Dynamic metal speciation in natural waters: theory, experimental validation and flux computations

ZHANG, Zeshi

Abstract
In this thesis, a rigorous theory of steady-state metal flux with one metal complex under both planar and spherical diffusions and ligand in-excess condition was firstly proposed. It was validated experimentally with Permeation Liquid Membrane (PLM) and metal complexes with different labilities. Dynamic parameter values have been compiled and theoretical approaches have been proposed to compute the missing parameter values. Dynamic metal speciation and metal fluxes of different metals to a planar perfect sink have been computed under typical natural freshwater conditions. The above results were compared to those under the spherical diffusion and the same conditions.

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Dynamic Metal Speciation in Natural Waters: Theory, Experimental Validation and Flux Computations

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Le Décanat
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Résumé de la thèse

Les modèles de « l’Ion Libre » et du « Ligand Biotique » sont couramment appliqués en laboratoire pour l’étude de l’internalisation des métaux traces par les micro-organismes. Néanmoins, dans de nombreux cas, les conditions expérimentales employées ne sont pas représentatives des milieux naturels. Par exemple, le milieu de culture contient souvent un complexant fort, tel que l’EDTA, qui forme des complexes non labiles avec les métaux traces. De plus, un nombre croissant de publications ont récemment rapporté des exceptions à ces modèles pour la bioaccumulation des métaux traces dans des systèmes aquatiques réels.

Dans ce contexte, la mise en place de modèles dynamiques est proposée pour une meilleure interprétation de la bioaccumulation, et l’étude dynamique de la spéciation des métaux apparaît comme nécessaire pour prédire la biodisponibilité et mettre en place des stratégies robustes pour l’évaluation des risques. Ces modèles dynamiques font intervenir des concepts tels que « la couche de réaction » ou « le degré de labilité », qui, pour des milieux environnementaux, ont encore besoin d’être clarifiés et validés expérimentalement. Actuellement, il n’y a pratiquement aucun exemple de modélisation des flux d’accumulation dans des conditions environnementales réelles, en particulier en présence d’un nombre important de ligands. Dans ces conditions, l’application des concepts mentionnés auparavant doit être revisitée. De plus, beaucoup de paramètres physico-chimiques sont nécessaires pour ces modèles en présence d’un nombre important de ligands (simples, fulviques et agrégats) et la plupart des valeurs des paramètres dynamiques ne sont pas disponibles (coefficients de diffusion, constantes de vitesse). Il est alors également nécessaire d’obtenir de telles données, à partir de modèles théoriques.

Sur cette base, le présent travail développe les points suivants :

1. Calcul et mesure du flux du métal en présence d’un ligand simple. Le concept de « couche de réaction » est revisité, et le comportement de la technique de ’Permeation Liquid Membrane’ (PLM) est étudié pour des complexes labiles, semi-labiles et inertes.

   a) tout d’abord, une théorie rigoureuse a été développée pour le flux en solution en présence d’un ligand et d’un complexe. Cette théorie permet de proposer une définition du concept de « couche de réaction » plus générale que la définition conventionnelle. Cette définition sert alors de base à l’étude des solutions environnementales contenant plusieurs ligands. Par ailleurs, un indice rigoureux de la labilité est proposé, applicable pour tout type de conditions hydrodynamiques, aussi bien dans le cas d’une diffusion plan que d’une diffusion sphérique (Chapitre 3).

   b) cette théorie a été validée expérimentalement pour la technique PLM, en présence de différents ligands formant des complexes de diverses labilités. La technique PLM a été choisie pour la validation, parce que le flux d’accumulation à son interface mimique d’une certaine manière celui à l’interface d’un micro-organisme. Les Chapitres 4 & 5 présentent donc l’étude du comportement de complexes labile, semi-labile et non labiles (inertes), en précisant en particulier le rôle de la diffusion, de l’hydrodynamique, de la spéciation à l’équilibre, et des paramètres influençant le transport à travers la membrane PLM (concentration du carrier, épaisseur de la membrane). Dans le Chapitre 5, la définition plus générale du concept de « couche de réaction » est également validée.
2. Calcul du flux de métal dans des systèmes environnementaux à plusieurs ligands, de la contribution relative des divers types de complexes et de leurs influences mutuelles.

Actuellement, seuls deux codes « conviviaux » sont disponibles dans ce but: Mhedyn et Fluxy (Chapitre 1). Mhedyn ne nécessite pas d’hypothèses a priori, mais repose sur de la simulation numérique, ce qui peut prendre relativement beaucoup de temps de calcul, selon de système étudié. Fluxy repose quant à lui, uniquement sur la résolution analytique et mathématique du flux à l’état stationnaire, et est beaucoup plus rapide. Néanmoins, Fluxy part de l’hypothèse a priori que le ligand est en large excès par rapport au métal et que les équilibres sont réalisés pour les différents complexes successifs. Ces deux codes apparaissent donc comme complémentaires. Seuls deux publications scientifiques font mention de leur application à des systèmes environnementaux. Dans ces deux articles, il est suggéré que dans un mélange, les interactions entre les différents complexes métalliques puissent affecter leur degré de labilité respectif. L’explication physique de cet effet n’est pas clair et encore mal compris. Dans ce contexte, les études suivantes ont été conduites dans le cadre de cette thèse :

a) Tout d’abord (Chapitre 7), le concept de « couche de réaction » développé dans le Chapitre 3 pour un ligand simple a été étendu à des systèmes multi-ligands. Cette approche théorique a été utilisée afin de comprendre les mécanismes physico-chimiques associés au changement du degré de labilité de deux complexes métalliques dans le cas de mélange. Différents systèmes environnementaux ont alors été considérés.

b) Le chapitre 8 détaille l’introduction du concept général de « couche de réaction » dans Fluxy. Le code modifié de Fluxy a permis de tester systématiquement, pour divers milieux environnementaux, les conditions de validité et les limitations de ses deux hypothèses de base (ligand en excès, équilibres parmi les complexes successifs).

c) Dans le Chapitre 9, Mhedyn est utilisé systématiquement pour modéliser les flux de trois métaux typiques formant des complexes labiles, semi-labiles et inertes dans des systèmes environnementaux, afin de comprendre dans chaque cas la contribution au flux total des complexes formés avec des ligands simples, des composés fulviques ou des agrégats. Le but de cette modélisation a permis de comprendre quels facteurs physico-chimiques contrôlent le flux du métal, et de prédire sa bioaccumulation, à partir de la composition du milieu.


Les valeurs des paramètres dynamiques des complexes métalliques, dans des eaux naturelles, n’ont été déterminées que pour quelques complexes formés avec des ligands simples. La plupart des paramètres sont encore inconnus, et souvent de nombreux ligands sont eux-mêmes mal définis (biopolymères, agrégats). Ce manque de données est une limitation majeure pour la modélisation des flux de métaux. Dans le Chapitre 6, toutes les données disponibles ont été compilées et des approches théoriques sont proposées afin d’estimer les paramètres manquants, en particulier pour les complexes formés avec les composés fulviques et les agrégats. Ces approches théoriques prennent en compte leur hétérogénéité chimique, leur structure physique, ainsi que la distribution de taille. En particulier, les cinétiques d’association/dissociation des métaux avec les agrégats poreux sont discutés en détail, en prenant en compte la diffusion du métal à l’intérieur et l’extérieur de l’agrégat.
Chapter 1

Introduction

1.1 Metal complex in natural waters.

1.1.1 Concentration of metals and complexants.

For a long time, trace metals, such as Cu(II), Pb(II), Cd(II) and Zn(II), in natural waters have been a central topic of environmental chemistry because of their great influences on human health and aquatic biota. These influences can be due to direct or indirect toxicity linked to the accumulation of metals in the aquatic food chain [1]. Only a small fraction of these heavy metals is present as free hydrated metal ions; most of them are bound to inorganic and organic substances whose nature depends on their environments. Figure 1.1 summarizes the major groups of complexants to which a metal ion (M) may be combined in an aquatic system: ‘simple’ organic or inorganic ligands; macromolecular organic ligands; suspended organic or inorganic particles or aggregates; organism cell walls or plasma membranes on which metals may be adsorbed [2].

![Diagram of metal complex in natural waters](image)

**Figure 1.1.** Schematic representation of the reactions of a metal ion, M, with the major types of aquatic system constituents[2].

The total concentration of a given trace metal is often below 1 μM and its free metal ion concentration may be even much lower. Figure 1.2 compares the total concentrations of the trace metals and some important organic and inorganic complexants in two different water systems.
Most ligands are in excess compared to heavy metals, and most of heavy metals are complexed and their effect thus seriously depends on the physicochemical properties of these complexants, and of the environmental conditions, in particular pH, pE, temperature and ionic strength of aquatic systems [2, 3]. The sizes of the metal ions and complexants can extend...
from several angstroms to micrometers as shown in Figure 1.3. In addition, their structure and the nature of their complexing sites are highly variable. Consequently, the values of their thermodynamic and dynamic parameters of the complexes vary over many orders of magnitudes (Table 1.1) which is a major difficulty for flux computation.

Table 1.1. Ranges of values of dynamic and thermodynamic parameters of natural metal complexes [2,4,5].

<table>
<thead>
<tr>
<th></th>
<th>Simple ligands</th>
<th>Fulvics</th>
<th>Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusion coefficient</td>
<td>$4 \times 10^{-10}$~$6 \times 10^{-9}$</td>
<td>$2~3 \times 10^{-10}$</td>
<td>$10^{-13}$~$10^{-10}$</td>
</tr>
<tr>
<td>Stability constant</td>
<td>$10^2$~$10^{10}$</td>
<td>$10^2$~$10^{17}$</td>
<td>$10^{-4}$~$10^{13}$</td>
</tr>
<tr>
<td>Association rate constant</td>
<td>$10^1$~$10^{11}$</td>
<td>$10^9$~$10^{10}$</td>
<td>$10^9$~$10^{11}$</td>
</tr>
<tr>
<td>Dissociation rate constant</td>
<td>$10^{-14}$~$10^{-10}$</td>
<td>$10^{-8}$~$10^{8}$</td>
<td>$10^{-7}$~$10^{9}$</td>
</tr>
</tbody>
</table>

Figure 1.3. Schematic classification, by size, of important organic and inorganic water components. Modified from [2].
The complexants of natural aquatic systems, in general, can be classified into three main categories[2,6,7].

### 1.1.2 Simple organic and inorganic ligands

They are small sized components (diameter < 1nm), typically with molar mass ≤ 300 Dalton (e.g., \( \text{OH}^-, \text{CO}_3^{2-} \), amino-acids, citrate…), and are often in large excess compared to environmental trace metals (Figure 1.2). Their molecular structure and properties are well characterized in all solution conditions. Their molar concentrations and those of their metal complexes can be unambiguously determined and related by well-known stoichiometric relationships and stability constants [3,8]. Many natural ligands have a single complexing site largely due to their small size. They often form 1/n successive complexes with trace metals, which are described by conventional coordination chemistry and diffuse quickly and are often labile or semi-labile, with weak to intermediate stability. These complexes can be expected to contribute to metal bioavailability.

### 1.1.3 The organic biopolymers

Important examples are peptidoglycans (like alginate) and fulvic (FS) and humics (HS). The latter two mostly include pedogenic refractory organic matter (PROM), i.e., fulvic and humic fraction of soil leached out by rainfall, and aquagenic refractory organic matter (AROM) groups produced in water bodies by recombination of amino acids, sugars, etc. released by plankton and bacteria [2,7]. Their molecular weights usually vary between several hundreds and thousands of \( 10^6 \) Daltons, but may take much larger values for HS. Table 1.2 lists four components of this group usually found in aquatic systems and their physical characteristics.

**Table 1.2. Physical characteristics of typical aquatic biopolymers [2,9].**

<table>
<thead>
<tr>
<th>Species</th>
<th>Molar mass (Da)</th>
<th>Size (nm)</th>
<th>Charge density (mequiv.g(^{-1}))</th>
<th>Diffusion coefficient ( (10^{-10} \text{m}^2.\text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Protein</td>
<td>&lt;10(^4)</td>
<td>Flexible</td>
<td>-2.1 to -5.5</td>
<td>0.1-2.0</td>
</tr>
<tr>
<td>Alginic acid</td>
<td>10(^5)-&gt;10(^3)</td>
<td>Thickness:1-3 length:100-&gt;1000</td>
<td>Minimum:0; typically:-0.35 to-0.83; maximum: ~-6</td>
<td>0.1-0.7</td>
</tr>
<tr>
<td>Fulvics</td>
<td>500-5000</td>
<td>Stokes radius: 0.4-1.4</td>
<td>-6 to -11</td>
<td>0.6-3.0</td>
</tr>
<tr>
<td>Humics</td>
<td>10(^3)-10(^6)</td>
<td>Gyration radius:1.5-15</td>
<td>-1 to -6</td>
<td>0.1-2.0</td>
</tr>
</tbody>
</table>

Peptidoglycans originate from microbial release of intra and extracellular products. Their supramolecular structures are fibrillar based on double or triple helix formation or sometimes coils or gels depending on nature of cation, pH, or ionic strength [9].

The most important group of biopolymers is composed of fulvic and humic compounds, which typically represent 40-80% of the natural organic matters (NOM) in natural waters. They have a stokes radius of 1-3nm and are highly hydrated and spheroids or aggregates of spheroids. The diffusion coefficients of non aggregated fulvics/humics is \( 2.5 \times 10^{-10} \text{m}^2.\text{s}^{-1} \) [9,14]. They bear many carboxylate (on average 3 per HS molecule, 8 per FS molecule) and phenolate groups (4 per HS molecule, 8 per FS molecule) and thus a high electric charge density at pH > 5 because of the deprotonated carboxylate sites. So, they have a
polyelectrolytic character. Fulvics/humics have many complexing sites of differing nature present on the same molecule, i.e., they are polyfunctionality [8]. Two types of complexing sites can be discriminated: i) the major sites which represent ≥ 90% of the whole of sites; they are also weak complexing sites, mainly composed of single carboxylic or phenolic groups [2], and ii) the minor sites which comprise ≤ 10% of the whole of sites; they have average to very strong complexing strength and their chemical nature is highly variable (e.g. salycilate, acetylacetone, N or S bearing chelating sites [2]). So the minor sites are chemically heterogeneous and trace metals are often bound to them. In general, fulvics and humics, can be visualized [4] as an ensemble of different but similar molecules having: i) the same size (the hydrodynamic radius \( r_H \approx 1\text{nm} \)), ii) similar density of carboxylate and phenolate groups, iii) a significant electric charge density resulting from the deprotonation of carboxylate groups in the usual pH range, which creates an overall electric field over the whole fulvic/humic molecule, that is, in a size domain significantly larger than the complexing site dimension, iv) one or no minor site (with moderate or strong complexation affinity) located in the above-mentioned electric field. Normally, 1/1 metal complexes are formed with these complexing sites, exhibiting a wide distribution spectrum of equilibrium and rate constants.

Unfortunately, due to the chemical and physical heterogeneities of the complexants of this group, our ability to measure, represent and interpret the complexation equilibria of such substances is severely limited. The corresponding complexation properties are often represented by means of average stability “constants” and “total” site concentrations[2]. For heterogeneous complexants, such parameters have no physical-chemical meaning, they are extremely operational and, consequently, they can be used for comparing the properties of different samples only under identical experimental conditions and interpretation assumptions and with much caution [10]. A rigorous way to solve the problem is to couple a Site Affinity Distribution Function (SADF), or its Cumulative form, the Site Occupation Distribution Function (SODF) with Differential Equilibrium Function (DEF) [8,11]. In this way, the proportion of ligand concentration corresponding to a small range of \( \Delta \log K \), around a specific \( \log K \) value is easily obtained. By discretizing the spectrum of \( \log K \) in the interesting range, the ensemble of the complexing sites of the heterogeneous complexant can be treated as a system of simple ligands. The proportion of metals complexed by various sites, strongly depends on the total metal/ligand ratio. Thus it can be expected that the corresponding contribution of these metal complexes, to the metal bioavailability, will largely depend on the chemical heterogeneity and the metal/ligand ratio.

### 1.1.4 The natural “particles”

They are more often aggregates of various types of solids or polymeric compounds. Particles are ubiquitous in all natural systems and play an important role in the control and fate of nutrients, pollutants and trace metals. Mass concentrations of suspended material range from \( 10^{-2} \) mg/L in the deep ocean to greater than a gram per liter in some rivers and estuaries [12]. The sizes of colloidal particles are from nanometers to micrometers (Fig. 1.3). The most important size fraction of particles is the small size fraction because they have large specific surface areas and high surface energies which facilitate sorption of significant quantities of substances, even though their mass percentage is low (only 10-15% of the total particle mass concentration [13,54]). The origin of submicron particles are from: (i) chemical and biochemical production; (ii) biological debris; (iii) resuspension of sediments; (iv) mechanical and chemical weathering of soils. They include inorganic colloids such as aluminosilicates (clays), silica and iron oxyhydroxyde particles, organic colloids, mixtures of them and microorganisms [9,15]. Their sizes often fall into 3-1000nm with diffusion coefficients
varying from intermediate to very low values (Table 1.1). The size distribution of particles is much broader than those in the former two groups, influencing significantly their diffusive transport. In addition, metal diffusion inside the aggregate may also affect the overall kinetics of metal-aggregate interaction. Thus, it is expected that their contribution to bioavailability will be largely dependent on the size class.

The size distribution of particle sizes in natural systems is the result of production mechanisms and of a number of processes which either bring the particles together (coagulation mechanisms) or disrupt existing aggregates. The size of colloids is of fundamental importance because this parameter controls many of the general properties of these materials. A knowledge of the size distribution is an essential information in particular for a satisfactory understanding of the processes governing both the kinetics of aggregation and the adsorption capacity [15].

A large body of measurements indicates that an important fraction of trace elements (e.g. Cu, Cd, Pb, Zn) introduced into the aquatic environment is found associated with suspended or bottom sediments (Table 1.3); this association can change their chemical activity and biological availability. The processes that govern the scavenging of trace elements by particulate matter and their release to the ambient water when the environmental conditions are changed must be understood if the impacts of trace elements on the environment are to be predicted [13].

Table 1.3. Examples of percentage of colloidally bound metals in natural waters [16].

<table>
<thead>
<tr>
<th>River/region</th>
<th>Colloidally bound metal%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>1. Northern Britain (Canada)</td>
<td>15-100</td>
</tr>
<tr>
<td>2. Nova Scotia (Canada)</td>
<td>75-85</td>
</tr>
<tr>
<td>3. Ochlochonee (USA)</td>
<td>&gt;65</td>
</tr>
<tr>
<td>4. Silone Channel (Italy)</td>
<td>44</td>
</tr>
<tr>
<td>5. Ob/Yenisey (Russia)</td>
<td>89-97</td>
</tr>
<tr>
<td>6. San Joaquin/Sacreament (USA)</td>
<td>99</td>
</tr>
<tr>
<td>7. Garonne (France)</td>
<td>69</td>
</tr>
<tr>
<td>9. West Neck Bay (USA)</td>
<td>58</td>
</tr>
<tr>
<td>10. Thur River (Switzerland)</td>
<td>5-30</td>
</tr>
<tr>
<td>11. Kagamigaike pond (Japan)</td>
<td>&gt;6</td>
</tr>
<tr>
<td>12. Rivers in Amazon basin</td>
<td>35-91</td>
</tr>
<tr>
<td>13. Several waters (Germany)</td>
<td>43</td>
</tr>
<tr>
<td>14. Delsö Creek (Sweden)</td>
<td>12</td>
</tr>
</tbody>
</table>
Several models have been developed for interpreting the adsorption of trace elements at metal oxide surfaces. The most widely accepted one, the surface complexation model, is based on an extension of solution coordination chemistry to the description of interactions of ions with reactive surface sites present at the solid-solution interface [13,16,17]. In the presence of water, the surface of particles, such as oxides, are generally covered with surface hydroxyl groups [16]. These functional groups contain the same donor atom (oxygen) as found in many functional groups of soluble ligands, such as hydroxides, carboxylates. In addition all $≡S-OH$ groups will be deprotonated, which will create a surface electric field. Thus, it is expected that metals will be bound to these functional groups via complex formation plus electrostatic attraction. Although there is possibility that bidentate surface complexes are formed where one metal is bound to two functional groups simultaneously, most often an inner-sphere metal complex forms by coordination of one metal to one surface functional group. Thus, the binding properties of particles can be modelled via the formation of 1/1 metal complexes in the presence of an electric field [13,16,17]. The thermodynamic description of surface complexation, usually considers that the Gibbs free energy of adsorption ($\Delta G_{\text{ads}}$) includes two terms: $\Delta G_{\text{intrinsic}}$ which accounts for the formation of a chemical bond between the adsorbate and a reactive surface site, and $\Delta G_{\text{coulombic}}$ which accounts for the electrostatic energy of interactions between the adsorbate ion and the charges that developed at the surface of the metal oxide. The surface complexation model can describe and predict the extent of surface binding as a function of adsorbent concentration, adsorbate concentration, solution pH, ionic strength, dissolved ligand concentrations, competing ion concentrations, and other solid and solution characteristics.

1.2 Trace metal biouptake by microorganisms

1.2.1 Biouptake by microorganisms

Uptake of nutrients by microorganisms occurs mainly by transport through ion channels, carrier mediated processes, active transport or endocytosis [18]. In addition microorganisms do not have specific transport systems for each compound. Depending on its chemical forms, a metal can pass the membrane via different routes: e.g. liposoluble complexes can pass directly the plasma membrane, while hydrophilic complexes must first dissociate (Figure 1.4).

![Figure 1.4. Schematic diagram of the physicochemical processes that take place near a consuming interface, (electrode or microorganism) [47].](image-url)
In general, the biouptake by microorganisms involve the following steps [18-20]:

a. advection or diffusion of the metal and its complexes from the bulk solution to the biological surface through the outer “protective” cell wall;
b. dissociation of hydrophilic metal complexes;
c. adsorption/surface complexation of the metal at passive binding sites within the cell wall, or at transport sites on the outer surface of the plasma membrane;
d. uptake or “internalization” of the metal (transport across the plasma membrane).

1.2.2 FIAM and BLM

Based on a large amount of experimental results, to describe the uptake of metal by microorganisms, the Free Ion Activity Model (FIAM) was formulated [21] as:

\[ J_{\text{int}} = k_{\text{int}} K_a \{X\} [M] \]  

(1.1)

where \( k_{\text{int}} \) is the internalisation rate constant, \( \{X\} \) is the surface concentration of the transport sites and \([M]\) is the activity of free M in the bulk solution. The flux \( J_{\text{int}} \), of metal internalisation is directly proportional to the free metal ion activity. Later, a similar model-Biotic Ligand Model (BLM) [22] was formulated as:

\[ J_{\text{int}} = k_{\text{int}} \{MX\} \]  

(1.2)

where \( \{MX\} \) is the surface metal-site complex concentration. When surface complexation kinetics at the biological interface are not rate-limiting, i.e., \( \{MX\} \) and \([M]\) are at equilibrium, these two model are equivalent via \( \{MX\} = K_a \{X\} [M] \). Both models assume that the free metal ion, its complexes in solution, and its complexes with the transport sites on the biological surface are in chemical equilibrium. The FIAM and BLM are mathematically equivalent. Their only difference is the way competition it taken into account. In the BLM, the determinations of \( \{MX\} \) will take competing ions into account implicitly whereas in the FIAM stability constants for the competing ions must be known explicitly, to compute the flux usually in FIAM, one also assumes that \( \{X\} \gg \{MX\} \) [19,22]. Both models predict that the formation of complexes in solution will reduce trace metal uptake and thus reduce metal bioavailability.

Despite the fact that they have been used in a wide range of conditions for a wide range of aquatic organisms, the above two models (FIAM, BLM) are only strictly applicable for cases where [19]:

i) the plasma membrane is the primary site of interaction of the trace metal with living organisms;
ii) mass transport in solution towards the membrane is not rate-limiting;
iii) chemical kinetics in solution are not rate-limiting;
iv) surface complexation kinetics at the biological interface are not rate-limiting;
v) in cases where competition occurs for transport sites, it can be predicted by thermodynamic constants;
vi) carrier ligands in the membrane generally remain undersaturated;
vii) the membrane surface is chemically homogeneous (i.e. it only contains on type of site);
viii) chemical reactions of solutes with the cell walls are either negligible or very fast (at equilibrium) compared with internalisation;
ix) the induced biological response is directly proportional to metal internalisation fluxes, $J_{\text{int}}$, or concentrations of the surface complex \{MX\}.

The central part of these two models is based on the hypothesis that dynamic external factors don’t affect the biouptake rate and only thermodynamic external factors influence biouptake through the free metal ion activity. However, there are more and more experimental evidences against this hypothesis [19, 21]:

1) organic ligands forming lipophilic complexes with the metal can passively diffuse through the plasma membrane, leading to a bigger biouptake than that predicted by FIAM and BLM;
2) when transfer through the plasma membrane is very fast, e.g. under starvation conditions, the maximum possible flux is controlled by chemical dissociation and diffusion of complexes in the external medium. If these metal complexes are in large proportions, the biouptake is proportional to the concentrations of these complexes but not of free metal ions;
3) complexes with low diffusion coefficient (particle/aggregate) might become limiting factor for the transport of the metal;

These exceptions suggest that more general dynamic models should be developed.

1.2.3 General model of biouptake

![Model of metal-organism interactions.](image)

For the purpose of simplicity, let us consider a simple system where the only dissolved species are the free metal ion $M$ and the complex $ML$ formed with the ligand $L$ (Figure 1.5). Combining all the steps a-d in section 1.2.1 and assuming that the cytoplasm is a perfect sink for $M$ and that steady-state concentration gradients are reached in solution and through the membrane, it can be shown that the flux $J$ is given by [18]:

$$J = \frac{k_dK_a[M_t]}{1 + AB}$$  \hspace{1cm} (1.3)

where $k_d = k_{\text{int}}\{X\}$ is the rate for the transport of $M$ across the plasma membrane, $K_a$ is the equilibrium constant for the adsorption of $M$ on the transport sites, $[M_t]$ is the total metal
concentration in the bulk solution, \( \alpha (=\frac{[M]}{[M]_0}) \) is the overall degree of complexation of \( M \) in the bulk solution, and \( A \) and \( B \) are given by:

\[
A = \frac{k_a K_a}{D / \delta}
\]

\[
B = 1 + \left(\frac{k_a [L] \delta^2 / D_M}{(k_a [L] \delta^2 / D_M)^{1/2} / \alpha}\right)^{1/2}
\]

where \( \overline{D} \) is an average molecular diffusion coefficient for species \( M \) and \( ML \), \( \delta \) is the diffusion layer thickness, i.e., the layer of solution in contact with the membrane, in which the concentration gradients are developed, \( D_M \) is the diffusion coefficient of free metal ion \( M \), \( k_a \) is the association rate constant between \( M \) and \( L \), \( \alpha \) is the degree of complexation.

Eq 1.3 should be considered only as a crude description of metal uptake since several assumptions were made: reaction layer approximation and planar diffusion. It is, however, useful to understand and compare the relative importance of the physical, chemical, and biological factors in biological metal uptake by means of the two terms \( A \) and \( B \) in the equation:

The term \( A \) provides the influence of the biological transport across the membrane \( (k_a K_a; \text{cm.s}^{-1}) \) relative to that of the physical transport \( (\overline{D} / \delta; \text{cm.s}^{-1}) \); The term \( B \) provides the influence of formation rate of the complexes \( (k_a [L]; \text{s}^{-1}) \) relative to that of physical transport \( (D_M / \delta^2; \text{s}^{-1}) \).

Based on Michaelis-Menten type of flux equation and the Best equation, van Leeuwen [23] explicitly indicates the biological flux from the bulk solution into microorganism for labile and inert complexes and bioavailability of these types of metal complex under different bioaffinity.

### 1.3 Permeation liquid membrane (PLM)

PLM is a dynamic speciation technique which measures metal flux under conditions which somewhat mimics those of biouptake by microorganisms. For that reason, it is a so called bioanalogical sensor [24].

#### 1.3.1 Trace metal speciation and sensors

The term metal speciation is often used as synonymous with equilibrium speciation which deals with metal species distribution in solution at equilibrium. It is linked with the bioavailability of trace metals when the conditions for the free ion activity model (FIAM) or the biotic ligand model (BLM) are met (section 1.2). However, under more general conditions, the biouptake of trace metals by microorganisms, involves the dynamics of metal complexes (diffusion and chemical kinetics). Thus methods for dynamic metal speciation in aquatic ecosystems are required. This field is new but emerging as a powerful basis for development of predictions of bioavailability and reliable risk assessment strategies [24]. The central part of dynamic metal speciation analysis is that the metal flux towards the consuming interface of the sensor is measured. Table 1.4 summarizes the features of dynamic metal speciation techniques and their comparisons with equilibrium-based sensors.
Table 1.4. Features of dynamic metal speciation techniques, and comparison with equilibrium-based sensors [24].

<table>
<thead>
<tr>
<th>Method</th>
<th>Name of the technique</th>
<th>Physicochemical basis</th>
<th>Type of technique</th>
<th>Species measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltammetries</td>
<td>Voltammetries</td>
<td>Diffusion in test medium</td>
<td>Dynamic</td>
<td>Free metals plus dynamic complexes</td>
</tr>
<tr>
<td>GIME</td>
<td>Gel-integrated microelectrode</td>
<td>Radial diffusion in gel</td>
<td>Dynamic</td>
<td>Free metal plus dynamic penetrating complexes</td>
</tr>
<tr>
<td>DGT</td>
<td>Diffusive gradients in thin film</td>
<td>Planar diffusion in gel</td>
<td>Dynamic</td>
<td>Free metal plus dynamic penetrating complexes</td>
</tr>
<tr>
<td>PLM</td>
<td>Permeation liquid membrane</td>
<td>Planar diffusion in sample and membrane</td>
<td>Dynamic</td>
<td>Free metals plus dynamic complexes</td>
</tr>
<tr>
<td>ISE</td>
<td>Ion selective electrode</td>
<td>Equilibrium or steady-state membrane potential</td>
<td>Equilibrium</td>
<td>Free metal ion</td>
</tr>
<tr>
<td>DET</td>
<td>Diffusive equilibrium in thin film</td>
<td>Equilibrium gel/sample</td>
<td>Equilibrium</td>
<td>All penetrating species</td>
</tr>
<tr>
<td>PLM</td>
<td>Permeation liquid membrane</td>
<td>Equilibrium source/acceptor solutions</td>
<td>Equilibrium</td>
<td>Free metal ion</td>
</tr>
<tr>
<td>DMT</td>
<td>Donnan membrane technique</td>
<td>Equilibrium sample/acceptor</td>
<td>Equilibrium</td>
<td>Free metal plus part of cationic penetrating complexes</td>
</tr>
<tr>
<td>CLE-ADSv</td>
<td>Competing ligand exchange-Adsorptive voltammetry</td>
<td>Equilibrium with MLad in sample</td>
<td>Equilibrium</td>
<td>Free metal plus complexes weaker than MLad</td>
</tr>
</tbody>
</table>

All the dynamic metal speciation sensors listed in Table 1.4 have one thing in common, i.e., their external medium is the same as that of microorganisms and thus they can indicate the bioavailability of metal species in aquatic systems when interfacial processes are not limiting. All the techniques presented are deployable in situ which is a major advantage over sampling-based, sequential step ‘kinetic speciation schemes’.

PLM will be used in this thesis and is then described in more details below.

1.3.2 Principle of PLM

Permeation liquid membrane techniques (PLM) are newly emerging procedures for separation and preconcentration of target elements or species. They are often called in the literature supported liquid membrane (SLM) techniques, based on the type of devices which is the most widely used for liquid membrane formation [25].

PLM is an aqueous-organic-aqueous extraction technique (Figure 1.6). The test solution (source solution) with the target element (e.g. the metal M) is introduced on one side of the membrane. The metal is then selectively transported to the strip (acceptor) solution through the organic phase by means of the lipophilic carrier, C. It is then trapped in the strip solution by a strong complexing agent, S which lowers the electrochemical potential of metal in the strip solution compared to the source solution. The driving force for this facilitated transport is thus the chemical potential gradient of the metal which decreases from the source to the strip solution. The diffusion of metal in two aqueous solutions and in the membrane is usually the main way of transport.
1.3.3 Experimental devices

Depending on the types of application, a number of PLM devices have been designed and utilized in laboratories, on line, on the field or in situ [25]. Figure 1.8 shows three kinds of typical PLM devices which are often used in laboratories. Most of these devices belong to one of the following two categories: flat sheet PLM and hollow fiber PLM, depending on the geometry of the supporting membrane.

The flat sheet PLM (FSPLM) consists of a microporous hydrophobic flat sheet membrane in which the organic liquid is held in the pores of the membrane by capillary forces. In practice,
the flat sheet PLM is sandwiched between two cells which hold the source solution and the strip solution. Usually, convection is applied to the source solution by stirring (Figure 1.8a) or by using a flow-through device (Figure 1.8b).

In the hollow fiber PLM (HFPLM), the organic solvent is impregnated in the wall of the fiber and the strip solution is in the lumen of the fiber. Because of the small volume of the strip solution compared to the source solution, a big accumulation can be achieved in the strip solution. So this technique is more amenable to analytical applications at trace levels.

![Diagram of various types of cells used with flat sheet and hollow fiber permeation liquid membrane.](Figure 1.8)

**Figure 1.8.** various types of cells used with flat sheet and hollow fibre permeation liquid membrane. (a) flat sheet with stirred source and strip solutions; (b) flat sheet with a flow-through cell made of two spiral channels machine grooved in PTFE blocks; (c) single hollow fibre with strip solution inside the lumen [25].

### 1.3.4 Enrichment factor

The metal enrichment by permeation liquid membrane was first proposed in 1970s [26] and then developed by P.R. Danesi [26] for industrial applications. Figure 1.9 illustrates the metal enrichments of the devices listed in Figure 1.8. Both Figure 1.9 a and b show that with the time evolution, the metal concentration in strip solutions increases until the chemical potential of free metal ion is equal in both source and strip solution. The preconcentration factor, \( F \), is defined as:
\[ F = \frac{c_{st}}{c_{so}^{0}} \]  

(1.6)

Where \( c_{st} \) is strip concentration at time, \( t \), and \( c_{so}^{0} \) is the source concentration at time \( t=0 \). High preconcentration factors can be achieved by using in particular a small volume ratio of strip over source solution [25].

For the simplest case of metal complexes, a labile metal complex is present in the source solution and planar diffusion occurs at the source/membrane interface, the strip solution is a perfect metal sink and transport in the strip solution is not rate limiting. At steady-state, the flux is then given by [25]:

\[
J = \frac{c_{so}^{b}}{\alpha_{so}^{b}} \left[ \frac{\delta}{D_{so}^{b} \alpha_{so}^{b}} + \frac{\ell}{D_{MC} K_{P} [C]} \right]^{-1} 
\]  

(1.7)

where \( c_{so}^{b} \) is the total metal concentration in the bulk of the source solution, \( \alpha_{so}^{b} \) is the degree of complexation of metal in the source solution, \( \delta \) is the diffusion layer thickness near the source/membrane interface, \( D_{so}^{b} \) is the average diffusion coefficient of M and ML in the source solution, \( \ell \) is the membrane thickness, \( D_{MC} \) is the diffusion coefficient of metal and carrier complex in the membrane, \( K_{P} \) is the partition coefficient of metal between the source solution and the membrane, \([C]\) is the carrier concentration in the organic solvent. As shown in Figure 1.10, after a short time-lag, linear concentration gradients prevail in the diffusion layer in the source solution and in the membrane and the resistance is only the diffusion in the source solution and the membrane.
1.3.5 Selectivity

The selectivity of PLM is realized via specific carriers. A large number of potential organic carriers for various analytes exist for PLM. They can be neutral, cation-exchange and anion-exchange extractants. The reagents used for analytical metal determination include in particular the macrocyclic extractants. Among these compounds, diaza crown ethers are known to complex well with transition metals as well as some alkaline metals. Thus it can be used as metal transport carrier in mode c of Figure 1.7, by back transporting a non perturbing alkaline metal ion (Na\(^{+}\)) in the source solution [27]. In this study, 1,10-didecyl-1,10-diaza-18-crown-6 with addition of alkyl side chains on the ring (22DD, Figure 1.11) together with palmitic acid (PAH) (1:1 ratio) were used as carrier for selectively transporting Cu(II), Pb(II) and Cd(II). Pb(II) and Cd(II) are complexed inside the ring of 22DD [27] and transported with anionic laurate or palmitate as counter ions, as depicted in Figure 1.6.

![Figure 1.10. Schematic concentration gradients of labile metal complex in PLM.](image)

![Figure 1.11. Structure of the carrier used for the PLM systems in this work: 1,10-didecyl-1,10-diaza-18-crown-6 ether (22DD).](image)

The mechanisms of Cu(II) transport by 22DD-LAH (LAH=Lauric acid) is more complicated and the mechanisms with PAH (Palmitic acid) is likely to be the same. As shown in Figure 1.13, the main steps are the following [28]:

1) 2DD is strongly surface active, whereas LAH is much less surface active. However, they can associate by hydrogen bonding, so that LAH is co-adsorbed with 22DD, at the organic/water interface.

2) Cu(II) ion is attracted by 22DD at the toluene-water interface, and incorporated in the organic solvent where it forms stable dimeric complexes with fatty acids (“paddlewheel” dimers). In absence of 22DD those complexes would aggregate and precipitate.

3) 22DD however can form ternary complexes with the “paddlewheels” complex, without dissociate it. This stabilizes the “paddlewheel” dimers kinetically against polymerization.
4) Cu(II) ions is thus transported primarily by a complex formed with laurate (or palmitate) but stabilized by 22DD.

Figure 1.12. Scheme of the key interfacial and bulk processes during the Cu(II) transport through the PLM with a mixture of LAH and 22DD in toluene/phenylhexane [28].

1.3.6 Analytical applications of PLM

PLM is mainly used in the field of industrial applications for recovery of metals from waste water treatment such as nuclear wastes. [26]. After the development by Danesi, it has been used by many researchers to selectively enrich certain chemicals[25] such as metals[29-31], proteins[32], or organic acids[33,34]. Cox et al. [35] are the first who used PLM for analytical preconcentration of metal where the preconcentration factor of Cu(II) is 10 after 1 h. The number of reports dealing with trace metal or organic analysis, by PLM, is comparatively small [36,37] and even less for metal speciation. Redox speciation of Cr(III/VI) [38] and As(III/V)[39] has been reported. Parthasarathy et al. [40,41] have shown that, under appropriate conditions, PLM is very useful to determine the thermodynamic degree of complexation of metals, in solutions with hydrophilic ligands, either synthetic or natural ones. Analytical applications of PLM to environmental samples have also been reported in refs [42] and [43] and a PLM system was specifically designed and coupled with voltammetric technique [45] to enable direct simultaneous dynamic speciation of trace metals (Cu, Cd, Pb, Zn) and on-line measurements in natural waters without any sample perturbation. Buffle et al. [44] have emphasized that PLM is very appropriate to determine metal complexation in complicated environmental systems [25] and can be used as a bioanalogical sensor, i.e., a
sensor whose response is controlled by the same environmental processes as those influencing metal uptake by organisms. However, for speciation studies, many reported PLM systems are not suitable either because the addition of a reagent is required for the co-transport of the target chemicals or because H⁺ is used for counter-transport which may change the species distribution of metal in the sample solution.

1.3.7 Similarity with microorganisms

The similarities between PLM and microorganisms are summarized below (Figure 1.13):

1) In PLM, the source and strip solutions are separated by an hydrophobic membrane which can well mimic the membrane separating the outside and inside of a microorganism.
2) The carrier in the membrane of PLM has the same function as the transport sites of microorganisms.
3) The diffusion layer thickness of PLM is 10-100 μm which is similar to that of microorganisms.
4) For both PLM and microorganisms, hydrophobic metal complexes can passively diffuse across the organic phase in the membrane of PLM and the plasma membrane.

However, differences of PLM and microorganisms also exist and caution should be used when interpreting the dynamic speciation results of PLM in terms of the uptake of metal by microorganisms. A major difference is that the geometry of the membrane of PLM is planar, while that of microorganisms is close to spherical. A second difference is the size. The radius of microorganisms is at the order of magnitude 1 μm which may cause the labilities of metal complexes decrease when working under the same conditions for PLM.

Eq 1.7 can be rewritten as:

\[ J = \frac{D_{MC}K_P[C]c_{so}^b}{\ell \alpha_{so}} \left[ 1 + \frac{D_{MC}K_P[C]}{\ell D_w \alpha_{so}} \delta \right] \] (1.7a)

Interestingly, eq. 1.7a is readily compared to eq. 1.3 developed for microorganisms, by choosing infinite \( k_a \) of eq 1.5, which correspond to planar diffusion of labile metal complex. Then \( B=1 \) in eq 1.5 and eqs 1.7a and 1.3 are fully equivalent if we realize that the term \( \frac{D_{MC}K_P[C]}{\ell} \) in eq. 1.7a is the analogue of \( k_aK_n \) in eq. 1.3. Thus, PLM is a bioanalogical sensor which may provide a flux which is a good surrogate of microorganism flux. The effect of the possible slow kinetics of metal complex formation/dissociation should however be studied. This is explained in chapters 3-5.

In eq 1.7a, when the rate of membrane transport is small, i.e., in practice at low carrier concentration, small partition coefficient or big membrane thickness, the processes in the source solution are at equilibrium, i.e., the flux measured by PLM is controlled by the free metal ion concentration, as for microorganisms under FIAM or BLM conditions. When the rate of membrane diffusion is very large, i.e., in practice at high carrier concentration, large
partition coefficient or small membrane thickness, the PLM and microorganisms uptake flux is controlled by the physicochemical dynamic processes of the external medium.

Figure 1.11. Schematic diagram of PLM flux as compared to uptake flux of metal at microorganism/solution interface.

