CHAPTER 4

Modelling Chemical Speciation: Thermodynamics, Kinetics and Uncertainty

Jeanne M. VanBriesen, Mitchell Small, Chris Weber and Jessica Wilson

4.1 INTRODUCTION

Chemical speciation refers to the distribution of an element amongst chemical species in a system. It is critical for understanding chemical toxicity, bioavailability, and environmental fate and transport. Despite the central importance of knowing the full speciation of a chemical in order to predict its behaviour in a system, it is generally not possible to determine a speciation analysis using analytical chemistry methods alone. Most techniques are focused on detection of free metal ion concentrations (e.g., Galceran *et al.*, 2004; Salaun *et al.*, 2003; Zeng *et al.*, 2003) or total metal concentrations (e.g., Wang *et al.*, 1998). Direct speciation measurement using traditional analytical methods requires significant complexity and generally hyphenated techniques (Sanzmedel, 1995; Yan and Ni, 2001; Moldovan *et al.*, 2004). A relatively new method, capillary electrophoresis (CE), allows direct measure of chemical speciation of some metals (Haumann and Bachmann, 1995; Beale, 1998; Dabek-Zlotorzynska *et al.*, 1998). However, because environmental concentrations of most metals of interest are low, and because many relevant forms of metals cannot be measured directly, analytical techniques often are not effective for determining overall speciation (Fytianos, 2001). Thus chemical speciation determination generally relies on utilising analytical methods in conjunction with chemical speciation models.

Modelling of Pollutants in Complex Environmental Systems, Volume II, edited by Grady Hanrahan. © 2010 ILM Publications, a trading division of International Labmate Limited.

4.2 CHEMICAL SPECIATION MODELLING

Multicomponent thermodynamic equilibrium speciation modelling has been described in detail (e.g., Morel and Morgan, 1972), and has been incorporated into publicly available and commercial modelling software (e.g., MINEQL;[1] Westall *et al.*, 1976). Components are selected such that all species can be formed by the components, and no component can be formed by a combination of other components. Mass balances can thus be written for each component (a proton balance is used for acidic hydrogen), and mass action equations define the interrelationships among the different components. For example, consider the system of EDTA with a limited set of environmentally relevant metals (Cu^{2+}, Zn^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, Mg^{2+}, Pb^{2+}, Co^{2+}, Al^{3+} and Fe^{3+}). Eleven mass balances (one for each component metal plus EDTA) and 28 mass action equations (one for each species formed by the components, including a protonated form, $HEDTA^{3-}$) define the system, and their solution predicts the equilibrium concentration of each species and component. Mass balances are set to equal the total concentration of each component in the system (generally measured analytically), and mass action equations are defined by equilibrium constants (K or β values, also determined experimentally). Thus the mass balances are defined as

$$M_j = \sum_{j=1}^{N_c} A_{ij} \frac{x_i}{\gamma_i} \tag{4.1}$$

where M_j is the total mass of component j; A_{ij} is the stoichiometric coefficient giving the number of moles of component j in species i; x_i is the activity of the aqueous species i; γ_i is the activity coefficient of species i; and N_c is the number of components.

The mass action equations are defined as

$$x_i = \beta_i \prod_{j=1}^{N_c} c_j^{A_{ij}} \tag{4.2}$$

where β_i is the overall equilibrium formation constant for species i. Table 4.1 provides the species and their reported formation constants from the Joint Expert Speciation System (JESS) thermodynamic database (May, 2000; May and Murray, 2001).

Although speciation modelling is use and highly informative, it involves significant uncertainties (Nitzsche *et al.*, 2000). Following the framework of Finkel (1990), uncertainty can, in general, be divided into four distinct types: decision rule uncertainty, model uncertainty, parameter uncertainty, and parameter variability (Finkel, 1990; Hertwich *et al.*, 1999). In the context of chemical speciation modelling, the latter three of Finkel's types are important. When we consider decision-making based on speciation, the first type is also important. Model uncertainty includes the decision of whether to include certain species or certain processes that may or may not be important in the given application. For speciation modelling of metals these might include humic complexation, changes in redox states, or adsorption to solids. Model uncertainty would also include the chosen models used for humic complexation or

Table 4.1: Species and reported log β values for the 10 metal/EDTA system

	log β^0		**log β^0**
H-EDTA^{3-}	10.61	Mn-EDTA^{2-}	15.38
H_2-EDTA^{2-}	17.68	Mn-EDTA^{-}	19.1
H_3-EDTA^{-}	19.92	Mg-EDTA^{2-}	10.27
H_4-EDTA	23.19	MgH-EDTA^{-}	15.1
Cu-EDTA^{2-}	20.36	Pb-EDTA^{2-}	19.67
CuH-EDTA^{-}	23.9	PbH-EDTA^{-}	21.86
CuOH-EDTA^{3-}	22.39	Co-EDTA^{2-}	17.94
Zn-EDTA^{2-}	18.15	CoH-EDTA^{-}	21.34
ZnH-EDTA^{-}	21.7	Al-EDTA^{-}	19.12
ZnOH-EDTA^{3-}	19.9	AlH-EDTA	21.6
Ni−-EDTA	20.13	AlOH-EDTA^{2-}	27.19
NiH-EDTA^{-}	24	Fe−-EDTA	27.52
NiOH-EDTA^{3-}	21.8	FeH-EDTA	29.2
Ca-EDTA^{2-}	12.38	FeOH-EDTA^{2-}	33.8
CaH-EDTA^{-}	16		

solid-phase adsorption (if applicable), in addition to the assumption of equilibrium conditions, which is of vital importance to the proper utilisation of speciation models (Fytianos, 2001). Finally, model uncertainty includes the models used to correct thermodynamic data for ionic strength, temperature and medium interactions, though this uncertainty could also be considered to be part of parameter uncertainty and variability, since cited thermodynamic data have usually already been corrected using these models (May, 2000). Chemical speciation modelling is thus strongly dependent on the presumption of equilibrium, and on the values of equilibrium constants determined experimentally.

4.2.1 Local equilibrium assumption

As described above, chemical speciation models rely on mass balance and thermodynamics to determine the concentration of each species that contains a given component. Chemical speciation is usually predicted with thermodynamic expressions, because the reactions involved take place in the bulk aqueous phase and are generally rapid (e.g., acid/base reactions). The local equilibrium assumption (LEA) states that, because aqueous-based reactions are reversible and generally rapid compared with other system processes, they may be assumed to reach equilibrium. The thermodynamics of the system components will be predictive of the final state of the system (Rubin, 1983). This assumption is generally accurate, although notable exceptions have been reported when complexation exchange reactions are slow (Xue *et al.*,1995; Pohlmeier and Knoche, 1996; Nowack *et al.*, 1997).

