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Determination of Cd(II), Cu(II), Zn(II), and Pb(II) speciation in aqueous solutions by electrochemical techniques

by

MOHAMED ABDEL SALAM

Ph.D. (Ain Shams University, Cairo, Egypt)

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

Department of Chemistry
Carleton University
Ottawa, Ontario
July, 2003

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submitted by

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Chair, Department of Chemistry

Thesis Supervisor

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ABSTRACT

This thesis examines of the applicability of the electrochemical method, Competitive Ligand Exchange Method (CLEM) with ethylenediamine as the competing ligand in conjunction with Differential Pulse Anodic Stripping Voltammetry (DPASV) for determining cadmium speciation in aqueous environmental samples. The samples tested were surface waters from lakes in Rouyen-Noranda (Quebec) and soil porewaters from Sudbury (Ontario).

The findings are as follows. At a given pH, the cadmium speciation depends on the mole ratio of cadmium / Dissolved Organic Carbon (DOC), and the competition of other trace metals and major cations for binding sites of DOC. The speciation parameters of cadmium, determined by CLEM/DPASV, generally agree with the predictions of an equilibrium computer model, Windermere Humic Aqueous Model (WHAM) V and VI. CLEM/DPASV was found to be a satisfactory method for determining cadmium speciation in lake freshwaters and soil porewaters.

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CHAPTER 1

INTRODUCTION

The use and dispersion of metals has increased vastly during the 20th century, and therefore the behavior of metals in the environment is a matter of rising concern. Metals are not biodegradable and can only be transformed from one chemical form (i.e. chemical species) to another. This transformation process is called 'chemical speciation'. Hence, there is a growing necessity to continuously monitor the levels of trace metals in the environment, and in particular, in aquatic systems, both to understand their long term physicochemical behavior and to check that the legislation related to the discharge of effluents containing waste metals is implemented. Even in low concentrations, heavy metals may present a severe hazard to the normal functioning of aquatic ecosystems as they are involved in biogeochemical cycles which distribute them among various physicochemical forms (e.g. simple inorganic species, organic complexes and metal ions adsorbed onto a variety of colloidal particles). The proportion of these different forms may vary continuously with space and time because of continuing physical, chemical and biological processes. Any variation in the speciation of a metal may affect its bioavailability, its rate of transport to bottom sediments, and its overall mobility in the aquatic system.

Chemical speciation: speciation parameters

The term chemical speciation has been used in the literature with two meanings: (i) the analysis or quantification of chemical species, and (ii) the chemical or physicochemical species distribution [1]. A given element may be present in aqueous solutions in different chemical forms, including neutral or ionic species. For example,

carbon may be present in the forms of H_2CO_3 , HCO_3^- and CO_3^{2-} . A chemical species has been defined as follows [2]: a specific form (monoatomic or molecular) or configuration in which an element can occur, or distinct groups of atoms consistently present in different compounds or matrices. Each chemical species has its own characteristic chemical reactivity and lifetime, and each reacts differently in different matrices or environments. Many chemical species have a group that is strongly bound to a central atom and other groups that are only weakly bound. The part of the species that remains unchanged through a matrix-generated transformation is called the “parent species”, or “conceptional species”. The chemical species that actually exists in the environment is the “matrix species” and it is actually an idealized concept. Analytical procedures generally convert the matrix species into a chemical form that is recognizable by the analytical instrument used for its quantification. The chemical species which is quantified is called the “analyte species” and quite often is operationally defined. As long as an operational definition of the species is considered only as a first approach to chemical species quantification, it is acceptable, but every effort must be made to identify and quantify the chemical species, or characterize them by determining their Speciation Parameters. Only then can a good understanding of the process under study be obtained.

Speciation may be loosely defined as the study of the occurrence and characterization of various species of an element [1]. More specifically, speciation is:

- (1) the analysis of chemical species leading to their identification and quantification in a defined sample;
- (2) the description of the abundance (or numerical distribution) of chemical species of an element in a defined sample;

- (3) the reactivity of a given chemical species;
- (4) the transformation of one chemical species into another.

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

Identification and quantification of extremely low concentrations of chemical species in freshwaters presents an enormous challenge that defies resolution [3]. Because of the absence of analytical techniques of extremely high sensitivity and selectivity, an alternative is to apply extremely expensive and enormously time-consuming techniques such as NMR and ESR for structural analysis, which militate against their routine applications. Therefore, recently a much better alternative has been developed for characterizing chemical species- the determination of speciation parameters which include: 1) Free Metal Ion concentration (i.e. aqua complex, often, the bioavailable metal species) concentration; 2) Stability Constants (give the measure of the equilibrium concentrations of Free Metal Ions); 3) Concentrations of organic complexants (ligand);

4) Dissociation Rate Coefficients (determines the reactivity of the metal complex and the time required for establishment of equilibrium in freshwaters); 5) Diffusion Coefficients (gives the measure of the mobility of chemical species). This thesis will present the results of determination of some of the Speciation Parameters of the complexes of Cd(II), Cu(II), Zn(II) and Pb(II) in freshwaters, through-fall precipitation samples, and in soil solutions (pore waters) by some newly-developed electrochemical techniques.

Determination of chemical species

The total concentration of an element can be used to assess its environmental impact only if it is present in the environment as a single species. This condition is met only rarely. The precise determination of the total concentration of an element is not an easy task. Very few analytical methods measure the total amount of an element in all its forms. Most analytical procedures actually measure only single species or groups of species, sometimes previously unrecognized.

The determination of chemical species is a more complex task than the determination of total element concentrations. Analytical procedures of sufficient sensitivity and specificity are not available to determine the chemical species of many environmentally significant elements, which frequently occur at very low concentrations. In fact, most efforts in species determination were directed towards the identification and quantification of chemical species in isolated samples. Since during sampling, storage, and analysis of the sample chemical-species, transformation of the chemical species may occur, appropriate action must be taken to ensure that the chemical species to be

determined does not change during the interval between sampling and analysis. Reliable methods for the preservation of the original distribution of the species do not yet exist, and the preservation of the sample integrity (i.e. the original distribution of species during sample storage) is not available and is urgently required. The ideal analytical method would determine chemical species directly *in situ* and *in vivo*, non-invasively and nondestructively, and would allow the transformation of the species to be monitored over time.

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

Chemical speciation, bioavailability and toxicity

Living organisms may regulate metal concentration by uptake and/or by extraction. In polluted waters, however, living organisms may show a tendency to bioconcentrate metals. Lipophilic metal species (e.g., methylmercury) may be biomagnified by a factor of 10^6 to 10^8 in fish [5]. Free and weakly-complexed metals show a bioaccumulation factor of 10^2 and 10^5 in biological cells [6-8]. Bioavailability is the ability of a chemical species of an element to be assimilated by an organism. It is

influenced by the efficiency of intestinal absorption, by transport of chemical species to sites of action, and the utilization of active sites. Three groups of chemical species have been identified as contributing to the bioavailable fraction: free metal ions (aqua complex) [9-11], metals in weak complexes [12,13] and lipid-soluble metals [14]. Two mechanisms of assimilation of dissolved species by unicellular organisms have been proposed and are illustrated [15] in Figure 1:

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

In Fig. 1, the latter mechanism (mechanism 2) depends on the chemical potential gradients between the external medium, the membrane surface, and the intracellular medium, with the displacement of **M** tending towards the phase wherein its chemical potential is the lowest. The transfer is also controlled by the availability of the hydrated, “free” form of metal ion **M**, which is limited by the type of complexing ligands, the concentrations of the complexing ligands, and the dissociation rates of the complexes in the external medium. These mechanisms indicate that the uptake tendency of the dissolved chemical species varies with the type of species present in the external medium.

When the capacity of a cell (organism) to detoxify accumulated metal is exceeded, damage to cytoplasmic constituents will occur. This is the toxic effect. Symptoms of intracellular toxicity may include ultrastructural deformities, reduction in cell division rate, respiration, photosynthesis, motility, electron transport activity and ATP production. Since only some forms of a given metal can penetrate the biomembrane to cause the toxic

Figure 1

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

effect, metal toxicity to aquatic organisms cannot be gauged by measuring the total metal concentration. Some studies of toxicity suggest that ionic or uncomplexed metal is the toxic form [16] and their complexations by organic complexants reduce the metal toxicity in oceans [17-19], rivers and lakes [20,21]. Since molecules of different sizes may have different complexing abilities and different kinetic properties, the molecular size of is an important component of metal bioavailability. For example, cadmium toxicity of *Simocephalus Serrulatus* decreases with increasing molecular size of natural organic materials [22], and the highest molecular-weight fractions of soil humics lower the availability of Cu to wheat [23].

Experimental determination of speciation parameters

Speciation parameters are quantitative measures of chemical characteristics of chemical species, which are independent of the chemical methods used to measure them. Full characterization of a system often requires the definition of a number of speciation parameters. Some important speciation parameters are given below:

(1) *Diffusion Coefficient*: The mobility of a particular chemical species plays a very important role in the biological impact the element may have in the natural environment. Before an element may elicit a toxic response, it must come into contact with a biological membrane and eventually penetrate it [24]. The diffusion coefficient is a direct measure of how quickly the chemical species can reach the biological membrane.

(2) *Stability constant*: The thermodynamic stability of a metal complex (which is a measure of the availability of free metal ions *at equilibrium*) is a very important property

for classifying the metal species in the aquatic and the terrestrial environment [25-27]. The determination of stability constants relies on an equilibrium or pseudo-equilibrium condition to be established before the measurement can be made. While stability constants are useful for strong complexes, they are not very useful for slowly-dissociating complexes, as equilibrium may not be established in a conveniently measurable time. Although measurement of this parameter is straightforward for homogenous systems (such as inorganic complexes), it may be difficult to measure this parameter for heterogeneous samples such as those containing naturally occurring organic complexants. Owing to the different types of functional groups in humic substances, which are ubiquitous in the natural environment, humic substances are heterogeneous complexants. This chemical heterogeneity is a strong characteristic which determines the metal ion binding, and hence, the stability constants of metal complexes of organic complexants. In such cases, instead of discrete values for stability constants, a large spectrum of stability constants is often observed and the interpretation becomes uncertain. Often, average conditional stability constants are estimated for groups of metal complexes having closely spaced values of stability constants. The measured stability constants are invariably 'conditional stability constants' for the particular set of experimental conditions of the sample (i.e. pH, ligand and metal present).

(3) *Dissociation rate constants*: The dissociation rate constant represents how rapidly a metal complex dissociates to form free metal ion (i.e. the metal-aquo complex) and hence is a very important speciation parameter, especially in the case where the free metal ion is the bioavailable species.

(4) Natural Organic Complexants: Natural Organic Complexants are the most important part of Natural Organic Matter (NOM). The metal-complexing characteristics of these complexants and their concentration determine which metal complexes are formed in freshwaters. Life on the earth is responsible for the occurrence of natural organic matter in soils and natural waters. NOM plays an important role in regulating trace metal speciation, bioavailability and toxicity to micro-organisms. It also regulates metal ion concentrations in freshwaters and soils, and their transport from one environment to another [28,29]. The nature of the NOM found in aquatic systems depends primarily on whether the sources are aquagenic (i.e., derived from water), or pedogenic (i.e., derived from soil) [30]. This organic matter consists of a mixture of plant and animal products in various stages of decomposition, of substances synthesized biologically and/or chemically from the breakdown products of decomposing organic matter and of micro-organisms and small animals along with their decomposing remains [31]. Since this work is concerned only with Natural Organic Complexants, for the sake of simplicity, NOM will be discussed only in terms of Natural Organic Complexants, which, for further simplification, will be further subdivided into two groups: (a) non-humic substances and (b) humic substances.

Non-humic substances include compounds that still exhibit recognizable chemical characteristics. These are predominantly polypeptides and polysaccharides, but also include common organic acids, amino acids, carbohydrates, tannins, resins and other low-molecular-weight organic substances [32-36]. However, these substances are easily degradable and their abundance is therefore very low. On the other hand, humic substances are high molecular-weight, polyelectrolytic macromolecules and are

degradation-resistant (refractory) materials. On average, humic substances constitute a major fraction of soil organic matter (60-70%) and of aquatic organic matter (30-50%) [37]. These humic substances are amorphous, brown or black, hydrophilic, acidic, polydisperse substances of molecular weights ranging from several hundreds to tens of thousands of g/mol [31,38].

Humic substances are commonly classified into three general categories based on their solubility in alkali and acid solution: humic acids (HA), fulvic acids (FA) and humin. The definitions for these categories are purely operational in nature. Humic acids are those components of humus which are soluble in dilute alkaline solution but are precipitated by acidification of the alkaline extract. Fulvic acids are soluble in both acid and alkaline solutions whereas humin is insoluble in both acid and alkaline solutions [39,40]. This insolubility of humin seems to be due to it being firmly adsorbed on or bonded to inorganic soil and sediment constituents [41]. From a wide variety of chemical degradation experiments, the major HA and FA degradation products are found to be phenolic and carboxylic acids. Experimental and theoretical studies have established that humic substances are not single molecules but rather associations or aggregates of these phenolic and carboxylic acids referred to as “building blocks” [42]. In higher molecular weight fractions, i.e.; HA and humin, the “building blocks” appear to be more complex and more stable [43]. This may arise from more energetic linkages of FA type and/or from additional chemical bonding via C-O and C-C bonds. The structure of the FA can be generally described as assemblies of covalently-linked aromatic and aliphatic residues carrying carboxyl, phenolic and alkoxy functional groups, although sulphate esters, alanine moieties, semiquinone, phosphate ester and hydroquinone groups [44] have been

Figure 2

A tentative structure of humic acid proposed by H.R. Schulten and M. Schnitzer [45].

proposed to exist in some humic isolates. Figure 2 shows a model of the structure of HA proposed by Schulten et al [45].

Metals in the environment

Heavy metals such as cadmium, copper, lead, and zinc are natural constituents of every compartment of the natural environment [46] (see Table 1). They take part in biogeochemical reactions and are transported between compartments by natural processes at rates that are frequently and greatly altered by human activity.

Cadmium falls in the group of so-called minor non-ferrous metals (the zinc subgroup elements) and it commonly forms six-coordinate complexes. The element cadmium exists in various forms throughout the lithosphere. Relatively rare (see Table 1), cadmium occurs in minerals and soils in association with Zn(II) to about 0.1%, and like Zn(II), cadmium occurs only as a divalent ion, Cd(II). Cadmium is a by-product in the refining of zinc and other metals. Hence, as soon as man started to extract metals from ore, he also started to pollute the environment with cadmium, releasing Cd emissions to air, soil, and water from mines, metal smelters, and industries using cadmium in alkaline accumulators, alloys, paints, and plastics. Two properties of cadmium lead to important environmental consequences: (1) its relatively high vapor pressure: 13 mm Hg at 500 °C [47], which accounts for its ready vaporization, for example, during smelting operations or coal combustion, and (2) its high solubility in water, especially at a slightly acidic pH. The wide distribution of cadmium in fuels, fertilizers, and mine tailings, together with its extensive use in non-recycled form in industry, accounts for a gradually increasing concentration of the metal in the environment. There is little evidence to

Table 1

Cadmium, copper, lead and zinc properties and distribution within the environment [46]

	Cadmium	Copper	Lead	Zinc
Atomic number	48	29	82	30
Atomic weight	112.40	63.546	207.2	65.39
Abundance in lithosphere	0.18 mg/kg	70 mg/kg	14 mg/kg	80 mg/kg
Group in periodic table	IIB	IB	IVA	IIB
Common valence state	Cd ²⁺	Cu ²⁺	Pb ²⁺	Zn ²⁺
Total content in soils	0.01-3.0 mg/kg	2-100 mg/kg	3-189 mg/kg	10-300 mg/kg
Soluble content in soils	0.1-14.0 mg/Kg	3-135 µg/L	5.0 µg/L	4-270 µg/kg
Content in sea water	1.1 x 10 ⁻⁶ to 38 x 10 ⁻⁶ mg/L	8.0 x 10 ⁻⁵ mg/L	3.0 x 10 ⁻⁵ mg/L	0.5-1.0 x 10 ⁻⁴ mg/L
Content in freshwater	0.01 mg/L	0.01-2.80 mg/L	0.01-5.6 mg/L	0.10 -240 mg/L
Essentiality	plants, yes animals, no	plants, yes Animal, yes	plants, no Animal, no	plants, yes Animal, yes

suggest that cadmium is an essential element in mammalian nutrition. Besides the industrial environment, the body burden of cadmium in animals and humans is derived mainly from food and water. An additional and significant source of body cadmium may be tobacco smoke. Like other heavy metals, cadmium reacts readily with proteins and other biological molecules. The cadmium exposure may result in adverse effects at multiple sites, including lungs, prostate, testes, heart, liver, and kidney. An especially serious form of Cd(II) poisoning has been described in Japan as 'itai-itai' (Japanese for 'ouch-ouch' disease) which causes pain in the back and legs due to bone calcification leading to easy fracturing. In Japan it was produced by ingestion of Cd(II)-laden water, either directly by drinking or by eating crops, especially rice, irrigated by the water over a period of many years [48].