1.4 Physicochemical principle of metal flux at a consuming interface in complexing medium

Figures 1.5 and 1.6 show schematically the most important physicochemical processes that take place in aquatic systems, near a consuming interface, represented by a bioanalogical sensor or a microorganism. In the external aquatic medium, trace metals are complexed with the highly chemically and physically heterogeneous natural complexants discussed in section 1.1.1. For the sake of simplification we shall discuss here the case where the solution contains only one ligand, L. The important processes controlling the metal flux are the following: the metal and its complexes diffuse from the bulk solution to the consuming interface; the metal and the ligand can associate and the metal complexes can dissociate in the diffusion-reaction layer. Finally a process which depends on the nature of the interface, occurs at the surface/solution interface. This is defined in the so-called boundary condition. Thus, the most important physicochemical parameters to consider are the diffusion coefficients \( (D) \) of metal.
ions, ligands and their complexes; the thermodynamic stability constants \( (K) \) of metal complexes and their chemical formation and dissociation rate constant \( (k_a, k_d) \). The bioavailable metal species can also be related to their lability index which is defined by, the ratio of the metal flux obtained when chemical reactions are the rate limiting steps over the flux obtained when diffusion in solution is rate limiting.

\[
\text{Lability index} = \text{fully kinetic flux} / \text{fully diffusion limited flux}
\]

### 1.4.1 Chemical kinetics

The complex formation and dissociation rate constants \( (k_a, k_d) \) are important parameters required for computing the flux at a consuming interface. However, for metal complexes in aquatic systems, these data are rare, except for small complexes with simple ligands, such as \( \text{OH}^-, \text{Cl}^- \), etc. These parameters are thus often estimated based on the so-called Eigen-Wilkins mechanism. For simple, not chelating ligands, it has been shown that the formation of ML starts with the formation of an outersphere complex \([M(H_2O)_q...L]\), in equilibrium with free \( L \) and free \( M(H_2O)_q \). The dehydration of \( M(H_2O)_q \) in the ion pair is often the rate-limiting step for the formation of the inner-sphere metal complex, \( ML \) \( [3,19,55] \) (eq. 1.8):

\[
M(H_2O)_q + L \rightleftharpoons K_{os} \rightarrow M(H_2O)\ldots L \xrightarrow{k_{aq}} ML(H_2O)_{q-1}
\]

Under these conditions, the association rate constant \( k_a \), can be estimated from the product of the outer sphere stability constant, \( K_{os} \), and the water loss rate constant, \( k_{-w} \).

\[
k_a = K_{os}k_{-w}
\]

The outer sphere stability constant can be estimated from the free energy of electrostatic interaction between \( M(H_2O)_q \) and \( L \) and the ionic strength of the medium. In Eigen-Wilkins model, \( K_{os} \) does not depend on the chemical nature of the ligand. A similar mechanism may also be applied to a chelating ligand (polydentate ligands), when the rate-limiting step is the formation of the first metal-ligand bond. \( K_{os} \) then depends on the geometries of the ligand and the complex in particular of the the position of the various electric charges \( [46] \). Values for the dissociation rate constant, \( k_d \), of a complex \( ML \), are usually estimated from the corresponding thermodynamic equilibrium constant, and the calculated values of \( k_a \):

\[
k_d = \frac{k_a}{K}
\]

### 1.4.2 Diffusion-reaction equations

Let’s assume that the system includes \( n_l \) ligands and \( j \) successive complexation reactions for each type of ligand \( [47] \), with \( j=1, \ldots, n_l \). We will consider a set of parallel and successive chemical reactions of the following kind:

\[
M^jL_{i-1} + i L \xrightarrow{j_{ia}k_{ia}} M^jL_i \quad i=1,\ldots, n
\]
Chemical reaction (1.10) takes place within the solution domain. Index \( i \) represents the stoichiometric number of \( j \) ligand in the complex and the superscript \( j \) is limited to the nature of the ligand. The chemical rate associated to each complex is given by:

\[
^j r_i = -^j k_{a,i}[M^j L_{i-1}]^j L + ^j k_{d,i}[M^j L_i] \quad i=1,\ldots,\, n
\]

(1.11)

where \(^j k_{a,i}\) and \(^j k_{d,i}\) are the association and dissociation rate constants respectively. They are related to the equilibrium constants of the corresponding reaction, \(^j K_i\),

\[
^j K_i = \frac{^j k_{a,i}}{^j k_{d,i}} = \frac{[M^j L_i]^j}{[M^j L_{i-1}]^j} \quad i=1,\ldots,\, n
\]

(1.12)

All the species diffuse within the solution domain following the usual set of reaction-diffusion equations [47]:

\[
\frac{\partial [M]}{\partial t} = D_M \nabla^2 [M] + \sum_{j=1}^{n} ^j r_i
\]

(1.13)

\[
\frac{\partial [M^j L_i]}{\partial t} = D_{M^j L_i} \nabla^2 [M^j L_i] - ^j r_i + ^j r_{i+1} \quad i=1,\ldots,\, n-1
\]

(1.14)

\[
\frac{\partial [M^j L_s]}{\partial t} = D_{M^j L_s} \nabla^2 [M^j L_s] - ^j r_s \quad s=\, n
\]

(1.15)

\[
\frac{\partial [L]^j}{\partial t} = D_{[L]^j} \nabla^2 [L]^j + \sum_{i=1}^{n} ^j r_i
\]

(1.16)

At \( t \leq 0 \), it is assumed that the solution is homogeneous, i.e., there is no concentration gradient or the concentration of any species \( X \) at the interface is the same as that in the bulk solution: \([X] = [X]^*\). The boundary conditions are discussed below.

1.4.3 Boundary conditions

There are two types of boundary conditions: very far from the interface and at the interface. Depending on the nature of the problem, either finite diffusion or semi-infinite diffusion condition is applied to species \( X \), far from the interface. When the solution is quiescent, the semi-infinite diffusion condition is applied. It is given by:

\[
[X](x,t) \rightarrow [X]^*(x,t) \quad x \rightarrow \infty
\]

(1.17)

However, in natural aquatic system or in a well-stirred solution, due to the hydrodynamics, a diffusion layer with thickness \( \delta \) is often built against the interface, then the boundary conditions are given by:

\[
[X](x,t) = [X]^*(x,t) \quad x \geq \delta
\]

(1.18)
In eqs 1.17 and 1.18, superscript * indicates bulk concentration. At the consuming interface, the boundary conditions are a little more complicated and depend on the nature of the processes at the consuming interface. Three boundary conditions at the interface which are useful in the thesis are summarized below:

### 1.4.3.1 Perfect sink

By definition a consuming interface is a perfect sink when the uptake rate of metal is sufficiently large compared to all other processes and never rate limiting. This is the case in DGT and Voltammetry at sufficiently negative potential [44]. Then the free metal ion concentration at the consuming interface is always nil, i.e.:

\[
[M] = 0 \text{ at } x = 0 \tag{1.19}
\]

In addition, in the following, the metal complexes are assumed to be inactive at the interface and their contributions to the total flux occur only via their dissociations in solution. So at the interface:

\[
\frac{d[M^i/L]}{dx} = 0 \text{ at } x = 0 \tag{1.20}
\]

Under the condition that the consuming interface is a perfect sink, the uptake of metal is fully dependent on the labilities of the metal complexes, i.e., it depends only on the physico-chemical parameters of the external medium. Maximum concentration gradients of the free metal ion and its complexes are built in the diffusion layer, and the corresponding flux is the maximum one which is allowed by the external medium.

### 1.4.3.2 Michaelis-Menten condition at microorganism surface

Prior to the internalisation of metal by microorganisms, free metal ion is firstly adsorbed by transporter sites located on the surface of the plasma membrane. This adsorption process is usually assumed to be fast enough (when compared with diffusion or internalisation process) and to be described by a Langmuir (equilibrium) isotherm relating the fraction \( \theta \) of transporter site occupied by \( M \) and the local concentration of free \( M \), \([M]_0\), at the microorganism surface [48]:

\[
\theta = \frac{K_a[M]_0}{1 + K_a[M]_0} \tag{1.21}
\]

where \( K_a \) is the adsorption constant. Thus the surface concentration of free metal ion is dependent on the surface concentration of transporter sites. It is linked to the general form of the Michaelis-Menten equation [48]:

\[
\{X\}_{tot} \frac{d}{dt} \frac{K_a[M]_0}{1 + K_a[M]_0} = D_M \left[ \frac{\partial [M]}{\partial x} \right]_{x=0} - k_{in} \{X\}_{tot} \frac{K_a[M]_0}{1 + K_a[M]_0} \tag{1.22}
\]

where \( \{X\}_{tot} \) is the total surface concentration of transporter sites. Again, the contributions of metal complexes to the total flux only occur via dissociation and the boundary conditions of metal complexes are described by eq 1.20.
The concentration gradients of free metal ion and its complexes depend on the internalisation rate constant $k_{int}$. An extreme case is when the internalisation rate is not the rate limiting step, the maximum concentration gradients are then developed in the diffusion layer and the maximum flux is obtained. At the other extreme, when internalisation is the rate limiting step, the consumption of free metal ion by the uptake is very small and no concentration gradients are built in the diffusion layer both for the free metal ion and for its complexes. This corresponds to the FIAM or BLM models.

### 1.4.3.3 The boundary conditions at PLM interface

Due to the large concentration of carrier used in PLM, the latter is always in excess compared to total metal concentration at the interface and it is usually assumed that the binding of free metal to the carrier is not rate limiting. At steady state, the specific concentration of free metal ion at the source/membrane interface [25]:

$$[M] = [M]_{surface} \text{ at } x = 0$$  \hspace{1cm} (1.23)

Results from the continuity of fluxes in the source solution and in the membrane, at $x=0$. These two fluxes are given by:

$$D_M \left( \frac{d[M]}{dx} \right)_{x=0} = \frac{K_p[C]D_{MC} ([M]_0 - 0)}{\ell}$$ \hspace{1cm} (1.24)

The right hand side of eq. 1.24 is a linear diffusion of metal complex in the membrane. Its driving force is the chemical potential of concentrations of metal carrier complex at source/membrane interface $([M]_0[C])$ and at strip/membrane interface $0$.

For the same reason as explained above, the boundary conditions of the metal complexes are given by eq 1.20.

As discussed in sections 1.3.3 and 1.3.7, PLM somewhat mimics microorganisms and can work under either equilibrium speciation or dynamic speciation conditions, depending on the rate transport through the membrane. When it is high and not rate limiting, the maximum concentration gradients of free metal ion and its complexes and the maximum flux are obtained, on the opposite, when it is low and it is rate limiting, no concentration gradient is built in the diffusion layer and a flux analogous to that of FIAM or BLM is obtained. The rate of membrane transport can be changed by tuning the carrier concentration and membrane thickness.

### 1.5 Environmental flux computation codes

Computations of metal fluxes at consuming interfaces like microorganisms or bioanalogical sensors are made difficult in natural aquatic systems due to the very large number of complexes and complexants and the interplay of many physical and chemical processes. Numerical codes are then needed. Up to now, only two user-friendly codes for metal flux computation in presence of an unlimited number of ligands are available. They are briefly discussed below.
1.5.1 Fluxy

Fluxy is available on the web at http://www.unige.ch/cabe/dynamic and is described in the user manual and in [49]. It is based on analytical solutions of diffusion-reaction equations under the conditions that all ligands are in excess with respect to the total metal concentration. It has two modes: Fluxy-RS is based on the rigorous solution of differential equations [50] but valid only for 1/1 ML complexes; the other mode, Fluxy-RLA is based on the reaction-layer approximation described in [49] and briefly in chapter 7, it can be applied to successive ML_n complexes provided all ML_n (n>1) complexes are in equilibrium with ML, which is frequently encountered with simple ligands [51]. In both modes, Fluxy computes the steady-state metal flux in systems including an unlimited number of complexes and ligands. In a complicated mixture, both Fluxy-RLA and Fluxy-RS provide the proportions of each species in the bulk solution, the total flux of the test metal, the individual contribution of each species to the total flux, and the degree of lability of each complex. Fluxy can work under planar and spherical conditions and a linear Michaelis-Menten boundary condition or perfect sink may be assumed to occur.

Fluxy is written in Microsoft visual C++ version 6.0 and contains about 40000 lines. It is related to a database, containing the dynamic and thermodynamic parameters required for computations. Those include in particular the thermodynamic stability constants of metal complexes with simple ligands, the rate constants for dehydration of metals, and the diffusion coefficients of free metal ions, simple ligands, fulvics and some complexes. The database also contains the parameters required to compute theoretically the dynamic parameters (diffusion coefficients and rate constants) not accessible in the literature, in particular for fulvics and aggregates complexants. The visualisation part runs under MS Windows.

1.5.2 Mhedyn

Mhedyn, (Multispecies HEtergeneous DYNamesics [47]), is based on a Lattice Boltzmann method for the numerical solution of the diffusion-reaction equations. It is coupled to a time splitting technique and a grid refinement method [52, 53] in order to treat physico-chemical systems with dynamic parameters varying over many orders of magnitude. Systems with unlimited number of ligands and complexes can be treated. The major characteristic of Mhedyn are the following: the contribution to metal flux and concentration profile of any species can be computed in the transient and steady-state regimes, without requirement of ligand excess compared to metal. Mhedyn can work under planar geometries with different boundary conditions such as: Michaelis-Menten boundary condition, Nernst boundary condition in Voltammetry, or a perfect sink. The user-friendly version is available at www.unige.ch/cabe/dynamic, however it is limited to planar diffusion with perfect sink or Michaelis-Menten conditions. The major drawback of Mhedyn is that it is computer-time consuming in presence of many complexants, particularly those (particles/aggregates) with low values of diffusion coefficients.

Fluxy and Mhedyn are complementary. Fluxy is a good alternative to Mhedyn for quick computations, when its basic hypotheses (excess of ligand and fast successive complexes) are acceptable for the test system. In presence of non excess of ligand, in particular in presence of fulvics or some particles, Mhedyn however is required, but Fluxy can provide quickly a good estimation of the metal flux and of the main contributors. Until now, neither Fluxy nor Mhedyn (or any other code) has been used to study systematically the relative importance of the various aquatic complexants or the capabilities/advantages of the codes.
1.6 References

[19] Wilkinson, K.J.; Buffle J. ‘Critical evaluation of the physicochemical parameters and processes for modelling the biological uptake of trace metals in environmental


Chapter 2

Objectives

The Free Ion Activity Model (FIAM) and Biotic Ligand Model (BLM) are applied in many laboratory studies of trace metal uptake by microorganisms. However, in many cases, the culture medium includes a strong complexant, such as EDTA, which forms non labile complexes with trace metals, and is not representative of the more labile natural complexants. In addition, more and more exceptions to FIAM or BLM have been found, when studying trace metal biouptake in real aquatic systems. Thus, dynamic models are required to interpret biouptake correctly and dynamic metal speciation should be used to predict the bioavailability and the reliable risk assessment strategies. For correct application of such dynamic models, some basis concepts such as the reaction layer or the degree of lability still need to be clarified under environmental conditions and checked experimentally. Presently, there is almost no example of flux computation performed in real environmental conditions, i.e., with a large number of often heterogeneous ligands. The application of the above concepts should also be revisited under such conditions. To perform such computations, a large number of physicochemical parameters are required due to the vast number of different natural ligands (simple, fulvic and aggregates) and most values of these dynamic parameters (diffusion coefficients and rate constants) are missing. Thus, there is an important need to collect such data.

So the purpose of this Ph.D thesis is to provide information on the above topics, to enable rigorous computation of fluxes in environmental media:

1. **Metal flux in presence of a single complex. The concept of reaction layer revisited and PLM behaviour of labile, semi-labile and inert complexes.**

   a). At the beginning of this Ph.D. study, there was no rigorous theory for the computation of flux in solution with one ligand and one complex with any lability, stability and diffusion coefficient, under finite diffusion boundary layer. The existing theories were developed mainly for Polarography and Voltammetries with semi-infinite diffusion boundary condition, for very stable complexes, with diffusion coefficient equal to that of free metal ion. However, in natural waters, a finite diffusion boundary layer is fixed by the convection, weak complexes may be important and some complexes have diffusion coefficients much lower than free metal. Furthermore, a rigorous theory for one ligand and one complex is important as it serves a basis for understanding the behaviours of multiligand system. Thus, the first aim is to develop a rigorous theory for the system with one ligand and one complex under environmental conditions, under both planar and spherical diffusion conditions (chapter 3). A rigorous definition of lability index and criteria of inert complex will be proposed based on the above rigorous theory.

   b). The proposed rigorous flux theory derived above should be validated by experimental studies. This can be accomplished by using the bioanalogical sensor: PLM described in chapter 1. In this part, various ligands forming complexes with variable labilities should be checked. PLM is chosen for such tests because in some respects, the flux at its interface mimics that at microorganism/solution interface. Studies will be focused on the behaviour of labile, semilabile and non labile metal complexes, by considering in particular the roles of diffusion, hydrodynamics, and equilibrium speciation in solution, as well as the factors influencing the transport through the membrane: carrier concentration and membrane thickness (chapters 4 and 5).
2. Computation of metal flux in environmental multiligand systems. The relative contributions of the various types of complexes and their mutual influences.

To the best of our knowledge, up to now, only two user friendly codes are available for metal flux computation: Mhedyn and Fluxy (chap.1). Mhedyn does not imply any a priori assumption, but is based on numerical simulations and may be time-consuming, depending on the test system. Fluxy is based on mathematical analytical solutions for steady-state flux only and is much faster, but it is based on the a priori assumptions that all ligands are in excess compared to the metal and that equilibrium exists among successive metal complexes. Thus, these codes are complementary. Their application to environmental systems however is very limited. In addition, these papers suggest that in a mixture, the interplay between the various metal complexes may affect their respective lability degrees. The detailed physical reasons of this effect however is presently ill-understood.

In this context, the objectives of this part of the thesis are multifold.

a) In a first step (chapter 7), systems with only two ligands should be studied, because this system is simple it is expected that the roles and interplay of different metal complexes will be easily understood. This study will help the understanding of multiligand systems in natural waters. Different environmental systems are to be considered.

b) The flux computations with Fluxy are time-saving. However, due to its two basic assumptions (ligand excess and equilibrium between successive complexes), Fluxy may give not precise or even wrong results when these two assumptions are not fulfilled. Thus, it is useful to test systematically its conditions of applications and its limitations with various environmental systems (chapter 8).

c) Our purpose is to understand the physico-chemical factors which control a metal flux and to make predictions on metal biouptake, for the various types of metals, based on the composition of the test medium. Thus, metal flux of various metals forming labile, semilabile and non labile complexes in environmental systems is to be computed systematically with Mhedyn, in order to understand in each case the contributions to the total flux of complexes formed with the simple ligands, the fulvics and the aggregates (chapter 9).

3. Dynamic parameter values for flux computation in environmental chemically and physically heterogeneous multiligand systems.

Dynamic parameter values of metal complexes in natural waters have been determined only for a few complexes formed with simple ligands. Most dynamic parameters are unknown and many complexants (biopolymers, aggregates) are ill defined. This is a major limitation in metal flux computation. To overcome this difficulty, we will compile the available data as much as possible. If they are not available, we will propose theoretical approaches to compute the missing parameters.
Part I

Metal flux in presence of a single complex. The concept of reaction layer revisited and PLM behaviour of labile, semi-labile and inert complexes
Chapter 3

General steady-state metal flux equations for solutions containing one complex. The reaction layer revisited

3.1 Overview

In this chapter, the metal flux equations at a consuming interface, in a solution containing one ligand, L, and one complex ML, are derived. In section 3.3, the physical problem is presented for a consuming interface corresponding to a perfect sink, by considering all the environmental physicochemical factors. In section 3.4-3.7, the flux equations for planar and spherical diffusion are given and a new general definition of reaction layer thickness is introduced.

3.2 Introduction

Diffusion-reaction processes are common in environmental chemistry and biological systems such as: biouptake of trace metals by microorganisms [1,2], bioanalogical sensors such as DGT[3], gel integrated voltammetric microelectrodes (GIME) [4,5] and Permeation Liquid Membrane (PLM) [6]. In all these cases, the response of the sensor or organism to the metal, M, depends not only on the equilibrium complexation by the complexants L (thermodynamic speciation), but also on the association and dissociation rates of ML, and its diffusion, i.e., on the dynamic speciation [7]. In multiligand environmental systems, the computation of metal flux at a consuming interface is made difficult due to the interplay of many physical and chemical processes. For that reason, former theories for metal flux computation were focused on specific sensors such as polarographic [8,9] and voltammetric ones [10] with only one ligand, using semi-infinite boundary condition in solution, i.e. a diffusion layer extending at infinity in solution, which implies the absence of convection. In addition, the studied complexes were quite stable, implying that the definition of reaction layer thickness, $\mu$, could be based on the rate of recombination of M with L and not on the dissociation of ML (see section 3.5). Furthermore, the studied complexes were such that $\mu << \delta$, where $\delta$ is the thickness of the diffusion layer.

However, in environmental systems, these conditions are usually not fulfilled. In the vast number of complexes, present in solution, some are not very stable or such that $\mu$ is of the same order of magnitude as $\delta$. In addition, microorganisms and sensors are usually under convective conditions which fix a certain value for the diffusion layer thickness at the surface of the sensor or organism. Thus, before studying multiligand systems, we have revisited the metal flux equations at steady-state, in the above conditions, for solutions containing a single ligand (chapter 3). These equations are applied to PLM sensors in chapters 4 and 5.

3.3 The physical problem

Let’s consider a solution containing a metal ion M, and a ligand L in excess with respect to M. As shown in Figure 3.1, M can form a complex ML with L via reaction (3.1):

$$M + L \xrightarrow{k_a} ML$$  \hspace{1cm} (3.1)
with equilibrium constant \( K = \frac{k_a}{k_d} \) and the association and dissociation rate constants \( k_a \) and \( k_d \). M, ML and L diffuse in solution with diffusion coefficients \( D_M, D_{ML} \) and \( D_L \). The nature of the consuming interface has no importance here, since it is considered as a perfect sink.

**Figure 3.1.** Schematic representation of the physicochemical problem.

For the above diffusion-reaction system, at steady-state, the conservation equations can be written as:

\[
D_M \nabla_{\text{dim}}^2 [M] + k_d [ML] - k_a [L][M] = 0
\]  
(3.2)

\[
D_{ML} \nabla_{\text{dim}}^2 [ML] - k_d [ML] + k_a [L][M] = 0
\]  
(3.3)

The dimensional Laplacian operator, \( \nabla_{\text{dim}} \), depends on the particular geometry considered. For a perfect sink, the boundary conditions can be written as follows:

at \( x = 0 \) for planar diffusion or \( r = r_0 \) for spherical diffusion:

\[
[M] = 0, \quad \frac{d[ML]}{d\rho} = 0
\]  
(3.4)

at \( x \geq \delta \) for planar diffusion or \( r \geq r_0 + \delta \) for spherical diffusion

\[
[M] = [M]^*, \quad [ML] = [ML]^*
\]  
(3.5)

where \([M]^*, [ML]^*\) denote the bulk concentrations. Since L is assumed to be in excess with respect to M, one also gets: \([L] = [L]^*\) at any distance from the interface.

In order to work with dimensionless parameters we define the normalized diffusion coefficients and concentrations:

\[
e = \frac{D_{ML}}{D_M}
\]  
(3.6)
\[
\begin{align*}
\theta &= \frac{[M]}{[M]} \\
\psi &= \frac{[ML]}{[ML]}
\end{align*}
\]  
\[(3.7)\]

3.4 Metal flux under planar diffusion conditions

Eqs 3.2 and 3.3 can be rewritten as follows:

\[
\begin{align*}
\frac{d^2\theta}{dx^2} + \frac{k_a[L]}{D_M} \psi - \frac{k_d[L]}{D_M} \theta &= 0 \\
\frac{d^2\psi}{dx^2} + \frac{k_s[L]}{D_M} \psi - \frac{k_d[L]}{D_M} \theta &= 0
\end{align*}
\]  
\[(3.9)\]

By multiplying the left-hand and right-hand sides of eq 3.10 by \(KL\) and rearranging with \(k_s[L] = k_j[L]\), one obtains:

\[
\varepsilon K[L] \frac{d^2\psi}{dx^2} - \frac{k_s[L]}{D_M} \psi + \frac{k_s[L]}{D_M} \theta = 0
\]  
\[(3.11)\]

By summing eqs 3.9 and 3.11 the kinetic terms cancel out and we get:

\[
\frac{d^2(\theta + \varepsilon K[L]\psi)}{dx^2} = 0
\]  
\[(3.12)\]

which shows that the sum of the gradients of \([M]\) and \([ML]\), weighted by their diffusion coefficients, is constant over the diffusion layer. This implies that, due to the chemical coupling of M and ML, a single depletion layer thickness applies to both M and ML, in spite of their different diffusion coefficients.

The boundary conditions now read:

\[
\begin{align*}
&\text{At } x = 0, \ \theta = 0 \text{ and } \frac{d\psi}{dx} = 0 \quad (3.13) \\
&\text{At } x \geq \delta, \ \theta = 1 \text{ and } \psi = 1 \quad (3.14)
\end{align*}
\]

By integrating eq 3.12 with these boundary conditions, we obtain:

\[
\begin{align*}
\theta + \varepsilon K[L]\psi &= (x - \delta) \left( \frac{d\theta}{dx} \right)_{x=0} + 1 + \varepsilon K[L] \text{ for } 0 < x < \delta \\
\theta + \varepsilon K[L]\psi &= 1 + \varepsilon K[L] \text{ for } x \geq \delta
\end{align*}
\]  
\[(3.15a)\]

The normalized concentration profiles of M and ML and the flux equation are found by combining eqs 3.9 and 3.15a to eliminate \(\psi\):
\[
\frac{d^2 \theta}{dx^2} - \frac{k_a[L](1+\varepsilon K[L])}{D_M \varepsilon K[L]} \theta + \frac{k_a[L]}{D_M \varepsilon K[L]} \left( \frac{d\theta}{dx} \right)_{x=0} + \frac{k_a[L]}{D_M \varepsilon K[L]} \left( 1+\varepsilon K[L] \right) - \left( \frac{d\theta}{dx} \right)_{x=\delta} = 0
\]  

(3.16)

In this equation, we recognize that \( J = D_M[M]^\varepsilon \left( \frac{d\theta}{dx} \right)_{x=0} \) is the metal flux through the interface. In addition, a combination parameter, \( \lambda \), appears as a physically meaningful parameter:

\[
\lambda = \frac{D_M \varepsilon K[L]}{\sqrt{k_a[L](1+\varepsilon K[L])}}
\]

(3.17)

which will be discussed in the next section. The general solution of eq 3.16 is:

\[
\theta = C_1 \exp(-x/\lambda) + C_2 \exp(x/\lambda) + \frac{\left( \frac{d\theta}{dx} \right)_{x=0} x}{1+\varepsilon K[L]} + 1 - \frac{\left( \frac{d\theta}{dx} \right)_{x=\delta}}{1+\varepsilon K[L]}
\]

(3.18)

where \( C_1 \) and \( C_2 \) are constants which can be found by using the boundary conditions 3.13 and 3.14:

\[
C_1 = \frac{1}{1-\exp(2\delta/\lambda)} \left[ 1 - \frac{\left( \frac{d\theta}{dx} \right)_{x=0} \delta}{1+\varepsilon K[L]} \exp(2\delta/\lambda) \right]
\]

(3.19)

\[
C_2 = \frac{\delta}{1+\varepsilon K[L]} \left[ \frac{1+\varepsilon K[L]}{1-\exp(2\delta/\lambda)} \right] - 1
\]

(3.20)

By combining eqs 3.18-3.20, we get the expression for \( J \):

\[
J = D_M[M]^\varepsilon \left[ \frac{\delta}{1+\varepsilon K[L]} + \frac{\lambda \varepsilon K[L]}{1+\varepsilon K[L]} \tanh \left( \frac{\delta}{\lambda} \right) \right]^\varepsilon
\]

(3.21)

3.5 General definition of the reaction layer thickness; lability of complexes

Eq 3.17 can be rewritten as:

\[
\lambda = \frac{D_M}{\sqrt{k_a[L](1+\varepsilon K[L])}} = \mu \frac{\varepsilon K[L]}{1+\varepsilon K[L]} = \sqrt{\frac{D_M}{k_a[L] + \frac{1}{\varepsilon} k_d}}
\]

(3.22)
where \( \mu = \sqrt{\frac{D_M}{k_a[L]}} \) is the conventional reaction layer thickness, as defined by Koutecky and other members of the Czechoslovak school [8], when they studied the kinetic contribution of dissociating complexes to the measured currents in polarography. It is based on the concept that free M must be able to cover the distance \( \mu \) to reach the interface, before recombining with L, i.e., during a life-time defined by \( \tau = \frac{1}{k_a[L]} \). This definition however, is only valid for a sufficiently large degree of complexation of M (\( K[L] \gg 1 \)). In volume reactions, the rigorous mean life time (relaxation time) of M for the reaction 3.1 is defined as \( \tau = \frac{1}{k_a[L] + k_d} \) [11], which also considers the dissociation of the metal complex ML. Indeed, when \( K[L] \gg 1, \ k_a[L] \gg k_d \), and \( \tau \) tends to the definition used by Koutecky et al. By analogy with the volume reaction, the definition of \( \tau \) at a consuming interface should consider both \( k_d \) and the diffusion of ML. Thus, the general life-time of M under this condition is \( \tau = \sqrt{\frac{1}{k_a[L] + k_d / \varepsilon}} \) (eq. 3.22), and the general definition of the reaction layer thickness is given by \( \lambda \) in eq. 3.22. When the degree of complexation is large (\( K[L] \gg 1 \), i.e., \( k_a[L] \gg k_d \)) and \( \varepsilon \sim 1 \) (\( D_{ML} \sim D_M \)), \( \lambda \sim \mu \). This corresponds to most of the cases treated in laboratory synthetic solutions. However in environmental systems containing many different kinds of ligands, the conditions \( K[L] \gg 1 \) and/or \( \varepsilon << 1 \) (colloidal complexes) are not uncommon and the general expression \( \lambda \) must be used.

In eq. 3.21, the term \( \tanh \left( \frac{\delta}{\lambda} \right) \) is a correction term which is due to a fixed diffusion boundary layer \( \delta \). Indeed, the general reaction layer thickness \( \lambda \) is the result of only diffusion prevailing in the solution, i.e., the semi-infinite boundary layer. When \( \delta \rightarrow \infty \), \( \tanh \left( \frac{\delta}{\lambda} \right) = 1 \) and there is no influence of this correction term. While when there is a fixed diffusion boundary layer \( \delta \) due to convection, the bulk solution is homogeneous and equilibrium exists between M and ML which results an enhanced flux to the consuming interface.

From eq. 3.21 a few limiting cases can distinguished:

a) when \( \lambda \ll \delta \), \( \tanh \left( \frac{\delta}{\lambda} \right) \rightarrow 1 \), and \( \frac{\lambda \varepsilon K[L]}{1 + \varepsilon K[L]} \tanh \left( \frac{\delta}{\lambda} \right) \ll \frac{\delta}{1 + \varepsilon K[L]} \), so
\[
J = \frac{D_{ML}[M]^*}{\delta} \left( 1 + \varepsilon K[L] \right) \] which is the maximum flux to the consuming interface, i.e., ML is labile.

b) when \( \lambda \gg \delta \), \( \tanh \left( \frac{\delta}{\lambda} \right) \rightarrow \frac{\delta}{1 + \varepsilon K[L]} + \frac{\lambda \varepsilon K[L]}{1 + \varepsilon K[L]} \tanh \left( \frac{\delta}{\lambda} \right) \rightarrow \delta \), so \( J = \frac{D_{ML}[M]^*}{\delta} \) which is the minimum flux to the consuming interface, i.e., ML is inert.

c) the intermediate values of \( \lambda \) result a flux \( J \) locates in between the maximum and minimum values and ML is semilabile.
3.6. Dissociation reaction layer, lability index and inert complexes

The lability index, \( \mathcal{L} \) expresses the ability of a complex ML to contribute to the supply of M to the interface, via diffusion and dissociation. It is defined [12] as the ratio between the purely dissociation-rate controlled flux and the flux determined by diffusion in solution only.

When \( \mathcal{L} \gg 1 \), the complex is fully labile, whereas for \( \mathcal{L} \ll 1 \), the complex is non labile. In intermediate cases, ML is semi-labile. The above ratio of fluxes can be computed as the ratio of the first over the second term of the denominator of eq. 3.21. By making algebraic rearrangement and defining:

\[
\chi = \varepsilon K[L] \quad (3.23)
\]

And

\[
\sigma = \delta (k_d/D_{ML})^{1/2} \quad (3.24)
\]

one gets:

\[
\mathcal{L} = \frac{\sigma \sqrt{1 + \chi}}{\chi \tanh \left( \frac{\sigma \sqrt{1 + \chi}}{1} \right)} \quad (3.25)
\]

Note that \( \sigma \) is the ratio between \( \delta \) and the ‘dissociation’ reaction layer, \( \omega \), given by:

\[
\omega = \sqrt{\frac{D_{ML}/k_d}{}} \quad (3.26)
\]

The physical meaning of \( \omega \) is understood by analogy to that of \( \mu \). It is the thickness of a solution layer in which ML can travel by diffusion, before re-dissociating, i.e. during its life-time. When \( \omega > \delta \) (\( \sigma < 1 \)), the complex has a very low probability to dissociate before reaching the consuming interface. When this probability is zero, the complex is inert by definition. Thus \( \sigma \) is a good parameter to evaluate whether or not a complex is inert. It is also easily verified that the condition \( \omega > \delta \) is equivalent with \( k_d t < 1 \), that is a condition for inertness in the time domain.

Equation 3.25 is a fully general expression for the lability index for inert, semi-labile and labile complexes. Figure 3.2 shows the relationship between \( \mathcal{L} \), \( \sigma \) and \( \chi \). Two limiting cases are interesting to discuss.

For \( \sigma \sqrt{1 + \chi} > 3 \) (roughly the right side of Fig. 3.2), \( \tanh(\sigma \sqrt{1 + \chi}) \sim 1 \), and eq. 3.25 reduces to:

\[
\mathcal{L} = \sigma \sqrt{1 + \chi} / \chi = \frac{k_d^{1/2} (1 + \varepsilon K[L])^{1/2}}{\varepsilon D_{ML}^{1/2} K[L]} \quad (3.27)
\]

which is the usual expression reported in the literature [12]. The lability index as defined in (3.27) indeed applies to the usual case of non-inert complexes (\( \sigma > 1 \)), and allows distinction between labile and non-labile complexes within the dynamic regime.

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For $\sigma \sqrt{1 + \chi} < 0.1$ (roughly left side of Fig. 3.2), the approximation $\tanh(x) \sim x$ can be used, so that:

$$\mathcal{L} = \frac{1}{\chi} \quad (3.28)$$

This case corresponds to inert complexes. Interestingly, for such complexes, not only is $\mathcal{L}$ independent of the formation/dissociation rate constants, but it may even be larger than 1 when $\chi = \varepsilon K[L] < 1$. Since only cases with $K[L] > 1$ are practically interesting, $\chi < 1$ implies that $\varepsilon = D_{ML}/D_M \ll 1$. This condition applies in particular for complexes with macromolecular or colloidal complexants [13]. Equation 3.28 shows that $\mathcal{L} = 1/\chi = D_M[M]^*/D_{ML}[ML]^*$, is just the ratio of the diffusive flux of M over that of ML (i.e. of total M for $K[L] >> 1$), by assuming that they are independent from each other. This limiting value of $\mathcal{L}$ is expected for an inert complex, since no dissociation occurs in the reaction layer.

![Figure 3.2](image_url)

**Figure 3.2.** Lability index as function of $\sigma = \delta (k_d D_{ML})^{-1/2}$ for various values of $\chi = \varepsilon K[L]$. The points on the curves corresponds to eq. 3.31. Their envelop is the threshold of inertia, and the hatched zone corresponds to the domain where complexes are inert.

The threshold conditions for inert behaviour can be found as follows, by referring to the flux equation for fully inert complexes:

$$J = [M]^* \left[ \frac{\delta}{D_M} \right]^{-1} \quad (3.29)$$

Equating the denominators of eqs. 3.21 and 3.29 shows that an inert complex obeys the condition:

$$\tanh(\delta/\lambda) \sim \delta/\lambda \quad (3.30)$$
This equality is never exactly fulfilled, but \( \tanh(x)/x \to 1 \) when \( x \to 0 \). This is expected since the dissociation rate of a reversible complex is never nil. However equality (3.30) allows definition of an arbitrary threshold for inertia. For instance, it is valid within \( \leq 1\% \) error for \( \delta \lambda \leq 0.1 \), which can be accepted as a limit of inertia. Introducing the expressions for \( \lambda \) and \( \mu \) (eq. 3.22) and expressing them in terms of \( \sigma \) and \( \chi \), gives the general condition for the so-called threshold of inertia, \( T_I \):

\[
T_I = \sigma \sqrt{1 + \chi} = \frac{\delta \sqrt{1 + \varepsilon K[L]}}{\sqrt{D_{ML}/k_d}} \leq 0.1
\]

(3.31)

By applying eq. 3.31 to each curve of Fig. 3.2, one gets a set of points whose envelope allows the definition of inert (left side) and non inert domains. Two cases can again be discriminated:

a) \( \varepsilon K[L] \ll 1 \). As discussed above this implies \( \varepsilon \ll 1 \). Then eq. 3.31 becomes:

\[
k_d \leq 0.01 \frac{D_{ML}}{\delta^2}
\]

which shows that the dissociation rate constant is the critical factor, irrespective of the specific nature and concentrations of M and L.

b) \( \varepsilon K[L] \gg 1 \). This condition applies to the small size, stable complexes. Then, rearranging eq. 3.31 leads to the threshold ligand concentration, \([L]_T\):

\[
[L]_T \leq 0.01 D_M/(\delta^2 k_a)
\]

The corresponding inert behaviour can be understood by realizing that \( K[L] \gg 1 \) implies that \([ML]^* \approx C^M = \text{cte} \), which is the total metal concentration, irrespective of \([L] \). Let’s explore Fig. 3.2, at a fixed value of \( \sigma < 0.1 \) (i.e. a fixed dissociation rate). If we start in the non inert domain and decrease \([L] \), \( \mathcal{L} \) will increase (even though it will stay below 1) reflecting an increase of the rate of reestablishment of the equilibrium between ML, M and L. This is due to an increase of the association rate, because of the increase of \([M] \) (corresponding to the decrease of \( K[L] \)), which more than compensates for the decrease of \([L] \). However if \([L] \) decreases below its threshold value (envelope in Fig. 3.2), the probability that this reaction occurs inside the reactive diffusion layer is so low, that ML can be considered as inert.

Combination of the Eigen mechanism [14] with the above considerations, enables to predict that \([L]_T \) should be independent of the chemical nature of the ligand or the complex. Indeed, as a first approximation, \( k_a \) can be estimated by:

\[
k_a = K_{os} k_{ow}
\]

(3.32)

where \( k_{ow} \) is the rate constant for removal of a water molecule from the inner shell of the hydrated metal ion M, and \( K_{os} \) is the stability constant of the outer-sphere complex. Values of \( k_{ow} \) are known for each metal ion and those of \( K_{os} \) can be computed [14,15]. They depend on the number of electric charges of M and L and on the ionic strength. Table 3.1 gives values of \([L]_T \) thus computed for various metals and charges of L, at I = 0.1M. Note that in Table 3.1, \([L]_T \) is the free ligand concentration. In case of protonation, the total ligand concentration may
be much larger and composite effective rate constants should replace the association and
dissociation rate constants discussed above.

Table 3.1. Predictions of the ligand concentration corresponding to the threshold of inertia,
\([L]_T\), for various charges of \(L\) and 1:1 metal complexes. \(\delta = 100\mu\text{m}, I = 0.1\ M\). Values of \(k_w\)
from [15].

<table>
<thead>
<tr>
<th>Metal</th>
<th>(D_M (\times 10^{-6} \text{ cm}^2\text{s}^{-1}))</th>
<th>(k_w (\text{s}^{-1}))</th>
<th>(\log ([L]_T/M))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(z=0)</td>
<td>(z=-1)</td>
<td>(z=-2)</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>9.5</td>
<td>7 \times 10^9</td>
<td>-12.37</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>7.6</td>
<td>2 \times 10^9</td>
<td>-11.92</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>7.2</td>
<td>1 \times 10^9</td>
<td>-11.64</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>7.2</td>
<td>3 \times 10^8</td>
<td>-11.12</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>7.2</td>
<td>7 \times 10^7</td>
<td>-10.49</td>
</tr>
<tr>
<td>Co(II)</td>
<td>7.0</td>
<td>2 \times 10^6</td>
<td>-8.96</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>6.9</td>
<td>3 \times 10^4</td>
<td>-7.14</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>5.9</td>
<td>2 \times 10^2</td>
<td>-5.03</td>
</tr>
<tr>
<td>Al(III)</td>
<td>6.0</td>
<td>1</td>
<td>-2.72</td>
</tr>
</tbody>
</table>

3.7 Metal flux under spherical diffusion conditions

For spherical diffusion, we introduce two new dimensionless parameters:

\[
\rho = \frac{r}{r_0} \tag{3.33}
\]

\[
\gamma = r_0 \sqrt{\frac{k_w}{D_M} \left( 1 + \varepsilon K[L] \right)} = \frac{r_0}{\lambda} \tag{3.34}
\]

Then eqs 3.2 and 3.3 can be rewritten as:

\[
\frac{d^2 \theta}{d \rho^2} + \frac{2}{\rho} \frac{d \theta}{d \rho} + \frac{k_w [L]}{D_M} \psi - \frac{k_w [L]}{D_M} \theta = 0 \tag{3.35}
\]

\[
\frac{d^2 \psi}{d \rho^2} + \frac{2}{\rho} \frac{d \psi}{d \rho} + \frac{k_w [L]}{D_M} \psi - \frac{k_w [L]}{D_M} \theta = 0 \tag{3.36}
\]

The boundary conditions now read:

At \(\rho = 1\), \(\theta = 0\) and \(\frac{d \psi}{d \rho} = 0\) \(\tag{3.37}\)

At \(\rho \geq \frac{\delta + r_0}{r_0} = a\), \(\theta = 1\) and \(\psi = 1\) \(\tag{3.38}\)

Following the same algebraic procedure as that in section 3.4.1, the normalized concentration
profile of \(M\) can be got to be:
\[
\theta = \frac{C_1}{\rho} \exp(-\gamma \rho) + \frac{C_2}{\rho} \exp(\gamma \rho) - \frac{1}{(1 + \varepsilon K ) \rho} \nu + 1 + \frac{1}{(1 + \varepsilon K ) a} \nu
\]

(3.39)

\[
\nu = \left(\frac{d \theta}{d \rho}\right)_{\rho=1}
\]

(3.40)

By using the boundary conditions 3.37 and 3.38, and combining eq 3.39, we get:

\[
C_2 = \frac{1}{(1 + \varepsilon K[L]) a} \nu - \frac{1}{1 + \varepsilon K[L]} \nu \exp[\gamma (2a - 1)] - \exp[\gamma]
\]

(3.41)

\[
C_1 = -\left\{ \frac{1}{(1 + \varepsilon K[L]) a} \nu - \frac{1}{1 + \varepsilon K[L]} \nu \exp[\gamma (2a - 1)] - \exp[\gamma] \right\} \exp[2\gamma a]
\]

(3.42)

with \( a = \frac{\delta + r_0}{r_0} \)

By combining eqs 3.39, 3.41 and 3.42, we get:

\[
J = D_M[J]^* \left\{ \left(1 + \varepsilon K[L]\right) \left(\frac{1}{r_0} + \frac{1}{\lambda \tanh\left[\frac{\delta}{\lambda}\right]}\right) \right\}
\]

(3.43)

\[
\varepsilon K[L] + \left(\frac{1}{\lambda \tanh\left[\frac{\delta}{\lambda}\right]}\right) \left(\frac{\delta}{\delta + r_0}\right)
\]

After some rearrangements, eq 3.43 reduces to:

\[
J = [M]^* \left[ \frac{r_0}{D_M (1 + \varepsilon K[L]) (r_0 + \delta)} \left(\frac{\delta}{r_0 + \delta}\right) + \frac{r_0 \lambda \tanh\left[\frac{\delta}{\lambda}\right]}{r_0 + \lambda \tanh\left[\frac{\delta}{\lambda}\right]} \frac{\varepsilon K[L]}{D_M (1 + \varepsilon K[L])} \right]^{-1}
\]

(3.44)

which takes the same form as that of eq 28 in Flucy-RLA when there is only one ligand in the system [16]:

40
\[ J = [M]^\dagger \left[ \frac{r_0}{D_M (1 + \varepsilon K[L])} \left( \frac{\delta}{r_0 + \delta} \right) + \frac{r_0}{D_M} - \frac{r_0}{D_M (1 + \varepsilon K[L])} \right]^{-1} \]

(3.45)

The only difference is that in eq. 3.44, \( \lambda \tanh \left( \frac{\delta}{\lambda} \right) \) replaces \( \mu \) in eq. 3.45, which is rigorous, i.e., the general reaction layer \( \lambda \) replaces the conventional one \( \mu \) plus a correction term \( \tanh \left( \frac{\delta}{\lambda} \right) \) which is due to the fixed diffusion boundary layer \( \delta \).

Planar diffusion is a specific case of spherical diffusion when \( r_0 \to \infty \). Indeed, we can see, under planar diffusion, eq 3.44 can be reduced to eq 3.21. And also, from eq. 3.44, the term \( \lambda \tanh \left( \frac{\delta}{\lambda} \right) \) also exists which reflects the chemical kinetics of the complex ML. Thus, the general definition of the reaction layer thickness, \( \lambda \), also applies for conditions of spherical diffusion.

