC

Quality control for metal determination included repeated injections and periodic (two in every two-hour operation of the instrument) analysis of the Standard Reference Material (SRM), NIST 1640 and NIST 1643-d. A prior set of water samples was re-run if the analyzed value differed from the Standard Reference Material value by >10%. The relative standard deviation (RSD) among replicate determinations was typically $\leq 5\%$.

RESULTS AND DISCUSSION

pH, ionic strength, conductivity, and Dissolved Organic Carbon (DOC)

Tables 18 and 19 present a description of the sampling sites: Rideau River (Ottawa, Canada) and Sudbury (Canada), and also some properties of the freshwater samples such as pH, conductivity, ionic strength, and DOC of the water samples from Rideau River Surface Water (Ottawa, Canada), Onaping River (Sudbury, Canada), and Copper Cliff Creek (Sudbury, Canada). The pH of the Rideau River water sample (8.2 ± 0.1) was higher than that of the Onaping River ($\text{pH } 7.2 \pm 0.1$) and Copper Cliff Creek ($\text{pH } 6.8 \pm 0.1$) water samples, probably because the latter streams received effluents from nickel refineries which had been chemically treated and their pH adjusted to 7 before they were released to the freshwater systems. The conductivity ranged from $340.0 - 480.0 \mu\text{S cm}^{-1}$ for the water samples of Rideau River, $1500 - 2000 \mu\text{S cm}^{-1}$ of Onaping River, $2700 - 3100 \mu\text{S cm}^{-1}$ of Copper Cliff Creek. The reason for the high conductivity values in both Onaping River and Copper Cliff Creek water samples was probably following: the nickel

Table 18. Sampling sites of Rideau River (Ottawa, Canada), Onaping River (Sudbury, Canada), and Copper Cliff Creek (Sudbury, Canada).

Sample #	Description of samples	Date of collection
1	Rideau River at Carleton University	May 23, 1998
2	Rideau River at Carleton University	June 26, 1999
3	Onaping River downstream of Moose Creek. Mixed water from Inco/Falconbridge and municipal pollution	October 26, 1998
4	Onaping River downstream of Moose Creek. Mixed water from Inco/Falconbridge and municipal pollution	June 8, 1999
5	Copper Cliff, wastewater treatment outflow	October 26, 1998
6	Copper Cliff, wastewater treatment outflow	June 8, 1999

Table 19. pH, ionic strength, conductivity and Dissolved Organic Carbon (DOC) of the water samples of Rideau River, Onaping River, and Copper Cliff Creek.

Sample #	pH		Conductivity ($\mu\text{S cm}^{-1}$)	DOC (mg/L)	Ionic strength (M)
	Sample as received	After adding Chelex (at the start of the kinetic run)			
1	8.2	7.9	480.0	6.5	6.1×10^{-3}
2	8.1	7.8	340.0	5.2	4.3×10^{-3}
3	7.3	7.5	1500	5.4	2.1×10^{-2}
4	7.2	7.6	2000	6.4	2.8×10^{-2}
5	6.6	6.9	2700	7.8	3.7×10^{-2}
6	6.8	7.1	3100	7.1	4.3×10^{-2}

refining processes included addition of acids and bases to the effluents for neutralization. There was no significant difference in the pH and the conductivity between the unfiltered and the filtered (through a 0.45 μm membrane filter) water samples.

The ionic strength and the pH of the water sample as received (i.e. before the Chelex resin was added to the sample) before the kinetic determination was started and at the end of the kinetic run are shown in Table 19.

Results of CLEM/GFAAS of the Rideau River surface water samples (Ottawa, Canada)

Aluminium

Figure 23 and Table 20 present the results of the aluminium kinetic speciation of the Rideau River surface water samples and show the presence of at least three kinetically distinguishable species of aluminium. The total aluminium concentration in the unfiltered water samples was 1.85×10^{-6} M, of which 15.7 % of the aluminium species was labile with a dissociation rate coefficient ($k_1 = 1.3 \times 10^{-3} \text{ s}^{-1}$), and 84.5 % was inert with a dissociation rate coefficient ($k_2 = 4.1 \times 10^{-6} \text{ s}^{-1}$). The filtrates from the 0.45 μm membrane filter contained both the truly dissolved fraction ($<0.05 \mu\text{m}$) and the colloidal fraction (0.05-0.45 μm). The filtrates from the 0.05 μm membrane filter contained only the truly dissolved fraction ($< 0.05 \mu\text{m}$). The large difference in the dissociation rate coefficients between the 0.45 μm fraction (i.e. the sum of the truly dissolved fraction plus the colloidal fraction) and the $< 0.05 \mu\text{m}$ fraction (the truly dissolved fraction)

Figure 23. Aluminium complexes remaining undissociated in the Rideau River water sample as function of time, determined by CLEM/GFAAS. (▽), unfiltered; (□), 0.45 µm; (◇), 0.05 µm; (△), 100,000 D MWCO; (○), 10,000 D MWCO; (◆), 1,000 D MWCO; pH, 8.1 ± 0.1 ; ionic strength, $\sim 6 \times 10^{-3}$ M.

Table 20. Kinetically distinguishable components of aluminium complexes in the Rideau River surface water sample (Ottawa, Canada), determined by CLEM/GFAAS. pH, 8.2 ± 0.1 ; ionic strength, $\sim 6 \times 10^{-3}$ M.

Fraction	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁶ s ⁻¹)	C ₃ (%)	k ₃ , (s ⁻¹)	R ² of fitting
Unfiltered	15.7±3.0	1.3±0.2	84.5±2.0	4.1±0.3	---	---	0.980
0.45 µm	21.8±2.0	5.9±0.9	78.1±2.0	8.8±2.0	---	---	0.985
0.05 µm	61.1±6.0	2.9±0.3	39.8±4.0	2.3±0.1	---	---	0.974
100,000 D MWCO	63.5±8.0	0.95±0.2	---	---	29.8±4.0	< 10 ⁻⁶	0.965
10,000 D MWCO	65.7±8.0	1.1±0.2	---	---	25.4±4.0	< 10 ⁻⁶	0.958
1000 D MWCO	69 ±9	1.7±0.3	---	---	25.9±2.0	< 10 ⁻⁶	0.986

--- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

suggests that 61.1% (0.05 μm) of the truly dissolved aluminium fraction and 21.8% (0.45 μm) of the mostly colloidal aluminium fraction were labile. The nearly same percentages of kinetically distinguishable components of aluminium species which are labile (with very similar dissociation rate coefficients) in the 0.05 μm fraction and the 100,000 MWCO, 10,000 MWCO and 1000 MWCO fractions suggest that aluminium was probably present in these fractions mostly as small, inorganic complexes (e.g. $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, $\text{Al}(\text{OH})_3^0$ and $\text{Al}(\text{OH})_4^-$). This is in agreement with the results of others [6,7] who reported that at alkaline pH's, the predominant species should be $\text{Al}(\text{OH})_4^-$, and below pH 4 the trivalent aqua ion, Al^{3+} (really, Al-aqua complex) should predominate [6]. The results also agree with WHAM calculations [8], which predict that the aluminium should be present as inorganic complexes under the experimental conditions of this work.

Iron

Figure 24 and Table 21 present the results of the iron kinetic speciation of the Rideau River surface water sample. In view of the fact that in the GFAAS results the rate coefficient of k_2 of 10^{-6} s^{-1} was hardly distinguishable from that of $k_3 < 10^{-6} \text{ s}^{-1}$, these two rate coefficients can be lumped together as extremely low (i.e. the species are inert). Using the above generalizations, Table 21 can be interpreted as follows. The labile fractions (C_1 %) increased gradually as one descended down Table 21, from the unfiltered fraction (the largest species) to the 1000 D MWCO (the smallest species); the inert fractions also decreased in a similar fashion. The gradual increase in the percentage

Figure 24. Iron complexes remaining undissociated in the Rideau River surface water sample as function of time, determined by CLEM/GFAAS. (●), unfiltered; (○), 0.45 μm ; (△), 0.05 μm ; (▼), 100,000 D MWCO; (◇), 10,000 D MWCO; (◆), 1,000 D MWCO; pH, 8.2 ± 0.1 ; ionic strength, $\sim 6 \times 10^{-3}$ M.

Table 21. Kinetically distinguishable components of iron complexes in the Rideau River surface water sample (Ottawa, Canada), determined by CLEM/GFAAS. pH, 8.2 ± 0.1 ; ionic strength, $\sim 6 \times 10^{-3}$ M.

Fraction	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁶ s ⁻¹)	C ₃ (%)	k ₃ , (s ⁻¹)	R ² of fitting
Unfiltered	25.5±6.0	0.6±0.1	73.3±10.0	6.3±2.0	---	---	0.975
0.45 µm	32.1±5.0	0.4±0.1	---	---	62.9±5.0	< 10 ⁻⁶	0.956
0.05 µm	31.6±3.0	0.4±0.1	---	---	66.6±3.0	< 10 ⁻⁶	0.945
100,000 D MWCO	44.8±8.0	0.3±0.0	---	---	49.4±8.0	< 10 ⁻⁶	0.966
10,000 D MWCO	56.1±9.0	0.8±0.1	---	---	44.3±2.0	< 10 ⁻⁶	0.959
1000 D MWCO	66±8	0.9±0.1	---	---	34.4±5.0	< 10 ⁻⁶	0.939

--- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

composition in the labile fraction with decreasing dimensions (MWCO) of the species—the greatest labile fraction being that of 1000 D MWCO—means that the labile fractions predominantly consisted of small iron species e.g. aqua complex or small inorganic or organic complexes of iron. Special features of Table 21 are that the 0.45 μm fraction and the 0.05 μm fraction are similar, suggesting that the so-called “dissolved phase” (the 0.45 μm fraction) consisted mostly of truly dissolved phase (the 0.05 μm fraction). Lastly, the unfiltered fraction (i.e. the original sample) had only about one-fourth of its iron species as labile, whereas the smallest ultrafiltered fraction had more than half of its iron species as labile. This can be interpreted in terms of the size of the iron species—the large ($>0.45 \mu\text{m}$) iron species were inert, whereas the small ($<0.05 \mu\text{m}$) iron species were labile. The calculations of the Windermere Humic Aqueous Model (WHAM) model V [9], predicting equilibrium speciation of the iron species as small inorganic complexes with 87 % of the species to be mononuclear $\text{Fe}(\text{OH})_3$, agree in general with the experimental results of Figure 24 and Table 21. It is quite possible that the labile fraction reported could amount to 87 % of the species, and is mononuclear $\text{Fe}(\text{OH})_3$, as predicted by WHAM model V.

Results of CLEM / GFAAS of the Copper Cliff Creek surface water samples (Sudbury, Canada)

Aluminium

Figure 25 and Table 22 present the results of the aluminium kinetic speciation of the Copper Cliff Creek surface water samples. The difference between the 0.45 μm and 0.05 μm fractions about 20% which suggest that most of the aluminium species in the Copper

Cliff Creek surface water samples present in dissolved phase. The labile aluminium species in the 100,000 MWCO, 10,000 MWCO and 1000 MWCO fractions were almost identical, and only slightly greater than the 0.05 μm fractions, suggesting that most of the aluminium species shown in Table 22 were small inorganic and/or organic complexes of aluminium. The results agree with the WHAM model V calculations, which predict 90% of the aluminium would exist as $\text{Al}(\text{OH})_4^-$. The labile fraction of aluminium species in the Rideau River surface water sample was less than the labile fraction of aluminium species in the Copper Cliff Creek water samples. This was probably because of the presence of high concentrations of major cations, such as Ca^{2+} , Mg^{2+} , Na^+ and K^+ , (8.83×10^{-3} M, 1.63×10^{-3} M, 1.26×10^{-2} M and 1.40×10^{-3} M, respectively) in the Copper Cliff Creek water samples; these major cations successfully competed with the aluminium species for the strong binding sites which were much smaller in number ($< 10\%$) in the naturally-occurring organic complexants (humic substances), resulting in the aluminium binding to the weak binding sites which were much larger in number ($> 90\%$). The consequence was that a larger fraction of the aluminium-complexes in the Copper Cliff Creek surface water samples was labile compared with that of the Rideau River surface water sample. The much higher values for the water exchange rate constants [10] for Ca^{2+} ($6.0 \times 10^8 \text{ s}^{-1}$) and Mg^{2+} ($6.0 \times 10^5 \text{ s}^{-1}$) compared to that of Al (1 s^{-1}) made the Ca^{2+} and Mg^{2+} much stronger complex-former than Al^{3+} ; the above was in addition to the effect of competition of Ca^{2+} and Mg^{2+} ions present in the latter sample, in which their concentrations were several orders of magnitude higher than that of aluminium. In addition to the competitive

Figure 25. Aluminium complexes remaining undissociated in the Copper Cliff Creek surface water sample as function of time, determined by CLEM/GFAAS. (□), 0.45 µm; (○), 0.05 µm; (△), 100,000 D MWCO; (◇), 10,000 D MWCO; (◆), 1,000 D MWCO; pH, 6.6 ± 0.1 ; ionic strength, $\sim 3 \times 10^{-2}$ M.