The LEA is an excellent foundation for modelling speciation when rapid exchange reactions are observed. However, speciation models using the LEA generally neglect reaction kinetics, and for some systems kinetics play a pivotal role (Xue *et al.*, 1995; Pohlmeier and Knoche, 1996; Nowack *et al.*, 1997; Brooks, 2005). For example, Xue *et al.*, performed a comprehensive study on ethylenediamenetetraacetate (EDTA) exchange kinetics, focusing on reactions of Fe-EDTA exchanging with Ca, Cu and Zn (Xue *et al.*, 1995). They observed that Fe-EDTA exchanges very slowly with higher-concentration, low-stability-constant metals (half-lives of 10 to 20 days), owing to its high stability and sometimes also to the relative unavailability of Ca, Cu and Zn, which complex with natural ligands such as HCO_3^- and organic matter. Hering and Morel (1988) found similar kinetic hindrances in the reverse reaction: the concentration of Ca in natural waters was found to be a master variable for controlling Ca-EDTA re-speciation to thermodynamically favoured Fe-EDTA and Zn-EDTA. This is due to a rate-limitation in the disjunctive step of the exchange, or the step where the ligand and metal first split apart before the ligand forms a complex with a different metal. This limitation is not a problem if the re-speciation takes place via the adjunctive pathway, where an intermediate dual complex is formed before the original metal is replaced with the new metal. These two mechanisms are shown below.

$$\text{Disjunctive pathway:}\quad \mathrm{AL} \xleftrightarrow{k_{-1}} \mathrm{A} + \mathrm{L}$$

$$\text{Adjunctive pathway:}\quad \mathrm{AL} + \mathrm{Me} \xleftrightarrow{k_{\mathrm{a}}} \mathrm{ALMe}$$

$$\mathrm{ALMe} \xleftrightarrow{k_{-\mathrm{b}}} \mathrm{A} + \mathrm{MeL}$$

When CaEDTA splits into Ca(II) and EDTA by the disjunctive mechanism, another Ca(II) will tend to take its place because of abundance, even though thermodynamics will favour the replacement of Ca(II) with a trace metal such as Cu(II). Such slow complexation reactions are important, because they can affect biodegradation rates of pollutants such as EDTA. Satroutdinov *et al.*, (2000) report slow re-speciation results in effective non-biodegradability of stable EDTA chelates. Willett and Rittmann (2003) report that cessation of biodegradation of EDTA corresponds to concentration of dissolved Fe(III), and that the non-biodegradability of this form along with the slow re-speciation to biologically available Ca-EDTA reduces EDTA biodegradation in the environment. Similar results by Kagaya *et al.*, (1997) indicate that slow re-speciation affects the photodegradation of metal–EDTA complexes. Brooks (2005) suggests that equilibrium speciation models are insufficient to understand chelate systems because of slow kinetics, which are clearly observed through direct speciation measurement using capillary electrophoresis.

When the LEA is not valid, kinetically controlled speciation reactions must be integrated into thermodynamically based speciation models. This has been done in the work of Willett and Rittmann (2003), who modify the CCBATCH model developed by VanBriesen and Rittmann (1999). Briefly, their kinetically controlled speciation model removes certain species from the list of complexes available for equilibrium speciation and instead solves for their concentrations over time, along with other kinetic reactions. This requires consideration of rate constants for the forward and reverse reactions controlling the exchange reaction of metals among the different chelates (e.g., k_a and k_{-b} or k_{-1} above).

4.2.2 Equilibrium constant values

Equilibrium constants are determined by measurement of the relevant concentrations of the species under differing experimental conditions. Concentrations of species can be measured in multiple ways, including potentiometrically, spectrophotometrically, and through NMR chemical shift measurement. Several papers report the use of these analytical techniques for determination of EDTA equilibrium constants under various conditions (Jawaid, 1978; Hering and Morel, 1988; Xue and Sigg, 1994). Equilibrium constants are determined at specific conditions for ionic strength and temperature, and the use of these values in modelling requires adjustment to the conditions in the system being modelled. These adjustments, as well as the differences in conditions and different methods for determination, can lead to uncertainty in chemical speciation constants.

Several databases exist that report experimental results for speciation constants, including the International Union of Pure and Applied Chemistry Critical Database (IUPAC, 2005), the National Institute of Standards and Technology standard reference database (Martell *et al.*, 2003) and the Joint Expert Speciation System thermodynamic database (May, 2000; May and Murray, 2001). Chelate-specific values were recently reviewed by Popov and Wanner (2005). These databases include experimental results, conditions of the experiments, and methods to adjust values for differing conditions, which is critical for real-time updating of constants within speciation models.

Most mainstream aqueous speciation programs, such as MINTEQA2, MINEQL+ and PHREEQC, come supplied with a standard thermodynamic database, which includes reaction constants, enthalpy values, and occasionally Debye–Huckel or specific interaction theory parameters for ionic strength correction (MINEQL). Unfortunately, many of these databases have been shown to contain significant errors (Serkiz *et al.*, 1996) Generally these speciation program databases offer only a single value for the overall formation reaction of each aqueous component, which has generally been calculated from accepted or so-called "critical" values in broader databases of thermodynamic constants such as the IUPAC Critical Database, the NIST standard reference database, or any of a number of other critical compilations of thermodynamic data (May, 2000; May and Murray, 2001; Martell *et al.*, 2003; IUPAC, 2005). These broader thermodynamic sources have been reviewed recently for chelate-associated thermodynamic data (Popov, 2005).

Use of these values for speciation calculations can lead to significant uncertainty. Several authors have investigated aspects of these uncertainties (Criscenti *et al.*, 1996) including examinations of the Fe(II)–Fe(III)–SO_4 aqueous system (Stipp, 1990), actinide speciation in groundwater (Ekberg and LundenBuro, 1997), and U(VI) aqueous speciation (Denison and Garnier-LaPlace, 2005). These studies have often relied on several assumptions, such as a fixed equation for ionic strength extrapolation (Denison and Garnier-LaPlace, 2005; Haworth *et al.*, 1998; Odegaard-Jensen *et al.*, 2004) and the assumption of statistical independence of model parameters (Schecher and Driscoll, 1987). We agree with Denison and Garnier-Laplace (2005) that the latter assumption of independence rarely holds, and recently we developed a new stochastic method specifically aimed at resolving these difficulties (Weber *et al.*, 2006).