3.8 Summary

In this chapter we have successfully derived the general flux equation for finite diffusion layer thickness in stirred solutions containing one ligand forming metal complexes of any stability and mobility, under either planar or spherical diffusion conditions. A new general expression for the reaction layer thickness is proposed based on rigorous physical concepts. With these equations, we can better understand the labilities of metal complexes in multiligand aquatic systems.

3.9 References


Chapter 4

Roles of metal ion complexation and membrane permeability in the metal flux through lipophilic membranes. Labile complexes at Permeation Liquid Membranes

4.1 Overview

Understanding PLM behaviour is important: i) because PLM may serve as bioanalogical device that helps to elucidate the environmental physicochemical processes occurring at the surface of biological membranes and ii) to optimise the application of PLM as metal speciation sensor in environmental media. The various physicochemical factors that influence the flux of carrier-transported metal ions through a permeation liquid membranes (PLM), in contact with a solution containing labile complexes of M, are studied systematically. Diffusion of free and complexed metal ions in solution, as well as diffusion of the metal carrier complex in the membrane are considered. The respective roles of diffusion layer thickness, ligand concentration, complex stability, carrier concentration, and membrane thickness are studied experimentally in detail and compared with theory, using various labile complexes, namely Pb(II)-diglycolate, Cu(II)-diglycolate, and Cu(II)-N-(2-carboxyphenyl)glycine. Conditions where either membrane diffusion or solution diffusion are rate limiting are clearly discriminated. It is shown in particular, that by tuning the carrier concentration or membrane thickness, either the free metal ion concentration or the total labile metal species are measured. PLM can thus be used to determine whether or not models based on the free ion activity in solution (such as BLM or FIAM models) are applicable to metal uptake by micro-organisms in a real natural medium.

4.2 Introduction

The principle and experimental devices used for PLM are described in chapter 1 (section 3). The main purpose of this chapter is to study systematically the factors that influence the flux of metal ion through the PLM, when ligands forming labile complexes are present in solution, in order to better understand the role of metal speciation on metal transport through membranes, and optimise speciation measurements by PLM for environmental applications.

In the presence of hydrophilic ligands L, both the free metal ion, M, and its complex, ML, are subject to diffusion in the test (or source) solution, but only free M can be exchanged at the solution/membrane interface (Fig. 4.1). M is then transported by diffusion through the membrane, in the form of the metal-carrier complex, MC, and finally exchanged and accumulated into the receiving (= strip) solution. The major processes and related physicochemical parameters that influence the metal flux through the PLM [1] are depicted in Fig. 4.1. The important parameters are the thickness of the liquid membrane (\( \ell \)) the partition coefficient (\( K_p \)) of the metal between the solution and the membrane and its diffusion coefficient (\( D_{MC} \)) in the membrane, the carrier concentration in the membrane [C], the diffusion coefficients of the free metal ion, M (\( D_M \)), and of the metal complex, ML (\( D_{ML} \)), in the source solution, the corresponding diffusion layer thickness (\( \delta_{so} \)) fixed by the hydrodynamic conditions in the source solution, and the degree of lability of ML. In this chapter only labile complexes will be considered, i.e. complexes that dissociate and reassociate so quickly that diffusion of M and ML is the only rate-controlling step in solution. As it will be shown later, the diffusion and complexation parameters related to the receiving
(or strip) solution (subscript \text{st}) are not relevant in this chapter because the conditions are such [1,2] that the corresponding processes are not rate limiting for the accumulation of M in the strip solution.

In this chapter the effects of the degree of complexation of M, the diffusion layer thickness, the partition coefficient, the membrane thickness and the carrier concentration on the metal flux, are specifically tested in the framework of a uniform theory, by using the labile complexes of Cu(II) with diglycolate, and N-(2-carboxyphenyl)glycine, and those of Pb(II) with diglycolate. The roles of \( \ell \), \( K_p \) and metal-carrier reaction in presence of a non-complexing source solution, as well as the role of the strip parameters, have been discussed elsewhere [2-5].

4.3 Theory

4.3.1 Stability and Lability of metal complexes

In the following, only 1:1 metal complexes are considered, with association and dissociation rate constants, \( k_a \) and \( k_d \) respectively, and the stability constant, \( K = k_a / k_d \) :

\[
M + L \xrightleftharpoons[k_d]{k_a} ML
\]  

(4.1)

The lability of complexes diffusing towards a consuming interface, can be compared through their lability index, \( \mathcal{L} \) [6]. When the ligand L is in excess with respect to M and diffusion occurs at a planar interface, \( \mathcal{L} \) can be expressed by:
\[ \mathcal{L} = \frac{k_1^{1/2}(1 + \varepsilon K[L])^{1/2}}{\varepsilon D_{ML}^{1/2} K[L]} \delta_{so} \]  

(4.2)

where \( \delta_{so} \) is the diffusion layer thickness, \( \varepsilon = D_{ML} / D_M \), and \([L]\) is the concentration of free L. \([L]\) is related to the total concentration, \([L]_t\), by:

\[ [L] = \frac{[L]_t}{(1 + \Sigma_i \beta_{H,i}[H]^i)} \]  

(4.3)

where the \( \beta_{H,i} \)'s are the cumulative acid-base stability constants of L (\( \beta_{H,i} = K_{H,i} K_{H,2} \cdots K_{H,i} \)). Physically, \( \mathcal{L} \) represents the ratio between the metal flux when it is fully controlled by the rate of ML dissociation (Fig. 4.1) to the flux entirely controlled by diffusion of M and ML in solution (i.e. assuming very fast dissociation of ML). When \( \mathcal{L} \gg 1 \), the metal complex is fully labile, whereas for \( \mathcal{L} < 1 \), the metal complex is non-labile (flux controlled by dissociation rate). For \( \mathcal{L} \) of order of 1, the complex is called semi-labile.

By assuming that the Eigen mechanism holds [7] (chapter 1, section 4), \( k_a \) and \( k_d \) can be computed by:

\[ k_a = K_{os} k_{w} \quad \text{and} \quad k_d = k_a / K \]  

(4.4)

where \( k_{w} \) is the rate constant for the water loss of the hydration shell of free M, and \( K_{os} \) is the stability constant of the precursor outer-sphere complex between the hydrated M and L.

The physicochemical parameters used in this chapter are listed in Tables 4.1 and 4.2.

**Table 4.1.** Acid-base stability constants of the tested ligands, \([8]\) \( I=0.1, T=25^\circ C \). \( K_{H1} \) and \( K_{H2} \) are successive stability constants

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Diglycolic acid</th>
<th>N-(2-carboxyphenyl)glycine</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \log K_{H1}(M^{-1}) )</td>
<td>3.94 ± 0.02</td>
<td>4.90 ± 0.01</td>
</tr>
<tr>
<td>( \log K_{H2}(M^{-1}) )</td>
<td>2.82 ± 0.01</td>
<td>3.33 ± 0.03</td>
</tr>
</tbody>
</table>

The lability index, \( \mathcal{L} \), of the three tested metal complexes were computed via eq. (4.2) for the minimum and maximum total concentrations of L used experimentally, by means of the values of Tables 4.1-4.2. Minimum and maximum values of \( \mathcal{L} \), \( \mathcal{L}_{\text{min}} \) and \( \mathcal{L}_{\text{max}} \) correspond to maximum and minimum concentrations of L respectively (eq. 4.2). For Cu and Pb diglycolate complexes, \( \mathcal{L}_{\text{min}} \) and \( \mathcal{L}_{\text{max}} \) are independent of pH in the pH range 5 to 7 and are given in Table 4.3. For Cu(II)-N-(2-Carboxyphenyl)glycine, \( \mathcal{L}_{\text{min}} \) and \( \mathcal{L}_{\text{max}} \) vary with pH, as shown in Fig. 4.2. Table 3 and Fig. 4.2 show that in all cases, \( \mathcal{L} \) values are much larger than 1, indicating that under the studied conditions, the test complexes are fully labile.
Table 4.2. Stability and rate constants of Cu(II) and Pb(II) complexes with the tested ligands. $K_{os}$ and the rate constants (except $k_{-w}$) were computed as explained in chapter 1, section 4. $I = 0.1$, $T = 25^\circ C$. The values of the diffusion coefficients of the complexes were taken as equal to those of free metal ions ($D_{ML} = D_M$), with $D_{Pb} = 9.5 \cdot 10^{-6} \text{cm}^2\text{s}^{-1}$ and $D_{Cu} = 7.8 \cdot 10^{-6} \text{cm}^2\text{s}^{-1}$.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ref.</th>
<th>Pb(II)-Diglycolate</th>
<th>Cu(II)-Diglycolate</th>
<th>Cu(II)-N-(2-carboxyphenyl)glycine</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log K_{os} (\text{M}^{-1})$</td>
<td>1.13</td>
<td>1.13</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>$\log k_{-w} (\text{s}^{-1})$</td>
<td>28</td>
<td>9.85</td>
<td>9</td>
<td>9</td>
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<tr>
<td>$\log k_{q} (\text{M}^{-1}\text{s}^{-1})$</td>
<td>11.0</td>
<td>10.13</td>
<td>10.13</td>
<td></td>
</tr>
<tr>
<td>$\log k_d (\text{s}^{-1})$</td>
<td>6.6 ± 0.1</td>
<td>6.18 ± 0.02</td>
<td>3.48 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>$\log K (\text{M}^{-1})$</td>
<td>26</td>
<td>4.4 ± 0.1</td>
<td>3.95 ± 0.2</td>
<td>6.65 ± 0.12</td>
</tr>
</tbody>
</table>

Table 3. Values of $\mathcal{L}_{\text{min}}$ and $\mathcal{L}_{\text{max}}$ computed from eq. 4.2 for the pH range 5-7. Total ligand concentrations (in mM) are given in parenthesis and correspond to extreme conditions used in this work.

<table>
<thead>
<tr>
<th></th>
<th>Pb(II)</th>
<th>Cu(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathcal{L}_{\text{max}}$</td>
<td>5034 (0.1)</td>
<td>2376 (0.5)</td>
</tr>
<tr>
<td>$\mathcal{L}_{\text{min}}$</td>
<td>606 (5.0)</td>
<td>770 (4.0)</td>
</tr>
</tbody>
</table>

Figure 4.2. pH dependence of $\mathcal{L}_{\text{min}}$ (dashed line, $[L]_t = 0.1 \text{ mM}$) and $\mathcal{L}_{\text{max}}$ (solid line, $[L]_t = 0.01 \text{ mM}$) for Cu(II)-N-(2-carboxyphenyl)glycine.

### 4.3.2 PLM metal flux for fully labile complexes in the source solution

The derivation of the theoretical equations for the flux of M in the presence of labile complexes has been described elsewhere [1,2]. It would be out of scope to discuss it here in detail, but it may be useful to recall that the PLM technique uses solvents with very low polarity (in our case, toluene/phenylhexane, with dielectric constant ~2), in which free ions cannot exist. Thus the carrier (C in Fig. 4.1) must include a lipophilic anion and a lipophilic complexant (in our case the anion of fatty acid: laurate or palmitate and the crown ether 22DD = 1,10 didecyl-1,10 diaza 18 crown 6). It has been demonstrated [4] that the complex MC is indeed neutral and includes one mole of 22DD and 2 moles of laurate per mole of divalent M.
The transport of M does not give rise to charge accumulation, because 2 moles of Na⁺ are back transported by the carrier, for each mole of diffusing divalent M. Thus no significant electrical potential difference is developed across the membrane.

Under such conditions, the steady-state metal flux, \( J \), through the membrane is given by eq. (4.5) [2], provided that any process at the membrane/solution interface as well as any chemical reaction inside the solution or membrane phases is fast compared to diffusion.

\[
J = \frac{C_{so}^b}{\alpha_{so}} \left[ \frac{\delta_{so}}{D_{so} \alpha_{so}} + \frac{\ell}{K_p[C]D_{MC}} + \frac{h_{st}}{2\delta_{st}\alpha_{st}} \right]^{-1} \times \exp \left[ -\frac{t}{h_{st}\alpha_{st}} \left[ \frac{\delta_{so}}{D_{so} \alpha_{so}} + \frac{\ell}{K_p[C]D_{MC}} + \frac{h_{st}}{2\delta_{st}\alpha_{st}} \right] \right] \quad (4.5)
\]

\( C_{so}^b \) is the total metal concentration in bulk source solution, and \( D_{so} \) is the average diffusion coefficient of M and ML in solution, given by [9]:

\[
D_{so} = D_M / \alpha_{so} + D_{ML} (\alpha_{so} - 1) / \alpha_{so} = D_M (1 + \varepsilon K[L]) / \alpha_{so} \quad (4.6)
\]

with:

\[
\alpha_{so} = 1 + K[L] \quad (4.7)
\]

\( \alpha_{st} \) and \( D_{st} \) are the equivalent of \( \alpha_{so} \) and \( D_{so} \), for the strip solution, and \( h_{st} \) is the depth of the strip channel.

Generally, a very strong ligand is used in the strip solution. For instance CDTA was used here. By using the typical parameters of the flow cell system (see “Experimental”), the stability constants of Pb(II) and Cu(II)-CDTA complexes, and taking \( \varepsilon \sim 1 \), one gets \( h_{st} / 2\delta_{st}\alpha_{st} = 1.6 \times 10^{-8} \text{ s cm}^{-1} \) for Cu(II) and \( 4.2 \times 10^{-10} \text{ s cm}^{-1} \) for Pb(II). These values are much smaller than the values of \( \ell / K_p[C]D_{MC} \) for Cu(II) (37.0) or Pb(II) (1.65). The strip solution term can thus be omitted from eq. 4.6. In addition, it is observed that the term in the exponential is extremely small for several hours, so that during that time, the flux is constant and equal to the flux, \( J^0 \), at \( t = 0 \):

\[
J^0 = \frac{C_{so}}{\alpha_{so}} \left[ \frac{\delta_{so}}{D_{so} \alpha_{so}} + \frac{\ell}{K_p[C]D_{MC}} \right]^{-1} = [M]^* \left[ \frac{\delta_{so}}{D_{so} \alpha_{so}} + \frac{\ell}{K_p[C]D_{MC}} \right]^{-1} \quad (4.8)
\]

or
\[ P = \frac{J^0}{[M]^*} = \frac{1}{\delta_{so\alpha_{so}} + \frac{\ell}{D_{so}\delta_{so} K_p[C]D_{MC}}} \]  

(4.9)

These expressions can be compared to that obtained in chapter 3 (eq. 3.21) for labile complexes \((\lambda \to 0)\), when the surface is a perfect sink. Equation 4.8 is then the same as eq. 3.21 except that the parentheses includes the additional term \(1/K_p[C]D_{MC}\) which corresponds to the additional resistance due to the transfer through the membrane. For very large values of \(K_p\), \([C]\) or \(D_{MC}\) or very low value of \(\ell\), this resistance tends to zero and eq. 4.9 and eq. 3.21 are the same.

Equations 4.8 and 4.9 enable us to define two useful parameters:

The permeability, \(P\): \(P = J^0 /[M]^*\) is a characteristic of the system under the experimental conditions used, independent of metal concentration. The parameter \(P'\) will also be used in this chapter:

\[ P' = \frac{J^0}{C^b_{so}} = \frac{1}{\delta_{so\alpha_{so}} + \frac{\ell}{D_{so} K_p[C]D_{MC}}} \]  

(4.9’)

The permeability index, \(\pi\): \(\pi\) is the ratio of the two terms in the denominator of eq. 4.9. It represents the relative importance of diffusion in solution and in the membrane, for the overall flux:

\[ \pi = \frac{K_p[C]D_{MC}}{D_{so} \ell \alpha_{so}} \]  

(4.10)

For \(\pi \ll 1\): diffusion in the membrane is the rate limiting step. Then the first term of the parenthesis of eq. 4.8 cancels and \(J^0\) is proportional to free \(M\) concentration, irrespective of the degree of complexation in solution.

For \(\pi \gg 1\): diffusion in solution is the rate limiting step. Then the second term of the parenthesis of eq. 4.8 cancels and \(J^0\) is proportional to the total concentration of labile \(M\) species, \(C^b_{so}\).

Note that this is valid for fully labile complexes only. For inert or semilabile complexes (see chapter 5), the expression of \(\pi\) is different. Also note that in principle, \(\pi\) can be manipulated by adjusting \([C]\), \(\ell\) or \(\delta_{so}\) (hydrodynamic conditions), so that in the same solution, one can determine either \([M]\) or \(C^b_{so}\) by measuring \(J^0\) under various conditions [12]. It is the purpose of this chapter to demonstrate the influence of the various parameters in \(\pi\), on \(J^0\).

It is useful to combine eqs. 4.8 and 4.9, with eq. 4.10, to give:
\[
J^0 = \frac{C_{so}^b D_{so}}{\delta_{so}} \left[ \frac{\pi}{\pi + 1} \right]
\]

and

\[
P' = \frac{D_{so}}{\delta_{so}} \left[ \frac{\pi}{\pi + 1} \right]
\]

where \( P' = J^0 / C_{so}^b = P / \alpha_{so} \). The plot of \( \log P' \) vs. \( \log \pi \) (see e.g. Fig. 4.10) tends to linearity for extreme values of \( \pi \). For \( \pi \gg 1 \) (in practice \( \pi > 10 \)), \( \log P' \) tends to the constant value of \( \log(D_{so} / \delta_{so}) \). For \( \pi \ll 1 \) (in practice \( \pi < 0.1 \)), \( \log P' = \log(D_{so} / \delta_{so}) + \log \pi \), i.e. a straight line with slope = 1. The transition between the two linear regimes occurs around \( \pi = 1 \). Thus, such plots, which can be obtained by varying any of the parameters determining \( \pi \) (eq. 4.10), clearly show in which regime the system is working.

### 4.4 Experimental

#### 4.4.1 Reagents and membrane

The following reagents, used for transport experiments, were analytical grade products: 2-(N-morpholino)ethanesulfonic acid (MES, Sigma), \textit{trans}-1,2-diaminocyclohexane-\(N, N', N''\)-tetraacetic acid monohydrate (CDTA, Fluka), sodium hydroxide and lithium hydroxide (Merck), palmitic acid (PA, Fluka). 1,10-didecyl-1,10-diaza-18-crown-6 ether (Kryptofix 22DD, Merck), diglycolic acid (Merck) and N-(2-carboxyphenyl)glycine (Aldrich) were pure for synthesis (> 98%). The solvents, toluene and phenylhexane, were Fluka analytical grade products. MilliQ water was used for preparing all the aqueous solutions.

The source solution contained the desired concentrations of Cu(II) or Pb(II) (usually 5 \( \mu \)M) in 0.01M MES (pH = 6 was adjusted with LiOH). The strip solution was composed of 0.01M CDTA (pH = 6.20 adjusted with NaOH). The membrane solution was made of 1:1 22DD/PA in 1:1 (v/v) mixture of phenylhexane and toluene. Note that, compared to previous work, palmitate was used instead of laurate in the present study. Indeed it was observed that, even though the 1:1 mixture 22DD/laurate works as a very good carrier at 0.1 M in organic solvent [3,10-12], its efficiency for Cu(II) transport decreases at lower concentrations and becomes nil at millimolar concentrations. This was attributed to the loss of laurate due to its solubility in water. Systematic studies with laurate, myristate and palmitate at low concentrations of 1/1 fatty acid/22DD mixtures have shown that the use of palmitate indeed results in excellent Cu(II) and Pb(II) transport, down to \( \sim 0.01 \) M carrier concentration, with flux characteristics stable for days.

Celgard 2500 polypropylene hydrophobic membrane (Celanese Plastic, Charlotte, NC) was used as flat sheet support. Its characteristics are the following: porosity = 0.45; thickness = 25 \( \mu \)m; average pore diameter = 0.04 \( \mu \)m.
4.4.2 The PLM device and its characteristics

A schematic view of the flow-through cell system used in this work, and its corresponding characteristics are shown in Fig. 4.3. A peristaltic pump (Gilson, Omnilab) was used to control the source volume flow rate. Standard tubings (Tygon R3607, internal diameter = 2.29 mm and 3.175 mm, Biosystems, Omnilab) were used to connect the source solution to the flow-through cell. This cell has been described in detail in [12]. The source solution flows through 4 channels in parallel. The metal from the source solution passes through the flat membrane (Fig. 4.3) and accumulates in the stagnant strip channel solution.

![Flow-through cell system diagram](image)

Figure 4.3. Flow-through cell system and its dimensions. $L =$ length of the source channels (12 cm), $W =$ width of the channels (1 mm), $h_{so} =$ depth of the source channel (0.6 mm), $h_{st} =$ depth of the strip channel (0.4 mm); effective strip volume: $192 \mu L$.

The strip channel is made of 4 arms positioned exactly opposite the source channels and connected to each other to form one single channel. The strip solution was collected by a pump at the end of the accumulation period and the corresponding metal concentration was measured by flame or flameless atomic absorption spectrometry (AAS) using a Pye Unicam SP9 or a Perkin-Elmer 4100 with HGA 700 graphite furnace spectrophotometers. The optimum geometries for the strip and source channels were based on the following...
considerations: the strip channel depth, $h_{st}$, should be sufficiently small to get a short response time and for eqs. 4.8-4.9 to be valid. The depth, $h_{so}$, width, $W$, and length, $L$, of the source channel (Fig. 4.3) together with the solution flow-rate, provide a well-defined thickness of the diffusion layer, $\delta_{so}$ [12]:

$$\delta_{so} = 0.901 \frac{D_{so}^{1/3} d^{1/3}}{h_{so}^{2/3} L^{1/3} \nu^{-1/3}}$$

(4.13)

where $d = W / 2$ = half width, $\nu$ is the volume flow-rate and the numerical coefficient is valid for CGS units.

The major advantages of this cell are the following: a small strip volume yields a high preconcentration factor (defined as $F = C_{st}^0 / C_{so}^0$) in a relatively short time; $\delta_{so}$ is well-controlled and tunable by the source flow rate; the total metal concentration in the bulk source solution can be kept constant since the volume of source solution may be very large.

$\alpha_{st}$ was calculated to be $10^{1.2}$ and $10^{2.7}$ for Cu(II)- and Pb(II) -CDTA complexes respectively, based on the stability constants given in [9]. Usually, one membrane ($\ell = 25$ $\mu$m) was used, but in some experiments, $\ell$ was varied by stacking several membranes together.

Values of $K_p$ and $D_{MC}$, for Pb(II) and Cu(II) with the system 0.1 M 22DD/0.1M palmitate were measured as described in [13], from extraction and flux experiments performed in the static diffusion cell shown in [4]. Formation of white microcrystals was observed on the source side of the membrane, at high concentrations ($\geq 50$ $\mu$M) of Pb(II) and at the end of flux experiments (2-7 h). ATR-IR analysis showed that this solid contained Pb-palmitate. Similar solid formation was observed with Cu(II). Such solids were never observed with the flow-through cell, which is probably due to a combination of two characteristics of flow-through cell experiments: i) the much lower total metal concentration used ($\leq 5$ $\mu$M), and ii) the much smaller contact time between the source solution and the PLM ($\leq 4$ s). On the other hand, due to the “static” conditions required for their measurement, $D_{MC}$ and $K_p$ may contain errors due to formation of colloidal solid, not visible by eye, even though conditions were used to minimize such solid formation. The values of $D_{MC}$ are obtained from the metal flux through the static diffusion cell mentioned above, by plotting $F = V_{st} / C_{so}$ as a function of time. At sufficiently large membrane thicknesses, the $F(t)$ curve shows a time lag at short time, which allows determination of $D_{MC}$. Because $D_{MC}$ is measured at very short times (few minutes), the possible surface precipitation can be considered as negligible or small during that time. The reproducibility of $D_{MC}$ values was tested by varying the overall membrane thickness, by stacking either 3 ($\ell = 75$ $\mu$m) or 6 Celgard membranes ($\ell = 150$ $\mu$m) together. Values of $3.6 \pm 1.2 \cdot 10^{-8}$ $\text{cm}^2/\text{s}$ and $4.9 \pm 1.0 \cdot 10^{-8}$ $\text{cm}^2/\text{s}$ were obtained for Pb(II) and Cu(II) respectively. These values are close to each other as expected, and the value for Cu(II) is also close to that obtained for Cu(II) with the 0.1M 22DD + 0.1M laurate system ($5.2 \cdot 10^{-8}$ $\text{cm}^2/\text{s}^{15}$).
Precise determination of the $K_p$ values by liquid-liquid extraction is more difficult, since the contact time between the aqueous and organic solutions is necessarily long. Experiments were performed, as discussed in [4], under conditions minimizing artefacts due to colloidal solid formation, as much as possible. Nevertheless the reproducibility of the obtained values of $K_p = [MC]_m/[M]_o[C]_m$ (subscript $m$ represents the membrane) was not good. Their ranges are $1.6 \times 10^5$ and $1.4 \times 10^4 \text{M}^{-1}$ for Pb(II) and Cu(II) respectively, at pH = 6 and ionic strength = 0.01 M. They should only be considered as orders of magnitude for comparison purposes. To get more precise values of $K_p$, the PLM data reported in the rest of the paper were fitted with theoretical equations (4.9)-(4.12), in which $K_p$ is the only adjustable parameter. For all Cu(II) data, a single $K_p$ value was obtained from these fittings. A similar procedure was used for Pb(II). The $K_p$ values obtained in this way were $4.2 \times 10^5$ and $1.37 \times 10^4 \text{M}^{-1}$ for Pb(II) and Cu(II) respectively, which are in reasonable agreement with the above orders of magnitude. Considering that the mechanism of transfer of metal at the membrane interface is not simple [5] (chapter 1, section 1.3.5) and not necessarily the same for extraction and PLM experiments, we believe that the $K_p$ values determined by the fitting procedure are the most appropriate for interpretation of PLM data.

4.4.3 Conditions of metal transport experiments

**Flow-through cell preparation and functioning.** A single membrane (or a set of several membranes stacked together) was impregnated with the membrane solution, as mentioned in [12]. After rinsing it with water to remove the excess solution, the membrane was clamped tightly and evenly between the source and strip half-cells by 10 screws. The strip solution was injected into the strip channel with a syringe and then the source solution with the test metal concentration was circulated with a constant flow rate. After preconcentration during a given period of time (typically 10 to 30 min), the strip solution was taken out and Pb(II) or Cu(II) was measured by AAS or flameless AAS. The source channel was then washed by flowing MilliQ water while the strip channel was washed by injecting a new strip solution. Circulation of MilliQ water was performed for up to 25 min, to minimize any carry-over effect. Then a new transport experiment was performed with the test source solution and a new strip solution. Usually the initial metal flux and permeability, under one given set of conditions, were computed from 4 preconcentration experiments performed with different preconcentration times. $J^0$ was obtained from the slope of the linear plot of the preconcentration factor, $F$, as a function of time [12]. Typically, such plots do not pass through the origin, since, at the beginning of the experiment, there is $\sim$ 1 minute time-lag (for a single membrane) which corresponds to the transient conditions required to establish the steady-state concentration gradients in the membrane and in solution.

**Transport experiments in the presence of complexants.** The nature of the complexes used as well as the experimental conditions (pH, ligand concentration) were chosen on the basis of the following criteria: a) only 1:1 complexes are formed, b) only fully labile complexes are present (see lability index), c) the nature of metals and ligands enable to span a range of $\alpha$ and $\pi$ values as wide as possible. For this reason, Cu(II) and Pb(II) complexes of diglycolate and N-(2-carboxyphenyl)glycine were studied in detail. The complexation properties of Cu(II) and Pb(II) with these ligands were determined by titrating a constant ligand concentration
with the metal ion, and following the Pb(II) and Cu(II) activities via the potentials of Pb(II) and Cu(II) ion-selective electrodes, with respect to a Ag/AgCl/sat KCl reference electrode. From the difference between these potentials and those measured in the absence of ligands, \( \alpha_{so} \) values were determined under the experimental conditions used here (e.g. [13]). We checked that these values compared well with those computed from the stability constants given in the literature.

Transport experiments in the presence of complexants were performed by keeping the total metal (Pb(II) or Cu(II)) concentration constant in the source solution. The total ligand concentration was then varied in such a way that the ligand was always in large excess over metal (0.1 to 5 mM for Pb-diglycolate and 0.5 to 4 mM for Cu-diglycolate) and that only the 1:1 metal/ligand complex was formed. For Cu(II)-N-(2-carboxyphenyl)glycine, a constant ratio \([\text{N-(2-carboxyphenyl)glycine}]/[\text{Cu(II)}] = 20\) was used, with the ligand concentration varying from 0.01 to 0.1 mM. The pH of the source solution was always buffered at \(pH = 6.00\) with 0.01M MES (pH adjusted with LiOH). A constant volume flow rate of 0.02 cm\(^3\)/s (corresponding to a linear velocity of 3.33 cm/s) was used for experiments with variable ligand concentrations.

The influence of volume flow rate on the permeability of the membrane in the presence of complexant was determined by varying the flow rate from 0.02 cm\(^3\)/s to 0.18 cm\(^3\)/s (3.33 to 30.0 cm/s). 5 \(\mu\)M metal with 0.5 mM diglycolate or 0.1 mM N-(2-Carboxyphenyl)glycine, at \(pH = 6.00\) was used for these tests. Other experimental conditions were the same as those discussed above.

The influence of the membrane thickness on the permeability of the membrane was tested in the presence of diglycolate. Several membranes of 25 \(\mu\)m thickness were stacked together and then impregnated with the carrier solution. The membranes stack well together [4]. They were rinsed with water to remove the excess of carrier solution, as explained above for a single membrane. Stacking of 1, 2, 4 and 6 membranes (corresponding to 25, 50, 100 and 150 \(\mu\)m thick membranes) were tested under both 0.1 M and 0.01 M carrier conditions. 5 \(\mu\)M metal with 0.5 mM diglycolate at \(pH 6.00\) was used here, as a test solution.

4.5 Results and discussion

4.5.1 Verification of lability of Cu(II)-Diglycolate

Preliminary test with the cyclic voltammetry of 5 \(\mu\)M Cu(II) in solution with and without 1mM of diglycollate, with \(I = 0.01M\) and \(T = 25^\circ C\) shows that the peak currents are the same both in presence and absence of ligand. From the shift of the peak potentials (-44 mV), we can compute the stability constant of Cu(II)-Diglycolate from the De Ford and Hume equation [9], by assuming that the complex is labile and \(D_{ML} = D_M\). A value of \(\log K = 4.49\) is found which is very close to that measured by titration with Cu(II) ion selective electrode (4.52). And also, the same peak currents were got for both with and without diglycolate. All these observations clearly demonstrate that Cu(II)-Dilglycolate is labile under the experimental conditions used and that the diffusion coefficient of Cu(II)-Diglycolate is the same as that of free Cu(II).
4.5.2 The metal permeability in the presence of ligands

Typical plots of metal preconcentration vs. time, in the absence and presence of ligand, and at two different carrier concentrations, are shown in Fig. 4.4. The experimentally determined preconcentration factor, \( F = \frac{C^{b}_{st}}{C^{b}_{so}} \), is related to the flux and permeability as follows. At sufficiently short times (scale of hours), the measured flux is equal to the initial steady-state flux, \( J^0 \), and is related to the increase of metal concentration in the strip solution by:

\[
J^0 = \frac{V_{st}}{A} \frac{dC^{b}_{st}}{dt} = h_{st} \frac{dC^{b}_{st}}{dt}
\]

(4.14)

where \( V_{st} \) is the volume of strip solution, \( A \) is the membrane area in contact with the source solution, and \( h_{st} \) is the depth of the strip channel. \( P' \) (eq. 4.12) is thus related to \( F \), as follows:

\[
P' = \frac{J^0}{C^{b}_{so}} = \frac{h_{st}}{C^{b}_{so}} \frac{dC^{b}_{st}}{dt} = h_{st} \frac{dF}{dt}
\]

(4.15)

\[\text{Figure 4.4.} \] Cu(II) transport under 0.1M and 0.01M carrier concentrations with and without diglycolate. Source solution: 0.01M MES, pH 6.00; Strip solution: 0.01M CDTA, pH = 6.20; volume flow rate: 0.02 cm³/s (≈ 3.33 cm/s). ● 0.1M carrier, without ligand; ○ 0.1M carrier, with 0.5 mM diglycolic acid; ▼ 0.01M carrier, without ligand; ▼ 0.01M carrier, with 0.5 mM diglycolic acid. 5 μM Cu(II) and room temperature in all cases.

Figure 4.4 shows that, under the experimental conditions used, the preconcentration factor, \( F \), increases linearly with time, i.e. \( P' \) and \( J^0 \) are constant. This indeed corresponds to the conditions of the initial flux which prevails under steady-state conditions (eqs 4.8-4.9). This result is also in agreement with experimental data reported in the literature [12].

Figure 4.4 illustrates a few important features of the PLM. For a given accumulation time, the value of \( F \) in the absence of diglycolate is much smaller for 0.01M carrier than for 0.1 M
carrier. This suggests that $P'$ is at least partially controlled by the transport through the membrane (eq. 4.9'), which depends on the metal distribution factor, $K_p[C]$, between the membrane and solution phases. Another observation is that, for a given accumulation time and carrier concentration, $F$ is smaller in the presence of diglycolate than in its absence, demonstrating that metal complexation reduces the amount of metal taken up by the membrane. For labile complexes, $J^0$ and $P'$ are inversely proportional to the degree of complexation, $\alpha_{so}$, when diffusion in the membrane is the rate limiting step for transport (eqs. 4.8, 4.9'). In such a case, $\alpha_{so}$ can be obtained, for a given time, by the ratio of the values of $P'$ with and without ligand. However, when these ratios are computed for $[C] = 0.1$ M and $[C] = 0.01$ M, for the data of Fig. 4.4, values of 0.69 and 0.14 are obtained respectively, i.e. a decrease by a factor of 5 instead of 10 is observed. Since the tested complexes are fully labile (Fig. 4.2, Table 4.3), the fact that $P'$ does not vary with [C] and $\alpha_{so}$ in a linearly proportional manner suggests that diffusion in both the membrane and in the solution are limiting steps (eqs. 4.8, 4.9'), i.e. $\pi$ is neither $>> 1$ nor $<< 1$. This behaviour is quantitatively studied and discussed below.

4.5.3 Changes in $P$ and $\pi$ with ligand concentration

When the ligand concentration increases, the degree of complexation, $\alpha_{so}$, increases, and accordingly, the value of $\pi$ decreases (eq. 4.10). It is then expected (see eq. 4.12) that, when the value of $\pi$ in the absence of ligand is not much larger than 1, the metal flux, $J^0$ (and consequently $P'$) will decrease, possibly passing from source diffusion limitation to membrane diffusion limitation. Figure 4.5 shows such experiments. Note that all figures 4.5-2 (a,b,c) represent the same data as the corresponding Figs. 4.5-1 (a,b,c). Only the ligand concentrations have been transformed into $\pi$ values through eqs. 4.7 and 4.10. Experiments were carried out at 0.1M carrier concentration, because under this condition, the permeability in the absence of ligand is fully controlled by diffusion in the source solution, both for Cu(II) and Pb(II). This is shown in Figs. 4.5a-2, 4.5b-2 and 4.5c-2. Indeed, in all cases, the highest $\pi$ values (which always correspond to $[L]_t = 0$ and $\alpha_{so} = 1$; eqs. 4.7, 4.10), are large enough for $P'$ to attain its maximum value (eq. 4.12). Diffusion in solution is then the only rate-limiting factor. Figures 4.5a-1, 4.5b-1 and 4.5c-1 also show that $P'$ decreases monotonically with $[L]_t$, but not to the same extent for the three metal-ligand systems. The decrease is very weak for Pb(II)-diglycolate, intermediate for Cu(II)-diglycolate, and very strong for Cu(II)-N-(2-Carboxyphenyl)glycin. This difference in behaviour results from the values of both $K_p$ and $\alpha_{so}$ in each case:

- For Pb(II), $K_p$ value is very large ($4.2 \times 10^5$) which reflects a strong uptake capability of the membrane. As a consequence, one always gets $\pi > 2$ (Fig. 4.5a-2), even for the largest value of $\alpha_{so}$ (or ligand concentration), over the studied concentration range ($6 < \alpha_{so} < 282$).

Thus $P'$ remains close to its maximum value, irrespective of $\alpha_{so}$ values, as expected from eq. 4.13. Physically, these results can be understood by considering that the uptake by the membrane is so large, that for any value of $[L]_t$, the free $M$ concentration at the membrane surface is nil. Since ML is fully labile (complete equilibrium in the diffusion layer), the surface concentration of ML is also nil and the overall flux is controlled by the sum of the
maximum concentration gradients of both M and ML. Thus $J^0$ and $P'$ only depend on $C^b_{so}$, through $D_{so}$.

Figure 4.5. The effect of ligand concentration on the permeabilities, $P'$, of Cu(II) and Pb(II). Source solution: 0.01 M MES, pH 6.00; carrier = 1/1 mixture of 0.1M 22DD/0.1 M PA; Strip solution: 0.01 M CDTA, pH 6.20; volume flow rate: 0.02 cm³/s (= 3.33 cm/s). 5 μM Pb(II) and Cu(II) in presence of diglycolate (Figs. 4.5a and 4.5b); [N-(2-carboxyphenyl)glycine]_{total}/[Cu(II)]_{total} = 20 (Fig. 4.5c). Solid lines are theoretical predictions from eq. 13). Figures 4.5a-1, 4.5b-1 and 4.5c-1 give the raw data $P'$ vs $[L]_t$, while Figs. 4.5a-2, 4.5b-2 and 4.5c-2 give log $P'$ vs log $\pi$, where $\pi$ depends on $[L]_t$ through $\alpha_{so}$ (Eq. 4.10).
- The Cu(II)-N-(2-carboxyphenyl)glycine system is the opposite case. The $K_p$ value ($1.37 \times 10^4$) is such that $\pi$ is significantly larger than 1 in the absence of ligand, but not in the presence of the strong ligand N-(2-carboxyphenyl)glycine (Fig. 4.5c-2). In the presence of ligand, one always gets $\pi \ll 1$, due to the large values of $\alpha_{so}$ ($86 < \alpha_{so} < 426$ in the tested range of $[L]_1$). Under such conditions, $P'$ is fully controlled by diffusion in the membrane, i.e., the metal flux is much smaller than what it would be if it were controlled by diffusion in solution.

Consequently, the gradients in the source solution are insignificant, and the free M concentration at the membrane surface is essentially equal to that in the bulk source solution, $[M]$. $J^0$ is then proportional to $[M]$ and not to $C^b_{so}$. Under such conditions log $P'$ is proportional to log $\pi$, with a slope of 1.0, as theoretically expected (eq. 4.12).

- The Cu(II)-diglycolate system (Fig. 4.5b) is an intermediate case. The values of $\alpha_{so}$ are not very large and $\pi$ only decreases from 2.12 to 0.28 when the diglycolate concentration varies from 0.5 mM to 4 mM. These values correspond to fluxes controlled by both diffusion in source solution and diffusion in the membrane, even though the membrane control becomes more and more important when $\pi$ decreases.

The full lines in Figs. 4.5a-2, 4.5b-2 and 4.5c-2 are theoretical predictions based on eq. (4.12) for $P'$ and eq. (4.10) for $\pi$. In these equations, $D_{so}$ was taken as $D_{so} = D_M$, which is acceptable, since all ligands are small. The value of $\delta_{so}$ was determined experimentally by using eq. 4.8, in the absence of ligands. Then:

$$\delta_{so} = D_M \times \left[ \frac{C^b_{so}}{J^0} - \frac{\ell}{K_p[C]D_{MC}} \right]$$  (4.16)

Values of 103 µm for Cu(II) and 110 µm for Pb(II) were obtained for the flow-rate used, which agree with values obtained from eq. (4.13). Figs 4.5a-2, 4.5b-2 and 4.5c-2 demonstrate a good fit between experimental data and theoretical curves.

4.5.4 The impact of the source solution flow rate (or diffusion layer thickness) on the permeability, $P'$, at different $\pi$ values

The value of $\delta_{so}$ is important since it influences both the lability of the complexes and the metal permeability of the membrane. The theoretical relationship between $\delta_{so}$ and the flow-rate of the source solution, for the flow-through cell used here (eq. 4.13), has been derived by Tomaszewski et al [12], and it has been shown that a well-defined diffusion layer thickness can be obtained by controlling the volume flow rate. Since the complexes used here are fully labile (Fig. 4.2, Table 4.3), equations (4.9') and (4.10) predict that $P'$ should depend on $\delta_{so}$ for $\pi >> 1$, while $P'$ should be independent of $\delta_{so}$ for $\pi << 1$. These predictions were checked by varying the volume flow-rate at constant Pb(II)-diglycolate and Cu(II)-N-(2-carboxyphenyl)glycine concentrations as shown in Fig. 4.6.
Figure 4.6. Effect of the volume flow-rate, \( \nu \), on the permeability, \( P' \), of Pb(II) in presence of diglycolate. Source solution: 0.01 M MES, pH 6.00; carrier = 1/1 mixture of 0.1 M 22DD/0.1M PA; Strip solution: 0.01M CDTA, pH 6.20; 5 \( \mu \)M Pb(II) with 0.5 mM diglycolate. Inset: \( P' \) vs. \( \nu^{1/3} \).

Due to the large \( K_p \) value for Pb(II), one gets \( \pi > 10 \) for the Pb(II)-diglycolate system at all flow-rates. Diffusion in the source solution is thus the rate-limiting step in all cases and \( P' \) is then predicted to be inversely proportional to \( \delta_{so} \) (eq. 4.9'), since \( \pi / (\pi + 1) \sim 1 \). An increase in the volume flow-rate, \( \nu \), decreases \( \delta_{so} \) (eq. 4.13; [12]) and should thus enhance \( P' \) and the Pb(II) flux. Fig. 4.7 shows that such a prediction is indeed observed. By plotting \( P' \) vs. \( \nu^{1/3} \), a good straight line is obtained (inset of Fig. 4.6), as expected from eq. 4.13.

Figure 4.7. Effect of the volume flow-rate, \( \nu \), on the permeability, \( P' \), of Cu(II), in presence of N-(2-carboxyphenyl)-glycin. Source solution: 0.01M MES, pH 6.00; carrier = 1/1 mixture of 0.1 M 22DD/0.1 M PA; Strip solution: 0.01M CDTA, pH 6.20; 5 \( \mu \)M Cu(II) with 0.1 mM N-(2-Carboxyphenyl)glycine; room temperature.

On the opposite, the \( \pi \) values for the Cu(II)-N-(2-Carboxyphenyl)glycin system (5 \( \mu \)M Cu(II), 0.1mM ligand) are much smaller than 1 at all \( \nu \) values (see Fig. 4.5c-2). So \( P' \) is...
independent of \( \delta_{so} \) (or \( \nu \); Fig. 4.7) as predicted theoretically by eq. (4.9'). This result also indicates that under such conditions, the equilibria in solution are not perturbed by the uptake of M at the solution/membrane interface and concentrations of all species are always the same as in the bulk.

4.5.5 Impact of membrane thickness and carrier concentration on metal permeability

By increasing the membrane thickness, \( \ell \), \( \pi \) decreases (eq. 4.10), which reflects the fact that diffusion through the membrane becomes more demanding. The role of this process, as rate-limiting step, thus increases. The same result should be obtained by decreasing the carrier concentration, [C]. Figure 4.8 shows that for Pb(II), either in the absence or the presence of 0.5 mM diglycolate, \( P' \) is independent of \( \ell \). This is coherent with the finding that, for all \( \ell \) values, experimental values of \( \pi \) were larger than 5, i.e. \( P' = D_M/\delta_{so} \) (eq. 4.12). Thus \( P' \) is never controlled by membrane diffusion under the current experimental conditions.