Table 22. Kinetically distinguishable components of aluminium complexes in the Copper Cliff Creek surface water sample (Sudbury, Canada), determined by CLEM/GFAAS. pH, 6.6 ± 0.1 ; ionic strength, $\sim 3 \times 10^{-2}$ M.

Fraction	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁵ s ⁻¹)	R ² of fitting
0.45 µm	58.0±6.0	3.7±0.4	43.5±4.0	6.2±1.0	0.975
0.05 µm	78.3±9.0	1.8±0.3	24.9±8.0	≤ 0.1	0.983
100,000 D MWCO	80.5±11.0	2.6±0.6	20.3±3.0	18.4±5.0	0.962
10,000 D MWCO	84.1±4.0	2.9±0.2	15.4±2.0	8.9±1.0	0.976
1000 D MWCO	84±5	4.3±0.6	16.2±4.0	14.6±3.0	0.968

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

advantage of the much greater water exchange rate constant, the extremely large concentrations of major cations (Ca^{2+} and Mg^{2+}) present in the sample screened the anionic charge on the organic ligand, thereby decreasing their electrostatic attraction (oligoelectrolyte effect) [10]. Since the total binding energy of aluminium complexation by naturally-occurring organic complexants (humic substances) is the sum of covalent bonding and electrostatic bonding, the above screening of the polyanionic charges on the humate ligands by Ca^{2+} and Mg^{2+} ions decreased the total binding energy by weakening the electrostatic component of the total binding energy [10].

Nickel

The results for the CLEM/GFAAS of nickel in the Copper Cliff Creek surface water sample are shown in Figure 26 and Table 23. In Figure 26, the curves for all the fractions were almost identical, the labile fractions having a dissociation rate coefficient $> 10^{-3} \text{ s}^{-1}$. The percentages of labile nickel species in the $0.45 \text{ }\mu\text{m}$ and $0.05 \text{ }\mu\text{m}$ fractions were about the same (88-89%), suggesting that the fraction that passed through the larger pore size ($0.45 \text{ }\mu\text{m}$) was the same as that passed through the smaller pore size ($0.05 \text{ }\mu\text{m}$). This means that in both cases, the nickel species was in the truly dissolved phase, consisting of small, inorganic and/or organic complexes of nickel. The concentration of nickel was high ($427 \text{ }\mu\text{g/L}$), and there was a large excess of nickel relative to the concentration of binding sites. The results suggest that approximately 95% of the nickel was present as the nickel-aqua complex and/or small, very weak inorganic nickel

Figure 26. Nickel complexes remaining undissociated in the Copper Cliff Creek surface water sample as function of time, determined by CLEM/GFAAS. (O), 0.45 μm ; ($\blacktriangle$), 0.05 μm ; ($\bullet$), 100,000 D MWCO; ($\triangle$), 10,000 D MWCO; ($\blacklozenge$), 1,000 D MWCO; pH, 6.6 ± 0.1 ; ionic strength, $\sim 3 \times 10^{-2}$ M.

Table 23. Kinetically distinguishable components of nickel complexes in the Copper Cliff Creek surface water sample (Sudbury, Canada), determined by CLEM/GFAAS. pH, 6.6 ± 0.1 ; ionic strength, $\sim 3 \times 10^{-2}$ M.

Fraction	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁴ s ⁻¹)	R ² of fitting
0.45 µm	88.2±2.0	3.9±0.2	11.6±2.0	3.1±0.5	0.988
0.05 µm	89.5±2.0	3.3±0.3	10.7±2.0	2.6±0.3	0.972
100,000 D MWCO	92.3±2.0	3.2±0.2	8.2±2.0	2.2±0.3	0.984
10,000 D MWCO	96.5±10.0	2.8±0.6	3.1±0.8	0.2±0.1	0.976
1000 D MWCO	95±4	4.3±0.4	5.9±1.0	2.0±0.7	0.985

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

complexes that were labile. The results agree with the WHAM model V calculations, which predict 97 % of the nickel species would occur as the nickel-aqua complex.

Results of CLEM/GFAAS of the Onaping River surface water samples (Sudbury, Canada)

Nickel

Figure 27 and Table 24 present the results of CLEM/GFAAS of the Onaping River water sample. The results suggest that the 'so-called dissolved' nickel species (0.45 μm) was labile; 13% (i.e. the difference between the fraction that passed through the 0.45 μm filter and that through the 0.05 μm filter) of the nickel consisted of colloidal species. The results for the 100,000, 10,000 and 1000 MWCO fractions were nearly identical, suggesting that 54-59 % of the 'truly dissolved' nickel species (from 0.05 μm to 1000 D MWCO) were labile, whereas the non-labile nickel species in these fractions were probably small, strongly-bound nickel-organic complexes that were inert ($k_d < 10^{-6} \text{ s}^{-1}$).

Results of CLEM/AdCSV of the Onaping River surface water samples (Sudbury, Canada)

Nickel

Figure 28 and Table 25 present the results of CLEM/AdCSV of the Onaping River surface water sample. The results suggest that 15% (i.e. the difference between the fraction that passed through the 0.45 μm filter and that through the 0.05 μm filter) of the nickel were colloidal species; this agrees with the results obtained by

Figure 27. Nickel complexes remaining undissociated in the Onaping River surface water sample as function of time, determined by CLEM/GFAAS. (O), 0.45 μm ; (▲), 0.05 μm ; (□), 100,000 D MWCO; (△), 10,000 D MWCO; (●), 1,000 D MWCO; pH, 7.3 ± 0.1 ; ionic strength, $\sim 2 \times 10^{-2}$ M.

Table 24. Kinetically distinguishable components of nickel complexes in the surface water sample from Onaping River (Sudbury, Canada), determined by CLEM/GFAAS. pH, 7.3 ± 0.1 ; ionic strength, $\sim 2 \times 10^{-2}$ M.

Fraction	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁶ s ⁻¹)	C ₃ (%)	k ₃ , (s ⁻¹)	R ² of fitting
0.45 µm	41.0±4.0	3.7±0.6	59.0±3.0	1.9±0.7	---	---	0.964
0.05 µm	54.0±6.0	1.5±0.3	41.0±3.0	41.0±0.6	---	---	0.957
100,000 D MWCO	59.0±4.0	3.3±0.4	---	---	45.0±4.0	< 10 ⁻⁶	0.945
10,000 D MWCO	59.0±4.0	3.3±0.4	---	---	42.0±0.9	< 10 ⁻⁶	0.961
1000 D MWCO	56.0±4.0	0.6±0.2	---	---	47.0±2.0	< 10 ⁻⁶	0.949

--- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

Figure 28. Lability (i_p/i_o) of nickel complexes in the Onaping River surface water samples as function of time, determined CLEM/AdCSV. (O), 0.45 μm ; (□), 0.05 μm ; (Δ), 100,000 D MWCO; (◇), 10,000 D MWCO; (▽), 1000 D MWCO; pH, 7.3 ± 0.1 ; ionic strength, $\sim 2 \times 10^{-2}$ M.

Table 25. Kinetic parameters of nickel complexes in the various ultrafiltered fractions of the Onaping River surface water sample (Sudbury, Canada), determined by CLEM/AdCSV. pH, 7.3 ± 0.1 ; ionic strength, $\sim 2 \times 10^{-2}$ M.

Fraction	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁶ s ⁻¹)	C ₃ (%)	k ₃ , (s ⁻¹)	R ² of fitting
0.45 µm	53 ± 1	2.2 ± 0.1	14 ± 1	3.7 ± 0.4	32 ± 1	< 10 ⁻⁵	0.968
0.05 µm	68 ± 2	2.6 ± 0.2	13 ± 1	5.0 ± 1.0	20 ± 1	< 10 ⁻⁵	0.972
100,000 D MWCO	70 ± 2	2.0 ± 0.2	29 ± 2	3.0 ± 0.3	-----	-----	0.983
10,000 D MWCO	76 ± 2	2.6 ± 0.1	23 ± 0	2.0 ± 0.1	-----	-----	0.981
1000 D MWCO	75 ± 2	3.1 ± 0.2	25 ± 1	2.0 ± 0.1	-----	-----	0.965

--- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

CLEM/GFAAS as shown in Table 24. The results for the 100,000, 10,000 and 1000 MWCO fractions were nearly identical (within the experimental error of measurement), suggesting that the non-labile ($k_d < 10^{-6} \text{ s}^{-1}$) nickel species in these fractions were probably small, strongly-bound nickel-organic complexes.

The Windermere Humic Aqueous Model (WHAM), model V.

The Windermere Humic Aqueous Model (WHAM) model V is an advanced, equilibrium-based speciation model, and was chosen because it represented a more commonly used approach in equilibrium modelling of metal complexation by dissolved organic matter. The WHAM model V, is a computer code for waters, sediments, and soils, and incorporates a discrete site/electrostatic model of ion binding by humic substances [8], which were used to predict the binding of metals by fulvic acid and to compare its predictions with the experimental results. The WHAM takes into account the interactions of metals with (i) inorganic ligands (OH^- , HCO_3^- , CO_3^{2-} , SO_4^{2-} , Cl^-), using conventional equilibrium formation constants (stability constants) from the literature, and (ii) humic substances using Humic Ion-Binding Model V [9]. The WHAM predictions presented in Table 26 agree reasonably well with the experimental results for nickel, but the experimental results for aluminium and iron do not agree very well with the WHAM predictions. Although WHAM reports the predicted concentrations of dissolved hydrolysis products of iron and aluminium, it does not take into account the precipitation of aluminium and iron when the solubility products of aluminium and iron hydroxides are exceeded. Hence, a significant fraction (e.g. 20-30%) of the soluble phase aluminium and

Table 26. WHAM predictions for the equilibrium speciation of aluminium, iron and nickel in the Rideau River surface water sample, the Copper Cliff Creek surface water sample and the Onaping River surface water sample.

<i>Sample location</i>	<i>WHAM PREDICTIONS</i>				<i>EXPERIMENTAL</i>
	Metal	Free metal ions plus other small metal-species (%)	Metal electrostatically bound (%)	Metal covalently bound (%)	<i>RESULTS</i> Free metal ions plus other small metal-species (%)
Rideau River	Al	95	-	5.0	69.4
Copper Cliff Creek	Al	99	-	1.0	83.5
Rideau River	Fe	87	-	13.0	65.7
Copper Cliff Creek	Ni	97	-	3.0	95.3
Onaping River	Ni	80.0	-	20.0	75.0

iron reported by WHAM was probably large colloidal species or insoluble aluminium and iron hydroxides that were non-labile.