Copper has long been known to be an essential component of many chemical compounds found in biological systems. Copper-containing enzymes and proteins are widely distributed in both animals and plants. They would appear to have two main functions, namely (1) electron transport and (2) dioxygen transport and metabolism. Although copper is an essential trace metal for organisms, it can be toxic in its ionic form at concentrations above 5 mg/L [49].

Lead [46] is one of the best known toxic heavy metals and is a major pollutant. It is primarily introduced into the atmosphere by the use of lead gasoline and is introduced into the food chain by atmospheric deposition on crop plants and by soil dust inhalation. Lead is the least mobile of the heavy metals in soils. It accumulates primarily on the surface, where its increasing presence may begin to affect soil microflora. Lead availability in soil is influenced by pH, decreasing with increasing pH of the soil. Lead is

not readily soluble in water and is found in relatively low concentrations. The maximum permissible level in drinking water is 0.05 mg/L. Lead is both carcinogenic and teratogenic. It adversely affects young children (2 to 3 years old), primarily impacting on their intellectual development. Lead primarily enters the body by soil dust inhalation, although it can enter through the skin or be ingested through contaminated food.

Zinc is an essential nutrient for virtually all living species [50,51]. Zn is an important constituent of dozens of metalloenzymes and metalloproteins [52,53]. It plays an essential role in a number of biological processes involved in normal growth and development [54]. Although zinc does not appear to be toxic to most freshwater invertebrates [55] it can become toxic at elevated levels [56].

Anthropogenic activity can result in greatly increased level of cadmium, copper, lead, and zinc in the environment. These elevated metal levels can have detrimental effects on both biota inhabiting the aquatic environment as well as people who utilize this environment for food, recreation and potable water. It is therefore essential that the contamination of freshwater systems by these metals be carefully monitored.

Hypothesis

The *hypothesis* to be tested is that in a polluted water (aqueous) environment, the occurrence of the free metal ions (reported to be toxic) is controlled by different factors such as the geographical location (distance from the pollution source), the wind direction, the metal to Dissolved Organic Matter ratio and the co-presence of other trace metal ions and major cations that compete with each other for the binding sites of natural organic complexants.

Objectives

The objectives of the present study is to test the above hypothesis using different polluted aqueous samples collected from different sources (lakes water samples, throughfall precipitation samples, and soil solution samples) to investigate the applicability of the electrochemical techniques: Competitive Ligand Exchange Method / Differential Pulse Anodic Stripping Voltammetry (CLEM / DPASV) and Differential Pulse Anodic Stripping Voltammetry (DPASV) for determining the total dissolved concentrations and the chemical speciation of cadmium, copper, lead, and zinc in various aqueous solutions.

Cadmium, copper, lead, and zinc have been chosen as the test elements because copper and zinc are essential to biological activity as nutrients but toxic at elevated concentrations, and lead and cadmium are toxic elements at any concentration.

Organization of the thesis

Chapter 1 gives a brief introduction for the chemical speciation and the metals in the environment. Chapter 2 describes the scientific background and the current knowledge about the different techniques used for the chemical speciation of cadmium, copper, lead, and zinc. Chapter 3 presents the Theory of Competing Ligand Exchange Method / Differential Pulse Anodic Stripping Voltammetry for determination of metal speciation in freshwaters. Chapter 4 presents the Applications of the Theory of the Competing Ligand Exchange Method / Differential Pulse Anodic Stripping Voltammetry for determination of Cd(II) speciation in aqueous solutions. Chapter 5 presents a comparison of the experimentally-observed speciation parameters with the WHAM-

predicted equilibrium speciation of Cd(II) in aqueous solutions. Chapter 6 presents the simultaneous determination and speciation of Zn, Cd, Pb, and Cu in aqueous solutions by Differential Pulse Anodic Stripping Voltammetry.

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CHAPTER 2

SCIENTIFIC BACKGROUND

Scientific background

It is well-known that trace metal speciation greatly influences metal circulation and bioavailability in aquatic media [1-5]. Heavy metals, such as cadmium, copper, lead and zinc, are one class of contaminants that can produce undesirable effects even if they are present in minute quantities [6]. All forms of ecological systems are affected to varying extents by heavy metals. They are the most insidious pollutants because of their non-biodegradable nature and ability to persist for long periods. The determination of ultra-trace levels of heavy metals in freshwaters is a challenging task for a chemist because of contamination problems and matrix effects. There is an increasing need to measure several heavy metals simultaneously and rapidly in the same sample with a single operation in various fields such as clinical chemistry and environmental and/or industrial control. Typically, simultaneous analyses have been usually based on chromatography [7,8], having detection systems based on spectrometry, anodic stripping voltammetry or potentiometric stripping. Although chromatographic techniques have been successfully used, they are usually time consuming, with the result that these techniques are not convenient for routine analysis of large sets of samples where rapid analysis is needed. Alternatively, multielement analysis for several analytes has successfully been done by energy dispersive X-ray fluorescence spectrometry [9], atomic spectrometry [10] and electroanalytical techniques. These techniques have several advantages over chromatography as they are faster, have reduced sample treatment time and the removal of interferences is not strictly required in many instances. In the last few years, electroanalytical techniques have attracted considerable attention for the determination of trace metals [11,12] as they combine the low cost of instrumentation and maintenance

with good accuracy and precision, and excellent sensitivity. The lower sampling rate of stripping voltammetry compared with atomic spectrometry is compensated by its ability for speciation studies and multielemental analysis.

Anodic stripping voltammetry (ASV) has always been regarded as one of the most sensitive techniques for trace metal analysis [13-18]. The very low detection limits achieved by ASV are due to the preconcentration of the analyte from the sample solution during the deposition step. By contrast with techniques such as atomic absorption spectrometry and inductively coupled plasma emission spectrometry, which can determine only total metal concentration, ASV can determine not only the total metal, but also 'reactive' or ASV-labile metal, which is the fraction of the total metal concentration that is measured by using a particular set of ASV and solution conditions. An aim of ASV speciation analysis is to adjust the solution and electrochemical conditions such that the measured ASV-labile fraction of the metal concentration approximates, as closely as possible, to the toxic fraction of metal [19]. This aim is most likely to be achieved when ASV-labile metal is equal to the electro-active fraction of the metal, i.e., the fraction of the metal that dissociates from complexes and is deposited onto the electrode during the deposition stage of ASV [20].

Florence [21] studied the trace element speciation, namely, of copper, cadmium and lead, in synthetic solutions containing a range of complexing agents, and in some polluted water samples using ASV to compare its results with those of the algal assays. The agreement was, in general, excellent, and provided confidence that ASV could be used to assess the potential toxicity of heavy metals in a water system. Linnik et al. [22] applied ASV to investigate the physico-chemical state of cadmium in surface water in

Ukraine and they found that the uncomplexed or free ions of cadmium did not constitute more than 26% of the dissolved cadmium because of the high concentration of Dissolved Organic Carbon (DOC), relative to the total cadmium concentration. Cheng et al. [23] have evaluated the dissolved speciation of copper, lead, cadmium and zinc in rain waters using a scheme combining physical characterization by size fractionation and chemical characterization by dissociation kinetics with final detection by DPASV. They reported that most of the dissolved cadmium (100%) and zinc (76%) was present in rain water as ASV_{labile} , whereas a part of copper (64%) and lead (51%) was present as ASV_{labile} . Abollino et al. [24] used two different techniques, namely adsorptive cathodic stripping voltammetry (AdCSV) and graphite furnace atomic absorption spectroscopy coupled with on line preconcentration for the determination of copper, cadmium, manganese, nickel, and zinc in Antarctic sea water. The results obtained for the same sample of Antarctic sea water with the two techniques were in very good agreement, and showed that both were suitable for the determination of heavy metal at ng/l levels. Scarponi et al. [25] investigated the Antarctic surface water of Terra Nova Bay (Ross Sea) by ASV to study the distribution and complexation of lead and cadmium. Samples were analyzed to determine the total metal content, the metal distribution between the free metal-ion fractions (ASV_{labile}), the metal –ligand complexes, and the related conditional stability constants. Their results revealed the presence of one class of ligands and a high proportion of bound metals (70-80% in the Adriatic Sea compared to about 50% in Oceanic and Antarctic waters) and a general agreement between values of conditional stability constants observed in different areas, leading to the hypothesis that the ligands were of natural origin. Bertt et al. [26] applied the batch injection analysis (BIA) to

determine copper, lead, zinc and cadmium in samples of volume $\leq 100 \mu\text{l}$ by square wave ASV and their results revealed nanomolar detection limits corresponding to sub-picomole quantities. Nimmo and Fones [27] applied adsorptive cathodic stripping voltammetry (AdCSV) for the detection of dissolved cobalt, nickel, copper, cadmium and lead in rain waters collected from an urban and a coastal site in northwestern England. The presence of metal organic complexing ligands in rain waters is indicated with an overall percentage of $\text{AdCSV}_{\text{non-labile}}$ dissolved metal of the total dissolved metal fraction ($=\% \text{AdCSV}_{\text{nl/t}}$) being 33% (33%); 28% (35%); 26% (32%); 33% (25%); 27% (34%): for cobalt, nickel, copper, cadmium and lead, respectively, for the urban site (and coastal site). Colombo and van den Berg [28] applied adsorptive cathodic stripping voltammetry (AdCSV) with mixed ligands for the simultaneous determination of copper, lead, cadmium, nickel, cobalt and zinc in sea water samples collected from the North Sea after ultra violet digestion (3 h). They found that these metals can be quantified at concentrations above 0.3 nM for copper, 0.2 nM for lead, 0.1 nM for cadmium, 0.4 nM for nickel, 0.6 nM for zinc and 0.02 nM for cobalt. Vascocelos et al. [29] applied differential pulse anodic stripping voltammetry (DPASV) for the determination of the total dissolved concentration of copper, lead, and cadmium in water samples collected from the shore of the Oporto Coast, Portugal, using pre-concentration in a Chelamine resin column. They found that the distribution of each metal in the different fractions (particulate and dissolved) were compatible with the data from literature [30]: lead and copper predominated in the particulate fraction, in the carbonate and hydroxide forms, whereas cadmium existed more in the dissolved fraction as the chlorocomplex form. ASV, using different mercury electrodes, was applied for the determination of trace

amount of lead, cadmium, zinc and copper leached from ceramics plates [31]. The amounts of metals leached were 0.1 to 25 $\mu\text{g/ml}$ of lead, 0.015 to 0.44 $\mu\text{g/ml}$ cadmium, 0.07 to 1.06 $\mu\text{g/ml}$ zinc and 0.14 to 0.40 $\mu\text{g/ml}$ copper. Tercier et al. [32] used a novel voltammetric in-situ profiling system (VIP system) for continuous, real-time monitoring of lead, cadmium and copper in seawater down to a depth of 500 meters using square wave anodic stripping voltammetry (SWASV). The results indicated that the VIP system was robust and reliable and that in-situ measurements of the mobile fraction of trace metals could be achieved down to very low concentration levels (ca. 5 ppt). Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), ion chromatography (IC), and differential pulse anodic stripping voltammetry (DPASV), were applied for the simultaneous determination of most common metallic impurities like iron, copper, zinc and cadmium, in industrial process control of the silicon used for solar cells [33]. The authors found that LA-ICP-MS was an expensive apparatus, but it directly performed the analysis of solid silicon with very good sensitivity, even though the results showed considerable standard deviation, probably because of the material defects. Both IC and DPASV need sample pre-treatment, but they are characterized by inexpensive and simple apparatus, suitable detection limits, good sensitivity and small standard deviation. Desmond et al. [34] used DPASV for the determination of zinc, cadmium, lead and copper to monitor discharge of the metals into waste waters. They optimized their procedure and they were able to determine those trace metals to parts per billion (ppb) levels. AdCSV was used for the determination of cadmium, using 5-Fluorouracil as the competing ligand in seawater collected from the Red Sea, Egypt [35]. A linear relationship between the peak current and cadmium concentration was obtained over the

range $5.0 \times 10^{-9} \text{ mol dm}^{-3}$ - $1.0 \times 10^{-7} \text{ mol dm}^{-3}$ with a correlation coefficient of 0.9973. A detection limit of $9.0 \times 10^{-11} \text{ mol dm}^{-3}$ was obtained with a coefficient of variation of 1.9%. DPASV was used for the simultaneous determination of copper, lead, cadmium and zinc in environmental matrices like estuarine and river sediments [36]. The precision, expressed as relative standard deviation (S_r), and the accuracy, expressed as relative error, were, in all cases, less than 5%. The detection limits, for each element and in the experimental conditions employed, were around 10^{-9} M . They also found that the standard addition technique significantly improved the resolution of the voltammetric method, even in the case of very high metal concentrations. Fischer and van den Berg [37] used SWASV with a mercury film electrode and thiocyanate in order to improve the sensitivity of the thin film mercury electrode for the determination of lead and cadmium in uncontaminated lake waters and certified sea water after UV digestion. The limit of detection (3σ) was 5 pM cadmium and 8 pM lead (coefficient of variation of 1.7% and 2%, respectively) using a deposition time of 5 min. Copper, lead, cadmium and zinc were determined by DPASV after sample digestion in whole blood samples from residents of the city Badajoz, Spain [38]. Elements levels found in the whole blood sample in a group of 82 people were $0.98 \pm 0.94 \text{ ng/ml}$ for cadmium, $46.7 \pm 28.6 \text{ ng/ml}$ for lead, $1.07 \pm 0.12 \text{ } \mu\text{g/ml}$ for copper and $6.95 \pm 1.08 \text{ } \mu\text{g/ml}$ for zinc. The analytical data were correlated to age, sex, smokers or non-smokers, drinking and food habits. DPASV was used for the determination of cadmium by standard addition method in sewage samples collected from the municipal sludge lagoon in Fort Wayne, Indiana [39]. The samples were found to have cadmium abundances ranging from 120 to 250 ppm, with most samples falling in the 120 to 170 ppm range. Van Staden and Matoetoe [40] applied DPASV in a flow

system for the simultaneous determination of copper, lead, cadmium and zinc in water used for boiler feeds in power stations. They found that the working ranges were 50-500 $\mu\text{g l}^{-1}$ for copper, 100-400 $\mu\text{g l}^{-1}$ for cadmium and lead, and 100-400 $\mu\text{g l}^{-1}$ for zinc, with detection limits of 39, 9.6, 16.6 and 14.7 $\mu\text{g l}^{-1}$ copper, cadmium, lead and zinc, respectively. Pei et al. [41] used SWASV for the simultaneous determination and speciation of zinc, cadmium, lead and copper in natural waters collected from Arve River, Switzerland. They determined the total metal concentrations, and the concentration of the mobile species for the four heavy metals under investigation. The total metal concentrations were found to be: 28.8 ± 3.2 nM for zinc, 0.27 ± 0.05 nM for cadmium, 3.9 ± 0.6 nM for lead and 16.1 ± 2.1 nM for copper, whereas the concentration of the mobile species were found to be: 9 ± 1 nM for zinc, 0.1 ± 0.02 nM for cadmium, 0.7 ± 0.1 nM for lead and 1.5 ± 1 nM for copper. Mikkelsen and Schrøder [42] studied the total determination of cadmium and lead using DPASV at a silver working electrode. Their results indicated that the silver electrode may be used for detection of cadmium, lead and copper coexisting in solution without any formation of the lead-copper intermetallic compound. The estimated detection limits were ca. 1 $\mu\text{g l}^{-1}$ for cadmium and 0.2 $\mu\text{g l}^{-1}$ for lead in 0.1 M HCl solutions. Abdelsalam et al.[43] determined total concentrations of cadmium, lead and copper in rain samples (5 samples, collected from Southampton, UK) by ASV at mercury microelectrode using two different methods; standard addition and stripping charge. There was a good agreement between the results of the two methods. The total cadmium concentration was in the range of 0.9 $\mu\text{g l}^{-1}$, 6.4 $\mu\text{g l}^{-1}$ for lead, whereas it was 4.4 $\mu\text{g l}^{-1}$ for copper. Lead and cadmium were determined in drinking water by subtractive anodic stripping voltammetry (SASV) in the square-wave mode at a

silver electrode without removal of oxygen [44]. Detection limits of 0.05 nM for lead and 1 nM for cadmium were achieved following 90 s electrodeposition. Locatelli and Torsi [45] used DPASV for the simultaneous determination of copper, lead, cadmium and zinc in seawater, sediments, algae and clams, at Goro bay, Italy. The analytical procedure was verified by the analysis of the standard reference materials and the precision and accuracy were found to be less than 5%.