Figure 4.8. Pb(II) permeability, \( P' \), as a function of membrane thickness and carrier concentration. Source solution: 0.01M MES, pH 6.00; Strip solution: 0.01M CDTA, pH 6.20; carrier: 1/1 mixture of 0.1 M 22DD/0.1 M PA. Volume flow rate: 0.02 cm\(^3\)/s (≈ 3.33 cm/s). 5 μM Pb(II). Membrane thickness: 25, 50 and 100 μm. Room temperature. ● 0.1M carrier, without ligand; ○ 0.1 M carrier, with 0.5 mM diglycolic acid.

Cu(II) shows a completely different behaviour (Fig. 4.9). In the absence of ligand, \( P' \) passes from a regime controlled by diffusion in solution (\( P' \) independent of \( \ell \)) at 0.1 M carrier, C, to a regime controlled by diffusion in the membrane at 0.01 M carrier. Indeed, by decreasing [C], \( \pi \) decreases accordingly, and becomes smaller than 1. When diffusion in the membrane is the only rate-limiting step, eq. 4.12 becomes: \( P' = D_M/\delta_{so} \sim \ell^{-1} \). In the presence of diglycolate, with both 0.1 M and 0.01 M carrier, the decrease of \( \pi \) is sufficient (as already seen in Fig. 4.5b) to change the rate controlling step from diffusion in solution to diffusion in the membrane. The corresponding curves in Fig. 4.9 confirm this prediction since straight lines are obtained for log\( P' \) vs log \( \ell \) with slopes of −0.78 for 0.1 M carrier and −0.94 for 0.01 M carrier, i.e. close to −1.
It seems useful to devote some remarks to the nature of the distribution parameter, $K_p$. The dependences of $\pi$ and $P'$ on the various parameters of the systems are generally well predicted by the theory explained in this chapter (see above) and the general equation $P' = f(\pi)$ (eq. 4.12). Overall correspondence between experimental data and theory can be evaluated from Fig. 4.10 a,b, where all the data of Figs. 4.5 and 4.8-4.9 are plotted again as $\log P' = f(\log \pi)$. It can be seen that for Pb, all data fall on the same curve. For Cu(II), all the data also follow theoretical predictions. However, the curve generated by the data of Fig. 4.8-4.9 is slightly shifted along the $\pi$ axis compared to the curve based on Fig. 4.5. These different data were obtained from different sets of experiments, and the shift between the two sets would correspond to a difference of a factor of ~2 in the $K_p$ values for the two cases.

This suggests that $K_p$ might not be a perfectly well-defined thermodynamic parameter, as is also suggested by other results [5] (chapter 1, section 3) which point at complicated interfacial and transport processes for Cu(II). Thus, for the carrier system used here, $K_p$ might have a partly operational nature which may depend somewhat on experimental conditions. Consequently, for precise and reproducible speciation measurements, the calibration must be
performed for each set of experiments, with the same experimental system and conditions. A study of the rigorous nature of $K_p$ is in progress.

**Figure 4.10.** The relation of Cu(II) (a) and Pb(II) (b) permeability, $P'$, with $\pi$ by varying $\ell$, [C] and $\alpha_{so}$. Conditions of Fig. 4.10a: ▲ see Fig. 4.5b, ▼ see Fig. 4.5c, ■ see Fig. 4.9 without ligand, ● see Fig. 4.9 with ligand. Conditions of Fig. 4.10b: ▲ see figures 4.5a, ■ see Fig. 4.8 (no ligand), ● see Fig. 4.8 (0.5 mM ligand).

### 4.5.7 Impact of carrier concentration on the permeability of metal complex

By decreasing the carrier concentration, [C], $\pi$ should decrease (eq. 4.10) and the rate-limiting step gradually passes from diffusion in solution to diffusion in the membrane. This effect is expected both in presence and absence of ligands forming labile complexes.
Figure 4.11. Cu(II) permeability as a function of carrier concentration. Source solution: 0.01M MES, pH6.00; Strip solution: 0.01M CDTA, pH6.20; carrier: 1/1 22DD/PA. Volume flow rate: 0.02 cm³/s (≈ 3.33 cm/s). Total Cu(II) concentration: 5 μM

Figure 4.11 shows that, for Cu(II), both in absence and presence of 0.5 mM diglycolate, $P'$ indeed decreases with decreasing carrier concentration, passing from a regime controlled by diffusion in solution ($P'$ independent of $[C]$) at 0.1 M carrier, to a regime controlled by diffusion in the membrane at 0.001 M carrier. This is due to the fact that when $[C]$ decreases, $\pi$ decreases accordingly, and becomes smaller than 1. When diffusion in the membrane is the only rate-limiting step, eq. 4.12 becomes: $P' = \frac{K_p[C]D_{MC}}{\ell \alpha_{so}}$. Thus from the ratio of permeability without diglycolate and with diglycolate, $\alpha_{so}$ can readily be obtained. A $\alpha_{so}$ value of 15.4, is found from Figure 4.11 at $[C] = 0.001$ M. This value is very close to the result of 17.6 obtained by titration with Cu(II) ion selective electrode and 16.4 obtained by cyclic voltammetry. This confirms that for $[C] < 10^{-2}$M, the rate-limiting step is really the diffusion in the membrane. A slope: 1.51 is found under membrane diffusion limited and with 0.5 mM Diglycolic acid. This partially confirms the observation in section 1.3.5: there is no single carrier (only 22DD) which undertakes the transport of Cu in the membrane. Otherwise, a slope 1 should be observed.

4.6 Comparison with metal flux at solution/organism interface

The present chapter shows that the factors of the test medium ($\delta_{so}$, $\alpha_{so}$, $\bar{D}_{so}$) which may affect the metal flux through PLM are quantitatively understood. It must be emphasized that they play the same role in the metal uptake by organisms, as in the metal flux through PLM. In fact, provided planar diffusion is valid in both cases, the permeability eqs. (4.10) and (4.12), developed for PLM, are equally applicable to biouptake. One simply has to replace the
PLM membrane rate constant \( (k_{PLM} = K_p[C]D_{MC}/\ell) \) in eq. (4.10), by a biological internalisation rate constant, \( k_{int} [14,15] \), while the rate constant for diffusion in solution, \( k_{so} = \bar{D}_{so}\alpha_{so}/\delta_{so} \) remains unchanged.

For microorganisms, spherical diffusion must be considered in the external medium. The general flux equation for a perfect sink and labile ML complex is then obtained from eq. 3.44 (chapter 3) with \( \lambda \to 0 \). If diffusion through the plasma membrane may also be a limiting step, then a resistance due to an biological internalisation rate constant, \( k_{int} \) should be added to the resistance term of diffusion in solution, as for planar geometry. Then the flux equation becomes:

\[
J = D_M c_M^* \left[ \frac{1}{k_m^* \alpha_{so} \ell} + \frac{r_0}{D_M (1 + \varepsilon K[L])} \left( \frac{\delta}{r_0 + \delta} \right) + \frac{r_0 \lambda \tanh \left( \frac{\delta}{\lambda} \right)}{n_0 + \lambda \tanh \left( \frac{\delta}{\lambda} \right)} \right]^{-1}
\]

Thus permeability vs \( \pi \) curves, with similar shapes as those of Fig. 4.5 or 4.10 are expected for both PLM and organisms. This has interesting implications:

First it is possible to predict that when the medium becomes more complexing (\( \alpha_{so} \) increases) or when convection increases (\( \delta_{so} \) decreases), the \( \pi \) value for a given organism will decrease, as for PLM. Thus the probability that the permeability will only depend on free M concentration (or activity), i.e. that uptake models such as the Free Ion Activity Model (= FIAM), or the Biotic Ligand Model (= BLM) [15] are valid, will increase. On the other hand, the chance that metal uptake will depend on the total concentration of labile metal species will increase with decreasing \( \alpha_{so} \) values, and in poorly mixed systems.

Above all, the results of this chapter demonstrate that PLM can be used to determine whether biouptake is controlled by free metal ion or by total labile species. Indeed, the PLM flux (permeability) can be tuned at the same value as that of metal uptake by the test organism, by choosing the right value of \( \pi, \pi_{organism} \), via the appropriate adjustment of \([C]\), \( \ell \), or \( \delta_{so} \) parameters. Then by measuring and plotting \( \log P' = f(\log \pi) \), for \( \pi \) values around \( \pi_{organism} \), it is possible to determine whether diffusion in solution (\( P' \) independent of \( \pi \)) or transport through the membrane (\( P' \) proportional to \( \pi \)) is the rate limiting step. This conclusion will be valid both for PLM and organism, provided the range of \( P' \) used is the same for both.

For experimental reasons, this capability of linking speciation to bioavailability is fairly unique for PLM compared to other dynamic speciation sensors. Thanks to its additional potential capability for in situ measurements in waters, this type of sensor might thus become a major tool in bioenvironmental monitoring.
4.7 References


Chapter 5

Roles of dynamic metal speciation and membrane permeability in the metal flux through lipophilic membranes. General theory and experimental validation with non labile complexes

5.1 Overview

A general theory is derived and checked experimentally, to interpret the role of dynamic metal speciation in aqueous solution, on its permeability through lipophilic membranes. The steady-state metal flux through a permeation liquid membrane (PLM), in solutions containing 1:1 metal complex under ligand excess conditions, is particularly studied, as model for metal biouptake, and as basis for PLM based bioanalaglogical sensors. From this theory, metal transport fluxes in the three rate-limiting conditions are readily derived, corresponding namely to, i) diffusion in the source solution, ii) diffusion in the membrane and iii) chemical kinetics of formation/dissociation of the metal complex in the interfacial reaction layer. The theoretical flux equations for fully labile complexes were validated in chapter 4. The general theory for semi- or non-labile complexes is validated in this chapter by studying the flux of Pb(II) through PLM in contact with solutions of Pb(II)-NTA and Pb(II)-TMDTA, at different pH’s and flow-rates.

5.2 Introduction

Figure 5.1. Schematic representation of PLM and the process of metal complex speciation. ℓ = membrane thickness, δso, δst = diffusion layer thicknesses in the source and strip solution respectively, DM, DML, DMC = diffusion coefficients of M, ML and MC respectively, ka, kd = association and dissociation rate constants for ML formation, KML = stability constant of ML, Kp = partition coefficient of M = [MC]/[M][C].

Figure 5.1 summarizes the important processes leading to the transport of a metal M from an aqueous solution through a lipophilic membrane. M is accumulated into the strip solution, at a rate which depends in particular on the physicochemical processes occurring in the source
solution. The amount of accumulated metal thus enables the determination of the overall flux through the source solution and the PLM, and thus the nature of the rate limiting factors. For example, if the transport through the membrane is slow compared to that in the source solution, the depletion of metal concentration at the interface is negligible and the flux through the PLM only depends on the free M concentration in solution (as assumed in the FIAM model for microorganism uptake). When, on the other hand, the transport processes in the source solution are slower than those in the membrane, the former become rate limiting. This may be due in particular to slow diffusion of the complex ML (low value of the diffusion coefficient of the complex, \( D_{\text{ML}} \), as for colloidal complexants) and/or to slow dissociation reaction of ML (low value of the dissociation rate constant, \( k_d \), as e.g. for some organic metal complexes). A complete study of the role of these factors is thus essential to understand metal biouptake as well as to develop well controlled bioanalogical PLM sensors.

In chapter 3, the effect of the dynamic processes in solution (diffusion and chemical kinetics) on the metal flux at an interface considered as a perfect sink has been studied. In chapter 4, the role of diffusion in solution and of transport in the membrane has been studied systematically, under conditions where the chemical reactions in solution are very fast compared to the other processes (labile complexes). In the present chapter, we develop a general theory and mathematical expressions providing the steady-state flux of metal ions through a lipophilic membrane, by considering all the important processes: the diffusion kinetics and thermodynamic properties of the metal complex in solution, in combination with its interfacial reaction and its transport inside the membrane. A general analytical expression for the flux is obtained, which simplifies into the expected limits for the fully inert and fully labile complexes. Experimental systematic verification for the labile systems has been reported in chapter 4, using Cu(II)-Diglycolic acid, Pb(II)-Diglycolic acid and Cu(II)-N-(2-Carboxyphenyl)-glycine complexes. Here the validation of the general equation is complemented by studying the metal flux in presence of semi-labile Pb(II)-TMDTA and Pb(II)-NTA complexes. The impact of pH and diffusion layer thickness has been investigated.

### 5.3 General theory for the PLM steady-state metal flux in complexing solution

#### 5.3.1 Derivation of the flux equation.

Let’s consider the metal complexation reaction (5.1), with the association and dissociation rate constants \( k_a \) and \( k_d \), and the equilibrium constant \( K = k_a/k_d = [\text{ML}]/[\text{M}][\text{L}] \):

\[
\text{M} + \text{L} \rightleftharpoons \text{ML}
\]  

(5.1)

In the following, the ligand will be assumed to be in large excess compared to M, i.e. \( C_L \gg C_M \), where \( C_L \) and \( C_M \) are the total concentrations of L and M in the source solution. In addition, the possible protonation of L will be assumed to be always at equilibrium, so that the free concentration of L, \([L] \), can be expressed as:

\[
[L] = \frac{C_L}{1 + \sum_i \beta_i^H [H]^i}
\]  

(5.2)

and is proportional to \( C_L \) at constant pH. (The \( \beta_i^H \)'s are the cumulative acid-base equilibrium constants of L).
The equations for the profiles of θ and ψ are obtained by using boundary conditions which correspond to a well-stirred solution, in which a fixed reactive diffusion layer with thickness, \( \delta_{so} \), is created at the membrane surface:

\[
\begin{align*}
\text{At } x = 0: & \quad \theta = \theta^0 = \frac{[M]^0}{[M]}, \quad \frac{d\psi}{dx} = 0 \\
\text{At } x \geq \delta_{so}: & \quad \theta = 1 \quad \psi = 1
\end{align*}
\]

(5.3) (5.4)

In the following we shall compute the flux at times long enough (typically >1 minute) so that steady-state concentration profiles are established, but short enough for the free M concentration to be much smaller in the strip than in the source solution, i.e. for the PLM system to remain far from equilibrium. With the flow-through cell described in this chapter, this condition is fulfilled for at least several hours after the start of the accumulation step [1].

On the other hand, the time required to get steady-state concentration profiles in solution and in the membrane are of the order of \( \delta_{so}^2/D_M = 10s \) (with \( \delta_{so} = 100 \mu m \)) and \( \ell^2/D_{MC} = 30s \) respectively. Under those conditions, the flux through the membrane is given by:

\[
J = D_{MC} \left( [MC]_1 - [MC]_2 \right) / \ell
\]

(5.5)

where \([MC]_1\) and \([MC]_2\) are the concentrations of the metal carrier complex in the membrane, at the source/membrane (subscript 1) and the strip/membrane interfaces (subscript 2; Fig.5.1). The strip ligand, S, is so strong that, during the steady-state, \([MC]_2 = 0\). In addition, \([MC]_1/[M]^0 = K_p[C]\), where \(K_p\) is the partition coefficient of M between the source solution and the membrane, and \([C]\) is the carrier concentration in the membrane phase, in large excess compared to MC. Thus eq. 5.5 can also be written:

\[
J = \frac{[M]^0 K_p [C] D_{MC}}{\ell} \theta^0
\]

(5.6)

This flux is equal to that on the source solution side of the membrane:

\[
J = D_M [M]^* \left( \frac{d\theta}{dx} \right)_{x=0}
\]

(5.7)

Combining equations 5.6 and 5.7 gives:

\[
\left( \frac{d\theta}{dx} \right)_{x=0} = \frac{K_p [C] D_{MC} \theta^0}{D_M \ell} = \phi \theta^0
\]

(5.8)

with:

\[
\phi = \frac{K_p [C] D_{MC}}{D_M \ell}
\]

(5.9)

By integrating eq. 3.12 with the boundary conditions 5.3, 5.4 and 5.8 we obtain:
\[ \theta + \varepsilon K[L] \psi = (x - \delta_\infty) \rho \theta^0 + 1 + \varepsilon K[L] \quad \text{for} \ 0 < x < \delta_\infty \] (5.10a)

and

\[ \theta + \varepsilon K[L] \psi = 1 + \varepsilon K[L] \quad \text{for} \ x \geq \delta_\infty \] (5.10b)

which reflects that the weighted sum of the normalised concentrations of M and ML is a linear function of x in the whole diffusion layer.

The concentrations profiles of M and ML, and the flux equation are found by combining eqs. 3.9 and 5.10 to eliminate \( \psi \):

\[
\frac{d^2 \theta}{dx^2} = -\frac{k_s[L](1+\varepsilon K[L])}{D_M \varepsilon K[L]} \theta + \frac{k_s[L]}{D_M \varepsilon K[L]} \rho \theta^0 x + \frac{k_s[L]}{D_M \varepsilon K[L]} (1+\varepsilon K[L] - \rho \theta^0 \delta_\infty) = 0
\] (5.11)

Equation 5.11, like eq. 3.16 (chapter 3) includes the combination parameter \( \lambda \) which represents the general expression for the reaction layer.

\[
\lambda = \sqrt{\frac{D_M \varepsilon K[L]}{k_s[L](1+\varepsilon K[L])}} = \mu \sqrt{\frac{\varepsilon K[L]}{1+\varepsilon K[L]}} = \frac{1}{\sqrt{\frac{k_s[L]}{D_M} + \frac{k_s}{D_{ML}}}}
\] (5.12)

where \( \mu = \sqrt{\frac{D_M}{k_s[L]}} \). \( \mu \) is the so-known reaction layer thickness [2]. It is the maximum distance from the interface, from which M can still diffuse to and be consumed at the surface, before being associated again with L into ML. For that reason we shall call it below ‘association’ reaction layer. \( \lambda \) is an even more general expression for the reaction layer thickness (chapter 3, section 3.5).

The general solution of eq. 5.11 is:

\[
\theta = C_1 \exp(-x/\lambda) + C_2 \exp(x/\lambda) + \frac{\rho \theta^0 x}{1+\varepsilon K[L]} + 1 - \frac{\rho \theta^0 \delta_\infty}{1+\varepsilon K[L]} + 1
\] (5.13)

where \( C_1 \) and \( C_2 \) are constants which can be found by using the boundary conditions (5.3) and (5.4):

\[
C_1 = \left(1 - \frac{\theta^0 (1+\rho \delta_\infty + \varepsilon K[L])}{1+\varepsilon K[L]}\right) \exp(2\delta_\infty / \lambda)
\] (5.14)

\[
C_2 = \frac{\theta^0 (1+\rho \delta_\infty + \varepsilon K[L]) - 1}{1+\varepsilon K[L]} - \frac{1}{1-\exp(2\delta_\infty / \lambda)}
\] (5.15)

From eqs. 5.13-5.15, we get \( (d\theta/dx)_{x=0} \) and \( \theta^0 \) which, combined to eqs. 5.6 or 5.7, provides the expression of \( J \):
\[ J = D_M [M] \left[ \frac{\delta_{so}}{1 + \varepsilon K[L]} + \frac{1}{\phi} + \frac{\lambda \varepsilon K[L]}{1 + \varepsilon K[L]} \cdot \tanh \left( \frac{\delta_{so}}{\lambda} \right) \right]^{-1} \]  

(5.16)

or

\[ J = [M] \left[ \frac{\delta_{so}}{D_M (1 + \varepsilon K[L])} + \frac{\ell}{K_p [C] D_{MC}} + \frac{\mu}{D_M} \left( \frac{\varepsilon K[L]}{1 + \varepsilon K[L]} \right)^{3/2} \tanh \left( \frac{\delta_{so}}{\mu} \sqrt{\frac{1 + \varepsilon K[L]}{\varepsilon K[L]}} \right) \right]^{-1} \]  

(5.17)

with \( \tanh(x) = \frac{\exp(2x) - 1}{\exp(2x) + 1} \). The denominator of equation 5.16-5.17 contains three terms, each one representative of a resistance to the flux. From left to right they correspond to i) the physical diffusion in the source solution, ii) the physical diffusion in the membrane, and iii) the chemical rate of dissociation/formation of metal complex in solution.

From eq. 5.17, a few important limiting cases can be distinguished:

5.3.2 Limiting case 1: membrane limited flux

When the second term in eq. 5.17 is much larger than the other two, diffusion inside the membrane is the only flux limiting process and eq. 5.17 simplifies into eq. 5.18 [1,3]:

\[ J = [M] \frac{K_p [C] D_{MC}}{\ell} \]  

(5.18)

Under this condition, the flux is proportional to the free metal concentration in the bulk of the source solution, \([M]^*\), irrespective of the degree of lability of the complex.

5.3.3 Limiting case 2: labile complexes

Complexes are fully labile if the association/dissociation rates of ML are much faster than the diffusion of M and ML in solution. This means that the third term of eqs. 5.24-5.25 is much smaller than the first one, i.e.:

\[ \lambda \varepsilon K[L] \tanh(\delta_{so}/\lambda) \ll \delta_{so} \]

For labile complexes, \(\delta_{so} \gg \lambda\) [2,4,5], so that, when \(\varepsilon K[L] \gg 1\) (i.e. \(\lambda \sim \mu\)), \(\tanh(\delta_{so}/\lambda) \to 1\), and one gets:

\[ \delta_{so} \gg \mu \varepsilon K[L] \]

The expression for the flux of fully labile complexes then simplifies into:

\[ J = [M]^* \left[ \frac{\delta_{so}}{D_M (1 + \varepsilon K[L])} + \frac{\ell}{K_p [C] D_{MC}} \right]^{-1} \]  

(5.19)

and , when diffusion in the membrane is much faster than in solution:

\[ J = [M]^* \frac{D_M (1 + \varepsilon K[L])}{\delta_{so}} = \frac{\bar{D} C^M}{\delta_{so}} \]  

(5.20)

where \(\bar{D}\) is the average diffusion coefficient of M, defined as [2]:

69
\[ D = \left( D_{ML}[M]^\dagger + D_{ML}[ML] \right) / C^M \]  

Under this last condition, \( J \) is proportional to the total rather than to the free concentration of \( M \). Equations 5.18-5.20 have been experimentally checked in detail in chapter 4. Note that, even for fully labile complexes, the flux can still be fixed by eq. 5.18, when the second term in the denominator of eq. 5.19 is much larger than the first one (see limiting case 1).

When \( \delta_{so} \approx \lambda \varepsilon K[L] \tanh(\delta_{so}/\lambda) \) the behaviour of the complex is in between that of a fully labile and a kinetically controlled complex, and it is called semi-labile.

5.3.4 Limiting case 3: kinetically controlled complexes

Under the condition:

\[ \delta_{so} << \lambda \varepsilon K[L] \tanh(\delta_{so}/\lambda) \]

The association/dissociation rates of \( ML \) are slow compared to its diffusion in the source solution and become the rate-limiting steps, provided the diffusion in the membrane is fast, i.e. \( 1/\phi \) is small compared to the third term of the denominator of eq. 5.17.

For the often encountered condition \( \varepsilon K[L] >> 1 \), which also implies \( \delta_{so}/\lambda \sim \delta_{so}/\mu \), three cases can be discriminated:

- When \( \delta_{so}/\lambda < 0.1 \), the complex can be considered as inert (see discussion in chapter 3, section 3.6)
- When \( \delta_{so}/\lambda > 10 \), \( \tanh(\delta_{so}/\lambda) \sim 1 \) in eq. 5.17. By taking also \( \varepsilon K[L] >> 1 \) into account, eq. 5.17 then reduces to:

\[ J = [M]^\dagger \left[ \frac{\ell}{K_p[C]D_{MC}} + \sqrt{\frac{1}{D_mk_s[L]}} \right]^{-1} \]  

(5.22)

i.e. the contribution of the complex \( ML \) (second term inside brackets of eq. 5.22) is limited by its chemical kinetics. A pure kinetically-controlled flux is obtained (\( J = D_{M}[M]^\dagger/\lambda \)) when the first term in brackets is negligible, i.e. the diffusion in the membrane is very fast with respect to chemical kinetics.

- When \( 0.1 < \delta_{so}/\lambda < 10 \), the behaviour of the complex is between that of an inert complex and that of a kinetically controlled complex (see chapter 3, section 3.6).

Note that the values of \( \delta_{so}/\lambda = 0.1 \) and \( \delta_{so}/\lambda = 10 \) are somewhat arbitrary, the only important conditions being that \( \tanh(\delta_{so}/\lambda) \sim \delta_{so}/\lambda \), and \( \tanh(\delta_{so}/\lambda) \sim 1 \) respectively.

5.4 Experimental section

5.4.1 Reagents and membrane

The following reagents used for transport experiments were analytical grade: 2-(N-morpholino)ethanesulfonic acid (MES, Sigma), \( trans \)-1,2-diaminocyclohexane- N, N', N'-
tetraacetic acid monohydrate (CDTA, Fluka), sodium hydroxide and lithium hydroxide (Merck), palmitic acid (PA, Fluka). 1,10-didecyl-1,10-diaza-18-crown-6 ether (Kryptofix 22DD, Merck) was pure for synthesis (> 98%). The solvents, toluene and phenylhexane, were Fluka analytical grade products. MilliQ water was used for preparing all the aqueous solutions.

The source solution contained the desired concentration of Pb(II) (usually 5 μM) in 0.01M MES (pH = 6 was adjusted with LiOH). The strip solution was composed of 0.01M CDTA (pH = 6.20 adjusted with NaOH). The membrane solution was made of 1:1 22DD/PA in 1:1 (v/v) mixture of phenylhexane and toluene. Note that, compared to previous work, palmitate was used instead of laurate in the present study, for the reason given in chapter 4.

Celgard 2500 polypropylene hydrophobic membrane (Celanese Plastic, Charlotte, NC) was used as flat sheet support. Its characteristics are as follows: porosity = 0.45; thickness = 25 μm; average pore diameter = 0.04 μm.

5.4.2 The PLM device and its characteristics

A schematic view of the flow-through cell system used in this work, and its corresponding characteristics are shown in Fig. 4.3. A peristaltic pump (Gilson, Omnilab) was used to control the source volume flow rate. Standard tubings (Tygon R3607, ID = 2.29 mm and 3.175 mm, Biosystems, Omnilab) were used to connect the source solution to the flow-through cell, whose characteristics and advantages have been described in detail in chapter 4 (section 4.4.2, Fig 4.3) [6]. The strip solution was collected by a pump at the end of the accumulation period and the corresponding metal concentration was measured by flame or flameless atomic absorption spectrometry (AAS) using a Pye Unicam SP9 or a Perkin-Elmer 4100 with HGA 700 graphite furnace spectrophotometers.

The driving force of the PLM is the free M activity gradient between the two solutions; thus the complexant S in the strip solution (Fig. 5.1) should be strong enough to maintain a free M activity lower than in the source solution, during the whole measurement period. In this chapter this was ensured, by using CDTA as ligand S, with a very large degree of complexation for Pb(II): based on the stability constants [7] (table 5.2), \( \alpha_{st} = C^{st}/[Pb^{2+}]_{st} \) was calculated to be \( 10^{12.7} \). Due to this large value the strip solution behaves as a perfect sink for Pb(II) under the experimental conditions used here. Values of \( K_p = 4.2 \times 10^5 \) M\(^{-1}\) and \( D_{MC} = 3.6 \pm 1.2 \times 10^{-8} \) cm\(^2\)/s, for Pb(II) with the system 0.1 M 22DD/0.1M palmitate, were used.

5.4.3 Conditions of metal transport experiments

Flow-through cell preparation and functioning. A membrane was impregnated with the membrane solution, as outlined in chapter 4, section 4.4.3 [6]. The procedure will not be repeated here. Usually the initial metal flux and permeability, under one given set of conditions, were computed from 4 accumulation experiments performed with different accumulation times. J was obtained from the slope of the linear plot of the accumulation factor, F (see section 5.5.3 for definition), as a function of time [6,8] (eq. 5.35). Typically, such plots do not pass through the origin, since, at the beginning of the experiment, there is \( ~1 \) minute time-lag which corresponds to the transient conditions required to establish the steady-state concentration gradients in the membrane and in solution [9].
Transport experiments in the presence of complexants. The nature of the complexes used as well as the experimental conditions (pH, ligand concentration) were chosen in such a way that only 1:1 complexes were formed, and for which, as much as possible, the value of lability index, $\mathcal{L}$, was $< 0.1$. Under this condition \[10\], a purely kinetic flux is expected. Pb(II) complexes of NTA and TMDTA were thus selected. Values of the degree of complexation of Pb(II), $\alpha$, in the presence of NTA and TMDTA were computed from the literature values of their stability constants (Table 5.1).

Transport experiments in the presence of complexants were performed by keeping the total Pb(II) concentration, $C^M \leq 50 \mu\text{M}$ in the source solution. The total ligand concentration $C^L$ was then varied in such a way that the ligand was always in large excess over metal. For $C^L \geq 1\text{mM}$, $C^M$ was equal to 50 $\mu\text{M}$. For $C^L \leq 1\text{mM}$, a constant ratio $C^L/C^M = 20$ was used, with $C^L$ varying from $5.1 \times 10^{-6}$ to $10^{-3}$ M. The pH of the source solution was buffered at pH = 5.0, 6.0, or 7.0 with 0.01M MES (pH adjusted with LiOH). Note that protonation/deprotonation reactions are usually very fast compared to complexation reactions and considered here as being always at equilibrium (section 5.3.1). Thus, under ligand excess and pH buffered conditions, free L concentration is constant (eq. 5.2) even when it is smaller than $C^M$. Unless otherwise stated, a constant volume flow rate of the source solution, of 0.02 ml/s (corresponding to a linear velocity of 3.33 cm/s), was used for experiments with variable ligand concentrations. In all cases, the ionic strength was kept constant at 0.1 M, by adding 0.1M LiNO$_3$. The carrier used was a 1:1 mixture of 22DD:PAH, at a concentration of 0.1M.

The influence of volume flow rate on the permeability of the membrane in the presence of complexant was determined by varying the flow rate from 0.02 ml/s to 0.4 ml/s (3.33 to 66.0 cm/s). 5 $\mu\text{M}$ Pb(II) with 0.1 mM total NTA at pH = 6.00 was used for these tests. Other experimental conditions were the same as those discussed above.

### 5.4.4 Physico-chemical parameters of the metal complexes

The acid-base and Pb(II) complex stability constants of the ligands used in this chapter are reported in Table 5.1. Other values are taken from the cited references, or as indicated below.

<table>
<thead>
<tr>
<th>CDTA</th>
<th>NTA</th>
<th>TMDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>log$K_{\text{H}}$</td>
<td>12.3</td>
<td>9.75 ± 0.18$^a$</td>
</tr>
<tr>
<td>log$K_{\text{H2}}$</td>
<td>6.07</td>
<td>2.49$^a$</td>
</tr>
<tr>
<td>log$K_{\text{H3}}$</td>
<td>3.49</td>
<td>1.84$^a$</td>
</tr>
<tr>
<td>log$K_{\text{H4}}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>log$K_{\text{Pb}}$</td>
<td>22.0</td>
<td>11.60$^a$</td>
</tr>
<tr>
<td>log$K_{\text{PbH}}$</td>
<td>1.85$^b$</td>
<td></td>
</tr>
</tbody>
</table>

In this table, $K_{\text{Pb}} (= k_d/k_a)$ refers to the equilibrium:

$$\text{Pb}^{2+} + \text{NTA}^{3-} \rightleftharpoons \frac{k_a}{k_d} \text{PbNTA}^-$$ (5.23)
whereas $K_{\text{Pb}}^H (= k_a^H/k_d^H)$ refers to the equilibrium:

$$\text{Pb}^{2+} + \text{HNTA}^{2-} \rightleftharpoons k_{a}^H \text{PbNTA}^- + H^+$$  \hspace{1cm} (5.24)

$k_a$, $k_d$, $k_a^H$, and $k_d^H$ are the corresponding association and dissociation rate constants. The value of $K_{\text{Pb}}^H$ in Table 5.2 was computed as $K_{\text{Pb}}^H = K_{\text{Pb}}/K_{\text{H}_1}$. There is no protonated Pb(II)-NTA complex under the conditions used here.

The important kinetic parameters used in this paper are listed in Table 5.2. The value of $k_d$ was obtained from $k_d = k_a/K_{\text{Pb}}$, using the value of $K_{\text{Pb}}$ given in Table 5.1 and the literature value for $k_a$. The value of $k_a^H$ is taken from \[11\] and $k_d^H$ was computed from $k_d^H = k_a^H / K_{\text{Pb}}^H$. Other parameters ($D_{\text{Pb}}, k_w$) are given in Tables 3.1 and 5.2.

**Table 5.2.** Kinetic parameters for the Pb(II) species used in this chapter. I=0.1 M, T = 20°C. References inside brackets. \[a\] computed from the value of $k_a$ and $K_{\text{Pb}}$ (Table 5.1). \[b\] computed from $k_a^H$ \[11\] and $K_{\text{Pb}}^H$ (Table 5.1). \[c\] computed from the Eigen mechanism (eq. 1.8a).

<table>
<thead>
<tr>
<th>Ligand, L</th>
<th>TMDTA</th>
<th>NTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>log$k_a$ (M$^{-1}$s$^{-1}$)</td>
<td>12.61$^c$</td>
<td>$&lt; 11.18$ [37]</td>
</tr>
<tr>
<td>log$k_d$ (s$^{-1}$)</td>
<td>-1.17$^a$</td>
<td>$&lt; -0.42^a$</td>
</tr>
<tr>
<td>log$k_a^H$ (M$^{-1}$s$^{-1}$)</td>
<td>6.64$^{[37]}$</td>
<td></td>
</tr>
<tr>
<td>log$k_d^H$ (M$^{-1}$s$^{-1}$)</td>
<td>4.79$^{[3]}$</td>
<td></td>
</tr>
<tr>
<td>$D_{\text{PbL}}$ ($\times 10^6$ cm$^2$s$^{-1}$)</td>
<td>7.3 $^{[38]}$</td>
<td></td>
</tr>
</tbody>
</table>

5.5 Results and discussion

5.5.1 Formation/Dissociation kinetics of PbNTA complexes

For the formation of PbNTA complex under the conditions described above, two parallel paths of reaction exist \[11\], where Pb(II) is combined either to NTA (eq. 5.23) or HNTA (eq. 5.24). The overall rates of association, $(d\text{[PbNTA]}/dt)_{\text{ass}}$ and dissociation $(d\text{[PbNTA]}/dt)_{\text{diss}}$ are then the sums of the two association rates and the two dissociation rates respectively, i.e.:

$$\left(\frac{d\text{[PbNTA]}}{dt}\right)_{\text{ass}} = k_a^H \text{[Pb][NTA]} + k_a^H \text{[Pb][HNTA]}$$  \hspace{1cm} (5.25)

and

$$\left(\frac{d\text{[PbNTA]}}{dt}\right)_{\text{diss}} = k_d^H \text{[PbNTA]} + k_d^H \text{[PbNTA][H]}$$  \hspace{1cm} (5.26)

By taking into account that acid-base equilibria of NTA are reached very quickly, the effective (or overall) association and dissociation rate constants are respectively:

$$\tilde{k}_a = k_a^H K_{\text{H}_1} [\text{H}]$$  \hspace{1cm} (5.27)

and

$$\tilde{k}_d = k_d^H [\text{H}]$$  \hspace{1cm} (5.28)

Thus eqs. 3.2 and 3.3 become:
\[
\frac{\partial [M]}{\partial t} = D_M \frac{\partial^2 [M]}{\partial x^2} + k_d [ML] + k_{dH}[ML][H] - k_a [M][L] - k_{aH}[M][L] 
\]  
(5.29)

\[
\frac{\partial [ML]}{\partial t} = D_{ML} \frac{\partial^2 [ML]}{\partial x^2} - k_d [ML] - k_{dH}[ML][H] + k_a [M][L] + k_{aH}[M][HL] 
\]  
(5.30)

Using the same procedure as in section 5.3.1, eqs. 5.29 and 5.30 get the following forms:

\[
0 = \frac{d^2 \theta}{dx^2} + \frac{\tilde{k}_a [L]}{D_M} \psi - \frac{\tilde{k}_a [L]}{D_M} \theta 
\]  
(5.31)

\[
0 = \frac{d^2 \psi}{dx^2} - \frac{\tilde{k}_d}{D_{ML}} \psi + \frac{\tilde{k}_d}{D_{ML}} \theta 
\]  
(5.32)

By multiplying the left hand and right hand sides of eq.5.32 by \( \varepsilon K[L] \) (with \( \varepsilon = D_{ML}/D_M \)), one gets eq. 3.12. Thus the rest of the derivation is the same as in section 5.3.1 and eqs. 5.16 and 5.17 are still valid. In these equations however, as for the lability index, \( \mathcal{L} \), (see below), \( k_a \) and \( k_d \) should be replaced by \( \tilde{k}_a \) and \( \tilde{k}_d \) respectively.

**5.5.2 Lability index of Pb-NTA and Pb-TMDTA complexes**

Equation 3.25 was used to compute the lability index of Pb-TMDTA (Fig. 5.3) and PbNTA complexes (Fig. 5.2).

Figure 5.2. pH dependence of Lability index of Pb(II)-NTA. Stability and kinetic constant values are taken from table 5.1 and 5.2. Diffusion layer thickness: 110 \( \mu \)m. The solid line corresponds to 10\( \mu \)M NTA and the dashed line corresponds to 0.1M NTA.

For the latter case, \( k_d \) or \( k_a \) (eq. 3.27) should be replaced by \( \tilde{k}_d \) and \( \tilde{k}_a \) respectively (eqs. 5.27, 5.28). Figures 5.2 and 5.3 show that, for both PbNTA and PbTMDTA, \( \mathcal{L} \leq 0.1 \) for the three tested pH’s, in most of the experimental domain of ligand concentrations used. Only at pH
5.0, for the lowest ligand concentrations used (~ 10μM), \( \mathcal{L} \) is larger than 0.1 but still well below unity, and at pH = 5, the flux is anyway controlled by membrane diffusion (see below). The thresholds of inertia, \( T_I \) (eq. 3.31) was also computed for PbNTA and PbTMDTA systems. They were respectively in the ranges 45 to 40000 (corresponding to 10μM NTA at pH 5 and 0.1M NTA at pH 7), and 1.6 to 170 (corresponding to 10μM TMDTA at pH5 and 1mM TMDTA at pH7). The whole of these results suggests that under the conditions used, the complexes are never inert (since \( T_I > 0.1 \)) and that purely kinetically controlled fluxes can be expected (\( \mathcal{L} \leq 0.1 \)).

![Figure 5.3](image.png)

**Figure 5.3.** pH dependence of Lability index of Pb(II)-TMDTA. Stability and kinetic constant values are taken from table 5.2 and 5.3. Diffusion layer thickness: 110μm. The solid line corresponds to 10μM TMDTA and the dashed line corresponds to 1mM TMDTA.

### 5.5.3 The influence of the ligand concentration on the metal flux through the PLM membrane: PbTMDTA complex

Experimentally, the flux, \( J \), through the membrane, is related to the total metal concentration in solution, \( C^M \), by the permeability \( P' \) defined as \( P' = J/C^M \) (chapter 4, section 4.5.2). The value of \( J \) can be computed from the accumulation of metal in the strip solution:

\[
J = \frac{V_{st}}{A} \frac{dC^M_{st}}{dt}
\]

(5.33)

where \( V_{st} \) is the volume of the strip channel, \( A \) the surface area of the membrane, \( C^M_{st} \) the total metal concentration in the strip solution, and \( t \) is time. Under the present conditions where \( J \) is independent of time, eq. 5.33 can be simply integrated to:

\[
C^M_{st} = \frac{P'C^M}{h_{st}} t
\]

(5.34)
where \( h_{st} = V_{st}/A \) is the depth of the strip channel (Fig. 4.3 chapter 4). By definition, the accumulation factor, \( F \), is equal to \( {C_{st}}^M / {C^M} \), so that:

\[
F = \frac{P^t}{h_{st}} = \frac{J}{h_{st} C^M t}
\]  

(5.35)

Figure 5.4. (a) accumulation factor as a function of time, for Pb(II) in presence of TMDTA, at pH=6.00, T=20°C, \( I=0.1 \). Total TMDTA concentration: ● 0.1mM ○ 0.2mM ▼ 0.5mM. (b) The corresponding permeability as a function of total TMDTA concentration. The ratio of total TMDTA concentration over Pb is kept equal to 20. Source solution: 0.01M MES, 0.1M LiNO\(_3\), pH6.00; Strip solution: 1mM CDTA, pH6.20; 0.1M 22DD-PAH. Flow rate : \( \nu=0.02\)ml/s.

Figure 5.4a shows that indeed \( F \) increases linearly with time. Different slopes are obtained for various concentrations of TMDTA, in excess to Pb(II). This is due to the decreasing lability of the PbTMDTA complex with TMDTA concentration (eq. 3.27). The corresponding fluxes or permeabilities can thus be computed from eq. 5.35. The slope of log\( P' \) vs log \( C_{TMDTA} \) in Fig. 5.4b is equal to -0.65, which is close to the theoretical value of -0.5 expected for purely kinetically controlled flux. This is shown by rewriting eq. 5.22 into:

\[
\frac{1}{P'} = \frac{\ell \alpha}{K_p[C]D_{MC}} + \alpha \sqrt{\frac{\alpha_{HL}}{D_M k_a C^L}}
\]

(5.36)

where \( \alpha = 1 + K_{PbCL}/\alpha_{HL} \) is the degree of complexation of Pb(II) by L in the source solution, and \( \alpha_{HL} \) is the degree of protonation of L at the given pH. When \( [ML] >> [M] \), \( \alpha \sim K_{PbCL}/\alpha_{HL} \), and eq. 5.36 becomes:

\[
\frac{1}{P'} = \frac{\ell \alpha}{K_p[C]D_{MC}} + K_{PbL} \sqrt{\frac{C^L}{D_M k_a \alpha_{HL}}}
\]

(5.37)

For a purely kinetically controlled flux, the first term of the right hand side of eq. 5.37 is negligible compared to the second, and thus : \( \log P' = -0.5 \log C^L + \text{cte} \), i.e. the slope of the log\( P' \) vs log\( C^L \) relationship should be -0.5.
5.5.4 Influence of the volume flow-rate on the metal flux through the membrane: PbNTA complexes

Figure 5.5. Permeability of Pb(II) through the PLM membrane in the Pb(II)-NTA system, with varying NTA concentrations. Source solution: 0.01M MES, pH6.00, 0.1M LiNO₃; Strip solution: 1mM CDTA, pH6.20; 0.1M carrier. A ratio \( C_{\text{NTA}}/C_{\text{Pb}} = 20 \) was maintained in all cases. \( T = 20^\circ C \). Volume flow-rate, ● 0.40 ml/s, ○ 0.02ml/s.

Figure 5.6. Permeability study of Pb(II) through the PLM, in the Pb(II)-NTA system, at varying volume flow rates. Source solution: 0.01M MES, pH6.00, 0.1M LiNO₃; Strip solution: 1mM CDTA, pH6.20; 0.1M carrier. \( C_{\text{NTA}} = 100\mu M \). A ratio \( C_{\text{NTA}}/C_{\text{Pb}} = 20 \) was maintained in all cases. \( T = 20^\circ C \).
The same results as in figures 5.4a,b were obtained for the Pb-NTA complex as shown in Fig 5.5. The slope of the obtained curve (= - 0.52) also suggests that the flux of Pb is purely kinetically controlled. This is confirmed by a study of the permeability as function of the source solution flow-rate. Changing the flow-rate, changes the thickness of the diffusion layer at the membrane surface (eq. 4.13). It can be seen that the curves of Fig. 5.5 are not influenced by the flow-rate. This is confirmed by a systematic study of the role of the volume flow-rate between 0.02 and 0.4 ml.s⁻¹ for which the diffusion layer thickness changes from 110μm to 40μm respectively (Fig. 5.6). This is in full agreement with the theoretical prediction of purely kinetically controlled flux which is independent of the diffusion layer thickness (eqs. 5.22, 5.35).