Conclusions

The experimental results were compared with the predictions of a computer-based, equilibrium speciation model, the Windermere Humic Aqueous Model (WHAM) model V. The good agreement of the results obtained in the ultrafiltration experiment with the WHAM predictions of nickel speciation suggests that there are no interactions between the filtration membrane and the nickel ion. For iron and aluminium, the extremely low solubility of their hydroxides makes the WHAM not appropriate under the experimental conditions of this work; and hence, the agreement was not good. This disparity in the results has been attributed to complications introduced by the formation of aggregated molecular species and the redox property of the system. Cascade ultrafiltration coupled with the kinetic speciation of the metal species in each molecular weight cut-off (MWCO) fraction provided a more comprehensive picture and an insight into the physical and the chemical characteristics of the metal species than either the ultrafiltration technique or the measurements of dissociation kinetics could do alone.

Environmental Significance

Since nickel free metal ions are reported to be toxic species, the presence of such a large fraction of the dissolved nickel species as free nickel ions in the freshwater samples is a matter of serious environmental concern. The presence of major cations, such as Ca^{2+} , Mg^{2+} , Na^{+} and K^{+} , which are ubiquitous in freshwaters, especially when the bedrocks are

calcium and/or magnesium carbonate, greatly increases the release of organically-bound, dissolved nickel species as free nickel ion, which is reported to be toxic.

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CHAPTER 7

THE EFFECTS OF Al(III) AND Fe(III) ON THE KINETIC SPECIATION OF Ni(II) IN MODEL SOLUTIONS AND FRESHWATERS INVESTIGATED BY CLEM/GFAAS AND CLEM/AdCSV

Experimental

Apparatus

Voltammetric measurements were made using a computer-controlled Bioanalytical System (BAS), 100 B/W with Controlled Growth Mercury Electrode (CGME-BAS) stand connected to a Pentium 166MMX personal computer (Gateway 2000), and a small size (size 4) static mercury drop electrode (SMDE) as the working electrode; the reference electrode was a Ag/AgCl electrode (BAS), filled with 3 M NaCl, and the counter electrode was a Pt wire (BAS). Analysis of voltammetric peaks was done using the BAS 100W windows control software v 2.1 (BAS). Graphite Furnace Atomic Absorption Spectrometry was performed using the apparatus described earlier in Chapter 5.

Square Wave Anodic Stripping Voltammetry (SWASV)

Each sample was purged with ultrapure nitrogen gas for 10 min. prior to the kinetic run. The experimental conditions used SWASV were as follows: initial potential -0.7 V, final potential -1.3 V, step potential -5 mV, deposition time 60 s, purge time 10 s, conditioning potential 0 V, equilibration time 5 s, frequency 50 Hz, modulation amplitude 25.0 mV, interval time 10 s.

Chemicals and Reagents

Stock solution (1000 $\mu\text{g/mL}$) of Ni^{2+} was prepared by dissolving an appropriate quantity of pure nickel metal powder (SPEX 99.999%) in ultrapure nitric acid (65-70% sub-boiling, distilled in a quartz still, Seastar Chemicals Inc., Sidney, BC, Canada) with heating, and diluting the solution to the appropriate volume with ultrapure water; the final solution contained 1% (v/v) ultrapure nitric acid. Standard solutions (1000 $\mu\text{g/mL}$) of Al^{3+} and Fe^{3+} were purchased from SPC Science Company, Canada. Ultrapure water (18.2 M Ω -cm) was obtained direct from a Milli-Q Academic water purification system (Millipore Corporation, USA), fitted with an organic purification column to remove organic matter.

Chelex-100 resin (Bio-Rad, 100-200 mesh, sodium form) was soaked and stored in ultrapure water; the Chelex resin was removed from of the water solution just prior to the kinetic run.

Samples

Two types of aqueous samples were used: (1) model solutions containing fixed concentrations of Ni(II) [8.5×10^{-7} M] and the FA [1.7×10^{-4} M] and varying concentrations of Al(III) and Fe(III), first singly and then together, to simulate freshwaters from the Sudbury mining area. Model solutions were prepared by spiking ultrapure water with appropriate volumes of standard solutions of the metals and of the FA solution. The spiked samples were equilibrated for 24 hours, and then the pH of the model solutions was measured using a Fisher Scientific Accumet 925 pH / ion meter. The pH meter was calibrated with three standard pH buffer solutions (pH 4, pH 7 and pH 10). For Graphite Furnace Atomic Absorption Spectrometry (GFAAS) and Adsorptive Cathodic Stripping Voltammetry (AdCSV), the pH of all the samples was adjusted to pH 5.0 ± 0.1 using 2M NaOAc/HAc. For GFAAS and AdCSV, the changes in the pH between the beginning and the end of the kinetic run were found to be $< \pm 0.5$ pH unit. Freshwater samples (6.6 L) were collected in June 1998 and in July 1999 from several sampling sites in the Sudbury mining area (Canada) using pre-cleaned Teflon bottles. The sampling sites were chosen with a view to studying the applicability of the nickel speciation techniques developed in our laboratories [1] using model systems to simulate nickel-polluted natural waters. The sites were chosen upstream and downstream of the nickel-tailing ponds, and outflows from the treatment tanks receiving effluents from nickel ore processing and smelting operations. Freshwater samples were collected in acid-cleaned Teflon bottles and filtered through 0.45 μm membrane filters (47 mm diameter, Gelman, Ann Arbor, MI) in our laboratory within 24 h of the sample collection. These filters, made of mixed cellulose esters, had the advantage of providing filtrates

having low blanks for the metals. Each 0.45 μm filter was able to filter ~ 500 mL water sample without clogging. Immediately after the filtration, subsamples (100 mL) of the filtrates were acidified with ultrapure nitric acid (HNO_3) to pH 1.0 to prevent loss of cations by adsorption on the container walls. The concentrations of trace metals: Ni^{2+} , Cu^{2+} , Pb^{2+} , Al^{3+} and Fe^{3+} , in the filtrates were determined by GFAAS or Inductive Coupled Plasma Mass Spectrometry (ICP-MS); major cations (Ca^{2+} and Mg^{2+}) were determined by Flame Atomic Absorption Spectrometry, and Na^+ and K^+ , by Flame Atomic Emission Spectrometry. The unacidified filtered samples were used to determine the total anions (NO_3^- , SO_4^{2-} , Cl^- , F^- , NO_2^- and Br^-) by Ion Chromatography. The remaining filtered samples were stored in the dark at 4°C and were used for the kinetic measurement within 24 h of filtration.

Kinetic Model

Methodology for Kinetic Measurement

The Kinetic Model presented in Chapter 3 was adopted. The method for the kinetic measurement is as follows. For the CLEM/GFAAS, the rate of Ni^{2+} ion release from Ni(II)-FA complexes was measured using GFAAS. For the measurement of the rate by GFAAS, the pretreated Chelex-100 resin was added to a 150 mL test solution placed in the Teflon Reactor, and the mixture was stirred with a Teflon-coated magnetic stirring bar. Test solutions for analysis were withdrawn from the Teflon Reactor through a nylon membrane filter placed at the end of the Teflon Reactor tube, which filtered out the Chelex-100 resin and injected a clear filtrate into the graphite furnace. The zero time for

the kinetic measurement was taken as the time at which the Chelex-100 resin first came in contact with the test solution in the Teflon Reactor. Total Dissolved Ni in all samples, $[\text{Ni}_{\text{diss}}]$, was determined by GFAAS using the filtrate from the 0.45 μm filter paper. Samples were analysed in triplicate using analytical calibration curves.

For the CLEM/AdCSV, a 25 mL aliquot of the sample was buffered to $\text{pH } 5.0 \pm 0.1$ using 2M NaOAc/HAOc buffer solution in a Teflon cell (Metrohm). It was deoxygenated for 10 min with purified nitrogen (UHP-Praxair Compressed Gas). Then 250 μL of 0.1M DMG solution was added to the above sample. The potential for the preconcentration step was applied for 30 sec on a new mercury drop electrode while the solution was stirred by an electric stirring bar at a rotational speed of 400 rpm. The sample was then allowed to become quiescent for 5 sec and the adsorbed $\text{Ni}(\text{DMG})_2$ complex was stripped using a square wave waveform. The dissociation rate coefficients of the $\text{Ni}(\text{II})$ -FA complexes were obtained from the i_p/i_0 versus time curves, where i_p and i_0 are the current for Ni^{2+} ion generated by dissociation of the nickel-FA complexes, and the reference current under conditions of no complexation of Ni^{2+} , respectively. The stripping conditions were as follows: purge time 5 s, deposition potential -0.7 V , deposition time 60 s, equilibration time 5 s, frequency 50 Hz, initial potential -0.7 V , final potential -1.3 V , step potential -5 mV , amplitude 25 mV. All kinetic experiments were performed at the room temperature ($\sim 20^\circ\text{C}$).

Analysis of the experimental kinetic data

The experimental data were analyzed for discrete values of the dissociation rate coefficients by a method based on non-linear regression analysis using the Marquardt-Levenberg algorithm. This method analyses the data assuming that the decrease in the metal concentration is represented by a sum of exponential terms. All the experimental data were used in the data fitting.

QA/QC

Quality control for metal analyses included repeated injections and periodic (two in every two-hour operation of the instrument) analysis of Standard Reference Material (SRM), NIST 1640 and NIST 1643-d. A prior set of samples was re-run if the analysed value differed from the Standard Reference Material value by >10%. The relative standard deviation (RSD) among replicate determinations was typically $\leq 5\%$.

Results and discussions

Effect of [Ni] / [FA] mole ratio on the kinetic lability of the Ni-FA complexes

The results for Ni(II) in model solutions of Laurentian fulvic acid are presented in Figure 29. The [Ni(II)] / [FA] mole ratios were varied by keeping the nickel concentration constant (8.5×10^{-7} M), and varying the FA concentration. The sharply falling section at the beginning of each curve can be attributed to the presence of the Ni-aqua complex and/or the rapid dissociation of weak inorganic and/or organic Ni-complexes that are labile. The slowly falling section of each curve is probably due to the slow dissociation of

strong Ni-complexes that are slowly labile or inert. Hence, the fraction of Ni- complexes remaining at the end of each kinetic run represents the fraction of Ni-complexes that are unable to dissociate within the experimental timescale.

The results shown in Figure 29 can be interpreted as follows. At the mole ratio of 0.005, the Ni(II) concentrations was much lower (10^{-7} M) than that of the FA (10^{-4} M), and the FA had therefore enough strong binding sites to bind all the Ni^{2+} ions, resulting in the formation of strong Ni-FA complexes, which were very slowly labile or inert. With further increase in the mole ratio to 0.05, and still further to 0.5, all the strong sites were completely filled, leaving the remaining nickel to bind to the weak binding sites of the FA, resulting in the formation of weak Ni-FA complexes, which were labile.

The experimental data presented in Figure 29 were fitted to the Kinetic Model (Chapter 3) by non-linear regression analysis to obtain the numerical values of the kinetically distinguishable components and the associated dissociation rate coefficients. The solid lines in Figure 29 represent the data that were fitted to the Kinetic Model by non-linear regression analysis. Table 27 shows kinetically distinguishable components: one labile component ($k_d \approx 10^{-3} \text{ s}^{-1}$) that dissociate rapidly, and one inert component ($k_d \approx 10^{-5} - 0^{-6} \text{ s}^{-1}$) that dissociate slowly. The measured dissociation rate coefficients do not necessarily imply the presence of only two distinct metal complexes: they represent only the minimum number of components required to describe the Ni-FA systems. The nickel complexes probably exist as distributions of closely-spaced nickel complexes [2,3], but

they group into recognizable individual sets which may be approximated by a small set of rate coefficients [4].