For total dissolved trace metal determination, it is necessary to release the trace metal from metal-organic complexes prior to analysis. Furthermore, the removal of Dissolved Organic Matter (DOM) from samples is often preferable, as enhanced concentrations of DOM (because of the pre-concentration step in ASV) may interfere with the trace metal analysis. In the case of stripping voltammetric methods, DOM may interfere with the physical and electrochemical processes occurring at the electrode surface and within its material. Traditionally, wet digestion has been used as a method for the destruction of DOM in natural waters, thereby liberating trace metal ions, followed by total dissolved trace metal determination. Wet digestion methods use chemical oxidants such as sodium peroxodisulphate, nitric acid, sulphuric acid, perchloric acid, or hydrogen peroxide to destroy organic matter [46]. A serious drawback of this approach is the addition of large concentrations of oxidants to the sample, and the often-used open digestion/evaporation procedures, which can introduce contamination. As trace metal concentrations in freshwaters are very low, wet digestion is not considered to be an acceptable sample preparation method. A preferred approach for the breakdown of dissolved metal-organic complexes and the removal of DOM involves treatment of the sample with ultra-violet (UV) radiation prior to trace metal determination [24, 25, 27, 29,

37, 44, 47-53]. The impact of the UV radiation on the character and function of surface waters has received considerable attention in several studies of the transformation and degradation of organic matter. Formation of CO₂, has, for example, been demonstrated when high molecular weight (HMW) organic matter is exposed to UV radiation [54, 55] Low molecular weight (LMW) carboxylic acids [56-58] have also been observed after exposure of natural waters to UV radiation. Thus, it is evident that UV radiation has the potential to affect both the concentration and function of the DOC. Papoff et al [59] have used UV irradiation in their study and have found that the following reaction steps are accomplished under UV irradiation: (i) decomposition of organic compounds that are generally present in natural waters and the voltammetric determination of Se(IV); (ii) quantitative reduction of Se(VI) to Se(IV); (iii) quantitative oxidation of Se(-II) to Se(IV). A high output low-pressure mercury lamp, 400 W L-Hg, was successfully used for the photolytic decomposition of dissolved organic compounds as the pretreatment for the determination of trace metal ions in aqueous solution by stripping voltammetry [60]. The authors found that various amino acids, which interfered with voltammetric determination of metal ions, could be removed quite easily by intensive UV irradiation at the room temperature. Samples from the Scheldt estuary were assayed for dissolved cadmium, copper and zinc using DPASV, either as total (after UV irradiation) or labile concentrations [61]. The labile concentrations ranged between 51-65% of the total copper, 16-66% of the total zinc and 53-91% of the total cadmium. The trace metals, cadmium, copper, lead and zinc, were determined in the Carmen-La Machona lagoon system, Tabasco, Mexico, on the basis of relative lability by using DPASV [62]. The samples were collected at 19 stations and the total soluble metals were found in a wide

range: 30-57% for zinc, 31-38% for lead, and 34-38% for copper. Soluble cadmium was not detected in the lagoon system. Most of the metals were in a very labile or moderately labile fraction with a small percentage of slowly labile, and no inert fraction was found. Alvarez et al [63] have proposed a speciation scheme based on the Nürnberg scheme [64] which makes an operational division in four categories: labile determined at natural pH by the voltammetric method, exchangeable (at pH 2), non-labile (after UV-irradiation), and particulate bound (after acid digestion) species of cadmium, copper, lead and zinc in natural waters. They [63] were able to simultaneously determine three of the trace metals, copper, lead and zinc, by ASV, whereas cadmium was not detected. The horizontal and vertical distribution of operationally defined species (labile, bound and total) of dissolved copper, cadmium and zinc were determined using DPASV in water samples obtained from 18 stations in Manila Bay, Philippines [64]. The results showed that more than 50% of the total dissolved copper and cadmium were labile, whereas 50% of the total dissolved zinc was organically bound, and elevated levels of these metals near point sources suggested anthropogenic inputs into the Bay.

Cadmium is considered in many regards as a significant anthropogenic pollutant because it has been introduced in large quantities into the environment and because it is one of the most toxic metals at elevated concentrations. The complexation of cadmium by natural organic ligands in the oceans and in estuaries has been studied [65-70]. Voltammetric techniques, especially DPASV, have been extensively used to determine the cadmium complexation parameters, using an equilibrium approach [67, 70], or a kinetic approach [68]. Erk and Raspor [71] have used DPASV for the evaluation of cadmium-metalllothionein stability constants. The capacity of metalllothionein (MT) to

complex cadmium and the stability constants of Cd-MT complex have been determined from the direct titration of the defined metallothionein. The calculated apparent stability constants of Cd-MT complexes is $K = (7.6 \pm 0.2) \times 10^8 \text{ dm}^3 \text{ mol}^{-1}$. Xue and Sigg [72] have studied the cadmium speciation and complexation by natural organic ligands in freshwaters using DPASV with the application of the competing ligand exchange method with ethylenediamine as the competing ligand. The dissolved cadmium concentrations range from 0.03 to 2 nM, the free cadmium ion concentrations expressed as pCd ($-\log[\text{Cd}^{2+}]$) = 10.5 to 12.2, and the conditional stability constants for stable organic complexes expressed as $\log K = 9.4\text{-}10.2$, with ligand concentrations of 1-6 nM in the water samples collected. Rollenmberg et al. [73] have determined the stability constants of labile heterogeneous complexes of cadmium with *Chlorella marina* cells using DPASV. They have found that *Chlorella marina* cells form complexes with cadmium (II) for surface coverages (θ) between 10^{-5} and 3×10^{-5} with $\log K$ values between 3 and 4. Another study has been done by Erk and Raspor [74] using DPASV for the evaluation of the conditional stability constants of cadmium-metallothionein, isolated from the mussel. The calculated conditional stability constants of the Cd-MT complexes are in the range of $K = (1.4\text{-}2.0) \times 10^{10} \text{ dm}^3 \text{ mol}^{-1}$. A study of cadmium complexation with the hexapeptide Lys-Cys-Thr-Cys-Cys-Ala thionein fragment (FT) was performed in the DPASV mode [75]. The study showed that the conditional stability constant, K_{CdFT} , had the value of $5.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1}$ with a satisfactory standard deviation of $1.9 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1}$. The interaction of fulvic acids with cadmium (II) ions was studied by DPASV, and the voltammetric data obtained during the titration of mixtures of cadmium (II) and fulvic acids at different concentrations were analyzed using multivariate curve resolution [76]. The average $\log K_{\text{app}}$ values obtained were 5.5 and 6.4.

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CHAPTER 3

COMPETING LIGAND EXCHANGE METHOD / DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMETRY FOR DETERMINATION OF METAL SPECIATION IN AQUEOUS SOLUTIONS

Anodic stripping voltammetry

Voltammetric methods, especially Anodic Stripping Voltammetry (ASV), are widely used for study of complexation of potentially toxic metals in natural waters. This is mainly due to their extremely low detection limits ($\sim 10^{-10}$ - 10^{-11} M), multielement and speciation capabilities, suitability for on-line and in situ measurements, and low cost. Stripping voltammetry is the best-known analytical method that incorporates an electrolytic preconcentration step [1-4]. Stripping Voltammetry involves two discrete steps: a preconcentration step and a stripping step. In the preconcentration step, the target analyte is accumulated into the working electrode. In the stripping step, the accumulated material is oxidized or reduced back into the solution. The response, recorded during this step, is proportional to the concentration of the analyte in the bulk solution (sample). Anodic Stripping Voltammetry (ASV) is the most common version of stripping analysis. As shown in Figure 3, it involves the reduction of a metal ion to dissolve it in mercury, forming an amalgam in the preconcentration step:

Preconcentration is followed by a positive-going potential scan to cause re-oxidation of the metal in the amalgam:

The amalgamated metals are thus stripped out of the electrode in an order that is a function of each metal's standard potential, and gives rise to anodic peak currents that are measured. Only those metals that are soluble in mercury can be determined by ASV. Differential pulse is one of the waveforms that is used in ASV. In Differential Pulse Anodic Stripping Voltammetry (DPASV), pulses of constant-amplitude potential,

Figure 3

A schematic diagram of Anodic Stripping Voltammetry for the determination of metal ion.

superimposed on a linear potential ramp, are applied to the working electrode (Static Mercury Drop Electrode (SMDE)) at a time just prior to the end of the drop, as shown in Figure 4. The current is sampled twice, just before the pulse application (at 1) and again late in the mercury drop life (at 2). The first current is instrumentally subtracted from the second, and this current difference [$\Delta i = i(t_2) - i(t_1)$] is plotted vs. the applied potential. The resulting differential pulse voltammogram consists of current peaks, the heights of which are directly proportional to the concentration of the corresponding analytes in the sample.

In Differential Pulse Anodic Stripping Voltammetry (DPASV), a distinction is made between electrochemically labile and inert species. The inert cadmium species are the complexes that are not dissociated in the diffusion boundary layer within the electrochemical timescale, and also those are not reduced at the deposition potential, which include strong cadmium organic complexes and cadmium adsorbed on colloids. The labile species include free aqua ions, and small inorganic and organic complexes that are rapidly dissociated.

The general concepts of metal speciation and bioavailability are currently being evaluated to define water quality criteria for metals in freshwaters [5,6]. A number of analytical methods have been developed to determine metal speciation in natural waters, such as voltammetric in-situ probe with microelectrodes [7], diffusive gradients in thin films [8,9], and metal ion selective electrodes [10-12]. For the determination of trace metal speciation parameters, including free metal-ion concentrations, natural organic ligand concentrations, conditional stability constants and diffusion coefficients, it is essential to have an analytical method that can be used at the natural low range of trace metal concentrations (nano-molar and lower range).

Differential Pulse Waveform

Figure 4

The differential pulse waveform

Competitive Ligand Exchange Method / anodic stripping voltammetry

The indirect methods of the Competitive Ligand Exchange Method (CLEM), followed by voltammetric measurements - cathodic stripping voltammetry (CLEM/CSV), anodic stripping voltammetry (CLEM/ASV) - have been applied to metal speciation at ambient levels in seawater and in freshwater [11, 13-27]. The CLEM is based on the addition of an excess of a competing ligand, with known complexation properties (complex stoichiometry and stability constants), to the test water sample. A new equilibrium develops between the original metal complexes and the metal complexes formed with this competing ligand. The concentration of the metal complexes with the competing ligand is determined specifically by CSV or ASV. Free aqua metal ion concentrations are obtained by equilibrium calculations and are then calculated for the original water samples. Trace metal complexation parameters (natural organic ligand concentrations, conditional stability constants) can be obtained by the titration of a water sample with the target trace metal. Since this Chapter deals only with ASV, no further mention of CSV will be made in this Chapter.

Competing Ligand Exchange Method with the application of Differential Pulse Anodic Stripping Voltammetry was used for the determination of the cadmium complexation by natural organic ligands in the presence of ethylenediamine (EN) as the competing ligand [20, 28]. As cadmium forms fully labile complexes with EN, the addition of EN increases the concentration of the labile cadmium complexes, and therefore increases the sensitivity of the method. When EN is present in excess compared with the natural organic ligands, and ligand exchange equilibrium is achieved in the freshwater sample, the less stable cadmium organic complexes consist mostly of Cd-EN

complexes whereas the more stable cadmium organic complexes remain inert. Therefore, the contribution to the measured current in presence of EN is due to free cadmium ions, inorganic and EN complexes of cadmium.

The CLEM involves titration of a freshwater sample with cadmium in the presence of an added competing ligand EN, and the determination of labile Cd by DPASV. The concentration of added ligand EN must just be sufficient to determine the metal complex of the added competing ligand EN. The free cadmium ion concentrations and the complexation parameters in the system then are obtained by equilibrium calculations [29-32]:

The mass balance in the original, unperturbed water sample is:

$$\begin{aligned} [\text{Cd}_T] &= [\text{Cd}^{2+}] + \sum [\text{CdI}_{i,x}] + \sum [\text{CdL}_i] \\ &= [\text{Cd}^{2+}](1 + \alpha_{\text{in}} + \sum K_i [\text{L}_i]) \end{aligned} \quad (3.5)$$

where I_i and L_i represent the i^{th} inorganic ligand and natural ligand, respectively, and $[\text{Cd}_T]$, $[\text{Cd}^{2+}]$, $[\text{CdI}_{i,x}]$, and $[\text{CdL}_i]$ represent the concentrations of total dissolved cadmium, free cadmium ion, inorganic Cd-complexes and natural Cd-complexes, respectively.

After the addition of the EN, the peak current i_p (A) is proportional to the concentration of labile species:

$$i_p/S = [\text{Cd}_{\text{labile}}] = [\text{Cd}^{2+}] + [\text{CdI}_{i,x}] + \sum [\text{Cd} - \text{EN}_z]$$

$$= [\text{Cd}^{2+}] (1 + \alpha_{\text{in}} + \alpha_{\text{EN}}) \quad (3.6)$$

where S refers to the DPASV sensitivity in A M⁻¹ where A stands for ampere; [Cd_{labile}], [Cd²⁺], and $\sum[\text{Cd} - \text{EN}_z]$ represent the concentrations of labile Cd, free Cd ion and Cd-EN complexes, respectively. The complexing coefficients α_{in} and α_{EN} of inorganic ligands and EN are equal to the ratio of the concentrations of the corresponding complexes to free Cd ions, as calculated from the major inorganic ion composition, pH and the added EN concentrations. Therefore, [Cd²⁺] in the presence of EN can be determined using equation (3.6). The mass balance at any point in the titration is given by:

$$\begin{aligned} [\text{Cd}_T] &= [\text{Cd}^{2+}] + \sum[\text{CdI}_{i,x}] + \sum[\text{CdL}_i] + \sum[\text{Cd} - \text{EN}_z] \\ &= [\text{Cd}_{\text{nat}}] + \sum[\text{Cd} - \text{EN}_z] \end{aligned} \quad (3.7)$$

where [Cd_{nat}] is the concentration of natural cadmium species at the new equilibrium and [CdL_i] is the concentration of natural organic complexes which are significantly more stable than Cd-EN and are not labile on the ASV timescale. [CdL_i] is equal to the difference between [Cd_T] and [Cd_{labile}]. [Cd_{nat}] is determined from the difference between [Cd_T] and $\sum[\text{Cd} - \text{EN}_z]$.

The inorganic complexing coefficient α_{in} , that includes the complexes of Cd with carbonate, hydroxide and chloride, is estimated from the Cd complex formation constants β_i and the concentrations of the major inorganic species *i*:

$$\begin{aligned} \alpha_{\text{in}} &= \beta'_{\text{OH}}[\text{OH}^-] + \beta''_{\text{OH}}[\text{OH}^-]^2 + \beta_{\text{CO}_3}[\text{CO}_3^{2-}] \\ &\quad + \beta_{\text{HCO}_3}[\text{HCO}_3^{2-}][\text{H}^+] + \beta_{\text{Cl}}[\text{Cl}^-] \end{aligned} \quad (3.8)$$

For freshwater conditions and pH around 8, α_{in} is usually in the range of 0.4-0.8.

The EN complexing coefficient α_{EN} is computed from the Cd-EN formation constants for CdEN and Cd(EN)₂ and the mass balance of EN:

$$\alpha_{EN} = \beta'_{EN}[EN] + \beta''_{EN}[EN]^2$$

$$[EN] = [EN_t] / (1 + K' [H^+] + K' K'' [H^+]^2) \quad (3.9)$$

where $[EN]$ and $[EN_t]$ stand for the free; uncomplexed, and total EN concentrations, respectively; β'_{EN} and β''_{EN} the formation constants of the CdEN and Cd(EN)₂ complexes; and K' and K'' the first and second protonation constants, respectively.

The relevant complexation parameters of the natural organic ligands are either obtained graphically [33-35], or are optimized numerically using fitting programs like FITEQL [36-38]. The addition of the competing ligand EN binds a portion of Cd in the sample and thereby reduces both $[Cd_{nat}]$ and $[Cd^{2+}]$.

$$\sum c_{CdI_{i,x}} = c_{Cd} \sum (\beta_{I_{i,x}} c_i^x) = c_{Cd} \alpha_{in} \quad (3.10)$$

$$\sum c_{Cd-EN_z} = c_{Cd} \sum (\beta_{EN} c_{EN}^z) = c_{Cd} \alpha_{EN} \quad (3.11)$$

where $\beta_{I_{i,x}}$ and β_{EN} are the stability constants for an x number of inorganic ligands, I_i , and a complex with a z number of added ligand, EN, respectively, and α_{in} and α_{EN} are the complexation coefficients of inorganic ligands and the competing ligand, respectively.

Since natural ligands are both physically and chemically heterogeneous, α_L varies continuously during the titration (i.e. with the metal-to-ligand ratio). When the concentration of $c_{M,nat}$ approaches the ambient total metal concentration, $c_{M,t,amb}$, $\alpha_{L,amb}$ reflects the complexation by the natural ligands at the ambient level.

The accuracy of the results from the competing ligand exchange method described above relies on the following assumptions being valid [28]:

1. Ligand exchange equilibrium is established between the added ligand and the natural ligands in the sample.
2. The concentration of the specific metal complexes with the competing ligand must be accurately determined.
3. Constant pH must be maintained using non-complexing pH buffers.
4. The complexation parameters of the competing ligand with the analyte metal M must be accurately known.