5.5.5 The influence of pH on the flux of Pb(II) through the PLM, in the Pb(II)-NTA system

When eq. 5.37 is applied to the PbNTA system, \(k_a\) must be replaced by \(\tilde{k}_a\) (eq. 5.27). Thus it is expected that \(J\) (or \(P\')) will depend on pH through both \(\tilde{k}_a\) and \(\alpha_{HI}\). A pH dependence is indeed observed on Fig. 5.7, which reports the change of permeability with NTA concentration, at pH = 4.99, 6.00 and 7.00.

The slopes of the curves \(\log P'\) vs \(\log C_{NTA}\) are –0.50, -0.52 and -0.94 at pH 7.00, 6.00 and 4.99 respectively. As explained above, the slopes at pH 6.00 and 7.00 correspond to the theoretical slopes expected for purely kinetically controlled fluxes (eq. 5.37). The slope of – 0.94 at pH 4.99 is explained by the fact that, as pH decreases, \(K_p\) decreases and the first term in the right hand side of eq. 5.37 may become larger than the second one. This means that under such conditions, diffusion in the membrane becomes rate-limiting irrespective of the chemical kinetics. In such a case, the slope of \(\log P'\) vs \(\log C\) should be –1.0, i.e. a value very close to the experimental one. The coherence of this explanation was checked by computing the values of \(\alpha_{HI}\) at the three tested pH’s, via: \(\alpha_{HI} = 1 + K_{HI}[H] + K_{HI}K_{HI}[H]^2 + K_{HI}K_{HI}K_{HI}[H]^3\) where \(K_{HI}, K_{HI}K_{HI}\) and \(K_{HI}\) are the acid-base constants of NTA (Table 5.1). The value of \(K_{pD_{MC}}\) was then obtained from the ordinate at the origin of the plot \(1/P'\) vs \(\sqrt{(C_{NTA}/\alpha_{HI})}\), at pH = 4.99. In turn, the value of \(k_d\) was obtained from the best fit of all the data at pH 7.0, 6.0, and 4.99, by using the values of \(k_a\) and \(K_{pD_{MC}}\) from tables 5.1 and 5.2. The corresponding value of \(k_d\) was obtained from \(k_d = k_a/K_{p}\). Values of \(k_a\), \(k_d\) and \(K_{pD_{MC}}\) thus obtained are given in table 5.3.

The values of \(k_a\) and \(k_d\) are close to those measured by NMR [11] at the ionic strength of 0.3 and \(T = 25\) °C (< 1.5 \(10^{11}\)M⁻¹s⁻¹ and < 0.6 s⁻¹ respectively). The value of \(k_a\) is about ten times lower than that which can be calculated on the basis of the Eigen mechanism (eq. 1.8a), when \(K_{os}\) is computed by considering the ligand as a sphere with a single overall charge localised at its center. This discrepancy however is expected since NTA is a multi-dentate ligand bearing several charges in different positions. When this is considered, the theoretical value becomes closer to the experimental one.

The obtained value of \(K_{pD_{MC}}\) is also in reasonable agreement with that reported. (1.51 \(10^{-3}\), chapter 4). In addition, when eq. 5.37 is combined with the values of \(k_a\), \(k_a\) and \(K_{pD_{MC}}\) given above, and those of stability constants given in table 5.1, the lines of Fig. 5.7 are obtained for the three pH’s, which shows that good fits are obtained in all cases. Thus these data confirm the validity of eq. 5.37, as well as the fact that, with this system, diffusion through the
membrane is the rate-limiting factor at low pH, due to the low value of $K_p$, whereas, at higher pH values, a flux controlled by pure chemical kinetics is obtained.

![Figure 5.7. Plot of permeability of the PLM for the Pb(II)-NTA system as function of total NTA concentration and pH. Source solution: 0.01M MES, 0.1M LiNO$_3$; Strip solution: 1mM CDTA, pH6.20; 0.1M carrier. Volume flow rate: 0.02 ml/s. When total NTA concentration $\leq$ 1mM, a ratio $C_{NTA}^{\text{c}}/C_{Pb}^{\text{c}} = 20$ was maintained constant. In other cases, a total Pb(II) concentration of 50$\mu$M was used. The lines are theoretical lines: solid pH4.99; dash pH6.00; dash dot pH7.00. ■ pH4.99; ● pH6.00; ▲ pH7.00. T = 20°C.](image)

**Table 5.3.** Values of $k_a$(M$^{-1}$s$^{-1}$), $k_d$ (s$^{-1}$) obtained from the best fit of data at pH 4.99, 6.0 and 7.0 and $K_pD_{MC}$ (cm$^2$s$^{-1}$) obtained at pH 4.99

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_a$(M$^{-1}$s$^{-1}$)</td>
<td>5.4±3.1 $10^{10}$</td>
</tr>
<tr>
<td>$k_d$(s$^{-1}$)</td>
<td>0.14±0.08</td>
</tr>
<tr>
<td>$K_pD_{MC}$(cm$^2$s$^{-1}$)</td>
<td>5.9±0.8 $10^{-4}$</td>
</tr>
</tbody>
</table>

5.6 General discussion

The general theory described here for the flux of a complexed metal through a permeable lipophilic liquid membrane by carrier-aided transport, is applicable to metal uptake from source solutions containing metal complexes with any degree of lability. A general analytical equation is obtained, which enables easy computation and from which the various limiting cases (flux control by membrane diffusion, solution diffusion, or chemical reactions) are readily derived. This general theory has been tested experimentally in the present work, for the non-labile complexes Pb(II)-NTA and Pb(II)-TMDTA, under varying pH and stirring conditions, for either membrane diffusion control or chemical dissociation/association control. The case of labile complexes was studied in detail in chapter 4.

These results show that the overall resistance to carrier aided metal ion permeability through a PLM is the sum of three resistances: diffusion in solution, association/dissociation rate of the complex, and diffusion in the membrane. This is very similar to the case of metal uptake flux
by microorganisms in natural waters. In this latter case, the membrane transport term is different, due to different mechanisms. When this mechanism is known, the present theory then enables to predict, the relative importance of free metal ion, labile and non-labile complexes on the metal biouptake flux. It also enables to interpret the signal provided by the PLM sensor in terms of metal flux through microorganisms plasma membrane, i.e. metal bioavailability.

5.7 References


Part II

Dynamic parameter values for flux computation in environmental chemically and physically heterogeneous multiligand systems.
Chapter 6

Critical evaluation and compilation of physico-chemical parameters for dynamic metal speciation and flux computation in environmental systems

6.1 Overview

The computation of metal flux, in aquatic systems, at consuming surfaces like organism membranes, must consider the diffusion of metal ions, ligands and complex species, as well as the kinetic and thermodynamic aspects of their chemical interactions. Many natural ligands however have complicated properties (formation of successive complexes for simple ligands, polyelectrolytic properties and chemical heterogeneity for macromolecular ligands, large size distribution and fractal structure for suspended aggregates). These properties should be properly modelled to get the correct values of the chemical rate constants and diffusion coefficients required for flux computations. The selection of the most appropriate models and parameter values is far from straightforward. This chapter discusses the various models and parameters to use for the three most important types of complexants: the small, simple ligands, the fulvic and humic compounds, and the colloidal “particles” or aggregates. The chapter also compiles selected values of the parameters required in these models. Such parameters are very much spread in the literature. They are gathered here and selected specifically for environmental applications. The chapter also discusses how to apply the concepts developed for simple synthetic soluble ligands and well characterizes metal oxide complexants, to fulvic or particulateaggregate complexants found in real aquatic systems.

6.2 Introduction

As it has been discussed previously, (chapter 1,3,5), metal biouptake in environment may be controlled by dynamic processes such as diffusion and/or chemical kinetics in solution. Modelling these dynamic processes is however presently difficult, because the parameter values required for such calculations are not always easily available. It is well known that the selection of thermodynamic constants for equilibrium models is sometimes difficult, in particular for complexes with fulvic or suspended particles. It is even more difficult with dynamic parameters since little reliable experimental data is available on diffusion coefficients of metal complexes and on complexation rate constants. As shown in the present chapter, theoretical estimation of their values is possible but it requires to use appropriate models as well as additional information on the complexant properties, such as the size distribution of particulateaggregate complexes, the structure of aggregates, or the site distribution and electrostatic properties of fulvic and humics substances.

A further complication is that environmental systems include many complexants with quite different properties [1]. They have been classified into three categories: a) the small size ligands, typically with molar mass ≤ 300 Dalton (e.g. OH−, CO3−, amino-acids, citrate..), which may form 1/n successive complexes. b) the organic macromolecules, often chemically heterogeneous with polyelectrolytic properties, in particular fulvic and humics. Their complexing sites react with metals to form 1/1 complexes, with a wide distribution of equilibrium and rate constants, and their electric charge should also be considered, c) the natural “particles”, which are more often aggregates. The properties of their complexing sites can also be modelled via the formation of 1/1 metal complexes. Their specificity however is that particle/aggregates size distribution usually covers several orders of magnitudes. This
distribution must be considered in dynamic modelling, since it is directly related to the diffusive transport of complexes. A homogeneous description of all the corresponding parameters to include them in a coherent code enabling to compute and compare the contribution of each metal species to the metal flux at a consuming interface, is not straightforward.

The purpose of this chapter is to provide, whenever possible, tables of such selected parameter values for flux computations, or the physico-chemical background required to compute these values when experimental information is not available. The considered dynamic constants are those required to compute the metal flux at a consuming interface such as a bioanalogical dynamic sensor [2, 3] or the plasma membrane of a microorganism (e.g. 4). The processes of diffusion and reactions of a metal M and a complex ML, for such a case, are summed up in Fig. 6.1. Only one ligand L and one complex, ML, are considered for the sake of clarity, but the concepts are extended in the chapter to systems with a large number of ligands with broadly varying dynamic properties.

Figure 6.1. Schematic representation of reaction-diffusion processes of metal complexes ML_{in}, at a consuming interface. $D_i$ = diffusion coefficient of species I, $K_i, k_{a,i}, k_{d,i}$ = equilibrium constant, formation and dissociation rate constants of the complex ML_{i}. $K_1^H$ and $K_2^H$ = acid-base equilibrium constants of L. $\overline{D}_L$ = average diffusion coefficient of L, LH and LH$_2$.

Figure 6.1 points out that the major parameters needed for flux computations are the diffusion coefficient of the hydrated ion M, $D_M$, the ligand L, $D_L$, and the complex ML, $D_{ML}$, the chemical rate constants for complex formation, $k_a$, and dissociation, $k_d$, and the thermodynamic equilibrium constant for complex formation $K_{ML} = k_a/k_d$ and ligand protonation, $K_H$. Flux computation also requires the definition of boundary conditions, at the organism or sensor surface (e.g. 5-8), and on the solution side. This latter is usually controlled by hydrodynamic conditions which fix the thickness, $\delta$, of a diffusion layer on the solution side of the consuming surface (Fig. 6.1). Concentration gradients exist within this layer ($x<\delta$), while the bulk solution is homogeneous ($x>\delta$). The relationship between hydrodynamics and $\delta$ can be found elsewhere [5, 9] and will not be discussed here.
The values of thermodynamic stability constants can be found in many tables [10-12]. In addition, when \( k_d \) values are not available, they can be computed from \( k_d = k_a / K \). Thus a large part of this chapter is focused on the following aspects:

- selection of the best values for the diffusion coefficients of free metal ions, small ligands, fulvics and their complexes, and computation of diffusion coefficients of metal complexes with aggregate/particulate material in aquatic systems
- critical selection of experimental \( k_a \) values for simple 1/1 and 1/n complexes, and description of the theoretical grounds for the computation of these values, when they are not available, as well as those for metal complexes with aggregate/particulate material.
- Quantitative description of a model relating the chemical heterogeneity of fulvic/humic compounds (i.e. their complexing site distribution) to coherent distributions of both the thermodynamic and kinetic formation constants of their metal complexes.

The chapter discusses successively the complexes with simple ligands, fulvic/humic compounds and natural aggregates.

6.3 Dynamic parameters for simple complexes

The so-called simple complexes are those formed with “simple” ligands (see introduction).

6.3.1 Diffusion coefficients

The best values of diffusion coefficients for free, hydrated metal ions in water, are listed in the Appendix (Section A.1.1 Table A.1.1a). Those for inorganic ligands and some organic ligands are listed in Tables A.1.1b, and A.1.2a-c. Reports on values of self-diffusion coefficients for specific metal complexes are not numerous. Some of them are given in Table A.1.3. The comments on these values can be found in section A.1.1 of Appendices.

6.3.2 Thermodynamic and conditional stability constants

Even though many tables of stability constants are available [10-12], the choice of the best values is not straightforward. This has been discussed elsewhere and is not the goal of this chapter. Let’s just point out that the values of logK registered in the database of common codes for calculation of metal species distribution (e.g. MINTEQ, MINEQL), are not always the best ones and should be checked carefully. Since the dissociation rate constant of a complex is often obtained from \( k_d = k_a / K \), the error on \( k_d \) will depend on both the errors on \( k_a \) and \( K \), which may both be significant. Thus every attempt should be done to minimize these errors. The recommended procedure to select the value of a stability constant is given in Appendix (Section A.1.2) with values of constants for inorganic complexes (Table A.1.4). The same approach is applicable to acid-base constants as well as any successive complex, ML, ML₂...MLₙ. In the following, the stability constants of the latter will be represented either by their successive constants, \( K_{n}^{ML} \) or their cumulative constants, \( \beta_{n}^{ML} \):

\[
K_{n}^{ML} = \frac{[ML_{n}]/[ML_{n-1}][L]}{}
\]

\[
\beta_{n}^{ML} = \frac{[ML_{n}]/[M][L]^{n}}{}
\]

\[(6.1)\]

\[(6.2)\]
When metal fluxes are computed under conditions where the ligand is not in excess compared to the metal ion, M, the transport of the ligand not bound to M must also be considered. Since ligands may have several protonated forms, the computation of the transport and reaction of all these species may become prohibitively computer-time consuming. In such a case, it is useful to recognize that i) the diffusion coefficients of the free ligand, L, and its protonated forms, LH\text{i} (i = 1-n) can usually be considered as equal unless conformation changes occur during protonation, and ii) the exchange of proton is usually a chemically very fast process, so that L and all its protonated forms can always be considered as being at equilibrium with each other. Under such conditions they can be treated as a whole (Fig. 6.1), with a concentration denoted as [LH]\text{t} = [L] + \sum_{i=1}^{i=n} [LH\text{i}] , with respect to their reaction with M and their diffusion process. Then it is convenient to express all metal complex equilibria by their conditional stability constant at the pH of interest and consider [LH]\text{t} as the concentration of a single species. For instance, for ML\text{n}, the relation between the thermodynamic stability constant \( \beta_{n}^{\text{ML}} \) and the conditional constant, \( \beta_{n}^{\text{ML}}' \), is given by:

\[
\beta_{n}^{\text{ML}} = \frac{[ML\text{n}]}{[ML][L]^{n}} = \frac{[ML\text{n}]}{[ML][L]^{n} \alpha_{\text{H}}^{i}} = \frac{\beta_{n}^{\text{ML}}}{\alpha_{\text{H}}^{i}}
\]

where \( \alpha_{\text{H}} = [LH]\text{t}/[L] = 1 + \sum_{i=1}^{i=n} \beta_{i}^{H}[H]^{i} \) is the degree of protonation of L. In most aquatic systems, the medium is sufficiently well pH buffered for \( \alpha_{\text{H}} \) to be constant, in the bulk solution and at an interface where M is consumed. When this is not the case, diffusion of H\text{+} and OH\text{-} have to be taken into account.

6.3.3 Association rate constants of 1/1 ML complexes, with unprotonated simple ligands

The important kinetic steps in the formation of the complex ML by reaction of M and L are depicted in eq. 6.3:

\[
M + L \xrightarrow{k_{a}^{\text{ox}}} (M,L) \xrightarrow{k_{d}^{\text{ox}}} ML
\]

\( k_{a}^{\text{ox}} \) and \( k_{d}^{\text{ox}} \) are the rate constants for the formation/dissociation of the outer-sphere complex (M,L), whereas \( k_{a}^{\text{in}} \) and \( k_{d}^{\text{in}} \) are the intrinsic rate constants for the formation/dissociation of the inner-sphere complex ML. In the classical Eigen-Wilkins mechanism [13], the formation of the outer-sphere complexes is supposed to be so fast that the corresponding equilibrium is always reached. The rate limiting step of complex formation is assumed to be that represented by \( k_{a}^{\text{in}} \), i.e. the elimination of a water molecule from the inner hydration shell of the metal ion (chapter 1). The corresponding pseudo-first order rate constant (often denoted by \( k_{a}^{\text{in}} = k_{w} \)) only depends on the nature of M and the solvent (here water). The best values as well as the range of reported values are given in Table A.1.5 for a number of metal ions. As it can be seen, the associated uncertainties are often significant and represent one of the major limitations on the accuracy of flux computations. The dissociation rate constant \( k_{d}^{\text{in}} \) is specific of the bond energy of ML. It can be obtained as discussed below.

It must be pointed out that in aquatic environmental systems, both the concentrations of M and L may be very low. This is the case for trace metals as well as for strong ligands, for which the free concentrations may be < 10\text{-}\text{9}M (sometimes by a few orders of magnitude). In addition, a number of natural ligands are supramolecular (see below), with small diffusion
coefficients and/or highly negative electric charge, which may result in lower values of $k_{a_{os}}$ and $k_{d_{os}}$. Under such conditions, the formation/dissociation of the outer-sphere complex by diffusion of M and L, may become the rate limiting step of eq. 6.3, as it is discussed below.

A general expression for the effective rate constants for the formation of ML, and its dissociation into M and L, can be obtained by applying the stationary-state approximation [14] to (M,L) in eq. (6.3), i.e. assuming that its concentration is independent of time. Then:

$$\frac{d[(ML)]}{dt} = k_{a_{os}}[M]L + k_{in}^a[ML] - k_{d_{os}}^o[(ML)] - k_{d_{os}}^p[(ML)] = 0$$ (6.4)

from which:

$$[(ML)] = \frac{k_{a_{os}}[M]L + k_{in}^a[ML]}{k_{d_{os}}^o + k_{d_{os}}^p}$$ (6.5)

By combining eqs 6.5 with that for the formation rate of the inner-sphere complex ML (eq.6.6),

$$\frac{d[ML]}{dt} = k_{in}^p[(ML)] - k_{d_{os}}^p[ML]$$ (6.6)

one gets:

$$\frac{d[ML]}{dt} = \frac{k_{a_{os}}k_{in}^a}{k_{d_{os}}^o + k_{in}^p}[M]L - \frac{k_{d_{os}}^o k_{d_{os}}^p}{k_{d_{os}}^o + k_{d_{os}}^p}[ML]$$ (6.7)

which shows that the effective association and dissociation rate constants are:

$$k_{a_{MS}}^d = \frac{k_{a_{os}}k_{in}^a}{k_{d_{os}}^o + k_{d_{os}}^p}$$ (6.8)

and

$$k_{d_{MS}}^d = \frac{k_{d_{os}}^o k_{d_{os}}^p}{k_{d_{os}}^o + k_{d_{os}}^p}$$ (6.9)

where the subscript MS refers to the complex of M with the site S of the ligand L (a general notation valid also for fulvic and particulate complexants). $k_{a_{MS}}$ can be readily computed from eqs (6.8, 6.13 and 6.14) with $k_{in}^a = k_{d_{w}}$.

Equation 6.8 shows that the expression for the effective rate constant of ML formation, derived in the classical Eigen mechanism where the outer-sphere complex is assumed to be at equilibrium with M and L, is obtained when $k_{a_{in}}^a << k_{d_{os}}^p$:

$$k_{a_{MS}}^d = k_{a_{os}}^d k_{d_{w}}$$ (6.10)

The stability constant, $K_{os}^d = k_{a_{os}}^d / k_{d_{os}}^p$, of (M,L) is given by the Fuoss equation (14-16):

$$K_{os}^d = \frac{4\pi N_{a_{v}}a_{v}^{3}\exp(-U(a)/kT)}{3}$$ (6.11)
where $N_A$ (mol$^{-1}$) is the Avogadro number and the units of $K^{\text{os}}$ are m$^3$mol$^{-1}$ if SI units are used for the other parameters. $a$ is the distance of closest approach of M and L and can be taken as the sum of the radii of M and L when L is a simple inorganic anion (see below for other cases). The value of $a = 5.10^{-10}$ m is usually accepted. For simple ligands, $U(a)$ is the coulombic energy between M and L, corrected for the ionic screening described by the Debye-Hückel term [14, 16, 17]:

$$U(a) = \frac{z_M^2 a}{4\pi\varepsilon_0 a}\left(1 - \frac{\kappa a}{1 + \kappa a}\right)$$  \hspace{1cm} (6.12)$$

where $z_M$ and $z_L$ are the charge numbers of M and L respectively, $\kappa$ is the reciprocal Debye length of the electrolyte solution, defined by $\kappa = \frac{2N_A e^2 I}{\varepsilon_0\varepsilon k_B T}$, $k_B$ is the Boltzmann constant (J.K$^{-1}$), $e$ is the charge of an electron (C), $\varepsilon_0$ is the vacuum permittivity (8.854×10$^{-12}$ J$^{-1}$C$^2$m$^{-1}$) and $\varepsilon$ is the relative permittivity of water (78.54 at 25°C). The ionic strength I is expressed in mol.m$^{-3}$.

As mentioned above however, for environmental applications, eq (6.8) cannot always be simplified into eq (6.10) and the independent knowledge of $k_a^{\text{os}}$ and $k_d^{\text{os}}$ is as important as that of $k_w$. It has been shown theoretically that they can be computed from eqs. 6.13 and 6.14 [14,17]:

$$k_d^{\text{os}} = \frac{4\pi N_A a(D_M + D_L)U(a)/kT}{\exp[U(a)/kT] - 1}$$  \hspace{1cm} (6.13)$$

$$k_d^{\text{os}} = \frac{3(D_M + D_L)U(a)/kT}{a^2\exp[U(a)/kT] - 1} \exp\left[\frac{U(a)}{kT}\right]$$  \hspace{1cm} (6.14)$$

where $D_M$ and $D_L$ (in m$^2$s$^{-1}$) are the diffusion coefficients of M and L and $k_a^{\text{os}}$ and $k_d^{\text{os}}$ are expressed in m$^3$.mol$^{-1}$.s$^{-1}$ and s$^{-1}$ respectively. $a$ (m) is the distance of closest approach, defined above for the simple inorganic ligands. The more complicated cases of multidentate ligands, fulvic/humic compounds and particulate complexants are discussed below. Note that when $U(a) \to 0$, $\frac{U(a)/kT}{\exp[U(a)/kT] - 1} \to 1$, in both eqs 6.13 and 6.14. Furthermore, as expected, the ratio of eqs 6.13 and 6.14 also provides the expression $K^{\text{os}}$ (eq.6.11).

Equation (6.14) shows that in some cases, $k_d^{\text{os}}$ may be small, in particular when the ligand is highly charged and the ionic strength rather low, i.e. when $U(a)$ is strongly negative. This case is usual under natural conditions. Then $k_a^{\text{in}}$ is not negligible compared to $k_d^{\text{os}}$ (eq. 6.8), and when $k_d^{\text{os}} \ll k_a^{\text{in}}$, eq. (6.8) tends to $k_a^{\text{MS}} = k_a^{\text{os}}$. Figure 6.2 compares the values of $k_d^{\text{os}}$ and $k_a^{\text{in}} = k_w$ for various metal ions and ligands with $z_L = 0$, -1, -2, or -3, at I = 0.01M. The figure also shows the values of $k_d^{\text{os}}$ for the complexes with fulvic acids, discussed in section 6.4. Clearly, the classical Eigen mechanism which assumes fast equilibrium for outer-sphere complex formation (i.e. $k_d^{\text{os}} \gg k_w$) should be used with caution: it is not rigorously applicable for the metals with the largest dehydration rate constant, with either simple ligands or fulvics. In such cases, eqs 6.13-6.14 should be used.
Figure 6.2. Comparison of the dissociation rate constant of the outer-sphere complex, $k_d^{os}$ (dotted and full lines), with the rate constant, $k_a = k_{a1}$, for elimination of a water molecule from the inner water shell of the cation (values on the right ordinate). The comparison is done for complexes with simple ligands (dotted lines for various number of charges of the ligand, $z_L$, eq. 6.14) and with fulvic compounds or aquatic particles or aggregates (eq.6.17). In such a case $k_d^{os}$ depends on the potential $\bar{\psi}$ inside the fulvics or at the solid surface.

6.3.4 Association rate constants of other complexes

Evaluation of the association rate constants of successive complexes, complexes with organic chelating agents, or complexes formed with protonated ligands is discussed in the A.1.4 of Appendix.

6.4 Dynamic parameters for metal complexes with humic substances

6.4.1 Nature of fulvic and humic complexants

The nature of fulvic and humic substances has been discussed in chapter 1. Two types of complexing sites can be discriminated [1,18]: i) the major sites which represent $\geq 90\%$ of the whole of sites; they are also weak complexing sites, mainly composed of single carboxylate or phenolic groups; and ii) the minor sites which comprise $\leq 10\%$ of the whole of sites; they have average to very strong complexing strength and their chemical nature is highly variable (e.g. salycilate, acetylacetone, N or S bearing chelating sites; 1,19). As far as trace metal complexation is concerned, the minor sites are the most important one to consider, under environmental conditions.
The site density of major sites is typically [1,20] 7 mol/Kg in HS to 10 mol/Kg in FS. Combined to an average molar mass, these site densities correspond to 3 (HS)-10 (FS) sites per molecule. Since the minor sites represent less than 10% of the major sites, each molecule of FS or HS statistically contains 0 or 1 minor complexing site. Thus, as far as the properties of minor sites are concerned, one can envision the FS or HS as an ensemble of different but similar molecules with:
- the same size ($r_{H} ~1 nm$),
- similar density of carboxylate (3 per HS molecule, 8 per FS molecule) and phenolate groups (4 per HS molecule, 3 per FS molecule),
- a significant electric charge density due to the deprotonation of carboxylate in the usual pH range, creating a significant overall electric field over the whole fulvic/humic molecule [21], i.e. in a region of space much larger than the complexing site dimension, and
- one or no minor site (with average or strong complexation strength) located inside the above electric field.

Because the nature of these minor sites is highly variable, the whole of the fulvic or humic molecules can be treated as an ensemble of $n$ classes of molecules, based on the nature of their minor complexing sites (the class zero corresponding to the fulvics or humics without minor complexing site). Thus the interactions of M with FS or HS corresponds to the reaction of M with a mixture of ligands, each one bearing one complexing site, $iS$, according to the reaction:

$$M + iS \rightleftharpoons MS \quad (6.15)$$

### 6.4.2 Diffusion coefficient of metal-humic complexes

The amount of data reported in the literature about the diffusion coefficients of fulvic and humic substances is rather limited. Some values of gyration radius or diffusion coefficients have been reported in the literature [22,23-26] but often with techniques like analytical centrifugation or transmission electron microscopy, which either may lead to artefacts or are not sensitive enough to work in dilute solution, in complete absence of aggregates. Only recently, sensitive reliable techniques (Fluorescence Correlation Spectroscopy, Flow Field Flow Fractionation, Atomic Force Microscopy) could be combined to get unambiguous values of diffusion coefficients and sizes of fulvic and humic substances as function of pH and ionic strength [27,28]. These works, combined to electrophoretic measurements [21], showed unambiguously that fulvic and humic molecules behave as rather rigid spheroidal molecules, and provided a detailed data base of values of diffusion coefficient and hydrodynamic radius ($r_{FS}$ and $r_{HS}$ for fulvic and humic substances respectively), in particular for Suwanee River fulvic and humic substances (Figures A.2.1, A.2.2). All the techniques used showed that the distribution of $r_{FS}$ is rather narrow for an environmental macromolecule (Fig. 6.3).

The representativity of these values for fulvics and humics of other aquatic systems has been confirmed by a systematic study of fulvic substances extracted from 18 different water bodies [29]. The corresponding variability of diffusion coefficient values was $\pm 20\%$, with an average value of $2.5 \times 10^{-16} \text{m}^2 \cdot \text{s}^{-1}$ ($r_{FS} ~1.6 \text{ nm}$), i.e. results very similar to those obtained with Suwanee river FS. In addition, the data strongly suggest that at the low concentration level found in natural waters and at pH $\geq 5$, FS and HS molecules are little or not aggregated with each other.
Figure 6.3. Distribution of the hydrodynamic radius of Suwanee river fulvic substances in solution, calculated from diffusion coefficient measured at pH = 8.5 and low ionic strength (5-27 mM), using the Stokes-Einstein equation. Techniques used are Fluorescence Correlation Spectroscopy (FCS), Flow Field Flow Fractionation (FIFFF) and NMR (PFG-NMR). Signal is normalised to give an equivalent total signal intensity. The bar histogram corresponds to the thickness distribution of the SWFA adsorbed on mica surfaces, measured by AFM. The Figure shows that the SWFA flatten somewhat, but not completely, when they are adsorbed at the surface. Modified from (27).

There are very few information in the literature about the diffusion coefficients of metal fulvic and metal humic complexes at natural, low concentration of fulvics or humics. In particular, values of \( D \approx 2 \times 10^{-10} \text{ m}^2\text{s}^{-1} \) have been determined by voltammetric techniques for Pb-fulvic complexes [78]. These values are similar to those reported for fulvics (Figures A.2.1-A.2.2), which is expected since the radii of hydrated fulvic and humic molecules are at least 10 times larger than those of the relevant dehydrated metal ions. Since in addition FS and HS are rather rigid molecules, only small conformation changes are expected during the metal complex formation. Consequently, as a good approximation, the diffusion coefficients of the metal-fulvic or metal-humic complexes can be considered as the same as those of fulvic and humic molecules.

6.4.3 Association and dissociation rate constants of metal fulvic complexes

For the sake of simplicity, in the following discussion, only the term fulvic will be used, even though the concepts discussed in the rest of section 6.4.3 are applicable to both humics and fulvics. First of all, consider the reaction between a metal ion M and a single type of minor sites (n° i) of the fulvic molecules. Three effects may influence the overall kinetics of reaction (Fig. 6.4):

i) The diffusion of M and FS towards each other, followed by diffusion of M inside FS, to form an outer sphere (M,S) complex with the minor complexing site S

ii) The electric field inside the FS, which influences the stability and formation/dissociation rates of the outer-sphere complex.
iii) The kinetics of formation/dissociation of the inner-sphere complex $\text{M}^\text{iS}$, which is controlled by the rate of elimination of a water molecule from the inner hydration shell of $\text{M}$, in the complex $(\text{M}, \text{iS})$.

\[
\text{M}_\text{aq}^{2+} \xrightleftharpoons{\psi} (\text{M}_\text{aq}^{2+}, \text{iS}) \xrightarrow{\psi} \text{M}^\text{iS}
\]

**Figure 6.4.** Schematic representation of the reaction of a metal ion $\text{M}$ with a spherical fulvic/humic macromolecule, $\text{FS}$, containing one single minor site, $\text{iS}$. $\overline{\psi}$ = average potential difference between the inside and outside of fulvic/humic macromolecule. A: approach of $\text{M}$ and $\text{FS}$ and penetration of $\text{M}$ in $\text{FS}$, by diffusion. B: formation of an outer-sphere complex between $\text{M}$ and $\text{iS}$. C: formation of an inner-sphere complex by elimination of a water molecule from the inner hydration shell of $\text{M}$.

In aquatic systems, the concentration of fulvic molecules containing the most strongly binding minor sites might be less than $10^{-9}$ M and the free $\text{M}$ concentration is often much lower. In addition, fulvics usually bear a strong negative electric field which slows down the dissociation of the outer-sphere complex. Thus the formation/dissociation rates of the outer-sphere complex may become the rate limiting step for $\text{M}^\text{iS}$ formation (Fig. 6.4), contrary to the assumption made in the classical Eigen mechanism (section 6.3.3). Hence, the generalized eqs. 6.8, 6.13, 6.14 should be used for computing the effective association rate constant of the complex, rather than eq. 6.10. For the fulvic complexes, the potential energy, $U(a)$, between $\text{M}$ and $\text{iS}$ results from the interaction of the positive charge of $\text{M}$ with the overall electric field of $\text{FS}$. Hence, $U(a) = z\text{Me}^+ \overline{\psi}(a)$, where $e$ is the elementary electric charge, $z\text{M}$ the number of charge of the ion $\text{M}$, and $\overline{\psi}(a)$ the electric potential at the distance $a$ of the site $\text{iS}$. Detailed profiles of $\psi$ inside the fulvics and humics, as function of pH and ionic strength, have been reported in [21] and are given in Fig. A.2.3. They are average profiles for the ensemble of fulvic (or humic) molecules. Besides, the position of a site $\text{iS}$ will vary statistically in the various $\text{FS}/\text{HS}$ molecules. Thus, there is no one single value of $U(a)$ for site type $n^0$, and an average value of $\overline{\psi}$, $\overline{\psi}$, obtained from Fig. A.2.3, should be used in preference, for computing $k_a$ and $k_d$. The values of $\overline{\psi}$ for various pH and ionic strength conditions, are given in Table 1. They are consistent with other observations of the literature [19, 30].

The table 6.1 shows that, at natural pH and ionic strength, $\overline{\psi}$ is always negative, having an absolute value $> 30$ mV. Under these conditions, the exponential term in the denominators of eqs. 6.13 and 6.14 becomes much smaller than one and the rate constants are given by:

\[
k_a \approx -\frac{4\pi N_A a (D_M + D_{FS}) z_M F \overline{\psi}}{RT}
\]

(6.16)

\[
k_d \approx -\frac{3(D_M + D_{FS}) z_M F \overline{\psi}}{a^2 RT} \exp\left[\frac{z_M F \overline{\psi}}{RT}\right]
\]

(6.17)
where \( a = 0.5 \) nm can be used for the distance of closest approach between \( M \) and the site. \( k_{a}^{\text{os}} \) and \( k_{d}^{\text{os}} \) are expressed in m\(^3\)mol\(^{-1}\).s\(^{-1}\) and s\(^{-1}\) respectively if SI units are used in eqs. 6.16-6.17.

### Table 6.1. Average value of the potential difference, \( \bar{\psi} \), between the inside and outside of fulvic macromolecules, for various values of pH and ionic strength, \( I \). \( \bar{\psi} \) values are calculated from Figures A.2.3-1 and A.2.3-2, by integrating \( \psi \) on the sphere of radius \( r_{FS} \) and dividing by its volume, i.e.:

\[
\bar{\psi} = \frac{3}{r_{FS}^{3}} \int_{r=0}^{r=r_{FS}} r^{2} \psi(r) dr.
\]

The values in the table correspond to experimental measurements under the given conditions. Other values at any pH and ionic strength, in the ranges \( 4<\text{pH}<11 \) and \( 0.005 \text{M}<I<0.15 \text{M} \), can be computed with the following empirical equation, derived in the Appendix (A.2.2):

\[
\bar{\psi} = -217.4 + 127.9 pH - 28.29 pH^2 + 2.496 pH^3 - 0.07685 pH^4 + 3.159 pH \log I - 3.654 \log I.
\]

<table>
<thead>
<tr>
<th>Ionic strength (mM)</th>
<th>( \bar{\psi} ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH=10.7</td>
<td>pH=4</td>
</tr>
<tr>
<td>5</td>
<td>-99.6</td>
</tr>
<tr>
<td>20</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>-86.9</td>
</tr>
<tr>
<td>40</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>-78.9</td>
</tr>
<tr>
<td>85</td>
<td>-66.4</td>
</tr>
<tr>
<td>135</td>
<td>-59.0</td>
</tr>
</tbody>
</table>

It must be emphasized that, for fulvic compounds, the value of \( \exp(zM F \bar{\psi} /RT) \) is usually very low, so that \( k_{d}^{\text{os}} \) may become smaller than \( k_{a}^{\text{in}} = k_{w} \) (Fig. 6.2). For instance, for \( \bar{\psi} = -0.1 \), \( k_{a}^{\text{os}} = 5.0 \times 10^7 \) m\(^3\)mol\(^{-1}\).s\(^{-1}\) and \( k_{d}^{\text{os}} = 9.5 \times 10^6 \) s\(^{-1}\); for \( Cu^{+} \), \( k_{a}^{\text{in}} = k_{w} = 10^9 \) s\(^{-1}\) and hence \( k_{a}^{\text{in}} >> k_{d}^{\text{os}} \), i.e., \( k_{a}^{\text{MS}} = k_{a}^{\text{os}} \) (eq. 6.8). In such a case, the overall formation rate of Cu-fulvic complexes is fully controlled by diffusion and electrostatic interactions between Cu and FS, and not by the water molecule loss in the hydration shell of Cu; consequently the classical Eigen-Wilkins mechanism (eq.6.10) is not applicable here.

The variations of \( k_{a}^{\text{MS}} \) as function of \( k_{w} \) (corresponding to various metal ions) are shown in fig. 6.5, for two extreme values of \( \bar{\psi} \), corresponding to extreme pH and ionic strength conditions. It is apparent that, for the metals having \( k_{w} > 10^7 \) to \( 10^{10} \) s\(^{-1}\) (depending on \( \bar{\psi} \) values) i.e., for most divalent metal ions, \( k_{a}^{\text{MS}} \sim k_{a}^{\text{os}} \), and hence the classical Eigen mechanism is not applicable.

It must be emphasized that, while \( k_{a}^{\text{MS}} \) is independent of the nature of the complexing site, \( ^{i}S \), it is not the case for the effective dissociation rate constant, \( ^{i}k_{d}^{\text{MS}} \), which depends on \( ^{i}k_{d}^{\text{in}} \) (eqs. 6.3, 6.9). \( ^{i}k_{d}^{\text{in}} \) is usually unknown, but can be obtained from \( ^{i}k_{d}^{\text{MS}} \), which in turn is given by:
Figure 6.5. Relationship between the effective formation rate constant, $k_{a}^{MS}$ (Eq. 6.4, 6.12, 6.13, with $U(a) = z_{Me} \bar{\psi}$), for metal-fulvic/humic complex, and the value of the rate constant, $k_{-w}$, for the elimination of a water molecule from the inner hydration shell of the metal, for two “extreme” values of the average potential, $\bar{\psi}$, of the fulvic/humic molecules. For fulvic compounds, $\bar{\psi} = 100$ mV corresponds to pH 10.7 and $I = 5$ mM, i.e. large charge density and low screening effect, while $\bar{\psi} = 30$ mV corresponds to pH = 4 and $I = 50$ mM, i.e. low charge density and large screening effect (Table 6.1).

6.4.4 Relationship between kinetic and thermodynamic complexation constants.

By substituting the expressions of $k_{a}^{MS}$ and $i k_{d}^{MS}$ (eqs. 6.8 and 6.9) in eq. 6.18, one gets:

$$iK = \frac{k_{d}^{os} k_{a}^{in}}{k_{a}^{os} k_{d}^{in}} = K_{in}$$  \hspace{1cm} (6.19)

where $iK_{in} = k_{a}^{in}/k_{d}^{in}$ is the equilibrium constant between the inner-sphere and the outer-sphere complexes (eq. 6.3). In addition, for fulvics, the ratio of eqs. 6.16 and 6.17 gives:

$$K^{os} = \left(\frac{4 \pi N_{A} d^{3}}{3}\right) \exp \left(-\frac{z_{Me} F \bar{\psi}}{RT}\right)$$  \hspace{1cm} (6.20)

which is identical to eq. 6.11 derived for the simple complexes (in eq. 6.20, $K^{os}$ is expressed in m$^3$/mol, when SI units are used for the other parameters). Since $iK_{in}$ is independent of $\bar{\psi}$, eqs. 6.19-6.20 can be rewritten as:
\[ iK = iK^0 \exp \left( -\frac{zMF\psi}{RT} \right) \]  

(6.21)

which shows the influence of the potential \( \psi \) of FS (or HS), on the stability constant of the complex \( M_i^i S \). \( iK^0 \) is the so-called intrinsic stability constant. The dependance of \( \log iK \) on \( \psi \) has been confirmed experimentally [19, 30]. Equations 6.19-6.21 enable to compute the unknown values of \( iK^0 \), and in turn of \( k_d^{in} \), from experimental values of \( iK^0 \).

6.4.5 The overall kinetic properties of metal-fulvic complexes, based on their kinetic and thermodynamic complexing site distributions

Since the fulvics include a large number of different site types, with different dissociation rate constants, \( k_d^{MS} \), the fulvic site distribution with respect to their \( k_d^{MS} \) values (i.e. the kinetic site distribution) must be considered to compute the overall metal flux. Since the association rate constant is site-independent, the latter distribution is directly related to that based on the stability constants, \( K \), which can be obtained as described below.

All experimental data show that under most environmental conditions, metal complexation by fulvics follows the so-called linear Freundlich isotherms [1, 31-34], over several orders of magnitude of \([M]\):

\[
\log \left( \frac{[MS]}{\{FS\}} \right) = \Gamma \log \left( K_o \Gamma \right) + \Gamma \log [M] \tag{6.22}
\]

where \([MS]\) is the total bound metal molar concentration, at a given value of \([M]\), and \{FS\} is the concentration of fulvic substances in kg.dm\(^{-3}\). \( K_o^* \) and \( \Gamma \) are constants characteristic of a given metal, at the conditions used (see below). Equation 6.22 is typically valid for all trace metals when \([MS]/\{FS\} < 0.5 \text{ mol/kg} \) (Fig. A.2.4-A,B, 32-35), i.e. for most aquatic systems. This \([MS]/\{FS\} \) range also corresponds to that of the minor sites of fulvics discussed in section 6.5.1.

\( \Gamma \) is a dimensionless parameter, linked to the chemical heterogeneity of fulvics, and consequently to their metal complexing buffering capacity, as discussed quantitatively in [36,37] and section A.2.3. Its value lies between 0< \( \Gamma \) < 1, and is often close to 0.5. \( K_o^* \) has units of stability constant, i.e. dm\(^3\).mol\(^{-1}\) when \([MS]/\{FS\}\) is expressed in mol/kg. Interestingly, both \( \Gamma \) and \( K_o^* \) depend on the nature of the metal ion and conditions (pH, ionic strength) but, within experimental errors, they can be considered to be independent of the origin of the fulvics (1, 31, 38; section A.2.3). It should be mentioned that various models have been proposed to interpret the observed isotherms in terms of metal-fulvics molecular interactions at equilibrium. These models are discussed in details elsewhere [1,19,35,39,40] and will not be repeated here. It must however be pointed out that the parameters \( \Gamma \) and \( K_o^* \) are model-independent, since they can be determined directly from the experimental data, without making any physico-chemical assumption. \( \Gamma \) and \( K_o^* \) data for aquatic fulvic substances are compiled in Table 6.2.
Table 6.2. Values of the parameters $\Gamma$ and $K_0^*$ of the Freundlich isotherms for the complexation of metal ions by fulvic substances. $K_0^*$ values correspond to $[\text{MS}]_t/\{\text{FS}\}$ values expressed in mol/kg and are average values resulting from the critical compilations of literature data for many water samples [a,b,c,d see footnote]. Due to significant dispersion of data from sample to sample, log$K_0^*$ values should only be considered as good estimates with a variability of 0.1 – 0.5. For intermediate pH’s, linear interpolation can be used. $T=25^\circC$, $I \sim 0.1\text{M}$.