Table 27 shows that with increasing mole ratios of $[\text{Ni}] / [\text{FA}]$, there is an increase in percentage of the labile Ni-FA complexes (including Ni-aqua complex) and a corresponding decrease in the percentage of slowly-labile Ni-FA complexes. The labile Ni-FA complexes may comprise Ni-aqua complexes, and other small inorganic or organic complexes of nickel. It is noteworthy that of the fraction of the Ni-FA complexes that are slowly-labile, the $[\text{Ni}]/[\text{FA}]$ mole fraction of 0.5 had a dissociation rate coefficient of $\sim 10^{-4} \text{ s}^{-1}$, which was an order-of-magnitude greater than that of the $[\text{Ni}]/[\text{FA}]$ mole fraction of 0.005 which had an associated dissociation rate coefficient of $\sim 10^{-5} \text{ s}^{-1}$ —a reflection of the nature of distribution of binding sites in the heterogeneous complexant, FA. These observation are in agreement with the hypothesis that as the $[\text{Ni}] / [\text{FA}]$ mole ratio is increased by keeping the nickel concentration constant and varying the FA concentration, the strong binding sites of the FA become saturated and the excess nickel then binds to the weaker sites of the FA, forming weak nickel complexes which are labile, releasing Ni-aqua complex, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, which has been reported to be toxic.

The kinetic lability of the Ni-FA complexes varied in a reasonable way with the $[\text{Ni}] / [\text{FA}]$ mole ratio, suggesting that the Kinetic Model has provided chemically significant metal species. **This is a test of the chemical significance of the Kinetic Model.** The change in the dissociation rate coefficient measured for each kinetically distinguishable

Figure 29. Ni(II)-FA complexes remaining undissociated in model systems containing varying concentrations of Laurentian FA, as a function of time, determined by CLEM/GFAAS. Concentrations of Ni(II) were same for all curves. pH, 5.0 ± 0.1 ; ionic strength, $\sim 5.97 \times 10^{-2}$ M; Chelex-100 was the competing ligand. (—), two-component fitting; (Δ), $[\text{Ni(II)}] 8.5 \times 10^{-7} \text{ M} / [\text{FA } 1.7 \times 10^{-4} \text{ M}] = 0.005$; ($\square$), $[\text{Ni(II)}] 8.5 \times 10^{-7} \text{ M} / [\text{FA } 1.7 \times 10^{-5} \text{ M}] = 0.05$; ($\circ$), $[\text{Ni(II)}] 8.5 \times 10^{-7} \text{ M} / [\text{FA } 1.7 \times 10^{-6} \text{ M}] = 0.5$.

Table 27. Kinetically distinguishable components of Ni(II)-FA complexes in model solutions of Laurentian fulvic acid, determined by CLEM/GFAAS. pH, 5.0 $\pm$ 0.1; ionic strength, $\sim 5.97 \times 10^{-2}$ M. [Ni (II) 8.5×10^{-7} M].

[FA], M	[Ni]/[FA]	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁵ s ⁻¹)	R ² of fitting
1.7×10^{-4}	0.005	52 $\pm$ 8	1 $\pm$ 0.2	48 $\pm$ 5	2.7 $\pm$ 0.4	0.991
1.7×10^{-5}	0.05	64 $\pm$ 7	2.6 $\pm$ 0.4	36 $\pm$ 5	16 $\pm$ 2	0.997
1.7×10^{-6}	0.5	83 $\pm$ 8	11.0 $\pm$ 0.4	17 $\pm$ 2	25 $\pm$ 3	0.997

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

component of the Ni-FA complexes provides experimental evidence of the polyfunctionality (i.e. chemical heterogeneity) of the fulvic acid. The results show how the Kinetic Model can detect the progressive occupation of strong and weak binding sites of a well-characterized FA and the existence of strong and weak binding sites in the fulvic acid, supporting the conclusion that the Kinetic Model has chemical significance. The dissociation rate coefficient ($\bar{k}_d$) increases with increasing metal-to-ligand ratios, suggesting that weaker complexing sites of the heterogeneous ligand (FA) are occupied with increasing metal concentrations, forming weaker complexes which are labile, and hence, have higher dissociation rate coefficients. The different values dissociation rate coefficient ($\bar{k}_d$) obtained by the two techniques (AdCSV and GFAAS) are attributable to their different analytical windows, which allow each to record only a narrow range of dissociation rate coefficient.

CLEM/GFAAS of Ni(II)-FA in model systems: the effect of Al(III) on the kinetic lability of Ni(II)-FA complexes.

Figure 30 and Table 28 present the results of varying concentrations of Al(III) on the release of the FA-bound Ni(II) and show that the top three curves group together with their most labile components ($C_1\%$) from 56 to 67% having a dissociation rate coefficient (k_1) of $\sim 0.4 \times 10^{-3} \text{ s}^{-1}$, whereas the fourth curve (bottom curve) was significantly different: its most labile component ($C_1\%$) 79% had a dissociation rate coefficient (k_1) of $\sim 1.0 \times 10^{-2} \text{ s}^{-1}$, which was about 25 times faster than the dissociation rate coefficient of top three curves. The above two groups were also significantly different in that top three

curves had the second kinetically distinguishable component ($C_2\%$) ranging from 32 to 40% as inert ($k_2 < 10^{-6} \text{ s}^{-1}$), whereas for the fourth curve (the bottom curve), the second kinetically distinguishable component ($C_2\%$) 21% was inert ($k_2 < 10^{-6} \text{ s}^{-1}$). The above grouping was probably the result of a single factor—the increasing mole ratios of Al(III) in the 2nd, 3rd and 4th curves from top, due to increasing Al(III) concentrations while the concentrations of all the components of the test solutions were held constant. The above effects are more noticeable in Fig. 30, in which the concentration of Al(III) was 10^{-6} M for the second curve (from top), which was then increased by one order of magnitude for each curve below (curves 3 and 4 from top). The result was a gentle following of the trend for the third curve (from top), whereas a further one order of magnitude increase in the Al(III) concentration for the fourth curve (bottom curve) resulted in a drastic change both in the $C_1\%$ and the k_1 value, making the system (bottom curve) about 25 times more labile than the first three systems. This drastic change can be interpreted as follows. The increasing concentrations of Al(III) from curve 2 to 4 (from top) successfully compete with Ni(II) for the strong binding sites (<10%) of the FA; the effect of this competition is that for the 3rd curve (from top) the strong sites are barely enough to bind all of the Ni(II) and Al(III). When the Al(III) concentration was increased by a further one order of magnitude for the 4th curve (from top), the concentration of Al(III) became so large as to displace Ni(II) from the strong binding sites (<10%) of the FA; the displaced Ni(II) then bound to the weak sites (>90%) of the FA, forming weak Ni(II)-FA complexes which were labile.

Figure 30. Ni(II)-FA complexes remaining undissociated in model systems containing varying concentrations of Al(III), as function of time, determined by CLEM/GFAAS. Concentrations of Ni(II) and FA were same for all curves. pH, 5.0 ± 0.1 ; ionic strength, $\sim 6.12 \times 10^{-2}$ M; Chelex-100 was the competing ligand. (—), two-component fitting; (□), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M]; (●), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Al(III) 1.51×10^{-6} M]; (△), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Al(III) 1.51×10^{-5} M]; (■), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Al(III) 1.51×10^{-4} M].

Table 28. Kinetically distinguishable components of Ni(II)-FA complexes in model solutions in the presence of varying concentrations of Al(III) and constant concentrations of Ni(II) and the FA, determined by CLEM/GFAAS. pH, 5.0 $\pm$ 0.1; ionic strength, $\sim 6.12 \times 10^{-2}$ M.

[Al (III)], M	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁶ s ⁻¹)	R ² of fitting
0	56 $\pm$ 8	0.42 $\pm$ 0.05	39 $\pm$ 5	<10 ⁻⁶	0.991
1.51 $\times 10^{-6}$	59 $\pm$ 9	0.37 $\pm$ 0.04	40 $\pm$ 7	<10 ⁻⁶	0.987
1.51 $\times 10^{-5}$	67 $\pm$ 9	0.41 $\pm$ 0.05	32 $\pm$ 6	<10 ⁻⁶	0.997
1.51 $\times 10^{-4}$	79 $\pm$ 13	10 $\pm$ 1	21 $\pm$ 3	<10 ⁻⁶	0.994

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

CLEM/AdCSV of Ni(II)-FA in model systems: the effect of Al(III) on the lability of the above systems

Figure 31 and Table 29 present the effect of Al(III) on the lability of Ni(II)-FA complexes—the i_p/i_o represents the fraction of Ni(II)-FA complex that is labile (i_p is the current given by the Ni(II)-FA complex, whereas i_o is the current given by the Ni(II) under the condition of no complexation). Table 29 shows the numerical values of the kinetically distinguishable components and their associated dissociation rate coefficients obtained from Fig. 31 by nonlinear regression analysis. In the absence of any Al(III), 38% of the Ni(II) probably existed as free Ni^{2+} ion, i.e. as Ni(II)-aqua complex (bottom curve); the percentage of Ni(II) existing as free Ni^{2+} ion increased with increasing concentrations of Al(III), as is seen in Fig. 31, (2nd and 3rd curves from bottom), and in Table 29. This effect is probably due to the Al(III) out competing the Ni(II) for the minor (< 10%), strong binding sites of the FA, which results in the Ni(II) binding the major (> 90%), weak binding sites of the FA, forming weak Ni(II)-FA complexes which were labile. The release of the free Ni^{2+} ion (i.e. Ni(II)-aqua complex) from the bound Ni(II)-FA complex as a result of the competition of Al(III) was 100% complete for the top curve in Fig. 31, in which the concentration of Al(III) is about the same as that of the FA, both of which are about 50-fold greater than the concentration of Ni(II). The above effect can be interpreted as the Al(III) out competing the Ni(II) for the minor (<10%), strong binding sites of the FA, saturating all the minor, strong binding sites, resulting in the Ni(II) binding to the major (>90%), weak binding sites, forming weak Ni(II)-FA complexes which are labile.

Figure 31. The lability (i_p/i_o) of Ni(II)-FA complexes in model systems containing varying concentrations of Al(III), as function of time, determined by CLEM/AdCSV. Concentrations of Ni(II) and FA were held constant for all curves. pH, 5.0 ± 0.1 ; ionic strength, $\sim 2.99 \times 10^{-2}$ M; DMG was the competing ligand. (—), two-component fitting; (Δ), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M]; ($\square$), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Al(III) 1.51×10^{-6} M]; ($\circ$), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Al(III) 1.51×10^{-5} M]; ($\bullet$), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Al(III) 1.51×10^{-4} M].

Table 29. Kinetically distinguishable components of Ni(II)-FA complexes in model solutions in the presence of varying concentrations of Al(III) and constant concentrations of Ni(II) and the FA , determined by CLEM/AdCSV. pH, 5.0 ± 0.1 ; ionic strength, $\sim 2.99 \times 10^{-2}$ M.

[Al (III)], M	C ₁ (%)	k ₁ , (10 ⁻² s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁶ s ⁻¹)	R ² of fitting
0	38±5	0.5±0.2	63±3	<10 ⁻⁶	0.945
1.51 × 10 ⁻⁶	48±4	0.73±0.08	49±3	<10 ⁻⁶	0.957
1.51 × 10 ⁻⁵	73±3	0.75±0.04	24±2	<10 ⁻⁶	0.979
1.51 × 10 ⁻⁴	100±9	1.33±0.01	--	--	0.901

--- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

Figure 31 and Table 29 show that the Ni(II)-FA complexes are 100% labile (almost all the Ni(II) are released within ~10 s) and have dissociation rate coefficients two order of magnitude greater than those Ni(II)-FA complexes that GFAAS with its narrow, limited window could observe (Table 28). The difference in the results between GFAAS and AdCSV is attributable to the difference in their respective analytical window [1]; GFAAS, because of its longer sampling time is capable of observing only relatively slower kinetics, whereas AdCSV because of its faster rate of sampling can observe faster kinetics.