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CHAPTER 4

DETERMINATION OF Cd(II) SPECIATION IN AQUEOUS SOLUTIONS BY COMPETING LIGAND EXCHANGE METHOD / DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMETRY

Reagents

Stock solutions of the trace metals (10 $\mu\text{g/mL}$) Cd(II), Cu(II), Zn(II) and Pb(II) were prepared separately for each metal by diluting appropriate quantities of a 1000 $\mu\text{g/mL}$ standard solution (Fisher, A.C.S. reagent) in ultrapure water containing 1% (v/v) HNO_3 (Seastar, Canada) to prevent metal loss by adsorption to the container walls. 2 M stock solution of ethylenediamine (EN) was prepared by diluting an appropriate quantity of EN liquid (Aldrich) in ultrapure water. A stock solution of 2.0 M HEPES-NaOH buffer at pH 7.5 was prepared by dissolving an appropriate quantity of HEPES (N-2-Hydroxyethylpiperazine-N'-3-ethanesulfonic acid, BDH 99%) in 2.0 M sodium hydroxide (ANACHEMIA) solution (previously purified by electrodeposition). The sodium hydroxide solution was purified by electrodeposition at -1.2 V vs. SCE (Standard Calomel Electrode) for at least 48 hours prior to use. A 2M stock solution of potassium nitrate (KNO_3) was prepared by dissolving an appropriate quantity of pure KNO_3 (Aldrich) in ultrapure water. Ultrapure water of resistivity 18.2 $\text{M}\Omega\text{-cm}$, obtained directly from a Milli-Q-Plus water purification system (Millipore Corporation) was used to prepare all standard and test solutions.

Cleaning procedure

All containers were soaked in 10% HNO_3 (AR grade), and were left to stand for one week at room temperature in order to leach out trace metals and other impurities. The containers were then rinsed five times with the ultrapure water, and left completely filled with the ultrapure water until they were used. The filling water was renewed periodically to ensure continued contact with the ultrapure water.

Study areas

Metal-impacted lake water samples were collected in June and July 2001, and in July and August 2002, from four lakes: Lake Opasatica, Lake Vaudray, Lake Dufault and Lake Osisko from the Rouyn-Noranda mining area, located in northwestern Québec (48°00'N, 79°00'W, Abitibi, Québec, Canada) (**Appendix 1**). The lakes in the study area were affected by acid and metal contamination from current metal mining operations, abandoned mines and atmospheric deposition from a large, nearby smelter that has been in operation since 1927 [1]. Many surrounding lakes are contaminated with heavy metals [1]. Lake Opasatica, which is located upwind from the smelter and is protected from atmospheric deposition, was used as a control (uncontaminated) site. Lake Vaudray is an intermediate-contaminated site and Lake Osisko and Lake Dufault are the most highly contaminated lakes based on data from previous studies [1-3]. In addition, Lake Osisko also received liquid effluents from the smelting operations during many years in the past. A detailed map of the study area was given by Brodeur et al. [3].

The natural environment around Sudbury (Ontario) was affected by cadmium and other metal contamination due to atmospheric deposition from nearby metal-refining operations. Throughfall collectors were used to collect throughfall precipitation samples from Sudbury sites (Site 1 and 2 located 10 km and 24 km from the metal Refinery, respectively) in November 2001, and in June and July 2002 (**Appendix 2**).

Total dissolved metal concentrations

The water samples were collected in pre-cleaned 2.2-L Teflon bottles. Immediately after the receipt of the water samples at the laboratory, they were filtered through 0.45 μm

mixed cellulose ester membrane filters. The filtered water samples were acidified to pH 1.5 with ultrapure nitric acid (Seastar, Canada), in order to preserve the concentrations of metals. Total dissolved metal concentrations were determined by inductively-coupled plasma mass spectrometry (ICP-MS).

QA/QC

Quality control for the determination of total metals by ICP-MS included replicate injections (typically $\leq 5\%$ relative standard deviation among metal concentrations determined in replicate injections) and periodic (two in every 2-h operation) analysis of NIST 1643d Certified Reference Material. A prior set of samples was reanalyzed if the analyzed value differed from the certified value by $> 20\%$.

Dissolved Organic Carbon (DOC) determinations

A Total Organic Carbon Analyzer (SHIMADZU, Model TOC-5000 or OI Analytical Model 1010 TOC Analyzer) was used to determine the concentrations of total carbon (TC) and inorganic carbon (IC) in the freshwater samples. The concentrations of DOC in the samples were calculated by subtracting the IC concentration from the TC concentration. For the TC determination, 25 μL of the freshwater sample was introduced into the analyzer and the TC components in the sample were combusted at 680°C using the catalyst for regular sensitivity measurement (P/N 017-42801-01) to form CO_2 , which was determined by a non-dispersive infrared gas analyzer (NDIR). For the IC measurement, 50 μL of the freshwater sample was injected into the analyzer, and the IC

components in the sample were decomposed by the IC reagent (a solution of phosphoric acid) to form CO₂, which was also detected by NDIR.

Cadmium titrations

A series of 10 mL sub-samples were transferred to 50 mL screw-top, Teflon cups (Savalex, USA), then buffered with 6 mM HEPES buffer (1 mol/L HEPES stock solution), and the pH was adjusted to 8.00 ± 0.05 using different concentrations of sodium hydroxide (2 mol/L NaOH stock solution). The sub-samples were spiked with cadmium to give a series of 10 to 12 spiked sub-samples containing 10^{-9} to 10^{-7} mol/L of cadmium. The spiked sub-samples were equilibrated in the dark for 18-24 h at 23.0 ± 1.0 °C, before analysis.

DPASV determinations of labile cadmium

For the cadmium titrations, Differential Pulse Anodic Stripping Voltammetry (DPASV) was used with a Static Mercury Drop Electrode (SMDE), a Ag/AgCl reference electrode, and a platinum counter electrode held in a Metrohm VA663 stand, combined with an Autolab PGSTAT12 potentiostat/galvanostat (Eco Chemie, The Netherlands). Ethylenediamine was added to each of the samples and equilibrated for 18 h. The samples were purged for 5 min. with ultra-high purity nitrogen gas immediately prior to analysis. Cadmium was preconcentrated by electrodeposition on the surface of the hanging mercury drop at -1.0 V. The experimental parameters were as follows: initial potential = -800 mV, final potential = -400 mV, pulse height = 50 mV, scan rate = 10 mV/s. The stripping peak for the labile cadmium occurred from -610 to -580 mV.

Results and Discussion

Metal-impacted lake water samples were collected in June 2001 from the four lakes (Lake Opasatica, Lake Vaudray, Lake Dufault and Lake Osisko). Figure 5 presents the voltammograms of the Cd(II) titration for Lake Dufault collected in June 2001 with EN as the competing ligand. It is clear from Figure 5 that the peak height increases as more cadmium is added to the lake water sample. Figure 6 presents the cadmium titration curve of the lake water sample collected from Lake Dufault in June 2001, in terms of DPASV peak current as a function of the total dissolved cadmium concentration. Figure 6 shows this type of titration curve, especially the curvature in the curve at the beginning of the titration that is observed in the DPASV titration of a freshwater sample with Cd. The curvature is due to a lack of equilibrium at the beginning of the titration because of an inadequate quantity of cadmium. It is clear from Figure 6 that the addition of a small amount of Cd^{2+} to the lake water sample causes the Cd(II) species in the original sample to be redistributed, resulting in a slow increase in the measured peak current at the beginning of the curve. At high concentrations of added Cd^{2+} , essentially all the cadmium is present as the free metal ion. Hence, the sensitivity, S , was determined from the slope of the titration curve at high added Cd^{2+} concentrations, as shown by the straight line in Figure 6. Figure 7 shows the cadmium titration data of the lake water samples collected in June 2001 from the four lakes with cadmium in terms of $\log [\text{Cd}^{2+}]$ as functions of $\log [\text{Cd}_{\text{nat}}]$. The dashed curves in the figure are calculated using the FITEQL fitting program based on one ligand model (for simplicity) [4-6]. The calculated conditional stability constants, the natural ligand concentrations, and the free cadmium ion concentrations are presented in Table 2. The conditional stability constants for the Cd(II)-DOC complexes increase

Figure 5

DPASV voltammograms of Cd(II) titration of the lake water samples, collected on June 2001 from Lake Dufault.

Figure 6

Titration curve of the lake water sample with Cd using DPASV. The lake water sample was collected from Lake Dufault in June 2001.

Table 2

Cadmium speciation parameters in the four lake water samples, collected in June 2001, determined by CLEM/DPASV at SMDE, with EN as the competing ligand, at pH 8.0 (HEPES/NaOH), and constant ionic strength (0.04 M); temperature 298 K.

Lake	DOC mg/L	[Cd]_{total} M	[Cd]_{total}/ DOC mol/g	[Cd²⁺] M	Log K_{CdL}	[L] nM
Dufault	6.9	8.0 x 10⁻⁹	1.2 x 10⁻⁶	(2.7 ± 0.3) x 10⁻⁹	8.1 ± 0.2	26 ± 1.0
Osisko	3.4	1.8 x 10⁻⁹	5.3 x 10⁻⁷	(6.0 ± 0.2) x 10⁻¹⁰	9.5 ± 0.4	6.4 ± 0.2
Vaudray	10	8.9 x 10⁻¹⁰	8.9 x 10⁻⁸	(5.7 ± 0.2) x 10⁻¹¹	9.9 ± 0.2	1.9 ± 0.1
Opasatica	9.4	8.9 x 10⁻¹⁰	9.5 x 10⁻⁸	(4.0 ± 0.1) x 10⁻¹¹	10 ± 0.2	3.3 ± 0.4

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- All the above samples were filtered through 0.45µm filter (Gelman Material No. 63077).
- [Cd]_{total} represents the dissolved cadmium concentration.
- [L] represents the natural ligand concentration.
- K_{CdL} is the conditional stability constant of CdL.
- SMDE: stands for Static Mercury Drop Electrode

from 8.1 in Lake Dufault to 10.0 in Lake Opasatica with decreasing total dissolved cadmium concentrations, from 8.0×10^{-9} M in Lake Dufault to 8.9×10^{-10} M in Lake Opasatica. Figure 8 shows the relationship of the free cadmium ion concentration with the conditional stability constants of the Cd(II)-DOC. Free cadmium ion concentrations increase from 4.0×10^{-11} M in Lake Opasatica, to 2.7×10^{-9} M in Lake Dufault, as the conditional stability constants of the Cd(II)-DOC complexes decrease, from 10.0 in Lake Opasatica, to 8.1 in Lake Dufault. The reasons for the decrease in the conditional stability constant and the increase in the free cadmium ion concentration may be explained as follows:

- 1) an increase in the total dissolved cadmium concentrations as a result of cadmium input to the lakes from different sources of contamination (effluents and/or atmospheric deposition) at nearly constant DOC concentrations (from 3.4 mg/L in Lake Osisko, to 10 mg/L in Lake Vaudray). The $[Cd]_{total}/DOC$ ratio for Lake Dufault was very high (1.2×10^{-6}) compared with the other three lakes (5.3×10^{-7} , 8.9×10^{-8} , and 9.5×10^{-8} for Lake Osisko, Lake Vaudray, and Lake Opasatica, respectively). With relatively high $[Cd(II)]/[DOC]$ ratios, the much less abundant strong binding sites of the DOC were saturated with Cd(II); the excess Cd(II) was then bound to the much more abundant, weaker binding sites of the DOC, forming weaker Cd(II)-DOC complexes which were labile.
- 2) As explained later in this paragraph, the co-presence of other trace metal ions such as Cu(II), Zn(II) and Pb(II) in higher concentrations than Cd(II) successfully competed with Cd(II) for the much fewer number of strong binding sites (<10%) of the DOC, resulting in a greater fraction of Cd(II) binding to the much larger number of weak

Figure

e 8

Relationship

ship of the free Cd ion concentrations and the conditional stability constant of the CdL complexes. Free Cd ion concentrations were determined by CLEM/DPASV.

$$pCd^{2+} = -\log [Cd^{2+}]$$

binding sites(>90%) of the DOC [7], forming weak Cd(II)-DOC complexes, which were labile. Table 3 presents the concentrations of the trace metals, Cu(II), Pb(II), and Zn(II) co-present with the cadmium ions in the four lake water samples collected in June 2001. Figure 9 shows the relationship of the free cadmium ion concentration with the other trace metal concentrations in the four lake water samples. It is clear from Figure 9 that the co-presence of the other trace metals, Cu(II), Pb(II), and Zn(II), in higher concentrations compared to Cd(II), increased the free cadmium ion concentration. This is a result of many factors such as the water exchange rate coefficients of the metal aqua complexes, i.e., the first-order rate coefficients for water exchange spans 16 orders of magnitude from Pb(II) and Cu(II) with $k_{-w} = 10^9 \text{ s}^{-1}$ to Cr(III) with $k_{-w} = 10^{-7} \text{ s}^{-1}$. For a given ligand, the metals such as Pb(II) and Cu(II), having very high water exchange rate coefficients, form strong complexes, which are inert, whereas the metals such as Al(III) and Cr(III), having very low water exchange rate coefficients form weak complexes, which are labile. When several metals, such as Cu(II), Pb(II), Cd(II), and Zn(II) are present with the DOC in lake water samples, the Law of Mass Action determines the equilibrium concentrations of the metal-DOC complexes. Depending on the mole ratios of metals to DOC the equilibrium will favor a metal such as Pb(II) which has much higher water exchange rate coefficient ($k_{-w} = 7 \times 10^9 \text{ s}^{-1}$) and Cu(II) ($k_{-w} = 1 \times 10^9 \text{ s}^{-1}$) than the metals such as Cd(II) which has a much lower water exchange rate coefficient ($k_{-w} = 3 \times 10^8 \text{ s}^{-1}$) [8].

The effects of the competition of the trace metal ions, Cu(II), Pb(II), and Zn(II) were to decrease the stability constant of the Cd(II)-DOC complex by competitive binding to the binding sites of the DOC (from prior work). For the metals Cu(II), Pb(II), Zn(II) and Cd(II), the effects of the above competition can be interpreted in terms of

Table 3

Concentrations of the other trace metal ions co-present with cadmium in the lake water samples collected in June 2001, determined by CLEM/DPASV.

Lake	[Cd]_{total} M	[Cd²⁺] M	[Cu]_{total} M	[Pb]_{total} M	[Zn]_{total} M
Dufault	8.0×10^{-9}	$(2.7 \pm 0.3) \times 10^{-9}$	2.1×10^{-7}	2.8×10^{-9}	1.3×10^{-6}
Osisko	1.8×10^{-9}	$(6.0 \pm 0.2) \times 10^{-10}$	9.6×10^{-8}	4.8×10^{-10}	2.6×10^{-7}
Vaudray	8.9×10^{-10}	$(5.7 \pm 0.2) \times 10^{-11}$	3.8×10^{-8}	6.3×10^{-10}	6.1×10^{-8}
Opastica	8.9×10^{-10}	$(4.0 \pm 0.1) \times 10^{-11}$	3.8×10^{-8}	5.3×10^{-10}	4.6×10^{-8}

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- [Cd²⁺] was determined by CLEM/DPASV
- [Cd]_{total} was determined by ICP-MS
- [Cu]_{total}, [Zn]_{total} and [Pb]_{total} were determined by ICP-MS

Figure 9

Dependence of the free Cd ion concentrations on the other trace metals concentrations in the four lake waters, samples collected in June 2001, determined by CLEM/DPASV.

the complex stability sequence of the metals: $\text{Pb(II)} > \text{Cu(II)} > \text{Zn(II)} \approx \text{Cd(II)}$. The above order for the transition metals Cu(II) , Zn(II) and Cd(II) is related to both the increase in effective nuclear charge with atomic number (which is due to imperfect shielding by the d orbital electrons). There are many factors governing the affinity of metal cations towards a poly-functional complexant, such as DOC, and the stabilities of these metal complexes are controlled by this affinity. One of the factors that affected the metal ligand stability is the charge to ionic radius ratio. The charge to ionic radius ratio is a convenient criterion for the estimation of the complexing ability of the metal ions [9]. The ability of the above metals to form M(II)-DOC complexes will increase according to the following order, $\text{Cu(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Pb(II)}$. Another factor that controls the stability of the M(II)-DOC complex is the hardness and softness of the cations and the functional groups. According to the classification of the Hard Acid Soft Base (HASB) theory, hard acids form strong complexes with hard bases and soft acids form stronger complex with soft bases. Pb(II) , Cu(II) , and Zn(II) are borderline acids whereas, Cd(II) is a soft acid. As was mentioned before, DOC contains various functional groups, with the majority of them containing oxygen groups in the form of carboxylic or hydroxyl (phenolic or alcoholic) groups, and other minor sites containing nitrogen, sulfur and sometimes phosphorous atoms. The order of the base hardness increases according to the following order: oxygen > nitrogen > sulfur > phosphorus. The functional groups that contain oxygen, which is considered a hard base, prefers to bind to Pb(II) , Cu(II) and Zn(II) , which are located at the borderline between hard and soft acids, more than Cd(II) , which is a soft acid. The other minor sites, containing nitrogen, sulfur and phosphorous, prefer to bind to Cd(II) . In addition, Cu(II) decreases the strength of the Cd(II)-DOC binding

because it forms a more stable complex than Cd(II). The stability of the Cu(II)-complex is enhanced by Ligand Field Stabilization Energy (LFSE), with further stabilization by Jahn-Teller effect. When Pb(II) is present with Cd(II) in freshwaters, Pb(II) forms stronger complexes than Cd(II) because of the higher effective nuclear charge of the Pb^{2+} compared with Cd^{2+} .