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH</th>
<th>$\Gamma$</th>
<th>log$K_0^*$ (dm$^3$.mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)$^a$</td>
<td>8.0</td>
<td>0.52</td>
<td>8.0</td>
</tr>
<tr>
<td>Cu(II)$^a$</td>
<td>7.0</td>
<td>-</td>
<td>6.6</td>
</tr>
<tr>
<td>Cu(II)$^a$</td>
<td>6.0</td>
<td>0.63</td>
<td>5.3</td>
</tr>
<tr>
<td>Cu(II)$^a$</td>
<td>5.0</td>
<td>-</td>
<td>4.0</td>
</tr>
<tr>
<td>Pb(II)$^{a,c}$</td>
<td>8.0</td>
<td>0.60</td>
<td>6.4</td>
</tr>
<tr>
<td>Pb(II)$^{a,c}$</td>
<td>7.0</td>
<td>-</td>
<td>6.1</td>
</tr>
<tr>
<td>Pb(II)$^{a,c}$</td>
<td>6.0</td>
<td>0.60</td>
<td>5.6</td>
</tr>
<tr>
<td>Pb(II)$^{b,c}$</td>
<td>5.0</td>
<td>0.62</td>
<td>4.8</td>
</tr>
<tr>
<td>Zn(II)$^a$</td>
<td>8.0</td>
<td>0.41</td>
<td>4.3</td>
</tr>
<tr>
<td>Zn(II)$^a$</td>
<td>7.0</td>
<td>-</td>
<td>4.2</td>
</tr>
<tr>
<td>Zn(II)$^a$</td>
<td>6.0</td>
<td>-</td>
<td>4.1</td>
</tr>
<tr>
<td>Zn(II)$^a$</td>
<td>5.0</td>
<td>-</td>
<td>3.8</td>
</tr>
<tr>
<td>Ni(II)$^d$</td>
<td>6-8</td>
<td>0.57</td>
<td>4.3</td>
</tr>
<tr>
<td>Co(II)$^d$</td>
<td>6-8</td>
<td>0.37</td>
<td>2.6</td>
</tr>
<tr>
<td>Mn(II)$^a$</td>
<td>6-8</td>
<td>0.42</td>
<td>2.6</td>
</tr>
</tbody>
</table>

$^a$ [1]; $^b$ [34]; $^c$ [41]; $^d$ [38]

In the present context, the striking feature is that a Freundlich isotherm (eq. 6.22), for the test metal ion, corresponds to a mathematically well-defined distribution of complexing sites (the so-called Sips distribution; 42), with regards to their thermodynamic stability constant ($\text{thermodynamic site distribution}$). In the linear regime of the isotherm (eq. 6.22), i.e. for the minor site types, the corresponding cumulative site distribution is given by [18]:

$$\log i^\chi = \log(\Phi/\sigma) + \Gamma \log K_0^* - \Gamma \log i^K $$  \hspace{1cm} (6.23)

By combining eqs 6.18 and 6.23, the $\text{thermodynamic site distribution}$ can be related to the corresponding $\text{kinetic site distribution}$, i.e. the distribution of sites with regards to $i^k_d$.

In eq. 6.23, $i^\chi$ is the cumulative mole fraction of sites i, i.e. the sum of the mole fractions of each site type ($=\Delta^\chi$), whose equilibrium constants lie between infinity and $i^K$. $\sigma = \sum_{i=1}^{\infty} [i^S_i]/\{\text{FS}\}$ is the total density of the sites in the FS (in mol.kg$^{-1}$), including the major ones. It is characteristic for a given type of fulvic substances, irrespective of its origin (typically for aquatic soil-derived FS, $\sigma \sim 6-10$ mol/kg of FS, i.e. $\sigma \approx 12-20$ mol/kg of C when $\{\text{FS}\}$ is expressed in terms of its equivalent of dissolved organic carbon (DOC); $I$). $\Phi$ is linked to the Sips distribution function and is given by:

$$\Phi = \left(\frac{\Gamma}{1-\Gamma}\right)^\Gamma \sin[(1-\Gamma)\pi] \Gamma \pi$$  \hspace{1cm} (6.24)
With a good approximation, $\log \Phi = -0.174$ in the range $0.2 < \Gamma < 0.8$. It must be pointed out that eq. 6.23 has been confirmed by theoretical computations [19, 43], also enabling the appraisal of the chemical nature of a few important complexing sites of the fulvics.

In practice, the kinetic and thermodynamic distributions of the metal-fulvic complexes under specific conditions can thus be computed as follows. The log $^iK$ scale is divided into equal $\Delta \log K$ intervals. The ($^k\chi, ^kK$) couple set, as a whole, is first computed from eqs. 6.23, 6.24 and the couples ($[^iS]_i, ^iK$) are obtained from:

$$[^iS]_i = (^{k-1}\chi - ^k\chi) \cdot \sigma \cdot \{FS\} \quad (6.25)$$

and

$$\log ^iK = 0.5 \log (^{k-1}K \cdot kK) \quad (6.26)$$

From this set of couples, the distributions of [M'S] and [$^iS$] with respect to log $^iK$ are obtained using any computer code (e.g., 44, 45). Flux computations can then be performed by using the expression for $k_a^{MS}$ (section 3.3) and the values of $^iK_d$ corresponding to the above set of ($[^iS]_i, ^iK$) couples, obtained from eq. 6.18. The following aspects are worth noting:

In order to get the correct site distributions, $\Delta \log K$ should be small enough so that the discrete distribution is close to the continuous one. The use of very small values, however, may need long computer times for flux computations. $\Delta \log K$ values between 0.1 and 0.5 (preferably not larger than 0.3) are recommended.

The selection of the log $^iK$ range, log $K_{\min}$ to log $K_{\max}$, (as well as the related log $^iK_d$ range) should also be made carefully. It should include site types for which, at the test value of log $[M'S]/\{FS\}$ (or log $[M]$), $^iK$ values are neither too low (unoccupied sites) nor too high (very strong and inert complexes). For this purpose, eqs 6.22 and 6.23 can be linked using the so-called Differential Equilibrium Function, $K^*$, which has a few salient features, as explained in section B3 of SI. First it can be readily computed from experimental data using eq. 6.27:

$$K^* = \frac{(1-\Gamma)}{\Gamma} [M] \quad (6.27)$$

And by combining eqs (6.22) and (6.27), $K^*$ can be related to the desired value of [M'S]/\{FS\}. In addition, it is theoretically well established [36] that $K^*$ is an average of the individual stability constants of all sites, weighted over their concentration and degree of occupation, in such a way that the value of $K^*$ is close to (or equal to, when $\Gamma=0.5$) that of $K$ for which [M'S] = [$^iS$]. On a logarithmic scale it is thus the center of the distribution (Figure A.2.4A, B). Finally, it has also been shown that the complexes with log $^iK \geq \log K^* + 2$ are saturated but are present in such low proportions that they do not play a significant role in the overall flux of metal fulvic complexes [46]. Furthermore, the contribution of complexes with log $^iK \leq \log K^* - 2$ is also small because the corresponding sites are almost unoccupied (section A.2.3 and discussion of fig. A.2.4 in Appendix). Thus for computation of thermodynamic distribution, the most useful range of log $^iK$ to explore is $\log K_{\min} = \log K^* - 2 \leq \log K \leq \log K^* + 2 = \log K_{\max}$. For flux computation, the limiting values of log $^iK_d$ of the kinetic distribution can be estimated from the limiting values of log $K$, although they should only be considered as guidelines. In particular in some cases, values of log $^iK_d$ corresponding to log $^iK < \log K^* - 2$ are required [46], because even minute proportions of the very weak but labile complexes may play a significant role in the total flux.

Finally, the selected range of $^iK$ or $^iK_d$ should preferably not lie beyond the range of log $[M]$ for which $\Gamma$ and $K_o^*$ have been determined (eq. 6.22). Until now, however, eq. 6.22 has been
found be valid over at least 3-5 orders of magnitude of log[M], and no limit to its validity has yet been found in the low [M] domain (corresponding to high $^1K$ values). Thus careful extrapolations of eq. 6.23 are even possible at high $^1K$ values.

### 6.5 Dynamic parameters for complexes with particles and aggregates

#### 6.5.1 Nature of aquatic complexing particles/aggregates

Aquatic “particles” are usually complicated aggregates of inorganic colloids and organic biopolymers in various proportions [47-49]. Frequent components are alumino-silicates, calcium carbonate, am-FeOOH, am-manganese oxide, SiO$_2$, microorganism debris, humic or peptidoglycan type biopolymers. Often they include a core composed of a “major” component (e.g. aluminosilicates), with “minor” components (e.g. am-FeOOH, am. manganese oxide, humics or peptidoglycans) adsorbed on it. Interestingly, as for humics, the “minor” components of aggregates are usually the strongest complexants. Thus, for the sake of simplicity we shall consider below the aquatic “particles” as fractal aggregates of non (or little) complexing basic particles (referred to below by subscript $b$), on which minor complexing components (denoted by subscript $X$) are adsorbed. As explained previously, the transport of trace metal ions, whose concentrations (typically $\leq 10^{-6}$M) are much lower than that of the major electrolyte, is not influenced by electrostatic migration [5]. Hence the most important parameters required for flux computations are the thermodynamic equilibrium constants for complex formation, $K$, the rate constants for complex formation, $k_a$, and dissociation, $k_d$, and the diffusion coefficients of the hydrated ion M, $D_M$, and of the complexes and complexants.

![Schematic representation of the diffusion of M towards a consuming interface and its reaction with complexing porous aggregates inside the diffusion layer.](image)

**Figure 6.6.** Schematic representation of the diffusion of M towards a consuming interface and its reaction with complexing porous aggregates inside the diffusion layer. $\delta$ = thickness of the diffusion layer (also called diffusio-reaction layer), at the boundary between the consuming surface and the solution. MS, S = complex and complexing site inside the aggregate. $k_a$, $k_d$ = formation and dissociation rate constants of MS. $D_{M\delta}$, $D_M$ = diffusion coefficient of M in solution and inside the aggregate. Note that the scheme is not at scale: in particular r is always much smaller than $\delta$. 

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When the complexant is a particule or an aggregate (Fig. 6.6), a few more complications, than those discussed for simple ligands or fulvics, arise. Each one, may contain and transport many complexing sites, S, and complexes, MS. In addition, a complexant L is much larger in size than M. Thus, $D_M >> D_{MS} \sim D_L$. Furthermore, since equilibrium is not always reached inside the diffusion-reaction layer, $\delta$, a particle/aggregate present in this layer may act as a consuming/releasing body, somehow competing for M, with the microorganism or sensor surface. In other words, the effective rates of association/dissociation of MS complexes, in the diffusion-reaction layer, will depend not only on the molecular rate constants $k_a$ and $k_d$ for the chemical reaction of M with a complexing site S, but also on the diffusion of M towards and possibly inside the particle/aggregate (Fig.6.6). Such a problem has been discussed in [74] for compact spherical and monodispersed particles. In nature, however, “particles” are more often aggregates of smaller subparticles, and their size distribution is very broad [49].

6.5.2 Distributions of diffusion coefficient and surface area of aquatic particles and aggregates

6.5.2.1 Relationship between structure and size distribution

As mentioned above, the size distribution of aquatic colloidal particles/aggregates usually follows the Pareto law (1,49-51; Fig. 6.7) given by:

$$\frac{dc_p}{dr} = \mathcal{A} r^{-\beta}$$  \hspace{1cm} (6.28)

where $c_p$ is the number concentration of particles/aggregates having an external radius, $r$, in solution. $\mathcal{A}$ and $\beta$ are constants. Experimental observations have shown that this law holds in the size range of nanometers to 10–100 \(\mu m\), with $\beta$ values ranging between 2.7 and 4.0 [48,52], being closer to 3.0 (Table A.3.1).

The peculiar feature of a natural suspension of aggregates following the Pareto law, is that the very low size aggregates, whose diffusion rate is significant but the number of complexing sites is low, are in very large number concentration (typically $10^{13} - 10^{16}$ dm$^{-3}$ for $r = \text{a few nm}$), whereas the larger size aggregates, whose diffusion is very slow, but the number of complexing sites very large, are in much lower number concentrations (typically $10^{7} - 10^{9}$dm$^{-3}$ for $r = 1 \mu m$). Thus, in order to predict the contributions of the metal bound to aggregates, to an overall metal flux, the distribution of M bound to the various size classes (or preferably classes of diffusion coefficient) must first be determined. This is explained in section 6.5.2 and 6.5.3.

The distribution of the diffusion coefficient, $D$, of aggregates can be derived from eq 6.30, provided the relationship between their external radius, $r$, and $D$ is known. For a spherical particle, $D$ is related to its hydrodynamic radius $R_h$, by the The Stokes-Einstein law [53]. On the other hand, the external radius, $r$, is related to the gyration radius $R_g$ of a fractal aggregate (with fractal dimension, $D_f$), by $r/R_g = \Xi D_f^{1/D_f} + 2/D_f$ [54], while $R_g$ is related to $R_h$ via $R_g/R_h = \Xi^{1/D_f} \sqrt{D_f + 2/D_f}$ (55), where $\Xi$ is the structure factor. When $D_f$ varies in the range 1.5 - 3.0, $\Xi$ varies between 0.8 - 1.29, and $r/R_h$ between 1.16 - 0.92. As these changes are rather small, $r= R_h$ will be assumed in the following. This leads to an error of less than 10% in most
environmental cases. Under such conditions, Stokes-Einstein law can be applied to aggregates, with \( R_h = r \), i.e.:

\[
R = \frac{RT}{6\pi \eta N_b D} \tag{6.29}
\]

The surface area available for the adsorption of \( M \) inside an aggregate of radius \( r \) is that of the major solid component, which one supposes to be comprised of \( N_b \) basic spherical subparticles of radius \( b \). Their total surface area, \( a_b \), inside an aggregate is \( a_b = 4\pi b^2 N_b \). For an aggregate of radius \( r \) and fractal dimension \( D_f \) [54]:

\[
N_b = \left( \frac{r}{b} \right)^{D_f} \tag{6.30}
\]

The distribution of the total surface area, \( A_b \), corresponding to the ensemble of aggregates, as function of \( r \), is obtained by combining the expression of \( a_b \) with eqs 6.28 and 6.30:

\[
\frac{dA_b}{dr} = a_b \frac{dc_p}{dr} = 4\pi b^2 - D_f A r^{D_f - \beta} \tag{6.31}
\]

Figure 6.7. Typical examples of particle size distributions in natural waters (Eq. 6.28). Modified from [52].
Note that $A_b$ (and $A_{b,t}$ below) is expressed in $m^2/dm^3$ of solution, since $c_p$ is the number of aggregate per liter of solution. Similarly the volume distribution, $V_b$, of the major solid component, as function of the aggregate size, $r$, is given by:

$$\frac{dV_b}{dr} = \frac{4}{3} \pi b^3 N_b \frac{dc_p}{dr} = \frac{4}{3} \pi b^{3-D_f} A r^{D_f-\beta}$$  \hspace{1cm} (6.32)

Equations 6.30-6.32 are also valid for compact spherical particles, with the condition: $b = r$.

### 6.5.2.2 Discretized size distribution of particle/aggregate concentration

In a given size class $j$, with a radius $r_j$ and an interval $\Delta \log r$ (supposed to be independent of $j$), the value of $j c_p$ can be obtained by multiplying the left and right hand sides of eq 6.28 by $r$ and discretizing it:

$$j c_p = 2.3 A r_j^{1-\beta} \Delta \log r$$  \hspace{1cm} (6.33)

The parameter $A$ is obtained by integrating eq 6.32 between the minimum and maximum values of $r$, $r_{\text{min}}$ and $r_{\text{max}}$. The results, $V_{b,t}$, is the total volume of the major solid component, $P$, per volume of solution and can be equated to $\{P\}_t/\rho_P$, where $\{P\}_t$ is the mass concentration of $P$ in solution, and $\rho_P$ its density. Thus one gets:

for $\beta - D_f \neq 1$

$$A = \frac{\{P\}_t}{\rho_P} \frac{D_f + 1 - \beta}{4 \pi b^{3-D_f} \rho_P \left( \frac{D_f + 1 - \beta}{r_{\text{max}}} - \frac{D_f + 1 - \beta}{r_{\text{min}}} \right)}$$  \hspace{1cm} (6.34)

for $\beta - D_f = 1$

$$A = \frac{3\{P\}_t}{4 \pi b^{3-D_f} \rho_P \ln(r_{\text{max}}/r_{\text{min}})}$$  \hspace{1cm} (6.34')

Note that equations 6.34,6.34’ are also applicable to compact particles, by using $D_f = 3$.

### 6.5.2.3 Specific surface area

The specific surface area of the ensemble of aggregates, i.e., the surface area per gram of aggregate, is a useful parameter to relate experimental observations to theoretical modelling. It can be obtained by computing $V_{b,t}$ and the total surface area, $A_{b,t}$, of aggregates per liter of solution, by integrating eqs 6.31 and 6.32 between $r_{\text{min}}$ and $r_{\text{max}}$. Their ratio is equal to that of eqs 6.31 and 6.32, and is given by:

$$\frac{dA_b}{dV_b} = \frac{A_{b,t}}{V_{b,t}} = \frac{3}{b}$$  \hspace{1cm} (6.35)

Eq 6.35 shows that the surface over volume ratio of the ensemble of basic subparticles is always equal to that of a single subparticle, irrespective of the size or fractal dimension of the aggregate. The specific surface area, $A_{ss}$, of the ensemble of aggregates is then given by:
\[ A_s = \frac{A_{b,t}}{V_{b,r} \rho_p} = \frac{3}{b \rho_p} \]  

(6.36)

If \( b \) and \( \rho_p \) are known (e.g., for pure am-FeOOH: \( b = 1-3 \) nm [79], \( \rho_p \sim 3 \) [80], \( A_s \) can be computed theoretically from eq. 6.36. For am-FeOOH one gets 333–1000 m\(^2\)/g, i.e., a value similar to that obtained experimental (\( \sim 700 \) m\(^2\)/g; Table A.3.3). More often \( b \) is unknown and an average value can be estimated from eq 6.36 and experimental values of \( A_s \).

\( A_s \) can be obtained similarly for compact particles. But contrary to fractal aggregates, it depends on \( r_{\text{min}}, r_{\text{max}} \) and \( \beta \).

### 6.5.2.4 Distribution of surface area in the various size classes

As mentioned above, the overall flux of M depends on the proportion of M bound to each size class of particles/aggregates, i.e., on the corresponding proportion of surface area available for complexation. By rearranging and discretizing eq 6.31, the surface area in each size class, \( \Delta A_{b,t} \), can be obtained

\[ j \Delta A_b = 9.2 \pi b^{2-D_f} \beta j r^{D_f+1-\beta} \Delta \log r \]  

(6.37)

The fraction of \( A_{b,t} \) in each class of \( r \) (interval \( \Delta \log r \)) can be determined by dividing eq. 6.31 by the result of its integration between \( r_{\text{min}} \) and \( r_{\text{max}} \) and discretizing. It can also be expressed as function of the diffusion coefficient (interval \( \Delta \log D, D_{\text{max}}, D_{\text{min}} \)), by combination with eq 6.31:

when \( \beta - D_f = 1 \):

\[ \frac{j \Delta A_b}{A_{b,t}} = \frac{\Delta \log r}{\log(r_{\text{max}}/r_{\text{min}})} = \frac{\Delta \log D}{\log(D_{\text{max}}/D_{\text{min}})} \]  

(6.38)

when \( \beta - D_f \neq 1 \):

\[ \frac{j \Delta A_b}{A_{b,t}} = 2.3(D_f+1-\beta) \frac{j r^{D_f+1-\beta}}{r_{\text{max}}^{D_f+1-\beta} - r_{\text{min}}^{D_f+1-\beta}} \Delta \log r \\
= 2.3(D_f+1 -\beta) \frac{j D_{\text{max}}^{D_f-1} - D_{\text{min}}^{D_f-1}}{D_{\text{max}}^{D_f-1} - D_{\text{min}}^{D_f-1}} \Delta \log D \]  

(6.38')

where \( D_{\text{min}} \) and \( D_{\text{max}} \) are the minimum and maximum values of \( D \) (corresponding to \( r_{\text{max}} \) and \( r_{\text{min}} \) respectively). In eqs 6.38 and 6.38’, \( \Delta \log r \) and \( \Delta \log D \) are absolute values. Tables A.3.1 and A.3.2 show that values of \( \beta \sim 3 \) and \( D_f \sim 2 \) are commonly found for aquatic aggregates [48], suggesting that eq 6.38 is a reasonable approximation for environmental systems. Interestingly, in such a case, the surface area available for metal adsorption is independent of the size class of the aggregates.

For compact particles, integration of eq 6.33 with \( b = r \) leads to

\[ \frac{j \Delta A_b}{A_{b,t}} = 2.3(3-\beta) \frac{j r^{3-\beta}}{r_{\text{max}}^{3-\beta} - r_{\text{min}}^{3-\beta}} \Delta \log r \]  

(6.39)
This equation can be directly obtained from eq 6.38’.

\[ J_A / A_{b,t} \] is the fraction of the total surface area of the major component P. Often, one or several minor components, X, adsorbed on the basic subparticles, P, constitute the strongest complexants for M inside the aggregate. For modeling purposes, the fraction of available surface area of each component X, A_X, as well as the remaining surface area of component P, A_P, are required. Assuming the minor component, X, to be adsorbed as patches of thickness h_X (typically 1 to a few nm) on the surface of the basic subparticles, A_X can be readily obtained from (Section A.3.1 in Appendices):

\[
A_X = A_{b,t} \frac{b}{3h_X} \frac{\{X\}_t \rho_P}{\{P\}_t \rho_X}
\]

(6.40)

All parameters in eq 6.40, except A_X and A_{b,t} are independent of r. Thus it is so for A_P/A_{b,t} (Section A.3.1 in Appendices). This is valid even when there are several minor complexants, provided that they are not adsorbed on each others. Thus, in any given size class, one has:

\[
\frac{i \Delta A_X}{A_X} = \frac{i \Delta A_P}{A_P} = \frac{i \Delta A_B}{A_{b,t}}
\]

(6.41)

and eqs 6.38 and 6.38’ or 6.39 are applicable to compute the proportions of the various types of complexing surfaces, in each size class of aggregates or particles. The total coarse-grained molar concentrations of the complexing sites of X and P in solution can be computed from (Section A.3.1 in Appendices):

\[
[S]^X = \{X\}_t \frac{n^X}{N_{Av} h_X \rho_X}
\]

(6.42)

and

\[
[S]^P = \frac{3n^P_{\{P\}_t}}{b \rho_P N_{Av}} - \frac{n^P_{\{P\}_t}}{N_{Av}} \sum h_X \rho_X
\]

(6.43)

where N_{Av} is the Avogadro number, and n^X and n^P are the number of complexing sites per surface area of compound X and P respectively (Table A.3.3). \{X\}_t and \{P\}_t are the mass concentrations of X and P and the summation is done over all the minor components, with the condition \Sigma A_X \leq A_{b,t}. The molar coarse-grained concentrations of sites in each size class are obtained by multiplying eq 6.41 with eqs 6.42 or 6.43.

6.5.4 Basic assumptions on metal reactions with aggregate sites

6.5.4.1 The chemical reaction

The reaction of M with the monoprotonated sites of metal oxides (e.g. \equiv Fe-OH, \equiv Si-OH, \equiv Al-OH, \equiv Mn-OH), symbolized by HS, will be mainly discussed hereafter. Other possible reactions (e.g. with unprotonated sites of metal oxides or organic complexants, competition reactions with other metals) are discussed in § 6.5.4.2, 6.5.4.3 and 6.5.6. In theory, HS may form MS and MS2 complexes with M \[ 56,57 \], but complexation with natural aggregates are
most often described by the formation of 1/1 MS complexes only [58-62], according to the reaction:

\[ M + HS \xrightleftharpoons[k_d^{-1}]{k_a} MS + H \]  

(6.44)

Equilibrium expression for this reaction can be written as:

\[ K = \frac{k_a}{k_d} = \frac{[MS][H]}{[HS][M]} \]  

(6.45)

(see section 6.5.4.2 for discussion). A pH dependant apparent equilibrium constant, \( K' \), defined as:

\[ K' = \frac{[MS]}{[HS][M]} \]  

(6.46)

where \( K' = K/[H] \), as reported in [62], will also be used below. It has been discussed [57,81,82] that the mechanism of complexation reaction, for sites of metal oxides, is similar to that for simple ligands, i.e. i) the formation of an outer-sphere complex (M,HS) and, ii) removal from a water molecule from the inner hydration shell of M, to form an inner-sphere complex, MS, followed by the fast release of a proton. The computation of the formation rate constant, \( k_a \), corresponding to reaction 6.46, in section 6.5.5, will be based on this mechanism.

6.5.4.2 Definition of equilibrium constants and species distributions between size fractions

The surface site, HS, may protonate or deprotonate to form a positively or negatively charged surface, depending on pH and ionic strength. The net effect is that a potential difference, \( \psi \), is usually set up between the surface and the solution (See Fig. A.3.1 and A.3.2A,B of Suppporting Information for Al$_2$O$_3$ and am-FeOOH), influencing the complexation of M. Various models for these processes have been developed for pure metal oxides [1,56,57,63-67], to i) relate the surface potential of particles to their electric charge and ii) define so-called intrinsic equilibrium constants, which are independent of \( \psi \) (Table A.3.4). Discussions of these models are out of the scope of this chapter, the focus being on natural aquatic particles/aggregates. These latter also develop an electric charge whose value varies between +0.5 to −1.5 mol.kg$^{-1}$, in the pH range 3-10 [60,68]. However, because of their physical and chemical heterogeneity, relating this charge to a surface potential is much more difficult than for pure metal oxides. In fact various studies [64,68,69] have suggested that the variability of the measured metal binding strength depends more significantly on these heterogeneities and the natural variability in chemical composition of particles than on their surface potential. Consequently, apparent equilibrium constants at a given ionic strength, not corrected for \( \psi \) effects, are usually reported in the literature for natural particles/aggregates (eqs. 6.45, 6.46).

Ranges of complexation stability constant values are reported in Table A.3.4 (Appendix: 1,58-63,70) for the binding of metal ions with natural particles/aggregates, together with values for a few pure metal oxides. Due to the chemical heterogeneity of natural particles/aggregates,
their K values may vary over a few orders of magnitudes, depending on location, sampling mode, or measurement conditions. In addition, in spite of their chemical heterogeneity, the data is most often interpreted in terms of one single average type of site. Thus these values should be considered as indicative. Nevertheless their comparison with those of pure complexants may help to assess the best parameters to use for model particle/aggregates in a given simulation.

For environmentally important metal oxides such as iron and aluminium oxides, HS is the dominant acid-base form of the complexing sites, at circumneutral pH’s [57]. When this is true for all types of complexants (P and X), in the particle/aggregate, then the following mass balance equation can be applied to each of them.

\[ [S]_t = [HS] + [MS] \]  \hspace{1cm} (6.47)

Combining eq. (6.47) with the expressions for \([S]_t\) (eqs. 6.42 or 6.43) and for \([HS]\) (eqs. 6.45,6.46), the distribution of M between free M and each type of surface complex can be obtained using computer codes (e.g. 44,45,71), for the particle/aggregate ensemble. Since, the proportion of sites in each size fraction, for both component types, X and P, is given by \(\Delta A_b/\Delta A_{b,t}\) (eqs 6.38–6.39, 6.41), the corresponding concentrations of sites non combined to M, \([HS]\), and bound to M, \([MS]\), are given by:

\[ ^j[HS] = [HS].\Delta A_b/\Delta A_{b,t} \]  \hspace{1cm} (6.48)

\[ ^j[MS] = [MS].\Delta A_b/\Delta A_{b,t} \]  \hspace{1cm} (6.49)

If the reactive site, HS, is not dominant in proportion, eg. when most sites are deprotonated, or if other metals compete for the sites, the constants for acid-base or competition reactions should be known to compute the concentrations of MS and HS, in each size fraction, using eq. 6.46 [62]. When M reacts with a chemical form of the site, different from HS (e.g. with deprotonated sites), the corresponding concentration is similarly computed, but in addition, the appropriate rate constant is required (§ 6.5.4.3, 6.5.6).

6.5.4.3 Reactivity inside the aggregates

The overall rate of formation of the complex, MS (Fig. 6.6), depends not only on the steps i) and ii) mentioned at the end of § 6.5.4.1, but also iii) on the diffusion of M in solution towards and inside the aggregate. This may slow down the overall formation rate compared to that occurring with simple ligands. Overall, the problem to solve includes processes of diffusion-reactions in a dynamic physically heterogeneous medium (the suspension of mobile porous aggregates). Sophisticated numerical methods are required to solve it rigorously. It has been shown however [74] that under certain conditions, an effective overall rate constant may be obtained by combining the diffusion of M surrounding the particles with the chemical rate constant. This effective rate constant can then be used to compute the metal flux at the consuming surface, as with simple ligands. The expression derived in [74], however, is limited to compact, non penetrable and monodispersed particles, and a steady-state flux of M is assumed to exist between the particle and the solution. In section 6.5.5, we generalise this concept to polydisperse systems of either compact particles or porous aggregates, for any time scale, and the conditions under which the steady-state approximation is applicable are discussed. This derivation requires a few definitions and assumptions which are briefly discussed below.
Let’s consider first a loose fractal aggregate with radius r. Its inside can be considered to be a separate medium, in which thermodynamic and kinetic processes are described using classical statistical concepts. M diffuses in this medium with the diffusion coefficient \(D_M\), which may or may not be the same as that in the solution phase (Fig. 6.6). Classical thermodynamic and kinetic concepts can be applied, provided that the total number of complexing sites inside the aggregate is sufficiently large. For example, consider the most restrictive case of a small aggregate of size r, in which the complexing sites only belong to a minor component X. The total number of sites, \(n_X\), of the complexant X, inside one aggregate of class j, is obtained by dividing the total number of sites in class j (eqs 6.38, 6.41, 6.42, 6.48), by the corresponding number of aggregates (eqs 6.33,6.34). By using \(D_t = 2\) and \(\beta = 3\), on gets:

\[
j_{nX} = \frac{4\pi h_X^2 \rho_P \{X\}_t}{3h_X \rho_X \{P\}_t} j_{r^2}
\]

For example, by substituting the typical values of \(b = 3\) nm, \(h_X = 1\) nm, \(n_X = 10\) site/nm\(^2\), \(\rho_P = 2\), \(\rho_X = 3\), and \(\{X\}_t/\{P\}_t = 0.1\) (i.e., the aggregate contains 10% of complexing component), the total number of sites of an aggregate with \(r = 10\) nm, is 800, which is large enough for using statistical concepts. Thus the lower aggregate size limit, up to which the model described below is valid, is of the order of a few nm and will depend on the proportion of complexing component. For colloids smaller than a few nm with a small number of sites, the classical approach of chemical kinetics can be applied.

In the following discussion, the concentrations of M, HS and MS inside the volume of an aggregate (denoted by \(C\): \(C_M, C_{HS}, C_{MS}\)) will be distinguished from the so-called coarse-grained concentrations of the same species, \([M], [HS], [MS]\), used earlier. In the bulk solution, all aggregates have the same internal concentrations, \(C_M, C_{HS},\) and \(C_{MS}\), and the coarse-grained concentrations are just average concentrations of M, HS and MS, in the whole suspension. Within the diffusion-reaction layer, the values of \(C_M, C_{HS}\) and \(C_{MS}\), inside an aggregate, vary with the distance between this aggregate and the consuming interface (Fig.6.6). Thus, in this layer, the coarse-grained concentrations are average concentrations within a given solution layer parallel to the consuming surface, whose thickness is small in comparison with \(\delta\), but large enough to accommodate many aggregates. In the following, we shall consider that, at equilibrium, \([S]_t \sim [HS] >> [MS]\), and \(C_{S,t} \sim C_{HS} >> C_{MS}\) inside the aggregate. These conditions hold when the free metal ion concentration, \([M]\), is such that \(K'[M] (= [MS]/[HS]) << 1\). With the typical values of \(K'\), which can be derived from Table A.3.4, and of \([M]\) valid for the most strongly bound metals (\([M] < 10^{-9}\) M), these conditions are often fulfilled in natural waters.

The following additional assumptions are made below for the computation of kinetic parameters:
- The pH remains constant and uniform inside the aggregates, which implies that the solution is well buffered.
- All the sites not bound to M are the reactive monoprotonated sites, HS, (see above) and [HS] \(\sim [S]_t\). When HS is not the dominant species, [HS] should be computed as mentioned in § 6.5.4.2 and [S] should be replaced by [HS] in eqs 6.73, 6.74, 6.76.
- M is supposed to react only with HS. When it also reacts with other types of sites, (e.g. the non protonated site, S, of the same complexant, or the site of another complexant), the overall rate for the reaction between M and the aggregate is the sum of all reaction rates. The expression derived for the effective association rate constants (section 6.5.5, eqs 6.73,
(6.76), under steady-state conditions, can also be used for other sites with slight modifications, as explained in section 6.5.6.

6.5.5 Effective formation/dissociation rate constants of complexes with particles/aggregates

6.5.5.1 Derivation of the effective rate constant for monodisperse aggregates, with a single complexing site type

Based on the above assumptions, the effective rate constants can be derived by solving the following conservation equations for a single aggregate having a radius r. In these equations, x is the distance from the centre of the aggregate (Fig. 6.6), C_M^{in} and C_M^{out} are respectively the concentrations of M inside and outside the aggregate, in particular within its external diffusion layer. In addition, since the pH is buffered (i.e. C_H = constant), the dissociation reaction of MS (eq. 6.44) is pseudo-first order and its rate can be written as rate = k_d C_H C_MS = k_d' C_MS, where k_d' is the pseudo-first order dissociation rate constant at the desired pH, and is related to k_a by k_a/k_d' = K' (K' defined by eq. 6.46). The conservation equations, then, are the following:

For 0 ≤ x ≤ r :
\[
\frac{\partial C_{MS}}{\partial t} = k_a C_M^{in} C_{HS} - k_d' C_{MS}
\]
(6.51)

\[
\frac{\partial C_M^{in}}{\partial t} = D_M^{in} \nabla^2 C_M^{in} + k_d' C_{MS} - k_a C_M^{in} C_{HS}
\]
(6.52)

\[
\frac{\partial C_{HS}}{\partial t} = k_d' C_{MS} - k_a C_M^{in} C_{HS}
\]
(6.53)

\[
C_{MS} + C_{HS} = C_{S,t}
\]
(6.54)

For x > r :
\[
\frac{\partial C_M^{out}}{\partial t} = D_M^{out} \nabla^2 C_M^{out}
\]
(6.55)

The initial conditions are:
\[
t=0, \quad 0 \leq x \leq r : \quad C_M^{in} = C_M^0, \quad C_MS = C_MS^0 \quad ; \quad x > r : \quad C_M^{out} = [M]
\]
(6.56)

and the boundary conditions are :
\[
t>0, \quad x=r : \quad C_M^{in} = C_M^{out} \quad ; \quad D_M^{in} \frac{\partial C_M^{in}}{\partial x} = D_M^{out} \frac{\partial C_M^{out}}{\partial x}
\]
(6.57)

\[
t>0, \quad x >> r : \quad C_M^{out} = [M]
\]
(6.58)

C_M^0 and C_MS^0 (eq 6.56), are the initial concentrations of M and MS (assumed to be uniform) in the aggregate; [M] (eq 6.56,6.58) is the concentration of M in the solution located at the same distance from the consuming interface (Fig.6.7) as the aggregate of interest, but far enough from any aggregate, in order not to be influenced by the concentration gradients existing around the aggregates. Note that eqs 6.51-6.58 are valid within the diffusion layer of the consuming surface (distance < δ; Fig.6.6), where a gradient of M is established. Thus [M] is usually less than the bulk concentration, [M]*. Since C_{HS} ~ C_{S,t} = constant, the formation of MS (eq 6.51) is a pseudo first order reaction. k_a is the association rate constant for reaction 6.44. It can be computed from the rate of formation of the outer-sphere complex (M,HS) and that for the elimination of a water molecule from the inner hydration shell of M [57, 72], i.e. k_a ≡ k_a^{MS} (eq 6.7).
By applying Laplace transforms to eqs 6.51-6.55 and to the initial and boundary conditions (6.56-6.58), the solutions of eqs (6.51-6.52) in the Laplace domain are:

\[ \overline{C}_M = \frac{c_i}{x} \exp(k_i x) - \frac{c_i}{x} \exp(-k_i x) + \frac{C_0^M}{s} \]  \hspace{1cm} (6.59)

\[ \overline{C}_{MS} = \frac{k_d}{k_d + s} \frac{c_i}{x} \exp(k_i x) - \frac{k_d}{k_d + s} \frac{c_i}{x} \exp(-k_i x) + \frac{C_0^{MS}}{s} \]  \hspace{1cm} (6.60)

with \( c_i = \frac{r [M]}{s} - r \frac{C_0^M}{s} \)  \hspace{1cm} (6.61)

and \( k_1 = \sqrt{\frac{(k_a + k_d)r + s^2}{D_M (k_a + s)}} \) and \( k_2 = \frac{s}{D_M} \).

In the following we are looking for the relationships between the effective rate constants, \( k_{a_{\text{eff}}} \) and \( k_{d'_{\text{eff}}} \), the corresponding chemical rate constants \( k_a \) and \( k_{d'} \) at the reactive site, the coarse-grained concentrations of the complex, \([MS]\), and of the sites not bound to \( M \), \([HS]\), and the total coarse-grained concentration of sites, \([S]\). By definition, the coarse-grained concentrations and the effective rate constants are related by eq. 6.62:

\[ \frac{\partial [MS]}{\partial t} = k_{a_{\text{eff}}} [M][HS] - k_{d'_{\text{eff}}} [MS] \]  \hspace{1cm} (6.62)

\( k_{d_{\text{eff}}} = k_{d_{\text{eff}}} [H] \) is the pH-dependant, effective pseudo-first order dissociation rate constant, for the above chemical reaction. The coarse-grained concentrations are defined in section 6.5.4.3.

In a monodisperse suspension of aggregates of radius \( r \), the coarse-grained concentration of MS in the solution is obtained by integrating eq 6.51 over the whole of the aggregate and multiplying by the aggregate number concentration in solution, \( c_P \):

\[ c_P \int_0^r 4\pi x^2 \frac{\partial C_{MS}}{\partial t} dx = c_P \int_0^r 4\pi x^2 k_a C_{MMS}^{\text{in}} C_{HS} dx - c_P \int_0^r 4\pi x^2 k_{d'} C_{MS} dx \]  \hspace{1cm} (6.63)

where \( x \) is the distance from the center of the aggregate (Fig. 6.7).

In eq. (6.63), by definition:

\[ [MS] = c_P \int_0^r 4\pi x^2 C_{MS} dx \]  \hspace{1cm} (6.64)

In addition, since \( C_{HS} \gg C_{MS} \) and by using eq. 6.61, the first term of the right hand side of eq. 6.63 can be written as:

\[ c_P k_a C_{HS} \int_0^r 4\pi x^2 C_{MMS}^{\text{in}} dx = \left[ \frac{[S]}{4} \right] \frac{k_a}{4\pi r^3} L^{-1} \left( \int_0^r 4\pi x^2 \left( \frac{c_i}{x} \exp(k_i x) - \frac{c_i}{x} \exp(-k_i x) + \frac{C_0^M}{s} \right) dx \right) \]  \hspace{1cm} (6.65a)
Combining eqs (6.61) and (6.65b) and the fact that the first term in the right hand side of eq. (6.63) is equal to $\frac{\partial [MS]}{\partial t} + k_d' [MS]$, eq (6.65b) becomes:

$$\frac{\partial [MS]}{\partial t} + k_d' [MS] = \left[ \frac{[S] k_d}{4 \pi r^3} \left( f_1(t) [M] + \frac{4}{3} \pi r^3 - f_1(t) \right) C_M^0 \right]$$  \hspace{1cm} (6.65c)

with: $[HS] = \frac{4}{3} \pi r^3 c_p C_{HS} = [S]_L$, since in most environmental systems, the sites not bound to M are in excess compared to M, and:

$$f_1(t) = L^{-1} \left( \frac{8 \pi \left( \frac{r^2}{k_1} \cos(k_1 r) - \frac{r}{k_1^2} \sin(k_1 r) \right)}{1 - \frac{D_m'}{D_m} \frac{1 - rk_1}{1 + rk_2}} \exp(k_1 r) + \frac{D_m'}{D_m} \frac{1 + rk_1}{1 + rk_2} \exp(-k_1 r) \right)$$  \hspace{1cm} (6.66)

The left hand side of eq (6.63) can also be obtained from the inverse Laplace transform of the spatial integration of $s \overline{C_{MS}} - c_M^0$, which is the Laplace transform of $\frac{\partial C_{MS}}{\partial t}$, where $\overline{C}_{MS}$ is given by eq. (6.60)

$$c_p \int_0^t 4 \pi x^2 \frac{\partial C_{MS}}{\partial t} dx = c_p L^{-1} \left[ \int_0^t 4 \pi x^2 \left( s \left( \frac{k_a'}{k_d + s} \exp(k_a x) - \frac{k_a'}{k_d + s} \exp(-k_a x) \right) \right) dx \right]$$  \hspace{1cm} (6.67a)

$$= c_p L^{-1} \left( \frac{k_s}{k_d + s} \left( 8 \pi c_1 \frac{a}{k_1} \cos(k_1 a) - 8 \pi c_1 \frac{1}{k_1^2} \sin(k_1 a) \right) \right)$$  \hspace{1cm} (6.67b)

Combining eqs. (6.61) and (6.64), with eq. (6.67b), one gets:

$$\frac{d [MS]}{dt} = c_p \left( f_2(t) [M] - f_2(t) C_M^0 \right)$$  \hspace{1cm} (6.67c)

with

$$f_2(t) = L^{-1} \left( \frac{8 \pi \frac{k_a'}{k_d + s} \left( \frac{r^2}{k_1} \cos(k_1 r) - \frac{r}{k_1^2} \sin(k_1 r) \right)}{1 - \frac{D_m'}{D_m} \frac{1 - rk_1}{1 + rk_2}} \exp(k_1 r) + \frac{D_m'}{D_m} \frac{1 + rk_1}{1 + rk_2} \exp(-k_1 r) \right)$$  \hspace{1cm} (6.68)

Set:

$$f_2(t) = B(t) \left( \frac{4}{3} \pi r^3 - f_1(t) \right)$$  \hspace{1cm} (6.69)

Combining eqs. (6.67c) and (6.69), one gets:
\[
\left(\frac{4}{3}\pi r^3 - f_i(t)\right)C_M^0 = \frac{f_z(t)[M] - \frac{1}{c_p} \frac{d[M S]}{dt}}{B(t)} \tag{6.70}
\]

\(C_M^0\) is eliminated by combining eqs (6.65c) and (6.70) to finally get:

\[
\frac{\partial [M S]}{\partial t} = \frac{k_u}{k_a[S]} [M][S]_r - \frac{k_d}{k_a[S]} [M S] + \frac{4}{3} \pi r^3 c_p B(t)
\]

\[
1 + \frac{1}{4} \pi r^3 c_p B(t)
\]

\[
\text{with}
\]

\[
B(t) = \frac{\frac{4}{3} \pi r^3 - f_i(t)}{f_z(t)} \tag{6.72}
\]

Thus, the effective rate constants \(k_a^{\text{eff}}\) and \(k_d^{\text{eff}}\) are:

\[
k_a^{\text{eff}} = \frac{k_u}{1 + \frac{k_u[S]}{4 \pi r^3 c_p B(t)}} \tag{6.73}
\]

and

\[
k_d^{\text{eff}} = \frac{k_d}{1 + \frac{k_d[S]}{4 \pi r^3 c_p B(t)}} \tag{6.74}
\]

\(B(t)\) varies with time and also depends on the parameters \(k_a, C_{\text{HS}}, K' = k_a/k_d, r, D_M\) and \(D_M^a\).