Effect of Fe(III) on the kinetic lability of the Ni-FA complexes

Figure 32 shows the effects of increasing concentrations of Fe(III) on the lability of Ni-FA complexes in model solutions under otherwise identical experimental conditions, and shows behaviour similar to Figure 30. In the absence of Fe(III), Ni(II) occupies the small number (< 10%) of strong binding sites of the FA, forming strong Ni(II)-FA complexes that are inert (top curve). However, the presence of high and sharply increasing concentration of Fe(III) (from 1.43×10^{-6} to 1.43×10^{-4} M) (increasing by one order of magnitude from top to bottom curve) has a dramatic effect on the lability of the Ni(II)-FA complexes because high concentrations of Fe(III) out compete the Ni(II) for the small number (< 10%) of strong binding sites of the FA, resulting in Ni(II) binding to the large number (> 90%) of weak binding sites of the FA, forming weak Ni(II)-FA complexes that were labile. The experimental data presented in Fig. 32 were analyzed using the non-linear regression method mentioned earlier. The values for kinetic parameters of the

Figure 32. Ni(II)-FA complexes remaining undissociated in model systems containing varying concentrations of Fe(III), as function of time, determined by CLEM/GFAAS. Concentrations of Ni(II) and the FA were held constant for all curves. pH, 5.0 ± 0.1 ; ionic strength, $\sim 6.60 \times 10^{-2}$ M; Chelex-100 was the competing ligand. (—), two-component fitting; (▼), $[\text{Ni(II)}] 8.5 \times 10^{-7}$ M + $[\text{FA}] 1.7 \times 10^{-4}$ M; (O), $[\text{Ni(II)}] 8.5 \times 10^{-7}$ M + $[\text{FA}] 1.7 \times 10^{-4}$ M + $[\text{Fe(III)}] 1.43 \times 10^{-6}$ M; (■), $[\text{Ni(II)}] 8.5 \times 10^{-7}$ M + $[\text{FA}] 1.7 \times 10^{-4}$ M + $[\text{Fe(III)}] 1.43 \times 10^{-5}$ M; (△), $[\text{Ni(II)}] 8.5 \times 10^{-7}$ M + $[\text{FA}] 1.7 \times 10^{-4}$ M + $[\text{Fe(III)}] 1.43 \times 10^{-4}$ M.

Table 30. Kinetically distinguishable components of Ni(II)-FA complexes in model solutions in the presence of varying concentrations of Fe(III) and constant concentrations of Ni(II) and the FA , determined by CLEM/GFAAS. pH, 5.0 ± 0.1 ; ionic strength, $\sim 6.60 \times 10^{-2}$ M.

[Fe (III)], M	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁴ s ⁻¹)	R ² of fitting
0	52±11	0.4±0.2	48±9	<10 ⁻⁶	0.981
1.43×10^{-6}	57±14	0.9±0.1	42±9	1.70±0.06	0.998
1.43×10^{-5}	72±4.0	3.8±0.1	28±3	4.3±0.8	0.987
1.43×10^{-4}	85±10	11±2	16±2	12.8±0.5	0.999

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

Figure 33. The lability (i_p/i_o) of Ni(II)-FA complexes in model systems containing varying concentrations of Fe(III), as function of time, determined by CLEM/AdCSV. Concentrations of Ni(II) and the FA were held constant for all curves. pH, 5.0 ± 0.1 ; ionic strength, $\sim 2.51 \times 10^{-2}$ M; Chelex-100 was the competing ligand. (—), two-component fitting; (O), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M]; (▲), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Fe(III) 1.43×10^{-6} M]; (●), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Fe(III) 1.43×10^{-5} M]; (▽), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Fe(III) 1.43×10^{-4} M].

Table 31. Kinetically distinguishable components of Ni(II)-FA complexes in model solutions in the presence of varying concentrations of Fe(III) and constant concentrations of Ni(II) and the FA, determined by CLEM/AdCSV. pH, 5.0 $\pm$ 0.1; ionic strength, $\sim 2.51 \times 10^{-2}$ M.

[Fe (III)], M	C ₁ (%)	k ₁ , (10 ⁻² s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁶ s ⁻¹)	R ² of fitting
0	55 $\pm$ 7	0.65 $\pm$ 0.01	44 $\pm$ 4	<10 ⁻⁶	0.993
1.43 $\times$ 10 ⁻⁶	58 $\pm$ 11	0.68 $\pm$ 0.02	40 $\pm$ 10	<10 ⁻⁶	0.973
1.43 $\times$ 10 ⁻⁵	100 $\pm$ 4	1.50 $\pm$ 0.08	--	--	0.988
1.43 $\times$ 10 ⁻⁴	102 $\pm$ 5	1.80 $\pm$ 0.02	--	--	0.961

--- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

Ni(II)-FA complexes in the presence of various concentrations of Fe(III) and constant concentrations of Ni(II) and the FA are presented in Table 30, which shows that in the presence of the relatively high concentration of Fe(III) (1.43×10^{-4} M), the Ni(II)-FA complex had a faster dissociation rate coefficient ($k_1 = 11.4 \times 10^{-3} \text{ s}^{-1}$) than in the presence of the relatively low concentration of Fe(III) (1.43×10^{-5} M) ($k_1 = 3.8 \times 10^{-3} \text{ s}^{-1}$); in the presence of a still lower concentration of Fe(III) (1.43×10^{-6} M), k_1 was $0.92 \times 10^{-3} \text{ s}^{-1}$, and in the absence of Fe(III) k_1 was $0.42 \times 10^{-3} \text{ s}^{-1}$. These results are consistent with the interpretation of the lability of the Ni(II)-FA complexes given above.

Figure 30 and Figure 32 show that in the competition for strong binding sites of the FA, Fe(III) wins over Al(III) presumably because the rate coefficient for water exchange for Fe^{3+} is $2 \times 10^2 \text{ s}^{-1}$, which is $\gg 1 \text{ s}^{-1}$ of that for Al^{3+} [5]. Also, in accordance with Hard and Soft Acid-Base Principle (HSAB) [6], Fe^{3+} is a soft acid, whereas Al^{3+} is a hard acid, and Ni^{2+} is on the borderline between soft and hard acids. Therefore, in a multiligand complexant (the FA), Fe^{3+} forms stronger covalent bonds with S, O and N ligand atoms than Al^{3+} and Ni^{2+} .

Figure 33 and Table 31 present the effects of the varying concentrations of Fe(III) on the release of Ni-aqua complex, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, from Ni(II)-FA complexes, measured by the AdCSV technique. The results of both GFAAS and AdCSV show the same trend of increasingly greater percentages of the Ni-FA complexes becoming more labile in the presence of increasing concentrations of Fe(III), for reasons stated earlier.

Effect of of Al (III) and Fe(III) on the lability of the Ni(II)-FA complexes

Figure 34 presents the effect of varying concentrations of a mixture of Al(III) and Fe(III) on the lability of Ni(II)-FA complexes in model systems, and shows a behaviour similar to that Figs. 30 and 32. In the absence of a mixture of Al(III) and Fe(III), Ni(II) occupies the small number ($< 10\%$) of the strong binding sites of the FA, forming strong Ni(II)-FA complexes which were inert (top curve). However, the presence of high and sharply increasing concentrations of the mixture of Al(III) and Fe(III) (from 1×10^{-7} to 1×10^{-4} M) (each curve from top to bottom) has a dramatic effect on the lability of the Ni(II)-FA complexes, when high concentrations of the mixture of Al(III) and Fe(III) out compete Ni(II) for the small number ($< 10\%$) of strong binding sites of the FA, resulting in Ni(II) binding to the much larger number ($> 90\%$) of weak binding sites of the FA, forming weak Ni(II)-FA complexes that were labile. The values for the kinetic parameters of the Ni(II)-FA complexes in the presence of varying concentrations of a mixture of Al(III) and Fe(III) and a constant concentration of Ni(II) and the FA are presented in Table 32. Comparison of Figs. 30 and 32 with Fig. 34 reveals that Ni(II)-FA complexes were more labile in the presence of the mixture of Al(III) and Fe(III), compared to the lability of the Ni(II)-FA complexes when only one of the two, Al(III) or Fe(III), was present. Whether this is simply a mass effect or a synergistic effect is an interesting question which maybe addressed as follows. Figures 32 and 33 and Tables 30 and 31 show that in the presence of 1.43×10^{-6} M Fe(III) alone (Fig. 32, second curve from top), the percentage of the labile Ni(II)-FA complexes ($C_1 = 57.0 \%$) was lower than that in the presence of 1.51×10^{-7} M Al(III) and 1.43×10^{-7} M Fe(III) when they were both present (Fig. 34, second

Figure 34. Ni(II)-FA complexes remaining undissociated in model systems containing varying concentrations of Al(III) and Fe(III) as function of time, determined by CLEM/GFAAS. Concentrations of Ni(II) and the FA were held constant for all curves. pH, 5.0 ± 0.1 ; ionic strength, $\sim 9.10 \times 10^{-2}$ M; Chelex-100 was the competing ligand. (—), two-component fitting; (▼), $[\text{Ni(II)}] 8.5 \times 10^{-7} \text{ M} + [\text{FA}] 1.7 \times 10^{-4} \text{ M}$; (○), $[\text{Ni(II)}] 8.5 \times 10^{-7} \text{ M} + [\text{FA}] 1.7 \times 10^{-4} \text{ M} + [\text{Al(III)}] 1.51 \times 10^{-7} \text{ M} + [\text{Fe(III)}] 1.43 \times 10^{-7} \text{ M}$; (●), $[\text{Ni(II)}] 8.5 \times 10^{-7} \text{ M} + [\text{FA}] 1.7 \times 10^{-4} \text{ M} + [\text{Al(III)}] 1.51 \times 10^{-6} \text{ M} + [\text{Fe(III)}] 1.43 \times 10^{-6} \text{ M}$; (□), $[\text{Ni(II)}] 8.5 \times 10^{-7} \text{ M} + [\text{FA}] 1.7 \times 10^{-4} \text{ M} + [\text{Al(III)}] 1.51 \times 10^{-5} \text{ M} + [\text{Fe(III)}] 1.43 \times 10^{-5} \text{ M}$ (▲), $[\text{Ni(II)}] 8.5 \times 10^{-7} \text{ M} + [\text{FA}] 1.7 \times 10^{-4} \text{ M} + [\text{Al(III)}] 1.51 \times 10^{-4} \text{ M} + [\text{Fe(III)}] 1.43 \times 10^{-4} \text{ M}$.

Table 32. Kinetically distinguishable components of Ni(II)-FA complexes in model solutions in the presence of varying concentrations of Al(III) and the Fe(III) and constant concentrations of Ni(II) [8.5×10^{-7} M], and the FA, [1.7×10^{-4} M], determined by CLEM/GFAAS. pH, 5.0 ± 0.1 ; ionic strength, $\sim 9.10 \times 10^{-2}$ M.

[Fe (III)], M	[Al (III)], M	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁴ s ⁻¹)	R ² of fitting
0	0	52±8	0.95±0.05	48±4	0.23±0.02	0.991
1.43×10^{-7}	1.51×10^{-7}	59±6	1.2±0.2	42±6	1.7±0.2	0.999
1.43×10^{-6}	1.51×10^{-6}	68±3	1.8±0.3	34±2	2.1±0.4	0.997
1.43×10^{-5}	1.51×10^{-5}	79±6	3.2±0.8	20±4	3.8±0.6	0.996
1.43×10^{-4}	1.51×10^{-4}	97±9	47±3	5±0.8	5.9±0.3	0.999

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

Figure 35. The lability (i_p/i_o) of Ni(II)-FA complexes in model systems containing varying concentrations of Al(III) and Fe(III), as function of time, determined by CLEM/AdCSV. Concentrations of Ni(II) and FA were held constant for all curves. pH, 5.0 ± 0.1 ; ionic strength, $\sim 2.49 \times 10^{-2}$ M; Chelex-100 was the competing ligand. (—), two-component fitting; (●), Reference solution [Ni(II) 8.5×10^{-7} M]; (○), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Al(III) 1.51×10^{-6} M] + [Fe(III) 1.43×10^{-6} M]; (▽), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Al(III) 1.51×10^{-5} M] + [Fe(III) 1.43×10^{-5} M]; (□), [Ni(II) 8.5×10^{-7} M] + [FA 1.7×10^{-4} M] + [Al(III) 1.51×10^{-4} M] + [Fe(III) 1.43×10^{-4} M].