It was also found that the lake water samples that have high free cadmium ion concentrations are associated with high concentrations of calcium and magnesium. As shown in Table 4, Lake Dufault has high concentrations of calcium (4.2×10^{-4} M) and magnesium (1.3×10^{-4} M) as well as a high concentration of free cadmium ions, whereas Lake Vaudray has low concentrations of calcium (9×10^{-5} M) and magnesium (4×10^{-5} M) as well as a low concentration of free cadmium ions. The co-presence of Ca(II) and Mg(II) in higher concentrations than that of Cd(II) decreased the stability of Cd(II)-DOC complexes; consequently, the Cd(II)-DOC complexes dissociated and free cadmium ions were released, resulting in the formation of free cadmium ions which are reported to be toxic. It is also well known that when a cation reacts with an acidic functional group of a molecule with multiple functional groups (a “polyanion” such as humic acid or a protein), the chemical free energy of interaction is augmented by the long-range coulombic attraction emanating from all neighboring, non-reacting negative sites as shown in Figure 10(a). This so-called polyelectrolyte effect, which can greatly strengthen the binding of metal ions by polyanions [10].

The free energy of reaction between Cd^{2+} and the functional group L^{m-}

is the sum of the chemical free energy due to the reaction with the functional group itself

Table 4

Concentrations of the major cations co-present with cadmium in the lake water samples
collected in June 2001.

Lake	pH	Conductivity mS/m	[Cd] _{total} M	[Cd ²⁺] M	[Ca] _{total} M	[Mg] _{total} M
Dufault	7.1	14.7	8.0×10^{-9}	$(2.7 \pm 0.3) \times 10^{-9}$	4.2×10^{-4}	1.3×10^{-4}
Osisko	9.0	33.3	1.8×10^{-9}	$(6.0 \pm 0.2) \times 10^{-10}$	6.2×10^{-4}	2.1×10^{-4}
Vaudray	6.2	30.4	8.9×10^{-10}	$(5.7 \pm 0.2) \times 10^{-11}$	9.0×10^{-5}	4.0×10^{-5}
Opasatica	7.1	90.3	8.9×10^{-10}	$(4.0 \pm 0.1) \times 10^{-11}$	2.4×10^{-4}	1.2×10^{-4}

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- [Cd²⁺] was determined by CLEM/DPASV
- [Cd]_{total} was determined by ICP-MS
- [Ca]_{total} and [Mg]_{total} were determined by ICP-AES

Figure 10(a)

Schematic diagram of the polyelectrolyte effect.

Figure 10(b)

Schematic diagram of the electrostatic screening effect

and the coulombic free energy due to electrostatic interactions between Cd(II) and all the charges on the polyanion.

$$\Delta G^0 = \Delta G_{\text{chem}}^0 + \Delta G_{\text{coul}}^0$$

and in terms of equilibrium constants,

$$K = e^{-\Delta G^0 / RT} = K_{\text{chem}} \cdot K_{\text{coul}}$$

Where

$$K_{\text{chem}} = e^{-\Delta G_{\text{chem}}^0 / RT}$$

$$K_{\text{coul}} = e^{-\Delta G_{\text{coul}}^0 / RT}$$

The co-presence of calcium and/or magnesium reduced the coulombic part due to the screening effect and decreased the stability constants of the cadmium complexes leading to the release of free cadmium ions, as shown in Figure 10(b).

In August 2001, another set of samples was collected from Lake Dufault, Lake Osisko and Lake Opasatica to study the chemical speciation of cadmium using the above mentioned method.

Figure 11 shows the cadmium titration data of the lake water samples collected in August 2001 from the three lakes (Lake Dufault, Lake Osisko, and Lake Opasatica) with cadmium in terms of $\log [\text{Cd}^{2+}]$ as functions of $\log [\text{Cd}_{\text{nat}}]$. The dashed curves in Figure 11 are calculated using the FITEQL fitting program. The calculated concentration of natural ligands, the free cadmium ions and the conditional stability constants are presented in Table 5. The total dissolved cadmium concentration of Lake Dufault decreased (from 8 nM to 2.7 nM) between the sampling dates and as a result, the free

Figure 11

Titration curves of lake waters (collected in August 2001) with Cd in presence of 1mM EN. The dashed line represents the fitting line using the FITEQL program.

Table 5

Cadmium speciation parameters of the lake water samples, collected in August 2001, determined by CLEM/DPASV at SMDE and EN as the competing ligand at pH 8.0 (HEPES/NaOH), and constant ionic strength (0.04 M); temperature 298 K

Lake	pH	Conductivity mS/m	DOC mg/L	[Cd] _{total} nM	[Cd] _{total} /DOC mol / g	[Cd ²⁺] nM	Log K _{CdL}	[L] nM
Dufault	7.1	90.3	5.5	2.7	4.9 x 10 ⁻⁷	0.2 ± 0.03	8.6	29.3
Osisko	9.0	33.3	3.6	1.8	4.8 x 10 ⁻⁷	0.2 ± 0.02	9.0	18
Opasatica	7.1	14.7	7.1	0.90	1.3 x 10 ⁻⁷	0.3 ± 0.01	10.2	0.73

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- All the above samples were filtered through 0.45µm filter (Gelman Material No. 63077).
- [Cd]_{total} represents the total dissolved cadmium concentration.
- [L] represents the natural ligand concentration.
- K_{CdL} is the conditional stability constant of CdL.

Cd^{2+} ion concentrations decreased from 2.7 nM in the samples collected on June 2001 to 0.2 nM in the sample collected on August 2001. At the same time, the total dissolved cadmium concentration for Lake Osisko and Lake Dufault remain unchanged and as a result, their conditional stability constants were nearly equal (9.0 and 10.2 for Lake Osisko and Lake Default, respectively). The change of the $[\text{Cd}]_{\text{total}}/\text{DOC}$ ratio was insignificant (4.9×10^{-7} for Lake Dufault to 1.9×10^{-7} for Lake Opasatica). Table 6 shows the total concentration of the trace metals and the major cations co-present with the cadmium in the three lake water samples collected in August 2001. Lake Dufault had higher concentrations of Cu(II), Zn(II), and Pb(II) than Lake Opasatica (one order of magnitude higher), which suggests that the formation of free cadmium ions might be due to the competition between the trace metals with cadmium for the strong binding sites and the formation of weak Cd(II)-DOC complexes which were labile.

Freshwater samples were collected from Lake Dufault and Lake Opasatica in July 2002 and August 2002 to study the chemical speciation of Cd(II) by CLEM/DPASV. The chemical speciation of Cd(II) can be determined from Figure 12. Table 7 presents the results derived from Figure 12. Table 8 presents the concentrations of other competing metal ions, both trace metal ions, Cu(II), Pb(II), and Zn(II), and also major cations, Ca(II) and Mg(II). The results shown in Figure 12 and Table 7 can be interpreted by referring to Table 8, and considering the effects of $[\text{Cd(II)}]/[\text{DOC}]$ mole ratio, and of competition by the other trace metals Cu, Pb and Zn, and of electrostatic screening of the anionic charges on humate and fulvate anions (of DOC) by major cations, Ca and Mg, as has been explained earlier.

Table 6

Concentrations of the other trace metal ions co-present with cadmium in lake water samples collected in August 2001.

Lake	[Cd] _{total} nM	[Cd ²⁺] nM	[Cu] _{total} M	[Pb] _{total} M	[Zn] _{total} M	[Ca] _{total} mM	[Mg] _{total} mM
Dufault	2.7	0.2 ± 0.03	1.9 x 10 ⁻⁷	1.8 x 10 ⁻⁹	3.7 x 10 ⁻⁷	0.3	0.1
Osisko	1.8	0.2 ± 0.02	1.2 x 10 ⁻⁸	5.3 x 10 ⁻¹⁰	4.6 x 10 ⁻⁸	0.6	0.2
Opasatica	0.90	0.3 ± 0.01	4.4 x 10 ⁻⁸	2.4 x 10 ⁻¹⁰	4.6 x 10 ⁻⁸	0.4	0.1

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- [Cd²⁺] was determined by CLEM/DPASV
- [Cd]_{total} was determined by ICP-MS
- [Cu]_{total}, [Zn]_{total} and [Pb]_{total}, were determined by ICP-MS
- [Ca]_{total} and [Mg]_{total} were determined by ICP-EAS

Figure 12

Titration curves of lake waters (collected in July 2002 and August 2002) with Cd in presence of 1mM EN, determined by CLEMDPASV. The dashed line represents the fitting line drawn with the FITEQL program.

Table 7

Cadmium speciation parameters of the lake water samples, collected in July 2002 and August 2002, determined by CLEM/DPASV using SMDE and EN as the competing ligand at pH 8.0 (HEPES/NaOH), and constant ionic strength (0.04 M); temperature 298 K. The data were collected from Figure 8.

Lake	collection date	DOC mg/L	[Cd] _{total} nM	[Cd] _{total} /DOC mol / g	[Cd ²⁺] M	Log K _{CdL}	[L] nM
Dufault	July 2002	10.9	3.2	2.9×10^{-4}	$(4.5 \pm 1.5) \times 10^{-10}$	8.7	9.0
Opasatica	July 2002	10.4	0.18	1.7×10^{-5}	$(1.2 \pm 0.1) \times 10^{-11}$	9.5	6.8
Dufault	August 2002	6.9	2.6	9.0×10^{-4}	$(3.3 \pm 5.4) \times 10^{-11}$	10.0	12.0
Opasatica	August 2002	7.9	0.06	4.0×10^{-6}	$(7.8 \pm 3.2) \times 10^{-13}$	10.3	4.4

- The uncertainty represents, 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).

- All the above samples were filtered through 0.45µm filter (Gelman Material No. 63077).

- [Cd]_{total} represents the total dissolved cadmium concentration, [L] represents the natural ligand concentration and K_{CdL} is the conditional stability constant of CdL.

Table 8

Concentrations of other trace metal ions co-present with cadmium in the lake water samples collected in July 2002 and August 2002.

	Dufault July 2002	Opasatica July 2002	Dufault August 2002	Opasatica August 2002
pH	7.2	7.7	7.3	7.6
Conductivity, mS/m	15.4	10.9	14.8	9.8
[Cu]_{total}, M	1.5×10^{-7}	4.2×10^{-8}	2.3×10^{-7}	4.6×10^{-8}
[Pb]_{total}, M	1.4×10^{-9}	7.3×10^{-10}	1.3×10^{-10}	9.7×10^{-11}
[Zn]_{total}, M	8.3×10^{-7}	5.7×10^{-8}	5.5×10^{-7}	4.0×10^{-8}
[Ca]_{total}, M	4.9×10^{-4}	3.3×10^{-4}	5.1×10^{-4}	1.6×10^{-4}
[Mg]_{total}, M	1.3×10^{-4}	1.3×10^{-4}	2.9×10^{-4}	1.3×10^{-4}

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- [Cu]_{total}, [Zn]_{total} and [Pb]_{total} were determined by ICP-MS
- [Ca]_{total} and [Mg]_{total} were determined by ICP-EAS

Throughfall precipitation samples were collected in November 2001 from the Sudbury (Ontario) sites (Site 1 and Site 2 were located from the metal refinery at a distance of 10 km and 25 km, respectively), and the speciation parameters of cadmium were determined using the previously mentioned procedure. Figure 13 presents the cadmium titration curves of the above samples, showing cadmium in terms of $\log [\text{Cd}^{2+}]$ as function of $\log [\text{Cd}_{\text{nat}}]$. The dashed curves in Figure 13 were calculated using the FITEQL fitting program. Table 9 presents the concentrations of natural ligands and the free cadmium ion and the calculated conditional stability constants of the cadmium complexes, and shows that the total dissolved cadmium concentration at Site 1 (nearest to the metal refinery) was higher (18 nM) than that at Site 2 (7.3 nM). The concentration of free Cd^{2+} ion at Site 1 (0.8 nM) was higher than that at Site 2 (0.3 nM) because of the high concentration of total dissolved cadmium while they had nearly the same DOC concentrations (≈ 10 mg/L), with the consequence that the Cd(II)/DOC mole ratio for Site 1 (1.7×10^{-6}) was higher than that of Site 2 (7.7×10^{-7}). The higher Cd(II)/DOC mole ratio meant that the [Cd] was more than enough to bind all the strong (< 1-10 % of the total) ligand sites of the DOC. The excess Cd^{2+} then bound to the weak (> 99-90 % of the total) ligand sites of DOC, forming weaker Cd(II)-DOC complexes which were labile. Table 10 shows that other trace metal ions and major cations were present with the cadmium in the throughfall precipitation samples.

The throughfall precipitation samples were collected from the Sudbury (Ontario) sites, Site 1 and Site 2, in June 2002 and July 2002, to study the chemical speciation of cadmium by CLEM/DPASV. Figure 14 presents the cadmium titration curves, from which the cadmium speciation parameters were determined (Table 11). Table 12 presents

Figure 13

Titration curves of throughfall precipitation samples (collected in November 2001) with Cd in presence of 1 mM EN. The dashed line represents the fitting line drawn with the FITEQL program.

Table 9

Cadmium speciation parameters in the throughfall precipitation samples, collected in November 2001, determined by CLEM/DPASV using SMDE and EN as the competing ligand at pH 8.0 (HEPES/NaOH), and constant ionic strength (0.04 M); temperature 298 K

Lake	DOC mg/L	[Cd] _{total} nM	[Cd] _{total} /DOC mol / g	[Cd ²⁺] nM	Log K _{CdL}	[L] nM
Site 1	10.4	18.0	1.7x 10 ⁻⁶	0.8 ± 0.2	8.6	68
Site 2	9.5	7.3	7.7 x 10 ⁻⁷	0.3 ±0.1	8.9	11

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- All the above samples were filtered through 0.45µm filter (Gelman Material No. 63077).
- [Cd]_{total} represents the total dissolved cadmium concentration.
- [L] represents the natural ligand concentration.
- K_{CdL} is the conditional stability constant of CdL.

Table 10

Concentrations of the other trace metal ions and major cations present with cadmium in throughfall precipitation samples collected in November 2001.

Throughfall sample	Site 1	Site 2
pH	5.0	4.5
Conductivity, mS/m	4.3	3.2
Cu(II), M	3.9×10^{-7}	3.6×10^{-8}
Pb(II), M	9.7×10^{-9}	3.9×10^{-9}
Zn(II), M	1.5×10^{-6}	6.3×10^{-7}
Ca(II), M	2.1×10^{-5}	7.7×10^{-6}
Mg(II), M	8.6×10^{-6}	2.3×10^{-6}

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- [Cu]_{total}, [Zn]_{total} and [Pb]_{total} were determined by ICP-MS
- [Ca]_{total} and [Mg]_{total} were determined by ICP-AES

Figure 14

Titration curves of throughfall precipitation samples (collected in June 2002 and July 2002) with Cd, in presence of 1mM EN.

The dashed line represents the fitting line drawn with the FITEQL program.

Table 11

Cadmium speciation parameters in the throughfall precipitation samples (collected in June 2002), determined by CLEM/DPASV using SMDE and EN as the competing ligand at pH 8.0 (HEPES/NaOH), and constant ionic strength (0.04 M); temperature 298 K

Site for sample	Date of collection	DOC mg/L	[Cd] _{total} nM	[Cd] _{total} /DOC mol / g	[Cd ²⁺] M	Log K _{CdL}	[L] nM
Site 1	June 2002	11.2	4.4	3.9×10^{-7}	$(2.4 \pm 1.7) \times 10^{-9}$	8.2	13.0
Site 2	June 2002	8.4	0.8	9.5×10^{-8}	$(1.0 \pm 0.1) \times 10^{-10}$	9.8	1.6
Site 1	July 2002	9.4	3.1	3.3×10^{-7}	$(1.4 \pm 0.8) \times 10^{-10}$	9.3	11.0
Site 2	July 2002	10	0.5	5.3×10^{-7}	$(2.8 \pm 0.1) \times 10^{-11}$	9.5	6.0

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- All the above samples were filtered through 0.45µm filter (Gelman Material No. 63077).
- [Cd]_{total} represents the total dissolved cadmium concentration.
- [L] represents the natural ligand concentration,
- K_{CdL} is the conditional stability constant of CdL.

Table 12

Concentrations of the other trace metal ions and major cations in the throughfall precipitation samples collected in June and July 2002.

	Site 1 June 2002	Site 2 June 2002	Site 1 July 2002	Site 2 July 2002
pH	6.1	5.8	5.9	5.7
Conductivity, mS/m	3.4	2.5	5.9	2.4
Cu(II), M	3.4×10^{-7}	4.8×10^{-8}	2.3×10^{-7}	4.3×10^{-8}
Pb(II), M	9.7×10^{-9}	1.9×10^{-9}	1.7×10^{-8}	2.0×10^{-9}
Zn(II), M	1.7×10^{-6}	2.8×10^{-6}	1.6×10^{-6}	1.9×10^{-6}
Ca(II), M	2.0×10^{-5}	6.7×10^{-6}	3.7×10^{-5}	2.0×10^{-6}
Mg(II), M	7.9×10^{-6}	2.1×10^{-6}	2.1×10^{-6}	9.0×10^{-7}

- The uncertainty represents 95.5 % confidence limits.
- [Cu]_{total}, [Zn]_{total} and [Pb]_{total} were determined by ICP-MS
- [Ca]_{total} and [Mg]_{total} were determined by ICP-AES

the concentrations of other competing metal ions, both trace metal ions, Cu(II), Pb(II), and Zn(II), and major cations, Ca(II) and Mg(II). The results shown in Figure 14 and Table 11 can be interpreted by referring to Table 12, and considering the effects of [Cd(II)]/[DOC] mole ratio, the competition by other trace metals (such as Cu, Pb and Zn), the electrostatic screening by major cations, (e.g. Ca and Mg), and the anionic charges on humate and fulvate anions (of DOC).