4.3 ANALYTICAL METHODS

As mentioned above, there are two ways in which speciation is determined: laboratory analysis provides a direct measure of different forms of a target chemical, whereas chemical modelling applies known thermodynamic relationships among chemical forms to predict the overall equilibrium distribution. Often, a combination is used when chemical analysis can only determine certain forms, and modelling is used to predict the other forms relative to the measured form. For example, metal ion concentrations can be measured in the laboratory by a variety of techniques, including graphite furnace atomic absorption spectroscopy (GFAA), inductively coupled plasma mass spectroscopy (ICP-MS), atomic emission spectrometry (AES), X-ray spectroscopy, and neutron activation analysis. Most existing as well as novel techniques are focused on the detection of free metal ion concentrations. Liquid membranes have been used for the separation of free metal ions, including Cd(II), Pb(II), Cu(II) (Parthasarathy and Buffle, 1994; Parthasarathy *et al.*, 1997; de Gyves and San Miguel, 1999) There are also fluorescence-based methods (Thompson *et al.*, 1996; Thompson *et al.*, 1999; Zeng *et al.*, 2003) and, more recently, electroanalytical techniques that use microelectrodes to measure the free metal ion concentration (Galceran *et al.*, 2004; Galceran *et al.*, 2007; Huidobro *et al.*, 2007). Total metal analytical methods include using electrochemical flow sensors or probes *in situ* to measure total metal concentrations (Wang *et al.*, 1995, 1998; Taillefert *et al.*, 2000).

Direct speciation measurement (beyond free ion or total metal) often requires combinations of complex analytical techniques. Certain speciation analyses include LC with ICP-MS (Rottmann and Heumann, 1994) and AES with both HPLC (Robards and Starr, 1991; Sanzmedel, 1995) and ICP (Sanzmedel, 1991; Xue *et al.*, 1995). Additionally, ICP-MS can be coupled with GC for the determination of metal concentrations (Sutton *et al.*, 1997). Capillary electrophoresis (CE) is a relatively new analytical method that allows direct measure of chemical speciation of metals. CE is an advanced analytical technique that separates species based on their mobility under an applied electric field. The CE system consists of electrolyte solution, power supply, capillary, electrodes, and detector (typically UV-Vis for environmental analyses). A sample is introduced into the capillary, filled with electrolyte solution by hydrodynamic or hydrostatic pressure. After the sample is introduced, the capillary ends and electrodes are submerged in the electrolyte solution. An electric field is applied across the electrodes, and the fluid migrates from one end of the capillary to the other. The addition of an electrolyte solution through the capillary allows for the complexes to separate based on their charge and size. The composition of the electrolyte solution (ionic strength, pH) affects the migration time and peak shape of the complexes (Reijenga *et al.*, 1996; Beckers and Bocek, 2003). The most common method of separating metal ions by CE involves the conversion of these ions into stable, negatively charged complexes prior to introduction into the column (Dabek-Zlotorzynska *et al.*, 1998; Timerbaev, 2004). Various derivatising reagents have been used for speciation of metals, including both organic and inorganic ligands. Organic ligands have been used extensively for the separation of metal complexes, and there have been a number of papers recently published that use aminopolycarboxylates because they form stable and water-soluble complexes with many metal ions (Burgisser and Stone, 1997; Padarauskas and Schwedt, 1997; Pozdniakova and Padarauskas, 1998; Owens *et al.*, 2000; Carbonaro and Stone, 2005). CE offers significant potential for direct chemical speciation measurement; however, it is still a developing technique, and not widely used in assessing environmental concentrations of metals.

4.4 EXPERIMENTAL AND MODELLING METHODS

In order to consider how chemical speciation determination is affected by uncertainty in analytical methods and chemical speciation models, we undertook a series of modelling and experimental studies.

4.4.1 Modelling methods

A statistical model was constructed using Markov chain Monte Carlo (MCMC) with Gibbs sampling (Weber *et al.*, 2006). The method is summarised here, and the reader is referred to Weber *et al.* (2006) for additional details.

Using the speciation system described above, includingT 10 metals and their EDTA chelates (Cu^{+2}, Zn^{+2}, Ni^{+2}, Ca^{+2}, Mn^{+2}, Mg^{+2}, Pb^{+2}, Co^{+2}, Al^{+3}, and Fe^{+3}) in addition to the protonated EDTA form, $HEDTA^{-3}$, we simultaneously fitted the 27 thermodynamic parameters that control this system. For each aqueous species, a non-linear regression of the parameters ($\log\beta_j^o$, b_j) was performed simultaneously on the available data. It was necessary to regress each of the species simultaneously to account for the correlation between the regression parameters for each species (correlation between $\log\beta_j^o$ and b_j) as well as the correlation between the regressed parameters for one species with each of the other species' regressed values. (i.e., correlation between $\log\beta_j^o$ and $\log\beta_k^o$, where j and k are two different aqueous species). The model treated the first kind of correlation directly through bivariate distributions, whereas the second kind of correlation was treated indirectly by regressing each primary constant before regressing the secondary constants. Modelling this correlation, which has not been done in previous studies, is imperative in order to avoid creating highly unlikely (very low values of the joint likelihood function) sets of either the two regression parameters for a specific species, or a highly unlikely set of two different $\log\beta_i^o$ values for two different species.

WinBUGS 1. 4 was utilised for the MCMC coding.[2] The standard errors of each of the sets of regression parameters were assumed to follow a bivariate normal distribution with a standard Wishart prior distribution on the precision matrix. Pseudo-informationless priors were utilised for all regression parameters (Gelman, 2004; Goyal and Small, 2005). Visual MINTEQ, a Windows version of the US EPA code

MINTEQA2, was used for the chemical speciation calculations.[3] An example aqueous speciation was examined for a simulated natural river water using data from US EPA's STORET database for Allegheny County, Pennsylvania, USA (US EPA, 2003).

4.4.2 Experimental methods

All solutions were prepared using distilled, deionised water (DDW) with a resistivity of 18 MΩ cm. All stock solutions were stored in polypropylene bottles prior to use. All glassware and plasticware was soaked in 5 M HNO_3 (Fisher Scientific) and rinsed several times with DDW prior to use.