Table 33. Kinetically distinguishable components of Ni(II)-FA complexes in model solutions in the presence of varying concentrations of Al(III) and the Fe(III) and constant concentrations of Ni(II) [8.5×10^{-7} M], and the FA [1.7×10^{-4} M], determined by CLEM/AdCSV. pH, 5.0 ± 0.1 ; ionic strength, $\sim 2.49 \times 10^{-2}$ M.

[Fe (III)], M	[Al (III)], M	C ₁ (%)	k ₁ , (10 ⁻² s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁶ s ⁻¹)	R ² of fitting
0	0	100*±3	5.20±0.05	--	--	0.993
1.43×10^{-6}	1.51×10^{-6}	47±2	0.62±0.04	51±3	<10 ⁻⁶	0.981
1.43×10^{-5}	1.51×10^{-5}	93±2	1.00±0.06	6±0.4	<10 ⁻⁶	0.991
1.43×10^{-4}	1.51×10^{-4}	100±3	1.52±0.01	--	--	0.984

--- Not detected

* Reference solution [Ni(II) 8.5×10^{-7} M]

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

curve from top, $C_1 = 59 \%$). Hence, the enhanced lability of the Ni(II)-FA complexes when Al(III) and Fe(III) were both present compared with the lability of the Ni(II)-FA complexes when only one of the two, Al(III) or Fe(III), was present, was due to synergy, and was not a mass effect.

Figures 30, 32 and 34 and Tables 28, 30 and 32 present the effects of varying concentrations of Al(III) and Fe(III) on the lability of the Ni(II)-FA complexes, as determined by CLEM/GFAAS. In Fig. 34, the curve with both Al(III) 1.51×10^{-4} M and Fe(III) 1.43×10^{-4} M (bottom curve) shows that almost 100% of Ni(II)-FA complex became labile ($k_1 = 4.7 \pm 0.3 \times 10^{-2} \text{ s}^{-1}$) probably as a result of the competition by a large excess of Al(III) and Fe(III). The CLEM studies were also done using the AdCSV technique and the results are presented in Figs. 32, 34 and 36 and Tables 29, 31 and 33. Figure 36 and Table 33 show that the reference solution Ni(II) without any complexing agent yields first-order dissociation rate coefficient $k_1 = 5.2 \pm 0.05 \times 10^{-2} \text{ s}^{-1}$, whereas Lavigne et al. [7] have reported that the labile component, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, that results from the dissociation of their Ni(II)-FA complex has a first-order dissociation rate coefficient (k_1) $= 6.2 \times 10^{-1} \text{ s}^{-1}$. The above difference is understandable as the $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ reported by Lavigne et al. [7] might have been mixed with other more labile species of Ni(II).

The results of both CLEM/GFAAS and CLEM/AdCSV show the same trend of increasing percentages of the Ni(II)-FA complexes becoming more labile in the presence of increasing concentrations of Al(III) and Fe(III). The difference in dissociation rate coefficients and the percentages of the labile Ni(II)-FA complexes obtained by the two

techniques is attributable to their respective analytical windows — the AdCSV technique allows measurement of faster kinetics and the associated kinetically distinguishable components, whereas the GFAAS technique allows measurement of only slower kinetics and the associated kinetically distinguishable components.

Freshwaters Samples from Sudbury (Canada) Area.

Competition of Al(III) and Fe(III) with Ni(II) for strong binding sites of the naturally occurring organic complexants in the Sudbury (Canada) area samples

Relevant properties of Sudbury (Canada) area freshwater samples are presented in Table 34. Figure 36 presents the result of the competition of three metals, Al(III), Fe(III) and Ni(II), for the strong binding sites of the naturally occurring organic complexants in the Sudbury (Canada) area freshwaters samples and shows that in the Onaping River sample downstream of the Sewage Treatment Plant, where the concentration of aluminium was $2.4\ \mu\text{M}$ and of iron was $1.6\ \mu\text{M}$ (top curve), about 30% of nickel was bound to the small number of strong binding sites of naturally occurring organic complexants, resulting in the formation of strong nickel complexes, which were inert. The remaining nickel was bound to the large number of the weak binding sites, resulting in the formation of weak nickel complexes, which were labile. However, in the Coniston Creek downstream sample where the concentrations of aluminium and iron were higher than those of the Onaping River (as shown in Table 34), and also with increasing concentrations of aluminium and iron, almost all the strong binding sites of the naturally occurring organic

Table 34. Some properties of Sudbury (Canada) area samples.

Sampling sites	pH	Conductivity μS/cm	DOC mg/L	Ni/DOC mol/g	[Al], μM	[Fe], μM
Coniston Creek downstream*	6.4	528	6.0	1.8×10^{-4}	7.6	1.9
Onaping River downstream of the Sewage Treatment Plant*	6.9	65	6.5	1.2×10^{-4}	2.4	1.6
Kelly Lake**	6.6	1250	6.3	6.8×10^{-4}	1.3	0.5
Moose Creek upstream**	6.6	1060	6.4	6.0×10^{-4}	3.1	2.0

* Samples collected in June, 1998

** Samples collected in July, 1999

Figure 36. Ni(II)-FA complexes remaining undissociated in the Sudbury (Canada) area water samples collected in June 1998, in the presence of Al(III) and Fe(III), as function of time, determined by CLEM/GFAAS. Chelex-100 was the competing ligand. (—), two-component fitting; (▼), Onaping River downstream of the Sewage Treatment Plant; (●), Coniston Creek downstream.

Figure 37. Ni(II)-FA complexes remaining undissociated in the Sudbury (Canada) area water samples collected in July 1999, in the presence of Al (III) and Fe(III) as function of time, determined by CLEM/GFAAS. Chelex-100 was the competing ligand. (—), two-component fitting; (▼), Kelly Lake; (●), Moose Creek upstream.

Table 35. Kinetically distinguishable components of Ni(II)-FA complexes in the Sudbury (Canada) area water samples, in the presence of different concentrations of Al(III) and Fe(III) and constant [Ni(II)]/[DOC] ratios, determined by CLEM/GFAAS.

Sampling sites	C ₁ (%)	k ₁ , (10 ⁻³ s ⁻¹)	C ₂ (%)	k ₂ , (10 ⁻⁴ s ⁻¹)	R ² of fitting
Onaping River downstream of the Sewage Treatment Plan	72±10	5.1±0.8	26±3	1.5±0.6	0.996
Coniston Creek downstream	97±12	8.5±0.3	---	---	0.998
Kelly Lake	76±8	5.4±0.2	25.0±2.0	1.3±0.2	0.997
Moose Creek upstream	89±9	7.8±1.0	12±1	3.3±0.1	0.995

--- Not detected

The uncertainties represent 95.5% confidence limits in the non-linear regression analysis, for an individual measurement.

complexants in the Coniston Creek downstream sample were saturated by aluminium and iron present in the sample. The result was that increasingly larger percentages of the Ni(II) were bound to much larger number of the weak binding sites of the naturally occurring organic complexants, forming weak nickel complexes which were labile.

Figure 37 presents the result of the competition by three metals, Al(III), Fe(III) and Ni(II), for strong binding sites of the naturally occurring organic complexants in the Sudbury area samples and shows almost a similar behaviour to that shown in Fig. 36. The results are interpreted as follows. In the Kelly Lake sample, where the concentrations of aluminium and iron lower were than those in the Moose Creek upstream sample, Ni(II) occupied the small number of the strong binding sites of the organic complexants, thereby forming strong nickel complexes, which were inert (top curve). However, when the concentrations of aluminium and iron in the Moose Creek upstream sample increased to about three times of those in the Kelly Lake sample (bottom curve), the effect was greater lability of Ni(II)-complex in the latter sample.

From Figs. 36 and 37 and Table 35 it is clear that the enhanced lability of the Ni(II)-complexes in the presence of aluminium and iron is the result of competition of aluminium and iron with nickel for the strong binding sites of the naturally occurring organic complexes in the Sudbury (Canada) area samples. This result agrees well with our studies with model aqueous solutions containing the above metals and a well-characterized fulvic acid.

Conclusions

Competitive binding by aluminium, iron and nickel for binding sites of fulvic acid has strong effects on the binding of Ni(II) by fulvic acid. This study has dealt with interactions in aqueous systems assumed to be at equilibrium. In real natural waters systems, there are a number of additional factors. With regards to Fe(III) in particular, the equilibrium assumption is certainly questionable, because of biologically or photochemically mediated redox cycling [8].

This work has shown that the effect of Al(III) and Fe(III), present in samples dose have an appreciable effect of releasing Ni^{2+} -aqua complex, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, from the DOC-bound Ni(II). The significance of these results is that in model solutions simulating freshwaters containing humic substances and the target trace metal Ni(II) and cations, Al(III) and Fe(III), the competitive binding of Ni(II), Al(III) and Fe(III) by humic substances makes Ni(II)-humate complexes are labile, releasing free Ni^{2+} -aqua complex, which are reported to be toxic. This knowledge will allow decision-makers to make better pollution risk assessment and to adopt environmental policies and regulations constraining discharge of effluents from mining and metallurgical operations into the aquatic environment, taking into considerations the presence of aluminium and iron in the surrounding bedrocks, and acid rains to dissolve the bedrocks in the aquatic environment.

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CHAPTER 8

THE INFLUENCE OF UV RADIATION ON DISSOLVED ORGANIC CARBON AND ITS EFFECT ON METAL SPECIATION AND BIOAVAILABILITY

Experimental

Chemicals and Reagents

Stock solutions of copper, lead, nickel and zinc (1000 $\mu\text{g/mL}$) were prepared separately by dissolving chemically pure metal or metal oxide in ultrapure nitric acid (Ultrex II), diluting the solution with ultrapure water, and acidifying the solution with ultrapure nitric acid to make the final solutions contain 1% (v/v) ultrapure nitric acid. In order to prepare a thin Mercury Film Electrode (TMFE), a stock solution of 5000 $\mu\text{g/mL}$ $\text{Hg}(\text{NO}_3)_2$ was prepared by dissolving pure mercury in ultrapure nitric acid and diluting the solution with 1% (v/v) nitric acid. A stock solution of 2.0 M sodium acetate electrolyte solution was prepared by dissolving an appropriate quantity of sodium acetate trihydrate (ACS grade/BDH) in ultrapure water. This solution was purified to be free of metals by mercury-cathode electrolysis at -1.4 V vs. E_{SCE} for at least 72 h using a mercury-pool cathode to remove heavy metals. A stock solution of 2.0 M acetic acid was prepared by diluting ultrapure glacial acetic acid (Aristar grade) with ultrapure water. Ultrapure water of resistivity 18.2 $\text{M}\Omega\text{ cm}$ was obtained direct from a Milli-Q UF Plus water purification system (Millipore Corporation), fitted with a purifying column to remove organic matter.

All test solutions (unless otherwise stated) were prepared by serial dilution of the above stock solutions with ultrapure water immediately prior to use.

Water samples

To study freshwaters containing different DOC concentrations, samples were taken from a brown-water site (head-waters of the Grand River), a clear-water site (Lake Simcoe), and from the St. Lawrence River. The Grand River (44° 05.807' N, 80° 22.445' W) originates in the highlands of Dufferin County and winds its way more than 300 km to Lake Eire. The Grand River Watershed is the largest in south western Ontario and includes all of the land drained by the Grand River and its major tributaries—the Nith, Conestogo, Speed and Eramosa rivers. Lake Simcoe is located in southern Ontario nearly 100 km north of Toronto with a surface area of 725 square kilometres; Lake Simcoe is southern Ontario's largest body of water exclusive of the Great Lakes. The St. Lawrence River flows 1000 km from Lake Ontario to the Gulf of St. Lawrence. It is the largest river draining the eastern seaboard of North America and, combined, the Great Lakes—St. Lawrence River system drains 25% of the world's freshwater supply [1].