Conclusion

In summary, the cadmium speciation in freshwaters depends on several environmental factors. One factor is the cadmium/ DOC mole ratio. Since less than 10% of the total binding sites are strong binding sites that form stable complexes with cadmium, an increase in the cadmium/DOC mole ratio results in the eventual saturation of these few strong binding sites, leading to the excess cadmium being bound to the numerous weak binding sites which are labile and can generate free Cd^{2+} ions. Another factor is the co-presence of the other trace metals, especially if their concentrations are greater than cadmium: These competing metal ions can outcompete cadmium for the less numerous strong binding sites that are available for complexation. Another factor is the presence of high concentrations of the major cations, such as Ca^{2+} and Mg^{2+} , which by electrostatic screening of the anionic charges on the DOC (electrostatic bonding), reduce the over-all binding energy of Cd(II) with DOC. Additionally, Ca^{2+} and Mg^{2+} also compete with Cd^{2+} for specific binding sites on DOC (covalent bonding) . All of the above factors act additively to decrease the overall energy for the binding of Cd(II) with DOC, resulting in

an increase in the concentration of labile Cd(II)-DOC complexes, and hence, in the concentration of free Cd²⁺ ions.

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CHAPTER 5

COMPARISON OF THE EXPERIMENTALLY-OBSERVED SPECIATION PARAMETERS WITH WHAM-PREDICTED EQUILBRIUM SPECIATION OF Cd(II)

Introduction

The speciation of Cd in natural waters is of great interest as it can be used to monitor the Cd output to the environment due to different anthropogenic activities. The free Cd^{2+} ion is reported to be the toxic species and it controls Cd-organism interactions. Furthermore, it is of interest to compare the experimental values of Cd-speciation and the model predictions. Chemical equilibrium models have often proved useful for describing and predicting speciation of trace metals in soil solutions and natural waters [1-4]. The Windermere Humic Aqueous Model (WHAM) [5] is a computer program based on the Humic Ion-binding model V [6], which is a discrete-site/electrostatic model of binding of protons and metal ions by humic substances. WHAM contains a large fixed database of binding constants, incorporating approximately 30 metals, which has been compiled from the analysis of ion-binding data from isolated fulvic acid (FA) and humic acid (HA). Here, I present a comparison between the free Cd^{2+} concentrations determined experimentally for the impacted lake water samples: Lake Opasatica, Lake Vaudray, Lake Dufault and Lake Osisko from the Rouyn-Noranda mining area, located in northwestern Québec, using the Competitive Ligand Exchange Method/Differential Pulse Anodic Stripping Voltammetry (CLEM/DPASV) (presented in the previous chapter; Chapter 4), and the predications of WHAM V and WHAM VI models. The main difference between Models V and VI is that the latter takes into account binding site heterogeneity, by incorporating tridentate sites, and by improving the description of the distributions of binding strengths [7].

Results and discussions

WHAM predictions

Table 13 shows the comparison between the experimentally determined free Cd^{2+} ion concentrations using CLEM/DPASV and WHAM models V and VI for the lake water samples collected in June 2001 from the Rouyn-Noranda mining area. It is clear from Table 13, that the WHAM models V and VI, generally, over predict the free Cd^{2+} ion concentrations at low concentrations of total dissolved Cd, as in the case of Lake Opasatica and Lake Vaudray, where predicted WHAM values were one order of magnitude higher than the experimentally determined values. However, at high concentrations of total dissolved cadmium for Lake Dufault and Lake Osisko, there was a good agreement between the predicated free Cd^{2+} ion concentrations and the experimentally determined values, and there was not a significant difference between the free Cd^{2+} ion concentrations predicted by either WHAM V or VI. Table 14 shows the comparison between the experimentally determined free Cd^{2+} ion concentrations using CLEM/DPASV and WHAM models V and VI for the lake water samples collected in August 2001 from the Rouyn-Noranda mining area. It is clear from Table 14 that WHAM V and VI slightly over-predicted the free Cd^{2+} ion concentrations relative to the experimental values obtained using CLEM/DPASV. Such slight differences between the experimental values and the predicted values were to be expected in light of the various assumptions (especially the equilibrium assumption) of the two models as well as the assumptions made in the kinetic model. To see what role the percentage of active DOC (assumed as 50% for the model-calculations) in the freshwater samples plays in the over-estimation of the free $[\text{Cd}^{2+}]$ by the models, a WHAM calculation was done using 100% DOC as active DOC instead of 50% DOC and the results are shown in Table 15.

Table 13

Experimental values of the free Cd^{2+} ion concentrations and those predicted by WHAM models V and VI, for the lake water samples collected in June 2001.

Lake	[Cd] _{total} , M	[Cd ²⁺], M	[Cd ²⁺], M	[Cd ²⁺], M
		CLEM/DPASV*	WHAM V	WHAM VI
Dufault	8.0×10^{-9}	2.7×10^{-9}	6.9×10^{-9}	6.6×10^{-9}
Osisko	1.8×10^{-9}	6.0×10^{-10}	1.1×10^{-10}	1.2×10^{-9}
Vaudray	8.9×10^{-10}	5.7×10^{-11}	6.9×10^{-10}	6.9×10^{-10}
Opasatica	8.9×10^{-10}	4.0×10^{-11}	7.4×10^{-10}	6.0×10^{-10}

* the $[\text{Cd}^{2+}]$ values were determined by CLEM/DPASV.

- $[\text{Cd}]_{\text{total}}$ determined by ICP-MS.
- 50% DOC was used in the WHAM calculations.
- Al(III) and Fe(III) were included in the WHAM calculations.

Table 14

Experimental values of the free Cd^{2+} ion concentrations and those predicted by WHAM models V and VI, for the lake water samples collected in August 2001.

Lake	$[\text{Cd}]_{\text{total}}, \text{M}$	$[\text{Cd}^{2+}], \text{M}$	$[\text{Cd}^{2+}], \text{M}$	$[\text{Cd}^{2+}], \text{M}$
		CLEM/DPASV*	WHAM V	WHAM VI
Dufault	2.7×10^{-9}	1.1×10^{-10}	2.7×10^{-9}	2.7×10^{-9}
Osisko	1.8×10^{-9}	1.5×10^{-10}	8.7×10^{-10}	1.2×10^{-9}
Opasatica	8.9×10^{-10}	3.5×10^{-10}	5.9×10^{-10}	4.5×10^{-10}

* the $[\text{Cd}^{2+}]$ values were determined by CLEM/DPASV.

- $[\text{Cd}]_{\text{total}}$ determined by ICP-MS.
- 50% DOC was used in the WHAM calculations.
- Al(III) was included in the WHAM calculations.

Table 15

Experimental values of the free Cd^{2+} ion concentrations and those predicted by WHAM models V and VI (100% DOC) for the lake water samples collected in August 2001.

Lake	[Cd] _{total} , M	[Cd ²⁺], M	[Cd ²⁺], M	[Cd ²⁺], M
		CLEM/DPASV*	WHAM V	WHAM VI
Dufault	2.7×10^{-9}	1.1×10^{-10}	2.7×10^{-9}	2.7×10^{-9}
Osisko	1.8×10^{-9}	1.5×10^{-10}	5.7×10^{-10}	9.0×10^{-10}
Opasatica	8.9×10^{-10}	3.5×10^{-10}	4.4×10^{-10}	2.5×10^{-10}

- * the $[\text{Cd}^{2+}]$ values were determined by CLEM/DPASV.
- $[\text{Cd}]_{\text{total}}$ determined by ICP-MS.
- 100% DOC was used in the WHAM calculations.
- Al(III) was included in the WHAM calculations.

There was no significant difference between the predicted free Cd^{2+} ion concentrations using WHAM Model V and VI when 100% DOC and 50% DOC was used. This leads to the question: “*Do the WHAM predictions generally over predict the free Cd^{2+} ion concentrations?*”. Bryan et al. [8] mentioned that the WHAM model was optimized to fit the data assuming that all binding by DOC was due by FA and there is an approximate 2:1 relationship between the optimized [FA] and [DOC]. They assumed that if Dissolved Organic Matter (DOM) is 50% carbon, then this ratio of 2:1 would suggest that 100% of the DOM behaves like isolated humic substances (HS). This was a reasonable hypothesis since the natural waters studied were from upland areas, where the major source of carbon is from humified material. They [8] concluded earlier that WHAM model V over estimated the free Cu^{2+} ions in natural water samples, especially at low total Cu concentrations. Table 16 shows a comparison between the experimentally determined free Cd^{2+} ion concentrations using CLEM/DPASV and those predicted by WHAM model V and VI for the lake water samples collected in July 2002 and August 2002 from the Rouyn-Noranda mining area. Table 16 shows that the predicted free Cd^{2+} ion concentrations using WHAM Model V and VI are higher than the experimentally determined values obtained by CLEM/DPASV.

In summary, it seems that in order to apply the models WHAM V and VI to freshwater samples and compare the WHAM-predicted values with those obtained experimentally, it is important to take into consideration the uncertainties inherent in the input data, and also the assumptions made in deriving the Equilibrium Model (DPASV/CLEM) adopted for the experimental determination, and how far these assumptions are valid in the case of the freshwater samples investigated.

Table 16

Experimental values of the free Cd^{2+} ion concentrations and those predicted by WHAM models V and VI for the lake water samples collected in June and August 2002.

Sample	[Cd] _{total} , M	[Cd ²⁺], M	[Cd ²⁺], M	[Cd ²⁺], M
		CLEM/DPASV*	WHAM V	WHAM VI
Dufault August 2002	2.6×10^{-9}	3.3×10^{-11}	2.4×10^{-9}	2.2×10^{-9}
Dufault July 2002	3.2×10^{-9}	4.5×10^{-10}	2.6×10^{-9}	2.2×10^{-9}
Opasatica August 2002	5.1×10^{-11}	7.8×10^{-13}	3.9×10^{-11}	2.3×10^{-11}
Opasatica July 2002	1.9×10^{-10}	1.2×10^{-11}	1.2×10^{-10}	7.4×10^{-11}

- * the $[\text{Cd}^{2+}]$ values were determined by CLEM/DPASV.
- $[\text{Cd}]_{\text{total}}$ determined by ICP-MS.
- 50% DOC was used in the WHAM calculations.
- Al(III) and Fe(III) were included in the WHAM calculations.

Experimental measurements, particularly those of solid-phase compounds, are operationally-defined and may not necessarily reflect the amounts of “active” binding species in the real system [4]. However, despite the fact that the WHAM Models slightly over-predicted the free Cd^{2+} ion concentrations in the lake water samples, they still provide a good approximation of the free Cd^{2+} ion concentrations in freshwaters.

van den Berg/ Ružić Method

Another way to test the validity of the cadmium speciation parameters (conditional stability constants, natural ligand concentrations, and free cadmium ion concentrations) that had been determined experimentally using the CLEM/DPASV and the FITEQL modeling program is to calculate the same speciation parameters using the van den Berg/Ružić [9,10] Method, which can be summarized as follows:

the conditional stability constant, K_{ML} , relates to the following equilibrium:

$$K_{\text{CdL}} = [\text{CdL}]/[\text{Cd}^{2+}][\text{L}] \quad (5.1)$$

where

$[\text{Cd}^{2+}]$ = concentration of uncomplexed Cd ion.

$[\text{CdL}]$ = concentration of the Cd complexed by organic complexing ligand L.

$[\text{L}]$ = concentration of the uncomplexed organic ligand.

K_{CdL} = conditional stability constant for the Cd organic ligand complex.

C_{L} is total concentration of the organic ligand L, given by

$$C_{\text{L}} = [\text{CdL}] + [\text{L}] \quad (5.2)$$

Substitution in Eq. (5.1) for [L] using Eq. (5.2) and rearrangement yields the following relationship:

$$[\text{Cd}^{2+}]/[\text{CdL}] = (1/C_L) [\text{Cd}^{2+}] + (1/K_{\text{CdL}}C_L) \quad (5.3)$$

In the presence of an added competing ligand (EN), ligand competition takes place and the metal becomes distributed between the added and the natural organic ligands present in the sample solution – the distribution being as follows:

$$C_{\text{Cd}} = \sum [\text{Cd-EN}] + [\text{Cd}'] + \sum [\text{CdL}] \quad (5.4)$$

where C_{Cd} = total Cd concentration.

$\sum [\text{Cd-EN}]$ = concentration of the Cd complexed by the competing ligand EN.

$[\text{Cd}']$ = concentration of the Cd complexed by inorganic ligands.

$\sum [\text{CdL}]$ = concentration of the Cd complexed by the organic complexing ligand L.

The concentration of labile Cd ion is that which equilibrates with the added ligand (EN) and is measured by DPASV. Thus, the labile $[\text{Cd}^{2+}]$ concentration is

$$[\text{Cd}^{2+}] = [\text{Cd-EN}] + [\text{Cd}'] \quad (5.5)$$

and

$$[\text{Cd}^{2+}] = i_p / \alpha S \quad (5.6)$$

$$[\text{CdL}] = C_{\text{Cd}} - i_p / S \quad (5.7)$$

where i_p is the current peak height, S is the sensitivity (peak current/[M]) of the DPASV technique, and α is the combined alpha-coefficient of M, for the metal side-reactions as follows:

$$\alpha_{Cd} = 1 + \sum (K_j^* [L_j]^j) + \sum (K_{a,i}^* / [H^+]^i) \quad (5.8)$$

where K_j^* is the stepwise stability constant for the complex of Cd with ligand L_j (Cl^- , CO_3^{2-} , $B(OH)_4^-$ or SO_4^{2-}), and $K_{a,i}^*$ is the stepwise acidity constant of Cd. These constants are valid at the specified ionic strength and for the free hydrogen ion scale [11].

Substitution of the appropriate terms in Eq. (5.3) yields the following relationship:

$$i_p / (S \cdot C_{Cd} - i_p) = (i_p / S) \cdot (1 / C_L) + \alpha / K_{CdL} C_L \quad (5.9)$$

The concentration of $[CdL]$ and $[Cd^{2+}]$ can be calculated from Equations (5.6) and (5.7), respectively. A plot of $i_p / (S \cdot C_{Cd} - i_p)$ as a function of i_p / S (i.e. $[Cd^{2+}] / [CdL]$ as a function of $[Cd^{2+}]$) gives a straight line, and C_L and K_{CdL} can be obtained from the slope and the y-intercept, respectively.

Figure 15 and Figure 16 show the plots of $[Cd^{2+}] / [CdL] = f[Cd^{2+}]$ obtained for Cd in the lake water samples collected in July 2002 and August 2002 from the Rouyn-Noranda mining area, respectively. The values of $\log K_{CdL}$ were calculated from the intercept of the linear regressions applied on these plots and the concentrations of the uncomplexed organic ligand $[L]$ were calculated from the slope. Table 17 and Table 18 show the comparison between the Speciation Parameters that had been calculated using the FITEQL program and the van den Berg/Ružić Method for the lake water samples collected in July 2002 and August 2002, respectively. The high value of the correlation coefficient (R^2) indicated good agreement between the experimental data points and showed validity of the van den Berg/Ružić Method and its applicability to natural systems. Table 5 and Table 6 show that there is a good agreement between the results calculated using the FITEQL program and those calculated using the van den Berg/Ružić

Figure 15

Plots of $[Cd^{2+}]/[CdL]$ vs. $[Cd^{2+}]$ obtained for Cd in the presence of 1mM EN, determined by CLEM/DPASV, in the lake water samples (collected in July 2002) from the Rouyn-Noranda mining area. The dashed line represents the fitting line obtained by the van den Berg/Ružić Method.

Table 17

Cadmium speciation and complexation parameters in the two lake-water samples, collected in July 2002, determined by CLEM/DPASV at SMDE, with EN as the competing ligand, at pH 8.0 (HEPES/NaOH), and constant ionic strength (0.04 M); temperature 298 K. Comparison between FITEQL Program and van den Berg / Ružić Method.

Sample name	[Cd] _{total} , M	[Cd] _{free} , M		Log K _{CdL}		[L], mole/L	
		FITEQL Program	van den Berg / Ružić Method	FITEQL Program	van den Berg / Ružić Method	FITEQL Program	van den Berg / Ružić Method
Dufault	32×10^{-10}	$(4.5 \pm 1.5) \times 10^{-10}$	$(7.2 \pm 0.2) \times 10^{-10}$	8.7 ± 0.1	8.5 ± 0.2	$(9.0 \pm 0.6) \times 10^{-9}$	$(20 \pm 0.07) \times 10^{-9}$
Opasatica	1.9×10^{-10}	$(12 \pm 0.01) \times 10^{-12}$	$(1.8 \pm 1.2) \times 10^{-12}$	9.5 ± 0.6	9.3 ± 0.6	$(6.8 \pm 0.1) \times 10^{-9}$	$(6.6 \pm 3.1) \times 10^{-9}$

- The uncertainties represent 95.5 % confidence limits for n replicate experiments (n=3)
- All the above samples were filtered through 0.45µm filter (Gelman Material No. 63077).
- [Cd]_{total} was determined by Inductively Coupled Plasma-Mass Spectrometry.
- K_{CdL} is the conditional stability constant of CdL.
- [L] = natural ligand concentration.