Ethylenediaminetetraacetic acid (H_4EDTA), $FeCl_3 \cdot 6H_2O$, $NiCl_2$, Na_2HPO_4, NaH_2PO_4, 3-(*N*-morpholino) propanesulfonic acid (MOPS) and tetradecyltrimethylammonium bromide (TTAB) were obtained from Fisher Scientific. 5.0 mM stock solutions of $FeCl_3 \cdot 6H_2O$ and $NiCl_2$ were prepared by weighing the crystals on a balance and dissolving them in DDW. The experimental solutions were prepared by adding the metals to an EDTA solution buffered in MOPS ($pH = 7.1$).

All separations were conducted using an Agilent capillary electrophoresis instrument equipped with a diode-array UV-visible detector. Bare fused-silica capillaries of 75 μm i.d. were used for all separations (Agilent). Capillaries were treated between separations using a rinse of 0.1 M NaOH for 1 min, followed by a water rinse for 1 min and then a rinse of BGE for 1 min. Samples were injected under positive pressure for 10 s at 34.5 mbar. Capillaries were 58.0 cm in total length. All separations were conducted in constant-voltage mode at -25 kV. Tetradecyltrimethylammonium bromide (TTAB; 0.5 mM) was used as an electro-osmotic flow (EOF) modifier. Detection at 192, 214 and 254 nm was employed, with the wavelength selected during method optimisation. The background electrolyte (BGE) used was phosphate (25 mM, $pH = 7.1$).

4.5 RESULTS AND DISCUSSION

In general, modelling results show that uncertainty in thermodynamic constants affects predicted speciation in chelate systems, and experimental results show slow speciation of chelates. The results suggest that chemical equilibrium models can be improved through consideration of uncertainty in model parameters, and that kinetic equilibrium models can be improved through experimental determination of kinetic exchange reactions.

4.5.1 Thermodynamic uncertainty in chemical speciation modelling

Results from our initial studies indicated that the uncertainty for thermodynamic values is much greater around the very dilute range and the more concentrated range, where data for the thermodynamic constants are comparatively sparse. This fact underscores the advantage of using a stochastic correction method, as calculations of stability constants at conditions far from laboratory conditions (such as the relatively small ionic strengths of natural waters) will tend to be much more uncertain than calculations performed at conditions close to laboratory conditions. Further, the results of the stochastic correction function give the user a much better idea of the thermodynamic uncertainty of the model at all levels of ionic strength. The use of all available measured values for different ionic strengths, different media, different temperatures and different reaction formulations provides much more information than a one-value model.

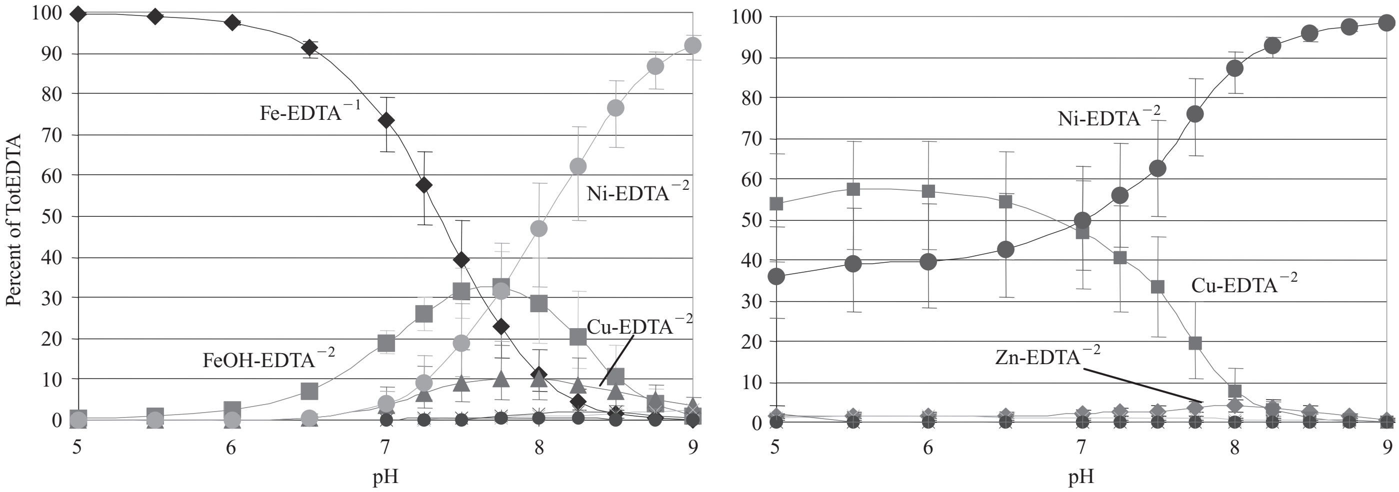
Stochastic chemical speciation diagrams are shown in Figure 4.1 for the simulated natural river water (a) without precipitation and (b) with precipitation (right). Also shown are the 90% credible intervals as a function of pH for both cases. Each of the simulations was run through a typical natural pH range of 5–9. The major conclusion from these diagrams is that the overall chemical system uncertainty is directly related to the system's competitiveness. Minimal uncertainty is predicted in conditions where one species is dominant over all others, such as Fe-EDTA$^-$ at low pH in the no-solids case. Mathematically, this result is caused by the simultaneous sampling of several marginal distributions of chemical importance. When one species is dominant, only uncertainty in its own stability constant is relevant, but when many species are close in stability, uncertainty increases substantially. The implication for policy and risk analysis is that it is probably defensible to use deterministic speciation modelling when chemical systems will be dominated by one species. In most cases, however, this is unlikely to be true, and thermodynamic uncertainty should be included in analysis.

4.5.2 Kinetic uncertainty in chemical speciation modelling

The dominant form of uncertainty in chemical speciation modelling involving kinetic exchange reactions is the uncertainty in the determination of the relevant kinetic constants. Here our work focused on the kinetics of iron and nickel exchange reactions. Figure 4.2 shows: (a) the slow re-speciation from the initial Fe-EDTA complex to the more stable Ni-EDTA complex over the 280 h of the experiment; and (b) the slow re-speciation from the initial Ni-EDTA complex to Fe-EDTA over the 325 h of the experiment. For the initial Fe-EDTA system (Figure 4.2a), the Fe-EDTA is exchanging with the Ni(II) in the solution, and the Fe(III) is precipitating out of the system, as evidenced by a yellow/orange tint in the solution after 200 h. For the initial Ni-EDTA system (Figure 4.2b), the exchange with Fe(III) is also slow, and a yellow/orange tint also developed in the solution, also indicating precipitation of Fe(III). If the decrease of Fe-EDTA is treated as a pseudo-first-order reaction, then a first-order reaction rate can be calculated based on this dataset, and by following the equations of Xue *et. al*.(1995). At pH = 6.7, the first-order reaction rate for Fe-EDTA loss, $k_{1,\mathrm{obs}} = 2.7 \times 10^{-3}\ \mathrm{h}^{-1}$. Similarly, the first-order reaction rate for Ni-EDTA loss can be calculated as $k_{2,\mathrm{obs}} = 1.9 \times 10^{-}\ \mathrm{h}^{-1}$.