It includes 2 complicated Laplace transform functions, and analytical solution is not possible. As explained below, this however can be circumvented by using the results of numerical inversion. A systematic study of the effect of the above parameters on \(B(t)\), in the ranges of values encountered in environmental conditions, has provided curves with shapes always similar to those of Fig. 6.8. They level off to a constant value, \(B_{ss}\), at large times, corresponding to steady-state conditions at the aggregate/solution interface, i.e. when the flux of M, inside or outside the aggregate, is independent of time.

It must be noted that for very large and very low times, the inversion of the function in eq (6.68) is not possible. Indeed, for very large times, which are equivalent to very low frequencies \((s \to 0)\), the function to be inverted in eq (6.68) tends asymptotically to \(\sqrt{s}\), for which the inverse Laplace transform does not exist. On the other hand, for very low times, corresponding to very large frequencies \((s \to +\infty)\), the function to be inverted in eq (6.68) tends asymptotic to a constant value, for which, again the inverse Laplace transform does not exist. Thus only the time domains where the numerical inversion provides physically meaningful values of \(B(t)\) are reported in figures 6.8A-D.
Figure 6.8. A: Log {B(t)} vs. log(t), for various values of aggregate radii, \( r \). \( D_M = D_M^a = 7 \times 10^{-10} \text{m}^2\text{s}^{-1} \). \( k_a = 3 \times 10^6 \text{m}^3\text{mol}^{-1}\text{s}^{-1} \), \( K^* = 10^6 \text{m}^3\text{mol}^{-1} \), \( C_{\text{HS}} = 3.73 \times 10^{-4} \text{M} \). \( r = \) (■) 893 nm, (●) 89.3 nm, (▲) 8.93 nm. B: Change of B(t) with time, for various values of \( D_M = D_M^a \). \( k_a = 3 \times 10^6 \text{m}^3\text{mol}^{-1}\text{s}^{-1} \), \( K^* = 10^6 \text{m}^3\text{mol}^{-1} \), \( C_{\text{HS}} = 3.73 \times 10^{-4} \text{M} \). \( r = 893 \text{nm} \). \( D_M = D_M^a = \) ■ 7 \times 10^{-9} \text{m}^2\text{s}^{-1} \), ● 7 \times 10^{-10} \text{m}^2\text{s}^{-1} \), ▲ 7 \times 10^{-11} \text{m}^2\text{s}^{-1}. C: Change of B(t) with time for different values of \( D_M^a \) (from 7 \times 10^{-11} to 7 \times 10^{-10} \text{m}^2\text{s}^{-1}) with constant values of \( D_M \) and other parameters. \( D_M = 7 \times 10^{-10} \text{m}^2\text{s}^{-1} \), \( k_a = 3 \times 10^6 \text{m}^3\text{mol}^{-1}\text{s}^{-1} \), \( K^* = 10^6 \text{m}^3\text{mol}^{-1} \), \( C_{\text{HS}} = 3.73 \times 10^{-4} \text{M} \). \( r = 893 \text{nm} \), \( D_M^a = \) ■ 7 \times 10^{-10} \text{m}^2\text{s}^{-1} \), ● 4 \times 10^{-10} \text{m}^2\text{s}^{-1} \), ▼ 1 \times 10^{-10} \text{m}^2\text{s}^{-1} \), ● 7 \times 10^{-11} \text{m}^2\text{s}^{-1}. D: Change of B(t) with time for different values of \( k_a \). \( D_M = 7 \times 10^{-10} \text{m}^2\text{s}^{-1} \), \( D_M^a = 7 \times 10^{-10} \text{m}^2\text{s}^{-1} \), \( K^* = 10^6 \text{m}^3\text{mol}^{-1} \), \( C_{\text{HS}} = 3.73 \times 10^{-4} \text{M} \). \( r = 893 \text{nm} \). \( k_a = \) ■ 3 \times 10^6 \text{m}^3\text{mol}^{-1}\text{s}^{-1} \), ● 3 \times 10^6 \text{m}^3\text{mol}^{-1}\text{s}^{-1} \), ▲ 3 \times 10^4 \text{m}^3\text{mol}^{-1}\text{s}^{-1} \), ▼ 3 \times 10^5 \text{m}^3\text{mol}^{-1}\text{s}^{-1}. Figures 6.8 A-D show B(t) decreases when time increases, but that a plateau is observed in the time domain from 0.1 s to 10^{-1} to 10^4 s, which corresponds to a steady-state transport of M between the solution and the inside of aggregates. In theory, the time dependant parameters \( k_a^\text{eff} \) and \( k_d^\text{eff} \) (eqs 6.73, 6.74) can be incorporated within codes allowing the computation of metal flux at the consuming surface (Fig. 6.6) by means of a numerical methods, provided the values of \( k_a^\text{eff} \) and \( k_d^\text{eff} \) can be changed at each time step, to follow the B(t) function. In the existing codes, however, \[k_a^\text{eff} \text{ and } k_d^\text{eff} \text{ should be kept constant, independant of time. In this case, eqs 6.73 and 6.74 should be used only in a time domain where } B(t) = B_{ss} \text{ is constant. On the other hand, the useful time domain for flux computations can be estimated as follows. Most often steady-state metal fluxes at the consuming interface are of interest (Fig. 6.6), and they are reached at } t > \delta^2/\pi D_M \text{, i.e., typically } t \geq 0.1 \text{ s for } \delta = 10 \mu\text{m. Thus in experiments lasting not more than an hour, the relevant time domain for flux computation is } 10^{-1} \text{ to } 10^3 \text{s. In this time scale, } B(t) = B_{ss} \text{ is found to be independent of } k_a, K^* \text{ (eq 6.46), and } D_M^a \text{ (Fig 6.8 A-D), at least in the following ranges: } 10^0 \leq k_a \leq 10^{12} \text{ M}^{-1}\text{s}^{-1}, 10^7 \leq K^* \leq 10^{12} \text{ M}^{-1}.\)
and $0.1 \leq D_M^a/D_M \leq 1$. These limits arise partly due to mathematical difficulties in the inversion of Laplace transforms, at extreme values of the parameters. Thus, the real domains of application might be larger. Nevertheless these ranges cover much of the useful environmental conditions. Then, $B_{ss}$ only depends on $D_M$ and $r$, as follows (Fig. 6.9):

$$B_{ss} = 3D_M/r^2$$

(6.75)

Figure 6.9. Plot of $\log(B_{ss})$ vs. $\log\{3D_M r^2\}$, at $t = 0.1$ s (□; $y = 0.989x + 0.00984$), $t = 1$ s (○; $y = 0.992x - 0.0333$), $t = 10$ s (△; $y = 0.984x - 0.0325$), and $t = 100$ s (▽; $y = 0.979x - 0.00307$), for values of $D_M^a$ and $r$ ranging from $7 \times 10^{-11}$ to $7 \times 10^{-10}$ m$^2$s$^{-1}$ and 8.93 to 893 nm respectively. Note that many points are superimposed.

$D_M^a/D_M$ is a crucial parameter for the validity of eq (6.75). The diffusion coefficient, $D_M^a$, of a free cation in a porous medium, may be lower than that in the solution, $D_M$, in particular owing to steric hindrance [75,76]. The corresponding value of $D_M^a/D_M$ can be estimated, based on the ratio, $\sigma$, of the metal ion and pore radii [73]. For example, the values of $D_M^a/D_M$ are 0.79 and 0.98 for $\sigma = 0.1$ and 0.01 respectively. In a fractal aggregate, the “pore size” decreases from the outside to the center of the aggregate. But in most of the aggregate, $\sigma < 0.2$, i.e. $D_M^a/D_M > 0.6$. Thus eq 6.75 usually holds, since it is valid in the range $0.1 < D_M^a/D_M < 1.0$.

6.5.5.2 The effective rate constant at steady-state and the impact of particle/aggregate size distribution

Under conditions where $B(t) = B_{ss}$, the effective formation rate constant of MS in the size class $j$ of polydispersed aggregates, is obtained by combining eqs 6.48, 6.73 and 6.75:

$$j_k^{eff} = \frac{k_a}{1 + k_a[S]_h/\Delta A_{h}/A_{p,t}} = \frac{k_a}{1 + j\Theta}$$

(6.76)
The corresponding pseudo-first order dissociation rate constant, at constant pH, is obtained via $k_d^{\text{eff}} = k_a^{\text{eff}}/K'$. Note that eq 6.76 is analogous to that obtained for monodispersed compact particles (74; only the term $[S]_t,^\text{}\Delta A_b/A_{b,t}$ in eq 6.78, is called $C_t$ in ref. 74). Equation 6.76 is valid when the particle/aggregate contains only one type of reactive site, with a total coarse-grained concentration $[S]_t$ (eqs 6.42 or 6.43). Multiple site type reactivity is discussed briefly in §6.5.6.

$k_a$ can be obtained as discussed in section 6.4.3 where HS is a complexing site bearing no charge. The parameter $D_l$ in equations 6.12 and 6.13, is now the diffusion coefficient of the particle/aggregate, and $U(a) = z_M \psi$ is the electrostatic energy of the ion M at the potential $\psi$ prevailing at the surface site. This term is analogous to that applicable to the ion M inside the charged fulvic/humic compounds. However, the distances between charged sites, inside an aggregate, are much larger than in a fulvic molecule. For instance, for an aggregate with $r = 1 \mu m$ and $D_l = 2$, the average distance, between the surfaces of two subparticles with radii $= 3$ nm, can be estimated using eq. 6.30, and is found to vary from a few nm at the center to $> 50$ nm at the edge of the aggregate. It is usually larger than the double layer thicknesses (e.g. 0.4, 3.0 and 10 nm at ionic strengths of 0.5, $10^{-2}$ and $10^{-3}$ M respectively). Hence, contrary to fulvic/humic molecules, an average $\psi$ value for the aggregate as a whole, is not physically relevant, and the local $\psi$ value of the surface site must be used to compute $U(a)$. This is however not known, in most cases. In absence of better value, and if the chemical nature of the complexing compound (X or P) is known, $\psi$ can be estimated from the data reported for the corresponding pure compound (e.g., Figures 6.8B-D). Note that, at pH close to 8, the $\psi$ values of iron and aluminium (hydr)oxides are very small and have only slight or negligible effects on the $k_a$ values.

In eq 6.76, $^1\Theta$ can be considered as a “corrective” term which accounts for the diffusion of M around and inside the aggregate. Even though $k_a$ is independent of the size class of the particle/aggregate, and $U(a) = z_M \psi$ is the electrostatic energy of the ion M at the potential $\psi$ prevailing at the surface site. This term is analogous to that applicable to the ion M inside the charged fulvic/humic compounds. However, the distances between charged sites, inside an aggregate, are much larger than in a fulvic molecule. For instance, for an aggregate with $r = 1 \mu m$ and $D_l = 2$, the average distance, between the surfaces of two subparticles with radii $= 3$ nm, can be estimated using eq. 6.30, and is found to vary from a few nm at the center to $> 50$ nm at the edge of the aggregate. It is usually larger than the double layer thicknesses (e.g. 0.4, 3.0 and 10 nm at ionic strengths of 0.5, $10^{-2}$ and $10^{-3}$ M respectively). Hence, contrary to fulvic/humic molecules, an average $\psi$ value for the aggregate as a whole, is not physically relevant, and the local $\psi$ value of the surface site must be used to compute $U(a)$. This is however not known, in most cases. In absence of better value, and if the chemical nature of the complexing compound (X or P) is known, $\psi$ can be estimated from the data reported for the corresponding pure compound (e.g., Figures 6.8B-D). Note that, at pH close to 8, the $\psi$ values of iron and aluminium (hydr)oxides are very small and have only slight or negligible effects on the $k_a$ values.

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When $^1\Theta \ll 1$, the chemical reaction at the particle surface or inside the aggregate is the rate limiting step, and $^1k_a^{\text{eff}} \rightarrow k_a$. This is particularly valid for metals with low $k_a$ values (e.g., low value of $k_a$; 57). As discussed below, however, relatively low values of $k_a$ (typically < $10^5$ M$^{-1}$s$^{-1}$) and/or $\{X\}/\{P\}$ (typically < $0.01$) are required to meet this condition.

If $^1\Theta >> 1$, diffusion around the particle/aggregate is the rate limiting step. Then $^1k_a^{\text{eff}}$ becomes independent of $k_a$, but it depends on particle/aggregate size via the parameters: $^1r$, $^1c_p$ and $^1\Delta A_b/A_{b,t}$ (depending on the values of $\beta$ and $D_l$; eqs 6.38 or 6.38'), as discussed below.

The specific impact of particle/aggregate size, on the effective rate constant $^1k_a^{\text{eff}}$, can be inferred from $^1\Theta$, as follows:

1) For fractal aggregates with Pareto law distribution, the combination of eqs 6.33, 6.34, or 6.34' and 6.38 or 6.38', with the expression for $^1\Theta$ in eq 6.76, gives:

$$j\Theta = \frac{k_a[S]_t\rho_P b^{3-D_f} j_D^{D_f-1}}{3D_M\{P\}_t} = \Theta_o b^{3-D_f} j_D^{D_f-1} (6.77)$$

where $\Theta_o$ is a constant which contains all the parameters independent of size. Interestingly, equation 6.77 is independent of $\beta$, for any value of $D_l$. When the complexing sites belong to a minor component X, $\Theta_o$ can also be expressed as function of its mass fraction, $\{X\}/\{P\}$, by
combining eqs 6.42 and 6.77. Figure 6.10 shows that with \( k_a = 10^8 \text{ M}^{-1}\text{s}^{-1} \) and typical values of the other parameters, \( \Theta \) is always \( \gg 1 \), even if a low value has been used for \( \{X\}_t/\{P\}_t \) (1%). Thus, as mentioned above, quite low values of \( k_a \) (typically \( < 10^5 \text{ M}^{-1}\text{s}^{-1} \)) are required to get \( \Theta < 1 \).

![Figure 6.10](image)

Figure 6.10. Plot of \( \Theta \) as function of \( r \) (eqs 6.42 and 6.77), for various values of \( D_f \). Other parameters: \( k_a = 10^8 \text{ M}^{-1}\text{s}^{-1}, \{X\}_t/\{P\}_t = 0.01, b = 3 \text{ nm}, h_X = 1 \text{ nm}, \rho_p = 3 \text{ kg dm}^{-3}, \rho_X = 2 \text{ kg dm}^{-3}, D_M = 7 \times 10^{-10} \text{ m}^2\text{s}^{-1} \).

ii) For compact particles following Pareto law distribution, the expressions for \( j_{cp}, A \) and \( \Delta A_b/A_{b,t} \) can be derived as for fractal aggregates. Combining these with \( \Theta \) in eq 6.76, leads to different expressions, depending on the value of \( \beta \):

\[
\beta = 3; \quad \Theta = \Theta_o \left( \frac{r_{\text{max}}^{4-\beta} - r_{\text{min}}^{4-\beta}}{(4-\beta) \ln(r_{\text{max}}/r_{\text{min}})} \right) j_r \quad (6.78)
\]

\[
\beta = 4; \quad \Theta = \Theta_o \left( \frac{(3-\beta) \ln(r_{\text{max}}/r_{\text{min}})}{r_{\text{max}}^{3-\beta} - r_{\text{min}}^{3-\beta}} \right) j_r \quad (6.79)
\]

\[
\beta \neq 3 \text{ and } 4; \quad \Theta = \Theta_o \left( \frac{(3-\beta)(r_{\text{max}}^{4-\beta} - r_{\text{min}}^{4-\beta})}{(4-\beta)(r_{\text{max}}^{3-\beta} - r_{\text{min}}^{3-\beta})} \right) j_r \quad (6.80)
\]

iii) For monodispersed compact particles, one gets:

\[
\Theta = \Theta_o r^2 \quad (6.81)
\]

Thus in all cases, \( \Theta \) (or \( j_{\Theta} \)) increases, and \( k_a^{\text{eff}} \) decreases, with increasing \( r^\alpha \), where \( 0 < \alpha \leq 2 \), depending on the aggregate structure (i.e., the value of \( D_f \)) or the size distribution of compact particles.

6.6 General discussions
This chapter provide concepts and parameter values to evaluate the diffusion coefficients and rate constants required for trace metal flux computations at consuming interfaces. A few additional effects might influence the metal flux. Some of them have been briefly discussed in the Section 6.2, namely electric migration, hydrodynamics, and aggregation/dissolution of colloids. In many cases they are expected to play a negligible role, but their precise influence should be studied in more details.

A few other processes may require further studies:
- A generalised version of the Eigens-Wilkins mechanism for the computation of association rate constants is presented in section 6.3.3. Its application to complexes with fulvics/humics is based on linear complexation Freundlich isotherms. Improvement of this approach would require a better knowledge of the nature of complexing sites and of the mechanism of complexation reaction. Similarly, a more detailed approach for particle/aggregates would require a better knowledge of their chemical composition and physical structure.
- The reaction of the test metal, M, with sites already occupied by another metal, M’, in particular Ca++, (competition reaction), is not discussed in detail, in particular because the corresponding rate constants are not available for natural complexants. It has been observed however, e.g. for the binding of Pb(II), Zn(II) or Cd(II) by EDTA in presence of Ca(II) as competing ion [77], that the dissociation of the complex Ca-EDTA is much slower than the dehydration rate of M. Thus it can be expected that sites already combined with a competing ion M’ will behave as “non reactive” sites in the time scale (< ~10 minutes) of diffusion-reaction processes. The contribution of these occupied sites however, may depend on their proportion compared to that of free sites.
- The effective rate constant for metal-aggregate complexes has been derived by assuming a single type of site. In presence of additional site types, their kinetic properties should be included in eq. 6.52 and in turn in the term B(t). Under steady-state conditions, however the corresponding term, Bss, is independent of any chemical kinetics (eq. 6.75). Then it can be inferred that in an aggregate with several site types, the effective rate constant for each site type can be computed from eq. (6.76), by replacing $k_a$, and $[S]_t$ by the corresponding values for each given site ($[S]_t$ then is replaced by the total concentration of that type of site). On this basis, the metal flux computation for aggregates containing adsorbed fulvics/humics would be feasible, provided the latter are considered as containing only site types in excess to M. On the other hand, the use of a complete fulvic site distribution, including sites which are not in excess compared to total metal concentration, is not compatible with the assumptions made to get eq. 6.76.

6.7 References


Burgess J. Metal ions in solution, Ellis Horwood, Chichester 1978.


Fuoss R. M. Ion association. III The equilibrium between ion pairs and free ions. J. Am. Chem. Soc. 1958, 80, 5059-5061.


[41] Town R. M., Filella M. Implications of natural organic matter binding heterogeneity


[62] Muller B., Duffek A. Similar adsorption parameters for trace metals with different


[70] Tonkin J. W., Balistrieri L.S., Murray J. W. Modeling sorption of divalent metal cations on hydrous manganese oxide, using the diffuse double layer model *Applied Geochemistry* 2004, 19, 29-53


Part III

Computation of metal flux in environmental multiligand systems. The relative contributions of the various types of complexes and their mutual influences
Chapter 7

The interplay of two complexes with different labilities: the impact on their metal flux understood by the reaction layer approximation

7.1 Overview

In this chapter we analyse two case studies: the Cu-OH-CO₃ and Pb-EDDA-CO₃ systems in freshwater. The simulation results show that metal complexes are not independent from each other: the more labile metal complex may strongly influence the degree of lability and individual flux of the less labile metal complex. In particular it may significantly increase the individual flux of the latter, even when it is present in very small proportion. In this chapter, we show that the use of the reaction layer approximation is very useful to understand the complicated interplay between the various factors which affect the flux. A mathematical model is proposed, based on this concept, which describe well the role of the various physico-chemical factors.

7.2 Introduction

Compared to metal speciation at equilibrium (i.e. thermodynamic metal species distribution), dynamic metal speciation (i.e. the determination of the contribution of each metal species to the overall metal flux) is a new field. It is of great importance for understanding the quantitative basis of the relationship between metal ion speciation at equilibrium, and metal ion bioavailability and biouptake, and thus for establishing the foundations for dynamic risk assessment [1]. The central part of dynamic metal speciation is flux measurement and computation. Most former theories for metal flux computation and their experimental tests have been focused on solutions containing only one ligand [2-7]. In environmental and biological media however, trace metal ions are present under a vast number of different species: the free, hydrated ion, as well as complexes with ‘simple’, macromolecular or colloidal, organic or inorganic, complexants [8]. The computation of metal flux at a consuming surface, such as a bioanalogue sensor (e.g. voltammetry, permeation liquid membranes (PLM) or diffusive gradients in thin films (DGT) [1,9,10]) or a microorganism surface, in such complicated systems comprising a large number of different types of ligands, is made difficult due to the interplay of many physical and chemical processes between the complexes. The different forms of metal species interconverse via the free metal ion, inside the diffusive-reactive layer near the consuming interface. For instance, in a solution containing only one ligand and one metal forming one 1/1 non labile complex, increasing the ligand concentration will always decrease the metal flux. We shall show below that in a multiligand system, even a binary one, the metal flux of the non labile complex may increase.

This chapter tries to understand the physico-chemical reasons of such unexpected behaviours. Simple systems (one single metal ion, two ligands and a few complexes) are used for such studies, in order to facilitate the understanding of the key processes: they are the Cu-OH-CO₃ and Pb-EDDA-CO₃ systems, under freshwater conditions. Rigorous flux computations are used, based either on a numerical method, the Lattice Boltzmann (LBGK) method [11] coupled to time splitting technique [12], or on a rigorous analytical solution applicable in presence of ligand excess [13]. These rigorous computations are compared to the results obtained via an approximate resolution of diffusion/reaction equations based on the so-called reaction layer approximation. It will be shown in this chapter that this approximation can be
rather good, and that in addition it enables to do a much easier physical-chemical interpretation of the factors which influence the metal flux.

7.3 Theory

7.3.1 Composite and overall reaction layer

Let’s assuming a multiligand system which contains n ligands forming n 1:1 metal complexes, M'L, M'2L, …, M'nL. The concentration of each ligand is in excess with respect to the total metal ion concentration. The n metal complexes are interrelated to each others via the free metal ion M, as shown in Figure 7.1

In Fig. 7.1, $k_a$ and $k_d$ are the association and dissociation rate constants of the complex M'L. The bulk solution is supposed to be homogeneous at a distance from the interface larger than the diffusion layer thickness, $\delta$. The concept of reaction layer thickness, $\lambda$, has already been discussed in chapter 3 for a solution with a single complex. It has been discussed for a multiligand system, and applied to the code for flux computation called FLUXY [14]. This concept is generalized and briefly discussed below.

The general expression for the reaction layer thickness (r.l.t.) is given by [6,7]:

$$r.l.t = \sqrt{(D_M \cdot \tau_{1/2})} \quad (7.1)$$

where $D_M$ is the diffusion coefficient of free M, and $\tau_{1/2}$ the life-time of free M in the reaction layer contacting the interface. The reaction layer thickness is thus the maximum distance which can be covered by M to reach the consuming interface before recombining to L, to form ML. Conventionally, it is expressed as $\mu$ (eq. 7.2 [3,6,7]), under conditions of most laboratory experiments, i.e. i) for sufficiently strong complexes ($K[L] = [ML]/[M] >> 1$ which also corresponds to $k_a[L] >> k_d$), ii) for $D_{ML} \sim D_M$ and iii) for $\mu << \delta$ (Fig. 7.1).
where \( k_a \) = association rate constant of ML, and \([L]\) = concentration of free L.

It has been shown however \([\S 6.5.2]\), that in environmental systems, where \( k_a[L] \) is not necessarily much larger than \( k_d \) (weak complexes) and/or where \( D_{ML} \) may be much smaller than \( D_M \) (complexes with colloidal complexants), the reaction layer of a complex ML is given by the more general expression, \( \lambda \):

\[
\lambda = \sqrt{\frac{D_M}{k_a[L] + k_d / \varepsilon}}
\]  

(7.3)

where \( \varepsilon = D_{ML}/D_M \). In addition, it has also been shown \([\S 3.4]\) that when the reaction layer is not much smaller than the diffusion layer, \( \lambda \) should be corrected by \( \tanh(\delta / \lambda) \) and becomes:

\( \lambda \cdot \tanh(\delta / \lambda) \rightarrow \lambda \). When \( \delta / \lambda \rightarrow \infty \), \( \lambda \cdot \tanh(\delta / \lambda) \rightarrow \lambda \), and when \( \delta / \lambda \rightarrow 0 \), \( \lambda \cdot \tanh(\delta / \lambda) \rightarrow \delta \).

By comparing eqs 7.1 and 7.3, one gets:

\[
\tau_{1/2} = \frac{1}{k_a[L] + k_d / \varepsilon}
\]  

(7.4)

In a mixture of \( n \) ligands, \( ^iL \), each one reacting with M to form a semi- or non-labile complex, \( M^iL \), M has only one single life time given by:

\[
\tau_{1/2} = \frac{1}{\sum_{i=1}^{n} (k_a[Li] + k_d / \varepsilon)}
\]  

(7.5)

to which corresponds a « composite » reaction layer, \( \bar{\lambda} \):

\[
\bar{\lambda} = \sqrt{\frac{D_M}{\sum_{i=1}^{n} (k_a[Li] + k_d / \varepsilon)}}
\]  

(7.6)

For metal flux computations, however, not all complexes of the mixture contribute to the reaction layer thickness. In fact a series of reaction layer thicknesses (\( ^1\bar{\lambda} \) to \( ^n\bar{\lambda} \); Fig. 7.2) are created (see below).

These are sorted from the thinner (\( ^1\bar{\lambda} \)) to the thicker one (\( ^n\bar{\lambda} \)). According to the reaction layer conceptual approximation, for \( ^n\bar{\lambda} < x < \delta \), all complexes are supposed to be fully labile, i.e. their formation/dissociation rates are supposed to be instantaneous. For \( ^{n-1}\bar{\lambda} < x < ^n\bar{\lambda} \), only the complex M^nL behaves in a semi- or non-labile manner and must be considered for the computation of the life-time of M. Reactions with other ligands are instantaneous and do not play a role on \( \tau \). Thus
\[
\tilde{\lambda}_n = \frac{D_M}{\sqrt{a k_a [a L] + a k_d / a e}} = \sqrt{\frac{D_M}{\lambda}}
\] (7.7)

For \( n-2 < \tilde{\lambda} < n-1 \), only the complexes \( M^nL \) and \( M^{n-1}L \) behaves in a semi- or non-labile manner. Thus:

\[
\tilde{\lambda}_{n-1} = \frac{1}{\sqrt{M_{n-1} + n - 1}}
\]

The general expression for the composite reaction layer \( n^0 j \) is thus:

\[
j \tilde{\lambda}_j = \frac{D_M}{\sqrt{\sum i \kappa}}
\] (7.9)

with the \( i \kappa \)'s sorted out in their decreasing order, from 1 to \( n \). In addition, in the general case where \( \delta \) is not very large compared to \( j \tilde{\lambda} \) (semi-infinite diffusion), each value of \( j \tilde{\lambda} \) should be corrected by the term \( \tanh(\delta / j \tilde{\lambda}) \), as discussed above and in chapter 3, i.e.,

\[
j \tilde{\lambda}^c = j \tilde{\lambda} \cdot \tanh(\delta / j \tilde{\lambda})
\]

In chapter 3, we have shown that for one ligand system system when the consuming interface is a perfect sink, the flux, \( J \), is given by:

\[
J = [M]^n \left( \frac{\delta}{D_M (1 + eK[L])} + \frac{\lambda eK[L]}{D_M (1 + eK[L])} \tanh \left( \frac{\delta}{\lambda} \right)^{-1} \right) = [M]^n \frac{1}{\tau}
\] (7.10)

where \( \tau \) is the resistance to the flux. For a multiligand system containing only 1/1 complexes, \( \tau \) is given by [14]:

Figure 7.2. Schematic reaction/diffusion processes for a system with two ligand, \( L^1 \) and \( L^2 \) and two complexes \( M^1L \) and \( M^2L \).
\[ "\tau = \frac{\delta}{D_\alpha \alpha_n} + \sum_{j=1}^{n} \frac{1}{\lambda} \left( \frac{1}{D_{j-1} \alpha_{j-1}} - \frac{1}{D_j \alpha_j} \right) \]  
(7.11)

where

\[ \bar{D}_j = \left( D_M [M] + \sum_{i=1}^{j} D_{M_i} L_i [M^j L^i] \right) \left( [M] + \sum_{i=1}^{j} [M^j L^i] \right) \]

and

\[ \alpha_j = \frac{1}{[M]} \left( [M] + \sum_{i=1}^{j} [M^j L^i] \right) . \]

Eq 7.11 can be rearranged as:

\[ "\tau = \frac{\delta}{D_m \beta} + \frac{\beta - 1}{D_m \beta} \left( \frac{D_m \beta}{\beta - 1} \sum_{j=1}^{n} \frac{1}{\lambda} \left( \frac{1}{D_{j-1} \alpha_{j-1}} - \frac{1}{D_j \alpha_j} \right) \right) \]  
(7.12)

where \( \beta = 1 + \sum_{j=1}^{n} \varepsilon_j K^j L^j \) and \( \varepsilon = \frac{D_{M_i} L_i}{D_M} \) which enables to draw an analogy between eqs. 7.10 and 7.12. Indeed \( \beta \) is similar to \( 1 + \varepsilon K[L] \) and \( \beta - 1 \) is similar to \( \varepsilon K[L] \). This implies that we can define an overall reaction layer thickness \( \tilde{\lambda} \), composed of the set of the above “composite” reaction layers, as follows:

\[ \tilde{\lambda} = \frac{D_m \beta}{\beta - 1} \sum_{j=1}^{n} \frac{1}{\lambda} \left( \frac{1}{D_{j-1} \alpha_{j-1}} - \frac{1}{D_j \alpha_j} \right) \]  
(7.13)

7.3.2 Metal flux, in presence of metal complexes formed with simple ligands

When only simple ligands are present, the diffusion coefficients of the metal complexes can be assumed to be the same as that of free metal ion. The reaction layer approximation can now be applied to the multiligand system, but using one single overall reaction layer. Between the bulk solution and the boundary of the (single) overall reaction layer, the metal flux is controlled by diffusion of all the metal species:

\[ J = \frac{D_m \alpha \left( [M]^* - [M]_j \right)}{\delta - \tilde{\lambda}} \]  
(7.14)

where \([M]^*\) and \([M]_j\) are the free metal ion concentrations in the bulk solution and at the boundary of overall reaction layer, \( \alpha = 1 + \sum K^j L^j \) is the total degree of complexation of M and the \( K = k_a / k_d \) are the equilibrium constants of the reactions in Figure 7.1. Inside the reaction layer, \( J \) is given by the diffusion of free M, since dissociation is supposed not to contribute to the flux:

\[ J = \frac{D_m [M]_j}{\tilde{\lambda}} \]  
(7.15)
At steady state, due to the continuity of flux, equations 7.14 and 7.15 are equal. In addition, when all the metal complexes are fully labile, the flux is equal to the total maximum flux, $J_{lab}$:

$$J_{lab} = D_M \frac{\alpha_t [M]^*}{\delta}$$ (7.16)

Combining eqs 7.14-7.16, a simple general expression for the flux is obtained:

$$J = \frac{J_{lab}}{1 + \frac{\lambda}{\delta} (\alpha_t - 1)}$$ (7.17)

Equations 7.15 and 7.17 are very simple equations which are applicable to complex mixtures of ligands, because $\lambda$ depends on all chemical kinetics and $\alpha_t$ on all thermodynamic parameters. It is shown below that these simple expressions provide good results when they are compared to rigorous computations. Their advantage is that they enable to do simple predictions, because $\lambda$ and $\alpha_t$ are very easily computed. A few limiting cases are briefly discussed below. Interestingly, the diffusion layer thickness $\delta$ is often kept constant. Thus the total flux is the result of an opposite effect of the overall reaction layer thickness, $\lambda$, and the total degree of complexation $\alpha_t$.

Eq 7.17 shows that when all complexes are labile, $\lambda$ tends to 0 (all chemical rate constants are very large), and $J \sim J_{lab}$ as expected.

- when all complexes are inert $\lambda / \delta \to 1$ and $\lambda (\alpha_t -1)/\delta \to \alpha_t -1$. Then $J = D_M[M]^*/\delta$, i.e. the flux indeed expected for inert complexes.

- On the other hand, if $\alpha_t >> 1$, and $\lambda/\delta >> 1$, while $\lambda/\delta << 1$, $J$ tends to $D_M[M]^*/\lambda$, which is a fully kinetically metal complexes system.

The most interesting feature of eq. 7.17, is that for a given multiligand system, the key point is that the values of $\lambda$ and $\alpha_t$ may be controlled by different ligands. Thus, increasing the concentration of one of them may for instance decrease $\tilde{\lambda}$ drastically while $\alpha_t$ remains approximately constant. The net effect will be an increase of total flux, even though intuitively an opposite effect would be expected. Such examples are discussed below.

7.4 The Cu(II)-OH-CO$_3$ system under freshwater conditions

7.4.1 Rigorous simulation of Cu(II) flux by MHEDYN

Making predictions of the bioavailability of Cu(II) is an important issue in ecotoxicology. Preliminary tests have shown that amongst the simple inorganic ligands (chapter 1) and under natural conditions, OH$^-$ and CO$_3^{2-}$ are the most important ones to study: many other simple complexes are either not stable enough to play a significant role, or fully labile so that they do not change significantly the total flux, with respect to that in absence of ligand, since their
Diffusion coefficients are close or equal to that of free M [Chapter 6]. Flux simulations have been performed with MHEDYN [Chapter 1] at various pH and carbonate concentrations [15]. They are reported here for the following specific conditions: total Cu(II) concentration, \([\text{Cu}]_t=10^{-8}\text{M}\), pH=9 and \([\text{CO}_3]_t\) varying between \(10^{-5}\) and \(10^{-1}\) M (for other conditions, see Table 7.1).

### Table 7.1. Dynamic parameters of species for the simulation if Cu-OH-CO_3 system. \([\text{Cu}]_t=10^{-8}\text{M}, \delta=20\mu\text{m}, \text{pH}=9.00\)

<table>
<thead>
<tr>
<th>Species</th>
<th>(D_x) ((\text{m}^2\cdot\text{s}^{-1}))</th>
<th>(k_a) ((\text{m}^2\cdot\text{mol}^{-1}\cdot\text{s}^{-1}))</th>
<th>(\log K) (M(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>(7.14 \times 10^{-10})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OH</td>
<td>(5.27 \times 10^{-9})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO_3</td>
<td>(9.20 \times 10^{-10})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuOH</td>
<td>(7.14 \times 10^{-10})</td>
<td>(4.98 \times 10^6)</td>
<td>6.22</td>
</tr>
<tr>
<td>Cu(OH)_2</td>
<td>(7.14 \times 10^{-10})</td>
<td>(4.15 \times 10^6)</td>
<td>6.87</td>
</tr>
<tr>
<td>CuCO_3</td>
<td>(7.14 \times 10^{-10})</td>
<td>(2.31 \times 10^7)</td>
<td>6.39</td>
</tr>
<tr>
<td>Cu(CO_3)_2</td>
<td>(7.14 \times 10^{-10})</td>
<td>(1.93 \times 10^7)</td>
<td>3.35</td>
</tr>
</tbody>
</table>

Species distribution Computed with MINTEQ2 shows that only the complexes Cu(OH\(^+\)), Cu(OH\(_2\))^0, CuCO\(_3\)^0 and Cu(CO\(_3\))\(_2\)^2\(^-\) are present in significant proportions (Figure 7.3) in the bulk solution, under those conditions.

![Cu(II) species distribution at equilibrium, at pH9.](image)

The ratios of steady-state metal fluxes at various values of \([\text{CO}_3]_t\) to the maximum flux obtained when all the complexes are fully labile, are shown in Fig 7.4. The diffusion coefficients of all complexes are assumed to be equal to that of Cu\(^{2+}\) \((7.14\times10^{-10}\text{ m}^2\cdot\text{s}^{-1})\). The values of the association rate constants, \(k_{a,i}\), were computed as discussed in [§6.3.3]. \(k_{d,i}\) values are obtained from \(k_{d,i}=k_{a,i}K_i\), where \(K_i\) is the stability constant of the complex \(M^i\text{L}_i\) (see table 7.1). Figure 7.4 shows that at constant pH9, by increasing \([\text{CO}_3]_t\), the total flux of Cu(II) through a consuming interface increases and takes a maximum value when \([\text{CO}_3]_t\) is in the range \(10^{-3}\) - \(10^{-2}\) M. This peculiar phenomenon is interesting, since the present opinion is that by increasing the ligand concentration, the lability and thus the flux of Cu(II) should
decrease. In the following section, this phenomenon is studied in detail by using the theory of the reaction layer approximation developed in section 7.3[14].

Figure 7.4. The normalized flux as a function of total CO$_3$ concentration, computed by MHEDYN and by the reaction layer approximation (eq. 7.17).

7.4.2 Explanation of flux in the Cu-OH-CO$_3$ system

Due to the definition of $\tilde{\lambda}$, equations 7.15 – 7.17 are applicable to 1/1 ML complexes only. On the other hand, in the Cu-OH-CO$_3$ system, the complexes Cu(CO$_3$)$_2$ and Cu(OH)$_2$ may be predominant (Fig. 7.3). Under certain conditions however, the whole of ML and ML$_2$ complexes may be treated as one single complex, as explained below.

7.4.2.1 CuOH and Cu(OH)$_2$ complexes

In that case, [CuOH] is always negligible (< 3%), at any carbonate concentration (Fig. 7.3). One can then assume that CuOH is at steady-state in the successive reactions:

$$
Cu + OH \stackrel{k_{d1}}{\rightleftharpoons} CuOH \stackrel{k_{d2}[OH]}{\rightleftharpoons} Cu(OH)_2
$$

(7.18)

Thus:

$$
\frac{d[CuOH]}{dt} = k_{d1}[Cu][OH] + k_{d2}[Cu(OH)_2] - k_{d1}[CuOH] - k_{d2}[OH][CuOH] = 0
$$

(7.19)

By combining the expression for [CuOH] obtained from eq 7.19 within the equation for the formation rate of Cu(OH)$_2$, (d[Cu(OH)$_2$]/dt=k$_{d2}$[OH][CuOH]-k$_{d1}$[CuOH]), one gets:

$$
\frac{d[Cu(OH)_2]}{dt} = \frac{k_{d1}k_{d2}[OH][Cu]}{k_{d1} + k_{d2}[OH]}[Cu][OH] - \frac{k_{d1}k_{d2}}{k_{d1} + k_{d2}[OH]}[Cu(OH)_2]
$$

(7.20)
Thus the interrelationship between Cu(OH)\(_2\) and Cu can be expressed with only the two following overall association and dissociation rate constants, which are used below for the computation of \(\bar{\lambda}\) and the metal flux:

\[
\begin{align*}
    k_a &= \frac{k_{a1}k_{a2}[OH]}{k_{d1} + k_{a2}[OH]} \\
    k_d &= \frac{k_{d1}k_{d2}}{k_{d1} + k_{a2}[OH]}
\end{align*}
\]  

(7.21)  

(7.22)

**7.4.2.2 CuCO\(_3\) and Cu(CO\(_3\))\(_2\) complexes**

In that case, the concentration of CuCO\(_3\) is non negligible at intermediate carbonate concentrations (Fig. 7.3). On the other hand, in the successive formation of CuCO\(_3\) and Cu(CO\(_3\))\(_2\), the slowest step corresponds to the formation/dissociation of CuCO\(_3\), while CuCO\(_3\) and Cu(CO\(_3\))\(_2\) are always at equilibrium, in the diffusive reactive layer (Table 7.1). Under this condition, it can be shown (see Appendix A.4) that the formation and dissociation rates of the whole of CuCO\(_3\) and Cu(CO\(_3\))\(_2\) complexes, can be related to Cu and CO\(_3\) expressed via the average rate constants:

\[
\bar{k}_a = k_{a1}
\]  

(7.23)

and

\[
\bar{k}_d = \frac{k_{d1}}{1 + K_2[CO_3]}
\]  

(7.24)

**7.4.2.3 The reason of the change of Cu flux with CO\(_3\) concentration.**

By using eqs 7.21 to 7.23, and eqs 7.15 and 7.17, one gets the results shown in Figures 7.4 and 7.5.

Figure 7.4 shows that the the flux computed by the reaction layer approximation, provides very good results, when they are compared to the rigorous results obtained from MHEDYN. In both cases, it is observed that the copper flux increases with the carbonate concentration, at constant pH, in the intermediate range of carbonate concentration. Figure 7.4 corresponds to pH = 9. However a similar maximum is observed at pH > 7 [15]. It is important to note that a significant increase of the flux starts at carbonate concentrations (10\(^{-4}\)M or below) where both CuCO\(_3\) and Cu(CO\(_3\))\(_2\) are negligible compared to Cu(OH)\(_2\), which is then by far the major Cu(II) species.

Figure 7.5 shows the change of the overall reaction layer thickness, \(\bar{\lambda}\) and of the free metal ion concentration at the boundary of the reaction layer, [Cu]\(_{\bar{\lambda}}\) with total carbonate concentration [CO\(_3\)]\(_t\). When [CO\(_3\)]\(_t\) increases in the low concentration range, [Cu]\(_{\bar{\lambda}}\) remains almost constant until [CO\(_3\)]\(_t\) \sim 0.002-0.003 M, because it is well buffered by Cu(OH)\(_2\) which is largely dominant. On the other hand, in the same concentration range, \(\bar{\lambda}\) decreases much more strongly because the life time of free Cu in the reaction layer becomes controlled by the carbonato complexes which form faster reactions than hydroxo complexes. This combination
of a constant $[Cu]_\lambda$ with a decreasing $\tilde{\lambda}$ results in an increasing flux, because the concentration gradient of free Cu increases at the consuming surface (see eq. 7.15). For $[CO_3]_t > 0.01$M, i.e. after the maximum flux, CuCO$_3$ and Cu(CO$_3$)$_2$ are the dominant complexes which buffer the free Cu concentration. Then, increasing $[CO_3]_t$ results in a decrease of $[Cu]_\lambda$ much faster than the decrease of $\tilde{\lambda}$, because $[Cu]/[Cu]_t = 1/\alpha_t$ decreases as $[CO_3]_t^2$, while $\tilde{\lambda}$ decreases as $[CO_3]^{1/2}$. This case clearly exemplifies the antagonistic roles of the degree of complexation and the overall reaction layer thickness on the total Cu flux.

![Figure 7.5. Changes of the overall reaction layer thickness, $\tilde{\lambda}$ (■) and of the free Cu concentration at the boundary of $\tilde{\lambda}$ (●).](image)

**7.5 Pb-EDDA-CO$_3$ system in freshwater at pH = 7.5**

In order to better understand the interplay of different types of complexes on the total flux at consuming interface, we have studied the case of Pb(II) in a mixture of two ligands forming complexes with very different lability degrees: the Pb-carbonato complexes (close to labile complexes) and the PbEDDA complex (close to inert complex). EDDA (= ethylene diamine-N,N'-diacetic acid) has a structure close to EDTA and may be seen as a decomposition product of EDTA. Such compounds may be present at total concentration of $10^{-6}$M or below, in natural waters.

In freshwater, the major cations are Mg$^{2+}$ and Ca$^{2+}$ and their concentrations (typically $10^{-3}$M) are orders of magnitude larger than that of EDDA as well as of a trace metals like Pb(II) (typically $10^{-9}$M). Nevertheless, by using the available stability constants of MgEDDA complex ($\log K = 3.95$ at $I=0.1$ and $T=25^\circ$C), it can be computed that at pH7.5, and for the total EDDA concentration used here ($[EDDA]_t = 10^{-6}$M), the proportion of EDDA complexed by Mg is negligible (2–3%) for $5.10^{-4}$M. The stability constant of CaEDDA complex has not been reported in the literature. However, the values of stability constants of Ca(II) and Mg(II) complexes are often similar. By using this value and a total concentration of Ca(II) of $10^{-3}$M,
the proportion of EDDA complexed by both Ca(II) and Mg(II) is ~ 7%. This effect is small and neglected below.