Figure 16

Plots of $[Cd^{2+}]/[CdL]$ vs. $[Cd^{2+}]$ obtained for Cd in the presence of 1mM EN, determined by CLEM/DPASV, in the lake water samples (collected in August 2002) from the Rouyn-Noranda mining area. The dashed line represents the fitting line obtained by the

van den Berg/Ružić Method.

Table 18

Cadmium speciation and complexation parameters in the two lake-water samples, collected in August 2002, determined by CLEM/DPASV at SMDE, with EN as the competing ligand, at pH 8.0 (HEPES/NaOH), and constant ionic strength (0.04 M); temperature 298 K. Comparison between FITEQL Program and van den Berg / Ružić Method.

Sample name	[Cd] _{total} , M	[Cd] _{free} , M		Log K _{CdL}		[L], mole/L	
		FITEQL Program	van den Berg / Ružić Method	FITEQL Program	van den Berg / Ružić Method	FITEQL Program	van den Berg / Ružić Method
Dufault	26×10^{-10}	$(3.3 \pm 5.4) \times 10^{-11}$	$(0.5 \pm 5.4) \times 10^{-11}$	10.0 ± 0.8	9.7 ± 0.7	$(1.2 \pm 0.01) \times 10^{-8}$	$(1.7 \pm 0.04) \times 10^{-8}$
Opasatica	0.5×10^{-10}	$(7.8 \pm 3.2) \times 10^{-13}$	$(7.1 \pm 8.0) \times 10^{-16}$	10.3 ± 0.4	10.3 ± 0.1	$(4.4 \pm 2.4) \times 10^{-9}$	$(6.8 \pm 0.2) \times 10^{-9}$

- The uncertainties represent 95.5 % confidence limits for n replicate experiments (n=3)
- All the above samples were filtered through 0.45µm filter (Gelman Material No. 63077).
- [Cd]_{total} was determined by Inductively Coupled Plasma-Mass Spectrometry.
- K_{CdL} is the conditional stability constant of CdL.
- [L] = natural ligand concentration.

Method, especially when cadmium was presents in high concentrations. The free Cd^{2+} ion concentrations calculated using the van den Berg/Ružić Method were mostly underestimated, especially at very low concentrations of total dissolved cadmium, as in the case of samples from Lake Opasatica. However, the calculated conditional stability constants, K_{CdL} , and natural ligand concentration, $[\text{L}]$, obtained by using the van den Berg/Ružić Method were within the experimental error of the CLEM/DPASV Method, and the FITEQL program.

The above results suggest that the speciation parameters for cadmium in the freshwater samples can be satisfactorily determined using CLEM/DPASV and the FITEQL program, as well as by the van den Berg/Ružić Method.

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CHAPTER 6

SIMULTANEOUS DETERMINATION AND SPECIFICATION OF Zn, Cd, Pb and Cu IN AQUEOUS SAMPLES BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY

Introduction

Toxic and persistent substances in the environment continuously increase owing to anthropogenic activities. In particular, rapid increase of potentially toxic metals, such as zinc, cadmium, lead and copper as environmental contaminants, has called for attention to their determination at trace and ultra trace levels [1,2] and especially for their speciation [3-5]. There is an increased need to determine the concentration of trace metals in environmental aqueous samples simultaneously and rapidly. Together with numerous sample treatment procedures [6,7], several methods have been described for simultaneous metal determination at low concentrations [1,2], although spectroscopic [8,9] and voltammetric [10,11] techniques have been the most frequently employed. In particular, voltammetric methods are a valid and effective option in the multicomponent analysis of metals because of their high sensitivity and selectivity [10-12].

The first objective of the research work was to develop and validate analytical methods for simultaneous determination of the total dissolved concentrations of the trace metals, namely Zn(II), Cd(II), Pb(II), and Cu(II), in samples of lake water and soil solutions using Inductively Coupled Plasma–Mass Spectrometry (ICP-MS) and Differential Pulse Anodic Stripping Voltammetry (DPASV), as well as different pre-treatment procedures, such as acidification and ultra-violet (UV) irradiation. The second objective was to develop and validate analytical methods for determination of chemical speciation of Zn(II), Cd(II), Pb(II), and Cu(II) in environmental aqueous samples by determining the ASV-labile fraction of the trace metals.

Experimental

The experimental procedures described in Chapter 4 were followed except those for sample pre-treatment and the voltammetric analysis, which are described below.

Sample pre-treatment procedures

UV irradiation

For total metal determination, quartz UV digestion tubes were used for holding the aqueous samples. The soil solutions and the lake water samples were irradiated continuously for 6 hours using 400 W medium-pressure Hg lamps, (Ultra-Violet Photo-Oxidation Unit, La Jolla Scientific Co., California, USA).

Sample Acidification

Prior to analysis, the soil solutions and the lake water samples were acidified with ultrapure nitric acid (Seastar, Canada) to pH 1.5, in order to preserve the integrity of samples.

Voltammetric analysis

For the voltammetric analysis of Zn(II), Cd(II), Pb(II), and Cu(II), Differential Pulse Anodic Stripping Voltammetry (DPASV) was used with a Hanging Mercury Drop Electrode (HMDE), a Ag/AgCl reference electrode, and a platinum counter electrode held on a Metrohm VA663 stand, and an Autolab PGSTAT12 potentiostat/galvanostat (Eco Chemie, The Netherlands). The samples were purged for 5 min. with ultra-high purity nitrogen gas immediately prior to analysis. The trace metals were preconcentrated by electrodeposition on the surface of the hanging mercury drop using a deposition potential of -1.2 V versus Ag/AgCl. The experimental parameters were as follows: initial

potential = -1.2 V, final potential = -0.2 V, pulse height = 50 mV, scan rate = 10 mV/s. The stripping peak for the labile zinc occurred from -1.00 to -0.93 V, labile cadmium from -0.61 to -0.58 V, labile lead from -0.41 to -0.38 V, and finally, labile copper from -0.01 to +0.01 V. All potentials mentioned above were measured versus Ag/AgCl.

Voltammetric procedure

10 mL of the aqueous sample was transferred to a 50 mL screw-top, Teflon cup (Savalex, USA), then buffered with 0.04 M acetic acid (using a stock solution of 2 mol/L acetic acid), and the pH was adjusted to 4.80 ± 0.05 using sodium acetate (2 mol/L sodium acetate stock solution). The analysis was performed on the acidified or UV-irradiated sample. The total dissolved trace metal concentrations were determined using the standard addition method. Prior to the determination, the solutions were purged for 5 minutes with ultra-high purity nitrogen gas.

Results and discussion

Preliminary studies

Deposition potential

The selection of the deposition potential for the simultaneous determination of all four trace metals (Zn, Cd, Pb and Cu) under investigation was determined by the metal that has the most negative peak potential (zinc at -0.98 V). Figure 17 shows the effect of deposition potential on the peak height of the four trace metals under investigation. The zinc signal increased as the deposition potential was made more negative. At the same time, the copper signal decreased slightly as the deposition potential was made

Figure 17

Effect of deposition potential on peak height for Zn, Cd, Pb and Cu.

more negative, whereas the peak height for cadmium and lead tended to be steady. A deposition potential of -1.2 V was therefore chosen for the four trace metals.

The effect of pH on the metal speciation

MINQEL (a Chemical Equilibrium Program) [13] was used to predict the equilibrium speciation of the four trace metals at different pH values. The results are presented in Figure 18, which shows that the % concentration of Cu^{2+} (aqua complex) decreased dramatically because of the formation of Cu(II)-inorganic complexes with CO_3^{2-} , SO_4^{2-} , Cl^- , and OH^- anions as the pH was increased from 6 to 7 [14]. The same effect was found for Zn(II), Pb(II) and Cd(II), but at higher pH values. For this reason, most of the experiments in this chapter were carried out at pH 4.8 (using acetic acid/sodium acetate buffer) to decrease the formation of the inorganic complexes.

Formation of intermetallic compounds

One of the serious problems associated with the simultaneous determination of trace metals ions is the formation of intermetallic compounds such as the formation of Cu-Zn intermetallic compounds [14-19] which may modify the relative peak currents and potentials of these trace metals with respect to those in the absence of this interference. Intermetallic compound formation is an equilibrium reaction, the importance of which increases with increasing metal concentrations in Hg and is expected to increase when passing from the hanging mercury drop to the Hg film electrode and to the Hg microelectrode [14]. To determine if there are any intermetallic effects among the four

Figure 18

The equilibrium distribution of the Cu(II)-, Zn(II)-, Pb(II)-, and Cd(II)- species as a function of pH. The metals were studied one at a time.

(○), Cu²⁺, (△), Pb²⁺, (▽), Zn²⁺, and (□), Cd²⁺

[Cu] = 10 nM, [Zn] = 100 nM, [Pb] = 5 nM, and [Cd] = 1 nM.

trace metals, simultaneous deposition for periods varying from 1 to 12 minutes was studied. The slopes of the test solution of Zn(II) (1×10^{-7} M), Cd(II) (1×10^{-9} M), Pb(II) (5×10^{-9} M) and Cu(II) (5×10^{-8} M) in their simultaneous determination were 0.040, 0.00027, 0.0014 and 0.0075 ($\mu\text{A min}^{-1}$), respectively. When test solutions containing each of the trace metals alone of the same concentrations were studied, the slopes for these solutions were 0.056 $\mu\text{A min}^{-1}$ for Zn(II), 0.00031 $\mu\text{A min}^{-1}$ for Cd(II), 0.0029 $\mu\text{A min}^{-1}$ for Pb(II), and 0.0057 $\mu\text{A min}^{-1}$ for Cu(II). The slope values obtained are representative of the sensitivity of this technique for each metal. The above differences in the slopes for the four trace metals indicates that the intermetallic effects were slight, especially between Zn(II) and Cu(II) as they were present in low concentrations in the test solutions. This may have resulted in minor over-estimation of copper concentrations determined by DPASV using a static mercury drop electrode (SMDE) .

UV Irradiation

It is well known that trace metals are complexed by organic ligands in freshwaters. The metal complexation by organic ligands causes those metals to be non-labile in their voltammetric determination. Dissolved Organic Matter (DOM) can affect the voltammetric signals as it acts as a surfactant, causing a decrease in the accessibility of the trace metals ions to the mercury drop electrode. Hence, removal of DOM from samples is preferable. UV- irradiation of the water samples prior to trace metals determination is considered a preferable approach for break-down of the metal-DOM complexes [20-28]. UV digestion is a clean sample preparation method, as it does not require the addition of any reagents, and it is very effective. Figure 19 presents the

effect of the UV-irradiation on an Open Field sample, Site No. 3, collected from the Sudbury area in November 2001. The sample was UV-irradiated for time periods of 1, 2, 3, 4, 5, 6, 7, and 8 hours, and the stripping peak current due to cadmium was measured using DPASV. Figure 19 shows that an increase in the irradiation time increased the peak current as a result of the break-down of cadmium-DOM complexes, and the release of labile Cd(II) species. The stripping peak current became nearly constant after 5 hours of UV-irradiation, which suggested that the break-down of most of the Cd organic complexes and the release of most of the Cd(II) ions from its complexes had reached their maximum limits at that time. Hence, 6 hours of UV-irradiation was adopted for digestion of water samples prior to the determination of the total dissolved trace metal concentration using DPASV.

In this work, three separate analytical procedures were used with the aqueous samples to determine the concentrations of dissolved trace metals, Zn, Cd, Pb, and Cu. The analytical procedures were: ICP-MS with the solution-nebulization procedure; Acid-DPASV, in which the sample was acidified to pH 1.3 with HNO₃, followed by measurement using DPASV; and UV-DPASV, in which the sample was UV-irradiated for 6 hours, followed by measurement using DPASV. The ICP-MS procedure is dependent on rigorous calibration for its accuracy. However, this rigorous calibration could not be done for these samples, as the ICP-MS was used for these samples as a part of the routine analysis program of the Geological Survey of Canada which owned and operated the instrument. Therefore, not much can be said with certainty about the accuracy of the ICP-MS results of these samples.

Figure 19

Effect of the UV-irradiation on the stripping peak current of cadmium in a water sample: Open Field sample, Site No.3, collected from the Sudbury area in November 2001.

DPASV results are generally reliable in terms of accuracy and precision, but this reliability is dependent on the sample integrity as elaborated below. In this work, the samples were studied by DPASV after they were subjected to two alternative sample-treatment procedures, both of which were designed to break down the metal-organic complexes in order to release 100% of the organic-bound metal as free metal for quantification by DPASV. Of the two sample-treatment procedures adopted for the above purpose, the one in which the sample is treated with HNO_3 to make its pH 1.5, should be able to break down the metal-organic complexes and to release 100% of the metal for the DPASV quantification. Hence, this procedure is likely to be the more reliable in terms of accuracy and precision. The alternative procedure of UV-irradiation to break down the metal-organic complexes to release 100% of the metal as free metal is not free from pitfalls, as can be suspected from Figure 19, which shows that the peak-height signal levels off at times longer than 5 hours of UV-irradiation. However, in Figure 19, this leveling-off of the peak-height signal cannot be interpreted as the release of 100% of the organically-bound Cd metal. For Figure 19, there was no easy way to prepare a CONTROL sample for the complete (100%) release of the organically-bound Cd, and hence, there was no such CONTROL sample of Cd. This uncertainty about the complete (100%) release of the bound metal is the Achilles' heel of the UV-irradiation procedure, which makes it the least reliable of the three analytical procedures adopted in this work for the determination of dissolved trace metal concentrations in aqueous samples.

Analytical parameters

To evaluate the use of DPASV in simultaneous determination of the concentrations of Zn, Cd, Pb, and Cu in water samples, some analytical parameters such as detection limits, accuracy and precision were determined. The detection limits, defined as the concentration that gave a signal three times the standard deviation of the blank signal, were calculated from the slopes of the standard addition curves, and the results are presented in Table 19. The Coefficients of Linear Regression (R^2) were good ($R^2 > 0.98$), and the precision of the method, expressed as % Relative Standard Deviation (%RSD), was satisfactory. The limits of detection (LOD) for the four trace metals were found to be lower than the total dissolved trace metal concentration present in the water samples. The DPASV was used for the simultaneous determination of Zn, Cd, Pb, and Cu in the SLRS-4 Certified Reference Material (Riverine Water for Trace Metals prepared by NRC, Canada), and the results are presented in Table 20. The total dissolved trace metal concentration determined by DPASV was very close to the certified values of SLRS-4, and the % recovery was 98% to 103%. This indicates that DPASV can be used satisfactorily for the simultaneous determination of the total dissolved Zn, Cd, Pb, and Cu with satisfactory accuracy and precision.

Simultaneous determination of the concentrations of Zn, Cd, Pb, and Cu, in soil solutions and lake water samples

DPASV was applied for the simultaneous determination of the concentrations of dissolved Zn, Cd, Pb, and Cu in soil solutions, collected from Sudbury area in May 2002. Figure 20 shows the voltammogram of Zn, Cd, Pb, and Cu standard additions to the soil

Table 19

Figures of Merit: Limit of Detection (LOD), Relative Standard Deviation (%RSD), and Coefficient of Linear Regression (R^2) for Zn, Cd, Pb, and Cu, determined by DPASV with a deposition time 10 min and pH 4.8 (acetic acid/sodium acetate buffer).

Metal	Slope (Sensitivity) (amp./ mole L⁻¹)	LOD (mole L⁻¹)	RSD (%)	R²
Zn	3.038	9.52×10^{-10}	2.76	0.982
Cd	2.253	2.38×10^{-11}	11.2	0.990
Pb	2.262	2.88×10^{-10}	7.19	0.982
Cu	1.981	3.44×10^{-10}	8.49	0.995

Table 20

Recovery of the SLRS-4 Certified Reference Material, determined by DPASV with a deposition time 5.0 min and pH 4.8 (acetic acid/sodium acetate buffer).

	Zn	Cd	Pb	Cu
	µg/L	µg/L	µg/L	µg/L
SLRS-4 (certified values)	0.930 ± 0.10	0.0120 ± 0.002	0.0860 ± 0.007	1.81 ± 0.08
DPASV	0.938 ± 0.10	0.0124 ± 0.002	0.0848 ± 0.002	1.861 ± 0.06
% Recovery	100.8	103.4	98.6	102.9
R²	0.977	0.979	0.993	0.991

- The uncertainty represents 95.5% confidence limits, i.e. 2 x standard deviation of n replicates (n = 3) for the DPASV determinations.

Figure 20

DPASV voltammograms of Zn, Cd, Pb, and Cu standard additions to the soil solution sample (Minerals 1), collected from Sudbury mining area, in May 2002.

solution sample (Minerals 1), collected from the Sudbury mining area in May 2002, and the response of the stripping peak current after each standard addition. Table 21 presents the concentrations of dissolved trace metals determined by ICP-MS and DPASV (after acidification to pH 1.5 using HNO₃ and UV-irradiation for 6 hrs, separately). Table 21 shows that the agreement between the ICP-MS and DPASV was generally satisfactory.