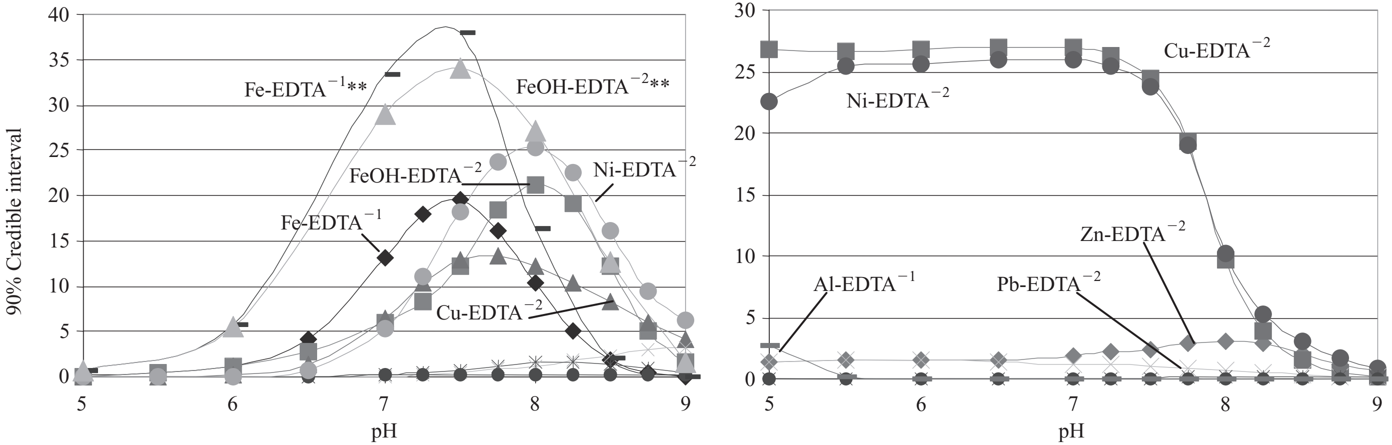
The first-order reaction rate for the loss of Fe-EDTA is greater than the first-order reaction rate for the loss of Ni-EDTA. Ni-EDTA is a stronger complex than Fe-EDTA, and thus is less likely to dissociate – hence the slower reaction rate. Additionally, the

Figure 4.1: Speciation diagrams (a and b) and 90% credible intervals (c and d) for simulated natural water with no precipitation (left, a and c) and allowing precipitation (right, b and d).



(a)

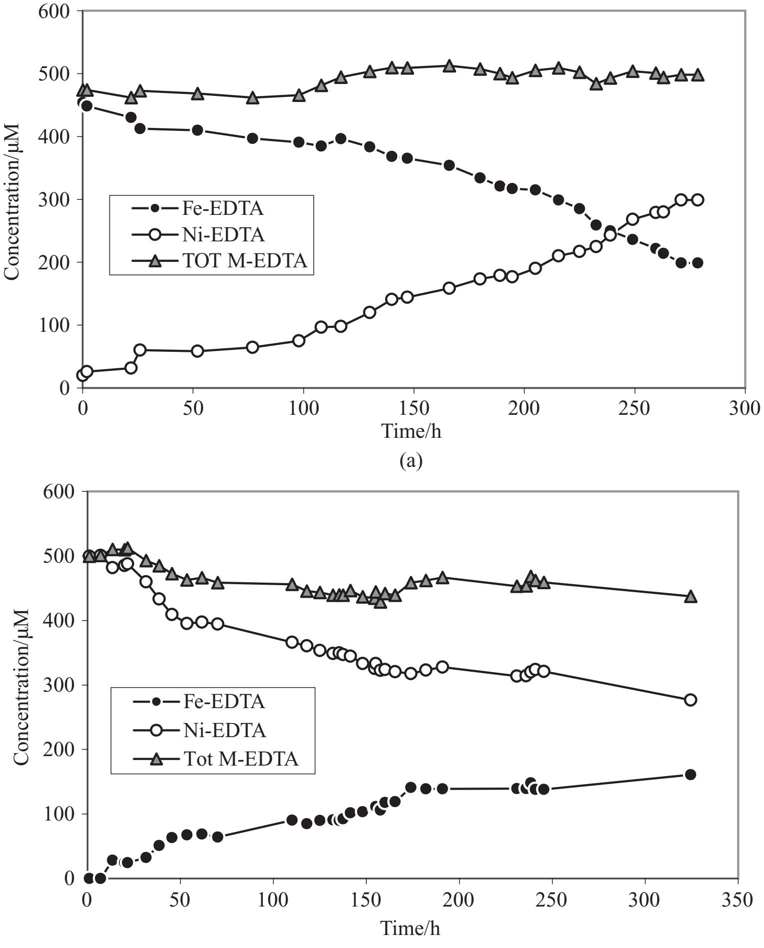
(b)



(c) (d)

Source: Reprinted with permission from Weber, C.L., VanBriesen, J.M. and Small, M.S. (2006). A stochastic regression approach to analyzing thermodynamic uncertainty in chemical speciation modeling. *Environmental Science & Technology*. 40: 3872–3878. Copyright 2006 American Chemical Society.

Figure 4.2: Capillary electrophoresis experiment to determine kinetic exchange constant for Fe-EDTA–Ni-EDTA reaction; (a) 500 µM Ni(II) added to 500 µM Fe(III)-EDTA buffered in MOPS (pH = 6.7); (b) 500 µM Fe(III) added to 500 µM Ni(II)-EDTA buffered in MOPS (pH = 6.7)



(a)

(b)

Fe(III) precipitates out of the system, and it is likely that the free EDTA will either sorb onto the Fe(III) precipitate, or recomplex with the Ni(II), given additional time. These results indicate that the slow exchange kinetics in certain M-L systems can contribute to the uncertainty in chemical speciation.