Immediately after the collection, the water samples were filtered through 0.45 µm Gelman mixed cellulose ester filters using a peristaltic pump and stored in dark at 4 °C prior to use. The water samples were irradiated under UV-B fluorescent lamps in 2.2 L Teflon bottles (11.5 cm diameter) in the laboratory for five and ten days. UV-B irradiance was measured using a OL754 spectroradiometer with dual monochromator (Optronics Ltd.), OL IS470-W submersible sphere, OL 730-7Q-WP waterproof fibre optic probe,

and operated with OptoLab 754 software. At the outside surface of the bottle (in air) the UV-B dose was 3.90 W/m^2 . The dose inside the bottle was measured by cutting a hole in the side of one of the bottles and sealing the probe's sensor inside the bottle with parafilm, then filling the bottle with deionized water. The UV-B dose (integrated over 280-320 nm) inside the bottle was 1.38 W/m^2 . Since the integrated UV-B irradiance in full sun ranges from approximately 0.80 to over 2.5 W/m^2 , the UV-B exposure inside the bottles was approximately half that of UV-B from summer solar radiation at the surface. Non-irradiated bottles were kept as controls. Irradiated water samples and non-irradiated bottles were stored in the dark at 4°C . A sheet of cellulose acetate between the Teflon bottles and the UV light source was used as a cut-off filter (wavelengths $< 280 \text{ nm}$ were excluded, while higher wavelengths were transmitted). The pH of the water samples were measured with an Accumet 925 pH/ion meter using a combination glass electrode containing an internal calomel reference electrode. The ionic strength of the sample was fixed with sodium acetate, which also functioned as the supporting electrolyte.

Apparatus

Voltammetric measurements were done using the Bioanalytical Systems (BAS) Electrochemical Analyzer, Model 100B/W analyzer and equipped with an RDE-1 Rotating Disk Electrode (BAS). The working electrode, a Glassy Carbon Electrode (GCE) of 3 mm diameter, was made of a glassy carbon substrate, surrounded by an epoxy resin insulating jacket. The reference electrode consisted of an Ag/AgCl electrode in a Teflon tube fitted with a porous Vycor tip filled with saturated with 3M KCl solution. The counter electrode was made of a coiled platinum wire. The data were acquired using

the BAS 100W windows control software version 2.3 (BAS), and were transferred to a 486 computer and saved for processing.

Electrochemical parameters

Each sample was purged for 15 min with ultra high-purity nitrogen gas (UHP, PRAXAIR) prior to use. The rotation electrode rate was from 25 to 7000 rpm. The experimental conditions were as follows: Linear Scan Anodic Stripping Voltammetry (LSASV); deposition time 180 s; equilibration time 15 s; step potential 2.0 mV/s; frequency 75 Hz, Scan rate 10 mV/s, Deposition potential: Cd(II) -0.80 V, Cu(II) -0.1 V, Pb(II) -0.80 V, and Zn(II) -1.2 V.

Formation of the Thin Mercury Film Electrode (TMFE)

The glassy carbon (GC) electrode was prepared by polishing with 0.05 μm alumina powder, wetted with ethanol, and cleaned in an ultrasonic bath for 5 minutes. The TMFE was formed by immersing the GC electrode into a 50 mL solution of deoxygenated, ultrapure water containing 0.04 M acetate buffer and 50 μL of 5000 $\mu\text{g/mL}$ Hg^{2+} solution. The samples were deoxygenated by purging with ultrapure nitrogen gas (BOC Gases, Extra Dry) for at least 10 min. With the electrode rotation rate set at 2000 rpm, the potential was held constant at -0.3 V for 10 min. as recommended in the literature [2]. After the 10 min. deposition period, the solution was allowed to become quiescent for 5 s and the potential ramped from -0.3 V to 0 V using a square-wave waveform (20 mV pulse height, 50 Hz frequency) to strip any impurities from the TMFE. The plating solution was then removed and the TMFE visually inspected. Non-uniform films or films

containing bubbles were wiped off and the TMFE re-formed. The plating solution was then replaced with a deoxygenated solution of the 0.04 M acetate buffer. Any excess mercury was removed from the electrode by dipping it in the above solution of the acetate buffer and rotating the electrode at 2000 rpm for 1 min.

Results and Discussion

Figure 38 shows the thickness of the diffusion layer as a function of the rotation rate. The thickness of the diffusion layer decreases with increase of the rotation rates and tends to reach a constant value of 4.94 μm at 7000 rpm. Fig. 38 shows that the diffusion layer thickness asymptotically approaches 0 at infinitely short timescales, as predicted from equation 35 (Chapter 3).

Since the concentration of copper, zinc, cadmium and lead in the three freshwater samples was below the limit of detection ($< 10^{-8}$ M) of GFAAS, the samples were spiked to contain equimolar (7.65×10^{-7} M) concentrations of copper, zinc, cadmium and lead, individually. The samples were allowed to equilibrate for 24 hours. The mean diffusion coefficient was calculated by fitting the experimental data to the Levich equation Eqn. 36 (Chapter 3) [3] for the straight part of the curve at low rotation rates when essentially all the complexes should be labile, as shown in Fig. 39. Results of the mean diffusion coefficients of the zinc, cadmium and lead complexes in the Grand River, Lake Simcoe and the St. Lawrence River are shown in Table 36. The most significant observation is an

Table 36. Mean diffusion coefficients of the cadmium, lead and zinc complexes in the freshwater samples determined by ASV-RDE.

Sample name	Metal	$D_{M^{2+}} \text{ (cm}^2 \text{ s}^{-1}\text{)}$	$D_{ML} \text{ (cm}^2 \text{ s}^{-1}\text{)}$
Grand River	Cd	7.17×10^{-6}	5.60×10^{-6}
	Pb	9.45×10^{-6}	5.60×10^{-6}
	Zn	7.15×10^{-6}	3.80×10^{-6}
St. Lawrence River	Cd	7.17×10^{-6}	3.70×10^{-6}
	Pb	9.45×10^{-6}	2.12×10^{-6}
	Zn	7.15×10^{-6}	5.46×10^{-6}
Lake Simcoe	Cd	7.17×10^{-6}	--
	Pb	9.45×10^{-6}	--
	Zn	7.15×10^{-6}	3.17×10^{-6}

$D_{M^{2+}}$ Mean diffusion coefficient for metal aqua complex

D_{ML} Mean diffusion coefficient for metal-NOM complex

--- Not measured

Figure 38. Thickness of the diffusion layer as a function of the rotation rate of the ASV-RDE. $[\text{Pb}] = 3 \times 10^{-7} \text{ M}$, $[\text{FA}] = 2.7 \times 10^{-4} \text{ M}$, ionic strength $\sim 2.3 \times 10^{-2} \text{ M}$, $T = 296.3 \text{ K}$.

Figure 39. Modified Cottrell plot of Zn(II)-NOM complexes in freshwater sample collected from Lake Simcoe in July 2001, (●), reference solution [Zn(II) 7.65×10^{-7} M], $r^2 = 1.0$; (○), Lake Simcoe water sample, [Zn(II) 7.65×10^{-7} M] + [DOC 4.4 ± 0.1 mg/L], pH = 4.97 ± 0.1 ; ionic strength, $\sim 4.75 \times 10^{-2}$ M, T = 297 K, $r^2 = 0.99$.

approximately 50 % reduction in the mean diffusion coefficients relative to those for the metal-aqua complexes [4], suggesting that metals were bound as large metal-NOM complexes.

The effect of charge-to-size ratio of metals binding

Figure 40 shows the effect of charge-to-size ratio of Cd(II), Cu(II), Pb(II) and Zn(II) complexes in model solution of a well-characterized fulvic acid (Laurentian fulvic acid) and in surface water sample from Grand River. The formation rate coefficient, k_f , is primarily a characteristic of the metal and was estimated from the rate coefficient for water exchange, k_w , which can be obtained from tables [5], as shown in Chapter 2. The dissociation rate coefficient, k_d , was calculated using experimental data, and $\log K$ was calculated from the ratio of k_f and k_d . The result was consistent with the Eigen mechanism. The linear relationship between the formation rate constant and the charge-to-size ratio of the metal ion suggests that the formation rate constant is primarily related to the electrostatic attraction between the metal cation and the coordinated ligands. The exception to the trend is Cu(II), the results of which are compounded of the Ligand Field Stabilization Energy (LFSE) and Jahn-Teller effect [6], which shortens the equatorial bonds and lengthens the axial bonds in octahedrally coordinated Cu(II). There was also the additional contribution of the very high rate coefficient for water exchange for Cu^{2+} , $k_w = 1 \times 10^9 \text{ s}^{-1}$ [5] to the observed result. A similar trend, but with a smaller slope, was also observed for the dissociation rate coefficient (k_d). These results are in agreement with those of I.I. Fafous et al. [7], who observed the same trend in dissociation rate

Figure 40. The effect of charge-to-size ratio on metals speciation in Grand River and fulvic acid samples, (●), Pb(II) 8.52×10^{-7} M; (□), Cd(II) 8.70×10^{-7} M; (▲), Cu(II) 1.57×10^{-6} M; (◆), Zn(II) 7.65×10^{-7} M; (—), fitting curve; pH, 5.0 ± 0.1 ; T = 297 K.

coefficients with a different technique, the competing ligand exchange method followed by ICP-MS to measure the dissociation kinetics. The main difference here is that (k_f) is primarily a function of the metal only, whereas the values for the dissociation rate coefficients depending on the various experimental conditions. Hence, the smaller observed dissociation rate coefficients in the model solution of Laurentian fulvic acid can probably be attributed to the fact that the metals were more strongly bound, forming strong complexes which were less labile. Although the speciation of copper was also studied, no result for Cu(II) was reported because the water sample did not give a measurable signal, suggesting that the Cu(II) complexes in water sample were nonlabile. This results is in agreement with results in Chapter 5 for the kinetic speciation of Ni(II), Cu(II) and Zn(II) in soil solutions (pore waters) samples, as would be predicated from the above discussion and other literature reports [8]. Similar results were observed by Town et al. [9] for Cu(II) in model solutions of Suwannee River fulvic acid.

The effect of metal-to-DOC ratio

Figure 41 shows the effect of metal-to-DOC ratio on the lability of metals in freshwater samples collected from the Grand River, Lake Simcoe and the St. Lawrence River in June 2001. Each freshwater sample is characterized by different concentrations of DOC, which is largely responsible for the colour of the water samples. The DOC concentrations in the Grand River, Lake Simcoe and the St. Lawrence River were 15.4 mg/L, 4.0 mg/L and 1.6 mg/L, respectively. The samples ranged in colour from brown to colourless. Figure 41 shows an increase in Zn^{2+} , Cd^{2+} and Pb^{2+} concentration with increasing metal-to-DOC

Figure 41. The effect of metal-to-DOC ratio on the lability of metals in freshwater samples exposed to UV-B radiation for 5 days, (●), Pb(II) 8.52×10^{-7} M, $K_{\text{Pb(II)}} = 6.73$; (▲), Cd(II) 8.70×10^{-7} M, $K_{\text{Cd(II)}} = 5.88$; (□), Zn(II) 7.65×10^{-7} M, $K_{\text{Zn(II)}} = 5.85$; (—), fitting curve; pH, 5.0 ± 0.1 ; T = 297 K.

ratio of the sample. The Grand River sample had the lowest metal-to-DOC ratio, resulting in the lowest free metal ion concentration. The results suggest that DOC has a continuous distribution of binding sites. The strong sites are saturated first. The free metal ion concentration becomes successively controlled by weaker sites as the strong sites become occupied. This is in agreement with work done by Mandal et al. [10,11] and Sekaly et al. [12] with model solutions of fulvic acid, which indicates that DOC has a continuous distribution of binding sites. The much lower values for Pb(II) indicate that Pb(II) may form much stronger complexes than Cd(II) and Zn(II). The relatively similar results for Zn(II) and Cd(II)- complexes suggest that they have similar stability constants.