The dissolved trace metal concentrations were determined in lake water samples collected from the Rouyn-Noranda mining area in August 2002 (Lake Dufault and Lake Opasatica) using DPASV (after acidification to pH 1.5 using HNO₃ and UV-irradiated for 6 hrs, separately). The results are presented in Table 22, which shows that the dissolved trace metal concentrations determined using DPASV were close to the values determined using ICP-MS (within the experimental error), especially in the case of Zn and Cu, which were present in Lake Dufault and Lake Opasatica in relatively high concentrations. The ICP-MS value for Pb concentration in the Lake Opasatica water sample was lower than those of ACID-DPASV and UV-DPASV. For reasons given earlier, this ICP-MS result should be rejected.

Simultaneous determination of the speciation of Cd(II), Cu(II), Zn(II), and Pb(II) using DPASV

ASV is considered one of the important techniques that can be used to determine the speciation of the “toxic fraction” of a metal in a water sample. The toxic fraction of a metal is defined [29-32] as the fraction of the total dissolved metal concentration that

Table 21

Comparison of the dissolved trace metals concentrations determined by ICP-MS and DPASV in soil solutions samples, collected from Sudbury area in May 2002.

Sample	Metal	ICP-MS	Acid-DPASV _{pH=1.5}	UV-DPASV _{pH=4.8}
Organic 1	Zn	$(2.06 \pm 0.2) \times 10^{-7}$	$(3.31 \pm 0.3) \times 10^{-7}$	$(2.40 \pm 0.2) \times 10^{-7}$
	Cd	$(5.45 \pm 0.4) \times 10^{-10}$	$(11.9 \pm 0.9) \times 10^{-10}$	$(6.19 \pm 0.1) \times 10^{-10}$
	Pb	$(1.16 \pm 0.2) \times 10^{-8}$	$(1.95 \pm 0.1) \times 10^{-8}$	$(1.28 \pm 0.1) \times 10^{-8}$
	Cu	$(7.81 \pm 0.3) \times 10^{-7}$	$(14.9 \pm 2.0) \times 10^{-7}$	$(10.6 \pm 4.0) \times 10^{-7}$
Organic 2	Zn	$(1.33 \pm 0.1) \times 10^{-6}$	$(0.216 \pm 0.2) \times 10^{-6}$	$(2.49 \pm 0.2) \times 10^{-6}$
	Cd	$(1.53 \pm 0.1) \times 10^{-9}$	$(2.65 \pm 0.3) \times 10^{-9}$	$(9.21 \pm 0.2) \times 10^{-10}$
	Pb	$(5.05 \pm 0.1) \times 10^{-8}$	$(6.20 \pm 0.2) \times 10^{-8}$	$(4.85 \pm 0.3) \times 10^{-8}$
	Cu	$(9.76 \pm 0.2) \times 10^{-7}$	$(53.2 \pm 1.0) \times 10^{-7}$	$(12.1 \pm 3.0) \times 10^{-7}$
Minerals 1	Zn	$(1.07 \pm 0.1) \times 10^{-6}$	$(1.70 \pm 0.1) \times 10^{-6}$	$(1.92 \pm 0.2) \times 10^{-6}$
	Cd	$(8.56 \pm 0.3) \times 10^{-9}$	$(8.98 \pm 0.2) \times 10^{-9}$	$(11.4 \pm 3.0) \times 10^{-9}$
	Pb	$(1.49 \pm 0.2) \times 10^{-7}$	$(2.22 \pm 0.1) \times 10^{-7}$	$(2.28 \pm 0.2) \times 10^{-7}$
	Cu	$(4.83 \pm 0.3) \times 10^{-7}$	$(6.47 \pm 0.2) \times 10^{-7}$	$(9.10 \pm 0.2) \times 10^{-7}$
Minerals 2	Zn	$(5.37 \pm 0.3) \times 10^{-6}$	$(1.34 \pm 0.2) \times 10^{-6}$	$(13.0 \pm 5.0) \times 10^{-6}$
	Cd	$(2.50 \pm 0.1) \times 10^{-9}$	$(3.23 \pm 0.3) \times 10^{-9}$	$(3.21 \pm 0.3) \times 10^{-9}$
	Pb	$(8.66 \pm 0.2) \times 10^{-10}$	$(11.7 \pm 3.0) \times 10^{-10}$	$(12.9 \pm 1.0) \times 10^{-10}$
	Cu	$(7.16 \pm 0.3) \times 10^{-8}$	$(5.46 \pm 0.2) \times 10^{-8}$	$(15.0 \pm 4.0) \times 10^{-8}$

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- All the above samples were filtered through 0.45µm filter (Gelman No. 63077).
- Acid-DPASV: the sample was acidified to pH 1.5 using HNO₃, followed by DPASV.
- UV-DPASV: The sample was UV-irradiated for 6 hours, followed by DPASV.
- all the concentrations are expressed in molar concentrations.

Table 22

Comparison of the dissolved trace metals concentrations determined by ICP-MS and DPASV in lake water samples, collected in August 2002.

Sample	Metal	ICP-MS	Acid-DPASV _{pH=1.5}	UV-DPASV _{pH=4.8}
Lake Dufault	Zn	$(5.50 \pm 0.1) \times 10^{-7}$	$(0.840 \pm 0.04) \times 10^{-7}$	$(4.94 \pm 0.2) \times 10^{-7}$
	Cd	$(2.58 \pm 0.3) \times 10^{-9}$	$(1.25 \pm 0.1) \times 10^{-9}$	$(3.39 \pm 0.2) \times 10^{-9}$
	Pb	$(1.45 \pm 0.1) \times 10^{-10}$	$(5.36 \pm 0.2) \times 10^{-10}$	$(6.79 \pm 0.1) \times 10^{-10}$
	Cu	$(2.32 \pm 0.1) \times 10^{-7}$	$(12.9 \pm 3.0) \times 10^{-7}$	$(1.04 \pm 0.3) \times 10^{-7}$
Lake Opasatica	Zn	$(4.01 \pm 0.1) \times 10^{-8}$	$(8.26 \pm 0.1) \times 10^{-8}$	$(4.16 \pm 0.2) \times 10^{-8}$
	Cd	$(0.45 \pm 0.01) \times 10^{-10}$	$(7.42 \pm 1.5) \times 10^{-10}$	$(6.07 \pm 0.8) \times 10^{-10}$
	Pb	$(0.10 \pm 0.01) \times 10^{-9}$	$(2.08 \pm 0.9) \times 10^{-9}$	$(2.53 \pm 1.3) \times 10^{-9}$
	Cu	$(4.58 \pm 0.2) \times 10^{-8}$	$(5.27 \pm 0.4) \times 10^{-8}$	$(3.36 \pm 0.4) \times 10^{-8}$

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- All the above samples were filtered through 0.45µm filter (Gelman No. 63077).
- Acid-DPASV: the sample was acidified to pH 1.5 using HNO₃, followed by DPASV.
- UV-DPASV: The sample was UV-irradiated for 6 hours, followed by DPASV.
- all the concentrations are expressed in molar concentrations.

is toxic to a living organism. ASV can determine not only the total dissolved metal concentrations, but also the ASV-labile metal, which is the fraction of the total dissolved metal concentration that is determined by using a particular set of ASV and solution conditions. The ASV-labile fraction of the dissolved metal is equal to the electroactive fraction of the metal, i.e., the fraction of metal that dissociates from complexes and is deposited into the electrode during the deposition step of ASV [32].

Two different methods were applied in order to determine the ASV-labile fraction. The first method used was the conventional ASV, one-point calibration curve, in which the ASV-labile fraction was quantified using peak-height calibration of solutions of salts of Zn(II), Cd(II), Pb(II), and Cu(II) in the same background electrolyte solution (acetic acid/acetate buffer and KNO₃) [33]. The second method is UV-DPASV which involves the comparison between the DPASV peak height before and after UV-irradiation of the sample for 6 hours [34].

ASV-labile fractions of Zn(II), Cd(II), Pb(II), and Cu(II) were determined in soil solutions, collected in May 2002, from the Sudbury area. The results are presented in Table 23, which shows the concentrations for the four trace metals in two different samples of soil solutions: the organic soil solution, which was used for monitoring the metal input to the sites (through the use of zero-tension lysimeters installed below the forest floor at 0 cm), and the mineral soil solution which was used for monitoring the metal output (through the use of zero-tension lysimeters installed below the forest floor at 30 cm). Table 23 shows that the dissolved metal concentrations for the two mineral samples (metal output) were very high compared with the total dissolved metal concentrations for the two organic samples (metal input).

Table 23

ASV-labile fraction determined by conventional DPASV and after UV-irradiation in soil solution water samples, collected from Sudbury area in May 2002.

Sample	DOC, mg/L	Metal	[M] _{total}	ASV-LABILE	
				UV-DPASV	Conventional DPASV
Organic 1	12.9	Zn (II)	$(2.06 \pm 0.2) \times 10^{-7}$	$(1.28 \pm 0.4) \times 10^{-7}$	$(1.11 \pm 0.4) \times 10^{-7}$
		Cd(II)	$(5.45 \pm 0.4) \times 10^{-10}$	$(14.0 \pm 3.0) \times 10^{-10}$	$(8.81 \pm 0.2) \times 10^{-10}$
		Pb(II)	$(1.16 \pm 0.2) \times 10^{-8}$	$(1.88 \pm 0.1) \times 10^{-8}$	$(5.19 \pm 0.1) \times 10^{-9}$
		Cu(II)	$(7.81 \pm 0.3) \times 10^{-7}$	$(5.57 \pm 0.3) \times 10^{-7}$	$(5.80 \pm 0.4) \times 10^{-7}$
Organic 2	18.1	Zn (II)	$(13.3 \pm 1.0) \times 10^{-7}$	$(5.35 \pm 0.3) \times 10^{-7}$	$(1.88 \pm 0.4) \times 10^{-7}$
		Cd(II)	$(1.53 \pm 0.1) \times 10^{-9}$	$(4.74 \pm 0.5) \times 10^{-9}$	$(2.67 \pm 0.4) \times 10^{-9}$
		Pb(II)	$(5.05 \pm 0.1) \times 10^{-8}$	$(6.42 \pm 0.3) \times 10^{-8}$	$(3.98 \pm 0.3) \times 10^{-8}$
		Cu(II)	$(9.76 \pm 0.2) \times 10^{-7}$	$(7.85 \pm 0.2) \times 10^{-7}$	$(7.28 \pm 0.4) \times 10^{-7}$
Minerals 1	2.3	Zn (II)	$(10.7 \pm 1.0) \times 10^{-7}$	$(3.62 \pm 0.3) \times 10^{-7}$	$(3.07 \pm 0.3) \times 10^{-7}$
		Cd(II)	$(0.856 \pm 0.3) \times 10^{-8}$	$(1.04 \pm 0.2) \times 10^{-8}$	$(1.41 \pm 0.3) \times 10^{-8}$
		Pb(II)	$(1.49 \pm 0.2) \times 10^{-7}$	$(1.52 \pm 0.3) \times 10^{-7}$	$(2.06 \pm 0.3) \times 10^{-7}$
		Cu(II)	$(4.83 \pm 0.3) \times 10^{-7}$	$(1.62 \pm 0.2) \times 10^{-7}$	$(3.83 \pm 0.4) \times 10^{-7}$
Minerals 2	N/A	Zn (II)	$(5.37 \pm 0.3) \times 10^{-6}$	$(1.05 \pm 0.4) \times 10^{-6}$	$(0.745 \pm 0.1) \times 10^{-6}$
		Cd(II)	$(2.50 \pm 0.1) \times 10^{-9}$	$(1.24 \pm 0.3) \times 10^{-9}$	$(1.79 \pm 0.4) \times 10^{-9}$
		Pb(II)	$(0.87 \pm 0.02) \times 10^{-9}$	$(1.09 \pm 0.5) \times 10^{-9}$	$(1.33 \pm 0.3) \times 10^{-9}$
		Cu(II)	$(7.16 \pm 0.3) \times 10^{-8}$	$(4.64 \pm 0.3) \times 10^{-8}$	$(3.39 \pm 0.4) \times 10^{-8}$

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- All the above samples were filtered through 0.45 µm filter (Gelman No. 63077).
- Total dissolved metal concentrations were determined by ICP-MS.
- N/A – not applicable due to insufficient sample volume.
- UV-DPASV: DPASV was applied after UV-irradiated for 6 hours.
- all the concentrations are expressed in molar concentrations.

The ASV-labile fraction for the mineral samples was generally higher than that for the organic samples. This probably was due to the fact that some of these metals were bound to natural organic matter present in the soil at both sites. This was confirmed by determining the DOC concentrations for all the samples (Site 1 and Site 2, organic and mineral samples). The results are presented in Table 23, which shows that the 'organic' samples had significantly higher DOC concentrations compared with the 'minerals' samples. As was discussed before, with increasing DOC concentrations, the number of the binding sites available for complexation increases, and consequently, the ASV-labile fraction of all the trace metals decreases. Table 23 shows good agreement between the two methods (conventional DPASV and UV-DPASV) which were applied for determining the ASV-labile fraction, especially at high concentrations of Zn(II), Pb(II) and Cu(II). In the case of Cd(II), which was present in very low concentrations, ASV-labile fractions, determined by both methods, were nearly the same or higher than the dissolved cadmium concentrations, which indicates that all the Cd(II) was ASV-labile. This, as explained before, was due to many factors such as the DOC concentrations and the co-presence of other trace metals in higher concentrations (2~3 orders of magnitude) that out-compete Cd(II) for the strong binding sites. Generally, most of the Zn(II) and Cu(II) was ASV-non labile, probably as a result of strong binding of Cu(II) compared with Pb(II) and Cd(II) for the binding sites of DOC.

The ASV-labile fraction for Zn(II), Cd(II), Pb(II) and Cu(II) complexes were determined in lake water samples by conventional DPASV and also by UV-DPASV. The results are presented in Table 24, which shows that Lake Dufault had higher concentrations compared with Lake Opasatica. This was probably a result of its geographical

Table 24

ASV-labile fraction determined by conventional DPASV and after UV-irradiation in lake water samples, collected in August 2002.

Sample	DOC, mg/L	Metal	[M] _{total}	ASV-LABILE	
				UV-DPASV	Conventional DPASV
Lake Dufault	10.9	Zn (II)	$(5.50 \pm 0.1) \times 10^{-7}$	$(3.54 \pm 0.7) \times 10^{-7}$	$(4.81 \pm 0.5) \times 10^{-7}$
		Cd(II)	$(2.58 \pm 0.3) \times 10^{-9}$	$(1.58 \pm 0.3) \times 10^{-9}$	$(2.45 \pm 0.4) \times 10^{-9}$
		Pb(II)	$(1.45 \pm 0.1) \times 10^{-10}$	$(2.61 \pm 0.4) \times 10^{-10}$	$(2.23 \pm 0.1) \times 10^{-10}$
		Cu(II)	$(2.32 \pm 0.1) \times 10^{-7}$	$(1.53 \pm 0.4) \times 10^{-7}$	$(1.08 \pm 0.3) \times 10^{-7}$
Lake Opasatica	10.4	Zn (II)	$(4.01 \pm 0.1) \times 10^{-8}$	$(2.04 \pm 0.3) \times 10^{-8}$	$(2.42 \pm 0.5) \times 10^{-8}$
		Cd(II)	$(4.45 \pm 0.1) \times 10^{-11}$	$(4.36 \pm 0.5) \times 10^{-11}$	$(5.05 \pm 0.6) \times 10^{-11}$
		Pb(II)	$(9.65 \pm 0.1) \times 10^{-11}$	$(1.55 \pm 0.4) \times 10^{-10}$	$(1.68 \pm 0.5) \times 10^{-10}$
		Cu(II)	$(4.58 \pm 0.2) \times 10^{-8}$	$(1.67 \pm 0.2) \times 10^{-8}$	$(1.88 \pm 0.5) \times 10^{-8}$

- The uncertainty represents 95.5 % confidence limits, i.e. 2 x standard deviation of n replicates (n = 3).
- All the above samples were filtered through 0.45 µm filter (Gelman No. 63077).
- total dissolved metal concentrations were determined by ICP-MS.
- N/A – not applicable due to insufficient sample volume.
- UV-DPASV: DPASV was applied after UV-irradiation for 6 hours.

Location, as Lake Dufault was closer to the Horne Smelter and the wind direction favoured transfer of the atmospheric deposition towards it. There was a good agreement between both methods used for the determination of the ASV-labile fraction, and as was expected, the ASV-labile fraction in Lake Dufault was higher compared with that of Lake Opasatica.

Conclusion

It can be concluded that DPASV can be used satisfactorily for the simultaneous determination of Zn(II), Cd(II), Pb(II), and Cu(II) with good selectivity and sensitivity. UV-irradiation is a powerful method to break down the metal-organic complexes to release metal ions which can be determined by DPASV. Also, DPASV can be used to determine the chemical speciation of Zn(II), Cd(II), Pb(II) and Cu(II) in soil solutions and lake water samples. Chemical speciation in aqueous samples depends on many factors. One factor is the DOC concentrations compared with the total metal concentrations, as well as the co-presence of the other cations for competitive binding with DOC.

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Appendix 1:

Location of the lakes in Rouyn-Noranda, Abitibi, Québec.

Appendix 2:

Location of the sites for soil solutions and throughfall precipitation samples collected from the Sudbury mining area, Copper Cliff, Ontario.