Xue *et al.* (1995) calculated a kinetic exchange constant for Fe-EDTA with Zn(II). Following the work of Xue *et al.* (1995), a second-order rate constant can be calculated from the overall equation for the two reactions in the experimental systems described above:

$$\text{Fe-EDTA} + \text{Ni(II)} \rightarrow \text{Fe(III)} + \text{Ni-EDTA} \qquad \text{(a)}$$

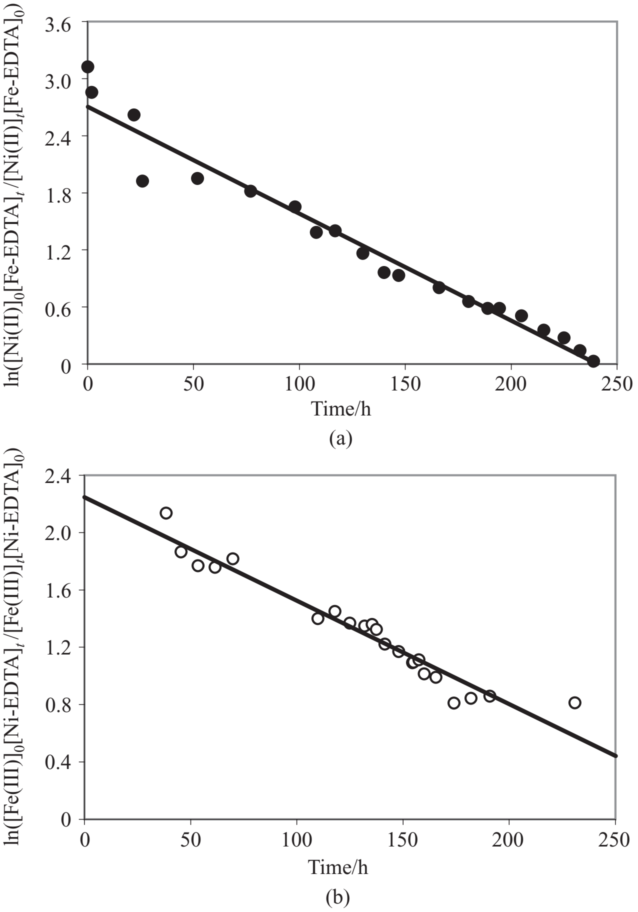
$$\text{Ni-EDTA} + \text{Fe(III)} \rightarrow \text{Ni(II)} + \text{Fe-EDTA} \qquad \text{(b)}$$

The rate law is then an expression of the rate on the concentrations of the reactants, Ni(II) and Fe-EDTA:

$$-\frac{\mathrm{d}[\text{Ni(II)}]}{\mathrm{d}t} = \frac{\mathrm{d}[\text{Ni-EDTA}]}{\mathrm{d}t} = k_{\text{obs}}[\text{Fe-EDTA}][\text{Ni(II)}] \qquad \text{(a)}$$

$$-\frac{\mathrm{d}[\text{Fe(III)}]}{\mathrm{d}t} = \frac{\mathrm{d}[\text{Fe-EDTA}]}{\mathrm{d}t} = k_{\text{obs}}[\text{Ni-EDTA}][\text{Fe(III)}] \qquad \text{(b)}$$

Figure 4.3: Second-order rate function of: (a) Ni–Fe-EDTA exchange, $k_{1,\text{obs}} = 0.0117\ \mu\text{M}^{-1}\ \text{h}^{-1} = 3.25\ \text{M}^{-1}\ \text{s}^{-1}$; (b) Fe–Ni-EDTA exchange, $k_{2,\text{obs}} = 0.0072\ \mu\text{M}^{-1}\ \text{h}^{-1} = 2.0\ \text{M}^{-1}\ \text{s}^{-1}$.



The k_{obs} for system (a) was then calculated by taking the slope of $\ln([\text{Ni(II)}]_0[\text{Fe-EDTA}]_t/[\text{Ni(II)}]_t[\text{Fe-EDTA}]_0)$ against time, and the k_{obs} for system (b) was calculated by taking the slope of $\ln([\text{Ni(II)}]_0[\text{Fe-EDTA}]_t/[\text{Ni(II)}]_t[\text{Fe-EDTA}]_0)$ (Figure 4.3)

The observed second-order rate constant for Ni(II) exchange with Fe-EDTA is calculated as $3.25\ \text{M}^{-1}\ \text{s}^{-1}$, and the observed second-order rate constant for Fe(III) exchange with Ni-EDTA is calculated as $2.0\ \text{M}^{-1}\ \text{s}^{-1}$.

4.6 CONCLUSIONS

Chemical speciation is critical for understanding the form of chemicals of interest in natural systems. It is crucial in assessing bioavailability and, ultimately, fate, transport and risk to humans and ecosystems. Chemical speciation is generally determined through analytical methods that measure free metal ion or total metal concentration, used in conjunction with thermodynamically based models. As discussed above, these models rely on the local equilibrium assumption, and on experimentally determined reaction constants. However, in chemical systems where the LEA is not valid (e.g., where speciation reactions are slow), or where the equilibrium constants are not certain, predictions from chemical speciation models show significant uncertainty.

Our results demonstrate that uncertainty in equilibrium constant values can be propagated into model predictions for speciation, and, further, that analytic methods based on CE can be used to evaluate the kinetic constants for slow reactions. Both sources of uncertainty (model uncertainty due to the LEA and parameter uncertainty in thermodynamic and kinetic constants) are clearly important for determining speciation. As far as possible, uncertainty analysis should be included in future risk assessments where speciation is important.

REFERENCES

Beale, S.C. (1998). Capillary electrophoresis. *Analytical Chemistry*. 70: 279r–300r.

Beckers, J.L. and Bocek, P. (2003). The preparation of background electrolytes capillary zone electrophoresis: golden rules and pitfalls. *Electrophoresis*. 24: 518–535.

Brooks, S.C. (2005). Analysis of metal-chelating agent complexes by capillary electrophoresis. *In* Nowack, B. and VanBriesen, J.M. (Eds), *Biogeochemistry of Chelating Agents*. American Chemical Society, New York, pp. 121–138.

Burgisser, C.S. and Stone, A.T. (1997). Determination of EDTA, NTA, and other amino carboxylic acids and their Co(II) and Co(III) complexes by capillary electrophoresis. *Environmental Science & Technology*. 31: 2656–2664.

Carbonaro, R.F. and Stone, A.T. (2005). Speciation of chromium(III) and cobalt(III) (Amino) carboxylate complexes using capillary electrophoresis. *Analytical Chemistry*. 77: 155–164.