It was expected that DOC concentrations would decrease with UV-B exposure, and that metal toxicity would be greatest in low-DOC waters, and that toxicity would increase following exposure to UV-B, particularly for high-DOC waters. The Grand River (brown-water) sample was found to be much richer in DOC than the Lake Simcoe (clear-water) sample, and DOC concentrations decreased by approximately 20% with irradiation in all samples (Fig. 42). This is not surprising, given that DOC is known to be photodegraded with exposure to UV-B radiation [13]. The large difference between the two samples is likely a result of the Lake Simcoe surface water being exposed to the sun's radiation for a much longer time than the Grand River surface water was.

Figure 42 shows DOC concentrations for subsamples from both locations. In the Grand River samples, DOC concentrations decreased from an initial concentration of 17.5 mg/L to 15.4 mg/L after 5 days of UV-B irradiation, and 14.5 mg/L after 10 days of UV-B

irradiation. Non-irradiated Lake Simcoe water sample had an initial DOC concentration of 4.4 mg/L, decreasing to 4.0 mg/L after 5 days of UV-B irradiation and to 3.4 mg/L after 10 days of irradiation. All measurements were subject to an error of ± 0.2 mg/L.

The influence of the UV-B radiation on the lability of metal-complexes

Figure 43 and Table 37 present the results of the influence of the UV-B exposure on the speciation of Zn(II), Cd(II) and Pb(II) in freshwater samples collected from the Grand River surface water sample. An increase in free metal ion concentration upon exposure to UV-B radiation was observed for Zn^{2+} and Cd^{2+} ; however, no significant trend was observed for Pb^{2+} ($r^2 = 0.14$). The results inversely parallel the change in DOC concentration after UV-B exposure. Although it is tempting to attribute the increase in the free metal ion concentration of Zn^{2+} and Cd^{2+} to the decrease in DOC, Figure 44 shows that the slope of the irradiated sample is much larger than for the unirradiated sample, suggesting that the small reduction in DOC concentration is not sufficient to account for the relatively large change in the free metal ion concentration. The results suggest that photochemical formation of reactive transients, such as H_2O_2 , superoxides, singlet oxygen, hydroxyl radical and organic peroxy radicals [14,15], as well as low-molecular-weight (LMW) carboxyl acids [16] may lead to the degradation of DOC, and significantly reduce the binding properties of DOC. Hence, it seems that UV-B radiation has the potential to affect both the concentration and function of the DOC. The interaction among light, trace metals and DOC is probably a major controlling factor in the geochemistry of surface waters [15].

Figure 42. The influence of UV-B exposure on DOC concentrations in freshwater samples; (□), Grand River surface water sample [DOC 17.5 ± 0.1 mg/L], pH, 7.5 ± 0.1 ; ionic strength, $\sim 2.16 \times 10^{-3}$ M, $r^2 = 0.98$; (▲), Lake Simcoe surface water sample, [DOC 4.4 ± 0.1 mg/L], pH, 8.3 ± 0.1 ; ionic strength, 2.17×10^{-3} M; $r^2 = 0.99$.

Figure 43. The influence of UV-B exposure on the lability of metal-complexes on Grand River surface water sample collected in June 2001, determined by ASV-RDE, (●), Pb(II) 8.52×10^{-7} M, $r^2 = 0.14$; (□), Cd(II) 8.70×10^{-7} M, $r^2 = 0.96$; (◆), Zn(II) 7.65×10^{-7} M, $r^2 = 0.99$; (—), fitting curve; pH, 5.0 ± 0.1 ; ionic strength $\sim 2.13 \times 10^{-2}$ M; T = 297 K.

Bioassay toxicity tests using the alga *Pseudokirchneriella subcapitata* (commonly known as *Selenastrum capricornutum*) were done by Winch et al. [17] in parallel with the metal speciation studies. Algae are environmentally important because they are part of the base of the food chain, which has implications for bioconcentration in the environment. The water was spiked with various concentrations of metals, and the algae were incubated in the spiked water samples for 72h. The endpoint was taken as the concentration of metal required to inhibit 50% of the algal growth (IC_{50}). In many cases, toxicity was found to increase with increasing free metal ion concentration as shown in Fig. 45, suggesting that the cooperative activity of the binding sites of DOC protects organisms by buffering them from sudden changes in free metal ion concentration. However, several cases of poor correlation between speciation results and toxicity were also observed as shown in Fig. 47. One potential problem is that the samples for the electrochemistry experiments and the bioassay toxicity tests were not treated in exactly the same way. In the electrochemistry experiments the samples were modified by adding buffer and electrolyte, whereas the samples for the toxicity tests were modified by adding nutrients and adjusting the pH to a level in which the organism could survive. In some cases the algae were found to modify the pH of the samples by 0.5 – 1 pH units. Humic substances could indirectly affect trace metal bioavailability (i) by adsorbing to the surfaces of the plankton [18-22]; (ii) by providing nutrient C [23,24], N [25,26], or P [27,28]; (iii) by complexing exoenzymes [29]; (iv) by modifying the membrane permeability [18,27,30]; or (v) by modifying the algal surface activity [31]. However, another important factor is likely the difference in the nature of the diffusion layer between the

Table 37. Metals parameters speciation in Grand River surface water determined by ASV-RDE.

Metal	UV-B	$k_f, (10^9)$	$k_d,$	log	$D_{ML},$	$C_M,$	RDE,	Algae
	(days)	($M s^{-1}$)	($10^3 s^{-1}$)	K	(10^{-10}	($10^{-8} M$)	($\Lambda_{ss}\delta \gg 1$)	($L \gg 1$)
				(M)	$m^2 s^{-1}$)			
Pb(II)	0	90.0	17.0	6.74	5.6	0.17	5	0.008
	5	90.0	17.0	6.73	7.2	0.19	4	0.007
	10	90.0	13.0	6.87	8.8	0.15	3	0.004
Cd(II)	0	4.0	4.1	6.00	5.6	0.92	5	0.008
	5	4.0	5.4	5.88	6.3	1.4	6	0.01
	10	4.0	8.6	5.67	7.0	2.3	9	0.01
Zn(II)	0	0.9	0.9	6.01	3.8	0.89	3	0.005
	5	0.9	1.3	5.85	4.4	1.4	4	0.007
	10	0.9	1.6	5.78	5.2	1.8	4	0.007

Figure 44. The effect of metal-to-DOC ratio on the lability of Zn(II)-complexes in Grand River surface water sample collected in June 2001, determined by ASV-RDE, (●), exposed to UV-B radiation for 5 days; (□), unirradiated; (—), fitting curve; Zn(II) 7.65×10^{-7} M; pH, 5.0 ± 0.1 ; T = 297 K.

Figure 45. The influence of UV-B radiation on Cu^{2+} -aqua ion concentration and the toxicity in the St. Lawrence River surface water sample.

Figure 46. The influence of UV-B radiation on Pb²⁺-aqua ion concentration and the toxicity in the St. Lawrence River surface water sample.

RDE: $R = 1.5 \text{ mm}$

Alga: $R = 2.5 \text{ }\mu\text{m}$

Figure 47. The effect of the nature of diffusion layer in the lability of metal complexes.

Adapted from van Leeuwen et al. [32].

two systems as shown in Fig. 47. Microorganisms such as algae are much smaller than the RDE, which has a diameter of about 3 mm. As the size of the biosurface approaches the thickness of the diffusion layer, the diffusion layer becomes spherical, and diffusion changes from planar for the macroscopic electrode to radial for microscopic such as algae. These combined effects lead to a significant decrease in the lability of the metal complexes compared to the macroscopic case. Table 37 shows that whereas the Pb(II), Cd(II), and Zn(II) complexes are labile at the rotating disk electrode, they are non-labile at microscopic surfaces such as algae. The results suggest that the equilibrium assumption at the biological surface is not satisfied; hence, FIAM may not apply.

Conclusions

Lability (and bioavailability) is defined by thickness and shape of the Nernstian diffusion layer. DOM such as humic substances is ecologically important since it buffers metal concentrations over several orders of magnitude that help organisms to adapt to gradual changes in free metal ion concentrations in the natural environment. UV-B radiation reduces the ability of DOM to bind metals. The DOC concentration is not strongly affected by exposure to UV-B radiation. This suggests that metal loading criteria should not be related to the DOC concentration in freshwaters.

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CHAPTER 9

CONCLUSIONS

The results of this work corroborates the following quotation: “The elucidation of the chemical speciation of trace elements in natural waters is probably the greatest challenge to analytical chemists; the objective is to demonstrate and quantify the existence of fractions of chemical constituents as picomolar concentrations of perhaps ephemeral species.” [1] Natural systems are dynamic and often far removed from equilibrium. The analytical timescale of measurement was identified as the critical parameter for defining the chemical species and predicting metal bioavailability.

For competing ligand exchange methods, the measurement timescale is simply the time required to complete the experiment (e.g. total run time for kinetic investigations). The timescale of measurement is useful for defining the nature of the metal species measured by analytical techniques. The kinetically-slow dissociation of certain transition metals such as Ni(II) and Cu(II), and trivalent metals such as Al(III) and Fe(III) observed in this work highlight the importance of considering the measurement timescale for interpreting metal speciation. In real systems with double exchange reactions, it is likely that the Ni speciation does not reach equilibrium for days or weeks [2].

The results suggest that Dissolved Organic Carbon (DOC) has a continuous distribution of binding energies. Kinetic studies revealed a general increase in lability with increasing metal-to-DOC ratio. Similar results were observed for several metals, and for Competing

Ligand Exchange Methods, quantified by GFAAS and AdCSV. Any exceptions were attributed to additional factors such as high concentrations of dissolved organic matter and competition by major cations (e.g. Ca^{2+} and Mg^{2+}) and other metals such as Al^{3+} and Fe^{3+} . At concentrations typically found in freshwaters, these metals can successfully compete with trace metals for metal binding by DOC, releasing trace metals as free metal ions. In view of the high concentrations of Al^{3+} , Fe^{3+} , Ca^{2+} and Mg^{2+} , compared to the trace metals, the competition effects of Al^{3+} , Fe^{3+} , Ca^{2+} and Mg^{2+} may be highly significant in natural freshwater systems. Clearly, therefore, a full understanding of metal chemistry in natural waters needs to take into account the competitive reactions of Al^{3+} , Fe^{3+} , Ca^{2+} and Mg^{2+} , and other metals with the target metals for binding sites in humic substances. With regard to Fe^{3+} in particular, the equilibrium assumption can certainly be questioned, because of biological or photochemically mediated redox cycling. In addition, the ageing of iron hydroxide colloids may lead to variations in the solubility product of iron hydroxide. Therefore, the equilibrium description of binding by humic substances and iron hydroxide precipitation is accurate only if these reactions take place rapidly compared to the redox and ageing processes [3].

The results in this thesis suggest that DOC probably helps to protect aquatic organism from the toxic effects of metal exposure by buffering metals over a large concentration range with only gradual changes in free metal ion concentration. However, exposure to UVB radiation was also found to alter the binding properties of DOC. The interaction between short-wavelength UVB radiation and DOC can lead to direct photolysis of DOC and the production of highly reactive intermediates, such as singlet oxygen ($^1\text{O}_2$), OH

radicals ($\text{OH}\bullet$), DOC-derived peroxy radicals ($\text{ROO}\bullet$), solvated electrons (e_{aq}^-), superoxide anions (O_2^-), triplet states of humic compounds and hydrogen peroxide. Hence, the protective effects of DOC may be relatively short-lived.

Accounting for the timescale of measurement can be used to verify the equilibrium assumption of the FIAM (i.e. equilibrium at the biological surface), and to shift the emphasis from ‘operationally-defined’ chemical species to quantitative physico-chemical speciation parameters (i.e. $[\text{M}^{2+}]$, K , k_d and D) which can be used to predict the lability, and hence, bioavailability of metal complexes to freshwater organisms. This approach can be useful for predicting the conditions under which the kinetics of metal complexation should be considered.

It is clear that the complex relationships between trace metal speciation and bioavailability and the complex nature of the heterogeneous metal complexing ligands will need to be addressed further if we are to understand the effects of metals on biota in natural waters. Understanding of the competitive reactions in complex systems is essential if the large body of laboratory-based knowledge about complexation reactions is to be applied to the natural environment.

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