Criscenti, L.J., Laniak, G.F. and Erikson, R.L. (1996). Propagation of uncertainty through geochemical code calculations. *Geochimica et Cosmochimica Acta*. 60: 3551–3568.

Dabek-Zlotorzynska, E., Lai, E.P.C. and Timerbaev, A.R. (1998). Capillary electrophoresis: the state-of-the-art in metal speciation studies. *Analytica Chimica Acta*. 359: 1–26.

De Gyves, J. and San Miguel, E.R. (1999). Metal ion separations by supported liquid membranes. *Industrial & Engineering Chemistry Research*. 138: 2182–2202.

Denison, F.H. and Garnier-LaPlace, J. (2005). The effects of database parameter uncertainty on uranium(VI) equilibrium calculations. *Geochimica et Cosmochimica Acta*. 69: 2183–2191.

Ekberg, C. and LundenBuro, I. (1997). Uncertainty analysis for some actinides under groundwater conditions. *Journal of Statistical Computation and Simulation.* 57: 271–284.

Finkel, A.E. (1990). *Confronting Uncertainty in Risk Management: A Guide for Decision-Makers*. RFF Press, Washington, DC.

Fytianos, K. (2001). Speciation analysis of heavy metals in natural waters: a review. *Journal of AOAC International*. 84: 1763–1769.

Galceran, J., Companys, E., Puy, J., Cecilia, J and Garces, J.L. (2004). AGNES: a new electroanalytical technique for measuring free metal ion concentration. *Journal of Electroanalytical Chemistry*. 566: 95–109.

Galceran, J., Huidobro, C., Companys, E. and Alberti, G. (2007). AGNES: a technique for determining the concentration of free metal ions. The case of Zn(II) in coastal Mediterranean seawater. *Talanta*. 71: 1795–1803.

Gelman, A. (2004). *Bayesian Data Analysis*. Chapman & Hall/CRC, Boca Raton, FL.

Goyal, A. and Small, M.J. (2005). Estimation of fugitive lead emission rates from secondary lead facilities using hierarchical Bayesian models. *Environmental Science & Technology*. 39: 4929–4937.

Haumann, I. and Bachmann, K. (1995). On-column chelation of metal-ions in capillary zone electrophoresis. *Journal of Chromatography A*. 717: 385–391.

Haworth, A., Thompson, A.M. and Tweed, C.J. (1998). Use of the HARPROB program to evaluate the effect of parameter uncertainty on chemical modelling predictions. *Radiochimica Acta*. 82: 429–433.

Hering, J.G. and Morel, F.M.M. (1988). Kinetics of trace-metal complexation: role of alkaline-earth metals. *Environmental Science & Technology*. 22: 1469–1478.

Hertwich, E.G., McKone T.E. and Pease, W.S. (1999). Parameter uncertainty and variability in evaluative fate and exposure models. *Risk Analysis*. 19: 1193–1204.

Huidobro, C., Puy, J., Galceran, J. and Pinheiro, J.P. (2007). The use of microelectrodes with AGNES. *Journal of Electroanalytical Chemistry*. 606: 134–140.

IUPAC (2005). Stability constants database and mini-SCDatabase. IUPAC, London.

Jawaid, M. (1978). Potentiometric studies of complex-formation between methylmercury(II) and EDTA. *Talanta*. 25: 215–220.

Kagaya, S., Bitoh, Y. and Hasegawa, K. (1997). Photocatalyzed degradation of metal-EDTA complexes in TiO_2 aqueous suspensions and simultaneous metal removal. *Chemistry Letters*. 2: 155–156.

Martell, A.E., Smith R.M. and Rotekaitis, R.J. (2003). *NIST Critically Selected Stability Constants of Metal Complexes Database*. National Institute of Standards and Technology, Gaithersburg, MD.

May, P.M. (2000). A simple general and robust function for equilibria in aqueous electrolyte solutions to high ionic strength and temperature. *Chemical Communications* 14: 1265–1266.

May, P.M. and Murray, K. (2001). Database of chemical reactions designed to achieve thermodynamic consistency automatically. *Journal of Chemical and Engineering Data*. 46: 1035–1040.

Moldovan, M., Krupp, E.V., Holliday, A.E. and Donard, O. (2004). High resolution sector field ICP-MS and multicollector ICP-MS as tools for trace metal speciation in environmental studies: a review. *Journal of Analytical Atomic Spectrometry*. 19: 815–822.

Morel, F. and Morgan, J. (1972). Numerical method for computing equilibria in aqueous chemical systems. *Environmental Science & Technology*. 6: 58–63.

Nitzsche, O., Meinrath, G. and Merkel B. (2000). Database uncertainty as a limiting factor in reactive transport prognosis. *Journal of Contaminant Hydrology*. 44: 223–237.

Nowack, B., Xue, H.B. and Sigg, L. (1997). Influence of natural and anthropogenic ligands on metal transport during infiltration of river water to groundwater. *Environmental Science & Technology*. 31: 866–872.

Odegaard-Jensen, A., Ekberg, C. and Meinrath, G. (2004). LJUNGSKILE: a program for assessing uncertainties in speciation calculations. *Talanta*. 63: 907–916.

Owens, G., Ferguson, V.K., McLaughlin, M.J., Singleton, I., Reid, R.J. and Smith, F.A. (2000). Determination of NTA and EDTA and speciation of their metal complexes in aqueous solution by capillary electrophoresis. *Environmental Science & Technology.* 34: 885–891.

Padarauskas, A. and Schwedt, G. (1997). Capillary electrophoresis in metal analysis investigations of multi-elemental separation of metal chelates with aminopolycarboxylic acids. *Journal of Chromatography A*. 773: 351–360.

Parthasarathy, N. and Buffle, J. (1994). Capabilities of supported liquid membranes for metal speciation in natural waters: application to copper speciation. *Analytica Chimica Acta.* 284: 649–659.

Parthasarathy, N., Pelletier, M. and Buffle, J. (1997). Hollow fiber based supported liquid membrane: a novel analytical system for trace metal analysis. *Analytica Chimica Acta.* 350: 183–195.

Pohlmeier, A. and Knoche, W. (1996) Kinetics of the complexation of Al^{3+} with aminoacids, IDA and NTA. *International Journal of Chemical Kinetics*. 28: 125–136.

Popov, K.I. and Wanner, H. (2005). Stability constants data sources: critical evaluation and application for environmental speciation. *In* VanBriesen, J. and Nowack, B. (Eds) *Biogeochemistry of Chelating Agents*. American Chemical Society, New York, NY, pp. 50–75.

Pozdniakova, S. and Padarauskas, A. (1998). Speciation of metals in different oxidation states by capillary electrophoresis using pre-capillary complexation with complexones. *Analyst*. 123: 1497–1500.

Reijenga, J.C., Verheggen, T., Martens, J. and Everaerts, F.M. (1996). Buffer capacity, ionic strength and heat dissipation in capillary electrophoresis. *Journal of Chromatography A*. 744: 147–153.

Robards, K. and Starr, P. (1991). Metal determination and metal speciation by liquid-chromatography: a review. *Analyst*. 116: 1247–1273.

Rottmann, L. and Heumann, K.G. (1994). Determination of heavy-metal interactions with dissolved organic materials in natural aquatic systems by coupling a high-performance liquid-chromatography system with an inductively-coupled plasma-mass spectrometer. *Analytical Chemistry.* 66: 3709–3715.

Rubin, J. (1983). Transport of reacting solutes in porous-media: relation between mathematical nature of problem formulation and chemical nature of reactions. *Water Resources Research.* 19: 1231–1252.

Salaun, P., Guenat, O., Berdondini, L., Buffle, J. and Koudelka-Hep, M. (2003). Voltammetric microsystem for trace elements monitoring. *Analytical Letters*, 36: 1835–1849.

Sanzmedel, A. (1991). Inductively coupled plasma-atomic emission-spectrometry: analytical assessment of the technique at the beginning of the 90s. *Mikrochimica Acta*. 2: 265–275.

Sanzmedel, A. (1995). Beyond total element analysis of biological-systems with atomic spectrometric techniques. *Analyst.* 120: 583–763.

Satroutdinov, A.D., Dedyukhina, E.G., Chistyakova, T.I., Witschel, M., Minkevich, I.G., Eroshin, V.K. and Egli, T. (2000). Degradation of metal-EDTA complexes by resting cells of the bacterial strain DSM 9103. *Environmental Science & Technology*. 34: 1715–1720.

Schecher, W.D. and Driscoll, C.T. (1987). An evaluation of uncertainty associated with aluminum equilibrium calculations. *Water Resources Research*. 23: 525–534.

Serkiz, S.M., Allison, J.D., Perdue, E.M., Allen, H.E. and Brown, D.S. (1996). Correcting errors in the thermodynamic database for the equilibrium speciation model MINTEQA2. *Water Research*. 30: 1930–1933.

Stipp, S.L. (1990). Speciation in the Fe(II)-Fe(III)-SO_4-H_2O system at 25°C and low pH: sensitivity of an equilibrium-model to uncertainties. *Environmental Science & Technology*. 24: 699–706.

Sutton, K., Sutton, R.M.C. and Caruso, J.A. (1997). Inductively coupled plasma mass spectrometric detection for chromatography and capillary electrophoresis. *Journal of Chromatography A*. 789: 85–126.

Taillefert, M., Luther, G.W. and Nuzzio, D.B. (2000). The application of electrochemical tools for *in situ* measurements in aquatic systems. *Electroanalysis*. 12: 401–412.

Thompson, R.B., Ge, Z., Patchan, M., Huang, C.C. and Fierke, C.A. (1996). Fiber optic biosensor for Co(II) and Cu(II) based on fluorescence energy transfer with an enzyme transducer. *Biosensors and Bioelectronics*. 11: 557–564.

Thompson, R.B., Maliwal, B.P. and Fierke, C.A. (1999). Selectivity and sensitivity of fluorescence lifetime-based metal ion biosensing using a carbonic anhydrase transducer. *Analytical Biochemistry*. 267: 185–195.

Timerbaev, A.R. (2004). Capillary electrophoresis of inorganic ions: an update. *Electrophoresis*. 25: 4008–4031.

US EPA (2003). *EPA STORET Database Access*. 03/09/2006 [cited 17 March 2009]. Available from: http://www.epa.gov/storet/dbtop.html

VanBriesen, J.M. and Rittmann, B.E. (1999). Modeling speciation effects on biodegradation in mixed metal/chelate systems. *Biodegradation*. 10: 315–330.

Wang, J., Larson, D., Foster, N., Armalis, S., Lu, J., Xu, R., Olsen, K. and Zirino, A. (1995). Remote electrochemical sensor for trace-metal contaminants. *Analytical Chemistry*. 67: 1481–1485.

Wang J., Tian, B.M. and Wang, J.Y. (1998). Electrochemical flow sensor for in-situ monitoring of total metal concentrations. *Analytical Communications*. 35: 241–243.

Weber, C.L., VanBriesen, J.M. and Small, M.S. (2006). A stochastic regression approach to analyzing thermodynamic uncertainty in chemical speciation modeling. *Environmental Science & Technology*. 40: 3872–3878.

Westall, J.C., Zachary, J.L. and Morel, F.M.M. (1976) Mineql: general algorithm for computation of chemical-equilibrium in aqueous systems. *Abstracts of Papers of the American Chemical Society*. 172: 8–8.

Willett, A.I. and Rittmann, B.E. (2003). Slow complexation kinetics for ferric iron and EDTA complexes make EDTA non-biodegradable. *Biodegradation*. 14: 105–121.

Xue, H.B. and Sigg, L. (1994). Zinc speciation in lake waters and its determination by ligand-exchange with EDTA and differential-pulse anodic-stripping voltammetry. *Analytica Chimica Acta*. 284: 505–515.

Xue, H.B., Sigg, L. and Kari, F.G. (1995). Speciation of EDTA in natural waters: exchange kinetics of Fe-EDTA in river water. *Environmental Science & Technology*. 29: 59–68.

Yan, X.P. and Ni, Z.M. (2001). Speciation of metals and metalloids in biomolecules by hyphenated techniques. *Spectroscopy and Spectral Analysis*. 21: 129–138.

Zeng, H.H., Thompson, R.B., Maliwal, B.P., Fones, G.R., Moffett, J.W. and Fierke, C.A. (2003). Real-time determination of picomolar free Cu(II) in seawater using a fluorescence based fiber optic biosensor. *Analytical Chemistry*. 75: 6807–6812.

NOTES

1. MINEQL: A computer program for the calculation of chemical equilibrium composition of aqueous systems. Department of Civil Engineering, MIT, Cambridge, MA.
2. WinBUGS ver 1.4. MRC Biostatics Unit, Cambridge, UK.
3. Visual MINTEQ ver 2.32. Stockholm Royal Institute of Technology (KTH), Stockholm.