Assuming a constant total Pb concentration of 1nM in the test freshwater of pH = 7.5, together with [EDDA]t = 10^{-6}M, equilibrium speciation calculation with Visual Minteq2 shows that the main Pb species are PbEDDA and PbCO_3 (Figure 7.6). The proportions of the other components are very low (less than 1 percent) and they can be omitted in simulation studies.

Figure 7.6. Pb speciation at pH7.5 in presence of EDDA 10^{-6}M, at variable carbonate concentrations. Stability constants: see Table 7.2.

Table 7.2. Dynamic parameters used for the simulation of Pb-CO_3-EDDA system. [Pb]_t= 10^{-9}M, [EDDA]_t=10^{-6}M, δ=20μm, pH=7.50, I=0.01, T=25°C.

<table>
<thead>
<tr>
<th>Species</th>
<th>(D_x) (m².s⁻¹)</th>
<th>(k_a) (m³.mol⁻¹.s⁻¹)</th>
<th>log(K) (M⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>9.45 × 10⁻¹⁰</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EDDDA</td>
<td>1.00 × 10⁻⁹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO_3</td>
<td>9.20 × 10⁻¹⁰</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbEDDA</td>
<td>9.45 × 10⁻¹⁰</td>
<td>3.20 × 10⁷</td>
<td>11.10</td>
</tr>
<tr>
<td>PbCO_3</td>
<td>9.45 × 10⁻¹⁰</td>
<td>3.08 × 10⁷</td>
<td>6.64</td>
</tr>
<tr>
<td>HEDDA</td>
<td></td>
<td></td>
<td>9.86</td>
</tr>
<tr>
<td>H₂EDDA</td>
<td></td>
<td></td>
<td>6.68</td>
</tr>
<tr>
<td>PbOH</td>
<td></td>
<td></td>
<td>1.03</td>
</tr>
</tbody>
</table>

Figure 7.7a shows the changes of total Pb(II) flux and of the Pb(II) fluxes due to each individual species, as function of total CO_3 concentration. Fig 7.7b shows the change of the degree of lability of the Pb-EDDA complex with [CO_3]. The degree of lability, \(ξ\), of ML, is defined in [16,17]. It can be computed by [18]:

\[
ξ = \left( \frac{[ML]^0}{[ML]} \right) / \left( 1 - \frac{[M]^0}{[M]^-} \right)
\]  

(7.25)
For $[\text{CO}_3]_t > 10^{-4} \text{M}$, the total flux increases with $[\text{CO}_3]_t$ largely because of the increase of the concentration of labile Pb$\text{CO}_3$ complex. The proportion of this complex is negligible with respect to PbEDDA, but its individual flux is a significant proportion of the total flux because Pb$\text{CO}_3$ is almost fully labile, while PbEDDA is almost fully non labile.

The most striking feature of figures 7.7a-b however, is that, for $[\text{CO}_3]_t < 3 \times 10^{-3} \text{M}$, both the degree of lability and the individual flux of PbEDDA increase by a factor close to 2, when $[\text{CO}_3]_t$ is increased, even though the proportion of carbonato complexes remains negligible (<5.6%). This behaviour is very similar to that observed for the Cu-OH-CO$_3$ system in section 7.4.

![Figure 7.7](image-url)  

**Figure** 7.7. Total flux and individual fluxes of each Pb(II) species (a) and lability degree of PbEDDA(b) as a function of total carbonate concentration. Computation with MHEDYN. Parameters see Table 7.2.

### 7.6 References


Chapter 8

Capabilities of FLUXY, a simple code for computing steady-state metal fluxes at consuming (bio)interfaces, in natural waters.

8.1 Overview

The computation of metal fluxes at consuming interfaces like microorganisms or bioanalogical sensors is of great importance in ecotoxicology. This chapter describes the application of the simple code, FLUXY, for the computation of steady-state metal fluxes in presence of a very large number of complexes, with broadly varying values of equilibrium constants, rate constants and diffusion coefficients. This code includes two major limiting assumptions, namely, i) the existence of excess of ligand compared to metal, and ii) the fact that in a series of successive ML_n complexes, the reaction ML ⇔ M is supposed to be the rate limiting step in flux computation. The domains of rate constants, for which these assumptions are valid, are tested systematically, and the corresponding errors are evaluated by comparison with the exact results given by another code: MHEDYN. FLUXY is then applied and compared to MHEDYN for case studies typical of aquatic systems, namely a) a culture medium containing simple ligands, b) solutions of fulvics including a broad distribution of complex stability and rate constants, and c) suspensions of aggregates with a broad size distribution. It is shown that FLUXY gives good results for cases a) and c). Application to case b) (fulvics) is also feasible under conditions which are clearly described. Altogether, FLUXY and MHEDYN are complementary. In particular FLUXY only computes steady-state fluxes and requires the fulfilment of a few conditions, but when these are met, computations require much less computer time than MHEDYN.

8.2 Introduction

In environmental and biological media, trace metal ions are present not only as free, hydrated ions, but often as complexes with ‘simple’, macromolecular or colloidal, organic or inorganic, complexants, adsorbed on or assimilated by living organisms [1]. The computation of metal flux at a consuming interface, such as a bioanalogical sensor (e.g. voltammetry, permeation liquid membranes (PLM) or diffusive gradients in thin films (DGT) [2,3]) or a microorganism surface, must consider the physico-chemical properties of each complex and ligand. In aquatic systems (Figure 8.1), as explained in chapter 1, the latter can be classified into three categories [4,5]: a) the “simple”, small size, organic or inorganic, ligands (denoted SL in Fig. 8.1); b) the organic macromolecules, often chemically heterogeneous with polyelectrolytic properties, in particular fulvic and humic substances (denoted FS in Fig. 8.1); c) the natural particles or aggregates (P and A in Fig. 8.1) made of metal oxides (SiO₂, alumino-silicates, iron oxides) on which organic macromolecules may be adsorbed.
Figure 8.1. Schematic representation of the contributions of the main groups of metal complexes to the flux of the metal M at a consuming interface in aquatic systems. Only free M is supposed to interact with the membrane, i.e. lipophilic complexes are not considered. SL = simple ligands, FS = fulvic substances, P,A = particles, aggregates (see text; note that in the rest of the chapter, L is used to denote any ligand). D = diffusion coefficient, $k_a, k_d$ = association/dissociation rate constant, $K$ = equilibrium constant. In aquatic systems, the thickness of the diffusion layer, $\delta$, is usually fixed by the hydrodynamic flow. The reaction layer thickness depends on the chemical kinetics. The consumption of M is supposed to follow the Michaelis-Menten process, as for organisms, i.e. a fast equilibration of M with a surface carrier site, R, followed by an internalisation with rate constant $k_{int}$ (cell wall is not drawn). When internalisation rate is much slower than diffusion and chemical reactions in solution, the FIAM or BLM models are applicable (no disturbance of equilibrium in solution) and the metal flux is minimum. When internalisation rate is very fast compared to diffusion-reaction, the free M concentration at the interface is nil and the metal flux reaches its maximum limit, only controlled by the whole of the processes external to the organism. This is the flux computed in this chapter. Note that the nature of the process at the consuming interface does not influence this maximum metal flux, which is the same for sensors or organisms, under the same geometric conditions.

In Figure 8.1, it is assumed that only free M can interact with the surface to pass through the membrane, i.e. complexes and ligands are assumed not to pass the membrane. Even though this is a limitation of the present code, which requires further improvement, this code enables to consider all hydrophilic complexes, which represent a large majority of complexes in aquatic systems. Figure 8.1 points out that under such conditions, the flux at an organism/solution interface depends in general on the kinetics of both a) the interaction of M at the interface ($k_{int}$) and b) the whole of the diffusion-reaction processes in solution. Only when the internalisation rate is very small compared to diffusion-reaction processes, are the FIAM or BLM models applicable. Under this condition, solution reactions are not disturbed and there are no concentration gradients at the interface. The corresponding flux is thus a minimum flux. It should be realised however that it is a limiting case. At the other extreme, when internalisation rate is very fast compared to diffusion-reaction in solution, then these processes become the rate limiting factors and a so-called maximum flux is reached. It is controlled only by the physico-chemical and hydrodynamic properties of the external medium, and it is the same for any organism or sensor under the same geometric conditions. The minimum and maximum fluxes are two limiting parameters of equal major importance to interpret the results of quality monitoring in terms of ecotoxicology. Even though there are many more reports in the literature, on biouptake following FIAM or BLM models (usually
under laboratory conditions) rather than diffusion-reaction processes, the latter also exist [4-6] and seems to be dominant under natural conditions, in particular close to organism starvation. Thus the availability of a code including all the dynamic processes of Fig. 8.1 is essential. This is the case of the code discussed here (FLUXY). In this chapter, the maximum flux is computed to emphasize its capability to deals with diffusion-reactions in solution, but some comparison with the minimum flux prevailing under FIAM or BLM conditions is also discussed at the end of the chapter.

The computation of metal flux at a consuming surface, in complicated systems comprising a large number of different types of ligands, is made difficult due to the interplay of many physical and chemical processes. Former theories for metal flux computation were focused on solutions with only one ligand [3,7-10]. Only recently, theories were extended to multiligand systems [11-15]. However, they require advanced mathematical operations, not easily usable by non-specialists, and are not directly applicable to complicated natural complexants like fulvics or particles/aggregates. The development of user-friendly codes for flux computations in environmental systems is of major importance. To the best of our knowledge, up to now, only two such codes for metal flux computation in presence of an unlimited number of ligands, are available (http//:www.unige.ch/cabe/dynamic/): FLUXY [16] and MHEDYN [17,18]. MHEDYN (see chapter 9) provides rigorous, time resolved solutions of the diffusion-reaction system, without any a priori assumption. Its characteristics are given in more details in section 8.3. It will be used here as a reference code, for FLUXY evaluation. Its drawback is that it is based on numerical methods and is thus computer-time consuming in presence of many complexants, particularly those (particles/aggregates) with low diffusion coefficient. FLUXY [16] is much quicker because it is based on the analytical solution of diffusion-reaction equations. It can deal with an unlimited number of complexes whose values of rate constants and diffusion coefficients vary in a very broad range, but it is valid only in presence of ligand excess compared to metal.

This chapter has two major goals:
  i) to discuss theoretically, by comparison with MHEDYN, the errors of FLUXY, caused by the two afore-mentioned limiting assumptions.
  ii) to show the capabilities and limitations of FLUXY in three typical types of environmental applications including many ligands forming complexes with wide ranges of stability and rate constants: a) Solutions containing only simple ligands, forming successive complexes. A culture medium based on AQUIL [19] which has been successfully used for trace metal studies of marine phytoplankton biouptake, will be taken as an example here. b) solutions with fulvic complexants only, with consideration of their broad chemical heterogeneity. In such solutions, the role of non excess of ligand can be tested; and c) solutions containing particle/aggregates only, with consideration of their broad size distribution. In such cases, the effect of complexes with widely variable diffusion coefficients is tested.

Flux computations in natural mixtures require the knowledge of a large number of parameters related to the properties of the complexes and complexants. They include the stability and association/dissociation rate constants for each complex, the diffusion coefficient of each species but also “complementary” parameters, such as the ligand electric charge density which influences the stability of complexes or the size distribution and fractal structure of aggregates which influence their diffusion coefficients and internal reactivity with metals. These parameters are linked to metal complexation via sometimes sophisticated physico-
chemical models. These parameters and models for dynamic speciation, are taken from or computed according to chapter 6.

8.3 The physical model and the computer code

Fluxy computes the steady-state metal flux in systems including an unlimited number of complexes, by using alternatively two mathematical approaches:

i) The first approach corresponds to the rigorous solution (RS) of the diffusion-reaction equations, as described in [12]. It is presently limited to a mixture of 1/1 ML complexes, where in the following, L denotes any ligand.

ii) The other approach is the so-called reaction layer approximation (RLA; [7,8,16]). It is assumed that a complex, ML, is at equilibrium with the free metal, M, and the ligand, L, at any distance from the consuming interface larger than the reaction layer thickness (Fig. 8.1). Inside the reaction layer the free M produced by dissociation of ML can be fully consumed at the interface because the time required for reassociation is longer than that to reach the interface by diffusion. Thus only in this layer, the formation/dissociation rate of ML plays a role on the metal flux. When successive complexes, ML\textsuperscript{n} (n>1), are present, they are included in flux computation by FLUXY-RLA, with the assumption that they are all at equilibrium with the corresponding 1/1 complex, ML. This assumption is discussed in § 8.4.1. The general expression for the reaction layer thickness discussed in chapter 3 [3,7,8], is included in the version of FLUXY (version 3.0) used in this chapter. It is more general than the conventional one. The application of this reaction layer concept to a solution containing many ligands and complexes is discussed in chapter 7 (section 7.3).

In a complex mixture, both FLUXY approaches provide the total flux of the test metal, the proportion of each species in the bulk solution, the individual contribution of each species to the total flux, and the corresponding degree of lability, \(\xi\), as defined and discussed in [10,11]. This parameter varies between 0 (fully inert complexes) and 1 (fully labile complexes) and corresponds to the ratio of the real flux of the test complex, to that which would be produced by this complex, if it was fully labile.

Both FLUXY-RLA and FLUXY-RS can work under planar and spherical diffusion conditions. The boundary conditions at the consuming interface are the following (see [18] for details):

a) Only free M can be transferred through the membrane (Fig. 8.1). This occurs via its binding to transfer sites. No ligand or complex can pass directly through the interface.

b) The metal of a complex can be transferred, but only after its dissociation at the solution side of the interface.

c) Linear Michaelis-Menten boundary condition is assumed to occur, for the transfer rate of M through the interface, i.e. the metal flux is assumed to be proportional to the surface concentration of transfer sites, R, to the complexation constant of the test metal with these sites, \(K_a\), and to an internalisation rate constant, \(k_{int}\) (Fig. 8.1). When these parameters are very large, the consuming surface is a perfect sink for M, and its transport dynamic is only controlled by diffusion-reaction processes in solution.

d) The flux is computed under conditions of finite diffusion in solution, i.e., the concentration of all species are assumed to be equal to those in the bulk solution, at any distance \(x \geq \delta\), where \(\delta\) is the diffusion layer thickness at the consuming surface (Fig. 8.1).
Former tests with simple ligands [16] have shown that in most cases, the differences between RLA and RS approaches are very small. Significant differences may occur when a solution contains complexes with close values of the corresponding reaction layer thicknesses.

In this chapter, the results provided by FLUXY-RS or FLUXY-RLA are compared to the rigorous results obtained with MHEDYN, whose major characteristics are the following [17,18]: the contribution to metal flux and concentration profile of any species can be computed in both the transient and steady-state regimes, in solutions containing many complexes whose rate constants and diffusion coefficients may vary over many orders of magnitude, without requirement of ligand excess compared to metal. Computations are based on the numerical solution of diffusion-reaction equations, using the so-called Lattice-Boltzman method coupled to time-splitting and grid refinement techniques [20,21]. Thus MHEDYN does not make the approximations used in FLUXY, but it may be much more computer time consuming, so that the two codes are complementary.

In this chapter, calculations are based on metal transfer through a planar interface, because comparison with MHEDYN is presently only possible under that condition. In addition, the transfer rate of M through the interface is assumed to be much faster than the diffusion/reaction processes in solution, i.e. the Michaelis-Menten parameters (c) above) are assumed to be very large. The limiting maximum flux is thus obtained (see introduction). Furthermore, δ was taken as 20μm, which corresponds to a typical diffusion layer thicknesses at the surface of bioanalogical sensors based on voltammetry, PLM or DMT[2,3], under stirred conditions.

8.4 Study of the major limitations of FLUXY

In this section, we determine in which domains of dynamic parameter values (diffusion coefficients and rate constants), the errors of FLUXY, due to i) non excess of ligands or ii) the hypothesis of full equilibrium between MLn (n>1) and ML complexes, are acceptable. The error, E, is based on the differences between the fluxes, J, or lability degrees, ξ, computed by FLUXY (either RS or RLA) and MHEDYN. It is defined as follows:

\[
E_J = \frac{J_{\text{Fluxy}} - J_{\text{Mhedyn}}}{J_{\text{Mhedyn}}} \tag{8.1}
\]

\[
E_\xi = \frac{\xi_{\text{Fluxy}} - \xi_{\text{Mhedyn}}}{\xi_{\text{Mhedyn}}} \tag{8.2}
\]

where the subscripts of J and ξ refer to the codes used, and E_J and E_ξ are the errors on J and ξ respectively.

8.4.1 Flux computations in presence of successive complexes

8.4.1.1 Simulation conditions

We consider the formation of successive complexes:

\[
M(H_2O)_6 + L \xrightleftharpoons[k_{-\text{j}}]{k_{\text{j}}} M(H_2O)_5L + L \xrightleftharpoons[k_{-\text{j2}}]{k_{\text{j2}}} M(H_2O)_4L_2 \tag{8.3}
\]
where \( k_{a1} \) and \( k_{a2} \) are assumed to be given by the Eigen mechanism [22], i.e.:

\[
k_{a} = K_{i}^{\text{os}} k_{w}
\]

\( K_{i}^{\text{os}} \) is the outer-sphere equilibrium constant of the complex ML\(_{i}\) and \( k_{w} \) is the dehydration rate constant of the metal M. When L is introduced inside the inner hydration shell of M, to form ML\(_{2}\)(H\(_{2}\)O)\(_{5}\), a water molecule is eliminated and the remaining ones are somewhat disorganized so that their binding energy is decreased. Thus the removal of a second water molecule, to form ML\(_{2}\)(H\(_{2}\)O)\(_{4}\) is much faster than that of the first one, and:

\[
k_{a1} < k_{a2}
\]

(8.5)

In addition, with few exceptions, the successive stability constants of ML and ML\(_{2}\) are such that [24]:

\[
K_{1} > K_{2}
\]

(8.6)

Equations (8.5) and (8.6) imply that:

\[
k_{d1} < k_{d2}
\]

(8.7)

Thus, in the whole stepwise formation of ML and ML\(_{2}\), the kinetics of formation/dissociation of ML are most often rate limiting, and it can often be assumed that ML\(_{2}\) is in equilibrium with ML. This reasoning is also applicable to ML\(_{n}\) (n>2) [24].

As mentioned above, this assumption is used in FLUXY-RLA. It is not always true however, and it is useful to know in which domain of dynamic parameters it is acceptable. It is tested below by studying the ML/ML\(_{2}\) system, since it can be expected that the formation/dissociation rate constants of ML\(_{n}\) increase with n. \( E \) is computed for the range \(-2 < \log(k_{a2}/k_{a1}) < 2\), which is the maximum range of variation found in chapter 6 and for varying values of the lability index of ML, \( \mathcal{L} \), [3]. This parameter can be expressed as:

\[
\mathcal{L} = \frac{\delta}{\lambda \varepsilon K[L]}
\]

(8.8)

where \( \varepsilon = \frac{D_{ML}}{D_{M}} \), and \( \lambda \) is the general expression for the reaction layer thickness (chapter 3 and 7). \( \lambda \) is equal to the conventional expression of the reaction layer thickness, \( \mu = \sqrt{(D_{M}/k_{a}[L])} \), under conditions where \( k_{a}[L] >> k_{d}/\varepsilon \), i.e. \( \varepsilon K[L] >> 1 \). This condition is used in section 8.4 and in addition \( \varepsilon K[L] \) is kept constant. Thus \( \mu/\delta \) is used as variable parameter in place of \( \mathcal{L} \), in Figs 8.2-8.3. \( \mathcal{L} \) is an index of the reactivity of ML at the consuming interface [3,9]: it is fully labile for \( \mathcal{L} >> 1 \) (\( \mu/\delta << 1 \) in our case) and non-labile or inert for \( \mathcal{L} << 1 \) (\( \mu/\delta > 1 \) in our case). The range 0.001<\( \mu/\delta < 1 \) is thus studied below.

Finally the following conditions have been used: \( \log K_{1} = 5, \log K_{2} = 4, [M]_{t} = 10^{-6}\text{M} \) and \( [L]_{t} = 10^{-3}\text{M} \). They are typical for major ligands forming successive complexes with weak to intermediate stabilities. Under such conditions, the ligand is in excess with respect to M, and
the species concentrations are: \([M] = 9.12 \times 10^{-10} \text{M}, [L] = 9.98 \times 10^{-4} \text{M}, [ML] = 9.10 \times 10^{-8} \text{M}\) and \([ML_2] = 9.08 \times 10^{-7} \text{M}\), i.e. \(ML_2\) is the major \(M\) species in the system \(([ML_2]/[M] \approx 0.91)\).

### 8.4.1.2 Results

Figure 8.2 is the contour plot of \(E_J\) as functions of \(\log(k_{a2}/k_{a1})\) and \(\log(\mu/\delta)\). It shows that under the conditions used, the errors on the total flux \(\dot{J}_t\) due to the assumption of the existence of a thermodynamic equilibrium between \(ML\) and \(ML_2\), hardly exceeds 10%. The largest error occurs at the lowest \(k_{a2}/k_{a1}\) values and only becomes significant for \(k_{a2} \leq k_{a1}\). This is expected, since, under this condition, the dissociation of \(ML_2\) to \(ML\) is the rate limiting step and \(ML_2\) is not in equilibrium with \(ML\) in the reaction layer. It is interesting that the error is small even for ratios of \(k_{a2}/k_{a1}\) as low as 1. It is probably due to the fact that, because \(K_2 < K_1\), \(k_{a2}/k_{a1} = 1\) still implies \(k_{d2}/k_{d1} > 1\), i.e. the dissociation of \(ML_2\) is faster than \(ML\). Anyway Fig 8.2 shows that, for most environmental ligands, for which \(k_{a2} \geq k_{a1}\), the error provided by FLUXY is less than 6% and often negligible.

**Figure 8.2.** Values of the relative error, \(E_J\) (in fraction) on the total metal flux, in presence of \(ML\) and \(ML_2\) complexes. \(E_J\) is based on the difference in fluxes computed by FLUXY-RLA and MHEDYN, \(\log(K_1/\text{M}^{-1}) = 5, \log(K_2/\text{M}^{-1}) = 4, D_M = D_L = D_{ML1} = D_{ML2} = 7 \times 10^{-10} \text{m}^2/\text{s}, \delta = 20 \mu\text{m}\).
corresponding individual errors, as function of $\log(k_{a2}/k_{a1})$ and $\log(\mu/\delta)$. Both figures reflect the same trend: the error increases with decreasing values of $\log(k_{a2}/k_{a1})$ and increasing values of $\log(\mu/\delta)$. Indeed, for large values of $k_{a2}/k_{a1}$ and low values of $\mu/\delta$, both ML and ML$_2$ tend to be fully labile and the approximation of equilibrium between ML and ML$_2$ is very good. Increasing values of $\mu/\delta$ correspond to slower formation/dissociation rates of ML, and decreasing values of $k_{a2}/k_{a1}$ correspond to slower interconversion rates between ML and ML$_2$. Since FLUXY-RLA assumes an instantaneous interconversion between ML and ML$_2$, the contribution of this latter complex to the total flux is overestimated by FLUXY (positive error; Fig. 8.3b). For the same reason, the reassociation rate of ML with L to form ML$_2$ is overestimated, and consequently the dissociation of ML into M and its contribution to the total flux is underestimated (negative error; Fig. 8.3a). These two errors compensate each other and the net result is a very small error on the overall flux (Fig. 8.2). It must be emphasized that anyway the condition $\mu/\delta \to 1$ usually corresponds to near inert complexes ML. Then the amount of ML and ML$_2$ dissociated because of metal consumption is very small, as is the total flux. Thus the largest individual errors shown in Fig. 8.3a,b also correspond to negligible errors on the fluxes.

**Figures 8.3.** Errors on the individual fluxes due to ML (Fig. 8.3a) and ML$_2$ (Fig. 8.3b) obtained as the differences between the individual fluxes computed by Fluxy RLA and MHEDYN. See Fig. 8.2 for parameter values.

Anyway, the maximum error on the total flux, $E_f$, which results from the combination of the above effects, occurs at intermediate values of $\mu/\delta$ (~0.006), as shown in Figure 8.2 and it is not larger than ~10% for $k_{a2}/k_{a1} > 0.01$.

### 8.4.2 The limitation due to non excess of ligand

#### 8.4.2.1 Simulation conditions

The computations of FLUXY are made by assuming that each ligand is in excess with respect to the total metal concentration. For trace metals ([M]$_t$ ≤ $10^{-6}$ M), this is valid for most of the simple inorganic ligands, such as carbonate, sulphate, OH$^-$ (in pH-buffered solutions), a few simple organic ligands (e.g. aliphatic acids), and many particulate ligands. However, a few strong organic complexants [25,26], including the fulvics bearing the strongest sites, may not fulfil this criterium. In absence of ligand excess, the concentration of free ligand, L at the
consuming interface may be larger than in the bulk, because free L is produced at the interface by the dissociation of ML and consumption of M. The degree of complexation of M then increases and the degree of lability of ML decreases, at the interface with respect to the bulk solution. Since this effect is linked to the build up of concentrations gradients at the interface, it will be influenced by the diffusion coefficient of ML, $D_{ML}$.

In the simulations below, the error due to the assumption of ligand excess is evaluated by comparing FLUXY-RS and MHEDYN calculations, by using solutions containing a single 1/1 ML complex. Based on the above considerations, the error is computed for variable $D_{ML}/D_M$ values in the range $10^{-3}$ to 1, which corresponds to complex sizes ranging from 1 μm (e.g. complexes with the largest colloids) to 0.4 nm (e.g. the smallest inorganic complexes). FLUXY does not require the knowledge of $D_L$. For computations with MHEDYN, $D_L = D_{ML}$ was used. The error is also computed for variable $μ/δ$ values, as surrogate of lability index, $ℒ$, (section 8.4.1), in a domain $(0.001 ≤ μ/δ ≤ 1)$ covering complexes with properties ranging from fully labile to inert, with a fixed value of $δ = 20$ μm. In waters, many ligands which are not in excess compared to M form intermediate or strong complexes. A stability constant value of log$K=7$, typical for such ligands, as well as a typical value of diffusion coefficient for free metal ion ($D_M=7 \times 10^{-10}$ m$^2$.s$^{-1}$) were used. The total concentrations in the bulk solution (superscript $*$) of M, $[M]^*$, and L, $[L]^*$, were chosen to get the conditions: $K[L]^*=[ML]^*/[M]^* >> 1$, thus $[ML]^*/[L]^* = \frac{1}{K(L)}$, in all cases below. Four conditions of $[M]^*$ and $[L]^*$ were studied to cover $[ML]^*/[L]^*$ ratios in solution, varying from 0.1 (excess of ligand) to 61 (non excess of ligand) (Table 8.1).

### Table 8.1. Conditions of ligand/metal ratios used to evaluate the error due to the assumption of ligand excess. log$K = 7$.

<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.001101</td>
<td>0.001</td>
<td>6.15 $10^{-6}$</td>
<td>1.62 $10^{-5}$</td>
<td>9.94 $10^{-4}$</td>
<td>61.5279</td>
</tr>
<tr>
<td>2</td>
<td>0.0011</td>
<td>0.001</td>
<td>9.89 $10^{-7}$</td>
<td>1.01 $10^{-4}$</td>
<td>9.99 $10^{-4}$</td>
<td>9.89225</td>
</tr>
<tr>
<td>3</td>
<td>0.002</td>
<td>0.001</td>
<td>1.00 $10^{-7}$</td>
<td>0.001</td>
<td>0.001</td>
<td>0.9998</td>
</tr>
<tr>
<td>4</td>
<td>0.011</td>
<td>0.001</td>
<td>1.00 $10^{-8}$</td>
<td>0.01</td>
<td>0.001</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Overall, the association rate constant varies between $10^{11}$ and $10^2$ M$^{-1}$.s$^{-1}$, i.e., for $[ML]^*/[M]^*$=61.5, $k_a$ varies between 1.08 $10^{11}$ and 4.30 $10^5$ M$^{-1}$.s$^{-1}$, for $[ML]^*/[M]^*$=9.89, $k_a$ varies between 1.73 $10^{10}$ and 6.90 $10^4$ M$^{-1}$.s$^{-1}$, for $[ML]^*/[M]^*$=1.00, $k_a$ varies between 1.75 $10^9$ and 6.97 $10^3$ M$^{-1}$.s$^{-1}$, and for $[ML]^*/[M]^*$=0.1, $k_a$ varies between 1.75 $10^8$ and 6.97 $10^2$ M$^{-1}$.s$^{-1}$.

#### 8.4.2.2 Results

Figure 8.4a-d shows the contour plots of the error on the flux, $J$, given by Fluxy-RS compared to MHEDYN (full lines), as well as the curves of iso-lability index (dashed lines with values of log($ℒ$)), as functions of $D_{ML}/D_M$ and $μ/δ$. Note that when $eK[L] >> 1$, $D_{ML}/D_M$ is inversely proportional to $μ/δ$, at constant values of $ℒ$ and $K[L]$ (eq. 8.8). The curves computed by FLUXY-RLA are almost the same as those provided by FLUXY-RS.
Figure 8.4. Contour plots of the relative errors (fraction of 1) on the total flux, \( J \), given by FLUXY-RS, due to the assumption of ligand excess.  

a: \([\text{ML}]/[\text{L}]^* = 61.5\),  
b: \([\text{ML}]/[\text{L}]^* = 9.89\),  
c: \([\text{ML}]/[\text{L}]^* = 1.00\),  
d: \([\text{ML}]/[\text{L}]^* = 0.10\), 

\( K = 10^7 \text{M}^{-1} \), 

\( D_M = 7 \times 10^{-10} \text{m}^2\text{s}^{-1} \), 

\( D_L = D_{\text{ML}} \).

It can be seen that, as expected, the error decreases when the value of \([\text{ML}]/[\text{L}]^*\) decreases (Fig 8.4a to 8.4d). In particular, for \([\text{ML}]/[\text{L}]^* = 0.1\), where the condition of ligand excess is almost met, the maximum error is less than 7\% and in most cases, \( E_J \) is negligible. Figure 8.4a-c also show that the error due to the absence of ligand excess is maximum for \( \mathcal{L} = 1 \) and tends to zero for very low or very large values of \( \mathcal{L} \). This is due to the following reasons. For \( \mathcal{L} >> 1 \), the complex is fully labile, and the total flux only depends on the diffusion of ML, but not on its chemical kinetics at the interface. Under such conditions, FLUXY provides correct results. When \( \mathcal{L} << 1 \), the metal complex is non labile, i.e. its dissociation at the interface is very small and consequently the ligand concentration at the surface is the same as in the bulk solution. Under such condition, the flux is due mostly to the diffusion of free M and is again ~ independent of chemical reactions. So the error is small or negligible. The error is maximum when \( \mathcal{L} = 1 \), i.e. under conditions where the rate of complex formation and dissociation is the same as that of diffusion.
The metal flux, in a solution where $[ML]/[M] >> 1$, depends on the degree of lability, $\xi$, of ML, as defined in [10,11]. It can be computed by [12]:

$$\xi = \frac{1 - \frac{[ML]^0}{[ML]}}{1 - \frac{[M]^0}{[M]}}$$

(8.9)

where the superscript $^0$ denotes the surface concentrations of M and ML. Fig 8.5 shows the error on the degree of lability as functions of $D_{ML}/D_M$ and $\mu/\delta$. It can be seen that as expected, the trends of errors on lability degrees are the same as those on total fluxes.

Figure 8.5. Contour plots of the relative errors (fraction of 1) on the degree of lability, $\xi$, given by FLUXY-RS, due to the assumption of ligand excess. a: $[ML]/[L] = 61.5$, b: $[ML]/[L] = 9.89$, c: $[ML]/[L] = 1.00$, d: $[ML]/[L] = 0.10$, $K = 10^7 \text{M}^{-1}$, $D_M = 7 \times 10^{-10} \text{m}^2\text{s}^{-1}$, $D_L = D_M$. 
8.5 Application of FLUXY to mixtures of simple ligands in culture media

An example of application of FLUXY to metal flux computation in culture medium, in which a large number of successive complexes are formed with simple ligands, is given below. A culture medium based on Aquil [19] has been chosen, in which EDTA is replaced by citrate. At the chosen pH (pH = 8) and concentration, Fe(III) is complexed by citrate, but the trace metals are in majority bound to inorganic anions. The composition of the medium is given in Table 8.2, and the species distribution of the metals, computed by MINTEQ2 [27] is given in Table 8.3.

### Table 8.2. The composition of the test culture medium. T= 25°C, I=0.576, pH=8

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (M)</th>
<th>Component</th>
<th>Concentration (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.4801</td>
<td>Cl</td>
<td>0.556</td>
</tr>
<tr>
<td>Mg</td>
<td>0.0546</td>
<td>SO₄</td>
<td>0.0288</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0105</td>
<td>CO₃</td>
<td>0.00283</td>
</tr>
<tr>
<td>K</td>
<td>0.01023</td>
<td>Br</td>
<td>8.40 10⁻⁴</td>
</tr>
<tr>
<td>Sr</td>
<td>6.38 10⁻⁵</td>
<td>H₃BO₃</td>
<td>4.85 10⁻⁴</td>
</tr>
<tr>
<td>Fe</td>
<td>4.51 10⁻⁷</td>
<td>NO₃</td>
<td>1.00 10⁻⁴</td>
</tr>
<tr>
<td>Mn</td>
<td>2.3 10⁻⁸</td>
<td>F</td>
<td>7.14 10⁻⁵</td>
</tr>
<tr>
<td>NH₄</td>
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</tr>
<tr>
<td>Cd</td>
<td>5 10⁻¹⁰</td>
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</tbody>
</table>

### Table 8.3. Species distribution of Pb, Cd and Zn in the test culture medium, as determined by MINTEQ2. Each column of metal distribution gives the proportion (in %) of metal species with respect to the total metal concentration. T= 25°C, I=0.576, pH = 8. The values of stability constants used are those of [23], by using a correcting factor b = 0.2 in the Davies equation. Total metal concentrations : see table 8.2

<table>
<thead>
<tr>
<th>Component</th>
<th>Pb (%)</th>
<th>Cd (%)</th>
<th>Zn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free metal ion</td>
<td>3.885</td>
<td>4.98</td>
<td>55.0</td>
</tr>
<tr>
<td>MOH</td>
<td>2.08</td>
<td>0.0131</td>
<td>1.83</td>
</tr>
<tr>
<td>M(OH)₂</td>
<td>0.17</td>
<td>0.0131</td>
<td>1.60</td>
</tr>
<tr>
<td>MCl</td>
<td>15.0</td>
<td>48.2</td>
<td>17.7</td>
</tr>
<tr>
<td>MCl₂</td>
<td>8.35</td>
<td>38.8</td>
<td>4.03</td>
</tr>
<tr>
<td>MCl₃</td>
<td>3.10</td>
<td>6.28</td>
<td>93.6</td>
</tr>
<tr>
<td>MCl₄</td>
<td>1.21</td>
<td>0.28</td>
<td>1.13</td>
</tr>
<tr>
<td>MSO₄</td>
<td>1.63</td>
<td>1.02</td>
<td>9.20</td>
</tr>
<tr>
<td>M(SO₄)₂</td>
<td>0.13</td>
<td>1.76</td>
<td>1.18</td>
</tr>
<tr>
<td>CO₃</td>
<td>62.5</td>
<td>0.194</td>
<td>5.13</td>
</tr>
<tr>
<td>Br</td>
<td>0.0373</td>
<td>0.135</td>
<td>0.00895</td>
</tr>
<tr>
<td>NO₃</td>
<td>0.00123</td>
<td>0.000336</td>
<td>0.00295</td>
</tr>
<tr>
<td>F</td>
<td>0.0048</td>
<td>0.00069</td>
<td>0.0096</td>
</tr>
<tr>
<td>Citrate</td>
<td>0.00269</td>
<td>0.000702</td>
<td>0.0935</td>
</tr>
<tr>
<td>PO₄</td>
<td>0.000675</td>
<td>0.00348</td>
<td></td>
</tr>
</tbody>
</table>
For each complex, the values of the association rate constants were computed as explained in chapter 6. Their values and those of thermodynamic stability constants and diffusion coefficients are listed in Table 8.4.

**Table 8.4.** Association rate constants and diffusion coefficients used in the modified AQUIL culture medium. Association rate constants are computed by using the generalized Eigen mechanism as explained in chapter 6. Diffusion coefficients are also taken from chapter 6.

<table>
<thead>
<tr>
<th>Species</th>
<th>$k_a$ (M$^{-1}$s$^{-1}$)</th>
<th>$D$ (m$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOH</td>
<td>6.05 $10^9$</td>
<td>3.55 $10^7$</td>
</tr>
<tr>
<td>Cl</td>
<td>1.78 $10^8$</td>
<td>5.22 $10^9$</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>7.86 $10^7$</td>
<td>2.62 $10^9$</td>
</tr>
<tr>
<td>Cl$_3$</td>
<td>3.33 $10^7$</td>
<td>1.19 $10^9$</td>
</tr>
<tr>
<td>Cl$_4$</td>
<td>4.97 $10^8$</td>
<td>1.27 $10^8$</td>
</tr>
<tr>
<td>CO$_3$</td>
<td>1.10 $10^{10}$</td>
<td>1.27 $10^8$</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>6.34 $10^8$</td>
<td>1.15 $10^{10}$</td>
</tr>
</tbody>
</table>

It has been shown elsewhere [16] that, in solution with only one ML complex, the metal flux computed by FLUXY-RS and FLUXY-RLA provide the same results, irrespective of the value of the chemical rate constants and diffusion coefficients values. This has been checked again for Zn (whose association rate constant and stability constants have intermediate values in the series of typical trace metals) and the multicomponent system of Table 8.2. For that purpose, all constants of ZnL$_n$ (n>1) complexes have been taken as zero, since FLUXY-RS can only deal with 1/1 ML complexes. Comparison of the fluxes obtained by FLUXY-RS, FLUXY-RLA and MHEDYN is given in Table 8.5. It can be seen that, as expected, the three computation modes provide the same results.

**Table 8.5.** Comparison of the fluxes of Zn(II) computed by FLUXY-RLA, FLUXY-RS and MHEDYN, for the solution of Table 8.2, in which only 1/1 ML complexes are considered. Total metal concentrations and pH: see table 8.2

<table>
<thead>
<tr>
<th>Components</th>
<th>Individual flux (mol.cm$^{-2}$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>FLUXY-RLA</td>
</tr>
<tr>
<td>Zn</td>
<td>8.71 $10^{-15}$</td>
</tr>
<tr>
<td>ZnOH</td>
<td>2.79 $10^{-16}$</td>
</tr>
<tr>
<td>ZnCl</td>
<td>4.49 $10^{-15}$</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>1.45 $10^{-15}$</td>
</tr>
<tr>
<td>ZnCO$_3$</td>
<td>8.04 $10^{-16}$</td>
</tr>
</tbody>
</table>

Table 8.6 provides the total metal flux by considering all successive complexes ML$_n$ ∀n, for Pb, Cd, and Zn, computed by FLUXY-RLA and MHEDYN. Only the metal complexes whose proportion is larger than 1% of the total metal concentration are listed in the table, because they are the only ones which contribute significantly to the total flux. Table 8.6 shows that the results of FLUXY-RLA and MHEDYN are in good agreement. The average differences in individual fluxes are 0.31%, 0.27% and 3.0% for Pb, Cd and Zn respectively. So under the conditions used, FLUXY-RLA satisfactorily computes fluxes in multicomponent systems, even in presence of significant contributions of successive complexes. This is in agreement with the results of Figs 8.2 and 8.3.
Table 8.6. Individual contributions of Pb, Cd and Zn species to the corresponding total metal fluxes at a consuming interface under condition of maximum flux, in the culture medium detailed in Table 1. Total concentrations: Pb: 2 × 10^{-9} M; Cd: 5 × 10^{-10} M; Zn: 4 × 10^{-9} M. Parameters: see Table 8.4

<table>
<thead>
<tr>
<th>Components</th>
<th>Pb</th>
<th>Cd</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fluxy-RLA</td>
<td>MHEDYN</td>
<td>Fluxy-RLA</td>
</tr>
<tr>
<td>M</td>
<td>3.43 × 10^{-16}</td>
<td>3.43 × 10^{-16}</td>
<td>8.77 × 10^{-17}</td>
</tr>
<tr>
<td>MOH</td>
<td>1.81 × 10^{-16}</td>
<td>1.80 × 10^{-16}</td>
<td>2.29 × 10^{-16}</td>
</tr>
<tr>
<td>M(OH)₂</td>
<td>5.50 × 10^{-15}</td>
<td>5.42 × 10^{-15}</td>
<td>6.60 × 10^{-16}</td>
</tr>
<tr>
<td>MCl</td>
<td>1.58 × 10^{-15}</td>
<td>1.58 × 10^{-15}</td>
<td>1.33 × 10^{-15}</td>
</tr>
<tr>
<td>MCl₂</td>
<td>8.82 × 10^{-16}</td>
<td>8.81 × 10^{-16}</td>
<td>1.07 × 10^{-15}</td>
</tr>
<tr>
<td>MCl₃</td>
<td>3.27 × 10^{-16}</td>
<td>3.26 × 10^{-16}</td>
<td>1.74 × 10^{-16}</td>
</tr>
<tr>
<td>MCl₄</td>
<td>1.27 × 10^{-16}</td>
<td>1.27 × 10^{-16}</td>
<td>2.35 × 10^{-16}</td>
</tr>
<tr>
<td>MSO₄</td>
<td>1.44 × 10^{-16}</td>
<td>1.44 × 10^{-16}</td>
<td>1.80 × 10^{-17}</td>
</tr>
<tr>
<td>M(SO₄)₂</td>
<td>1.53 × 10^{-16}</td>
<td>1.53 × 10^{-16}</td>
<td>1.53 × 10^{-16}</td>
</tr>
</tbody>
</table>

8.6 Application of FLUXY to Cu-Fulvic complexes

8.6.1 Basic complexation relationships, between metal and fulvics

Experimental results [1,25,26] and former simulations [17,18] have shown that fulvic substances are a major group of ligands for Cu(II) and other trace metals and that their metal complexes may be major contributors to the total metal flux at a consuming interface. Metal-fulvic complexes can be treated as 1/1 complexes. However fulvics contain a large number of different types of complexing sites, some of them, usually the strongest ones, being at very small concentrations. Thus the condition of ligand excess is not necessarily fulfilled for all the complexing sites. In this section we examine under which conditions FLUXY is applicable to fulvics.

Table 8.7. Parameters used for computation of the Cu(II) flux in presence of fulvic acids. Cases A and B correspond to different values of pH and ratios of [Cu]/[FS] (Parameters taken from [17]). T=25°C, Ionic strengh =0.01M.

<table>
<thead>
<tr>
<th>Input parameters</th>
<th>Case A</th>
<th>Case B</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>[Cu]₀ (M)</td>
<td>10^{-6}</td>
<td>10^{-8}</td>
</tr>
<tr>
<td>{FS}ₗ (mg C/L)</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Ψ (mV)</td>
<td>-78</td>
<td>-114</td>
</tr>
<tr>
<td>δ(μm)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>kₐ (m³mol⁻¹s⁻¹)</td>
<td>1.92 × 10⁷</td>
<td>3.31 × 10⁷</td>
</tr>
<tr>
<td>D_{FS} (m²s⁻¹)</td>
<td>2.50 × 10⁻¹⁰</td>
<td>2.80 × 10⁻¹⁰</td>
</tr>
<tr>
<td>Γ</td>
<td>0.63</td>
<td>0.52</td>
</tr>
<tr>
<td>logK₀⁺</td>
<td>5.06</td>
<td>8.04</td>
</tr>
<tr>
<td>logK⁺</td>
<td>6.2</td>
<td>13.2</td>
</tr>
</tbody>
</table>

The physico-chemical bases and parameters required to compute the metal flux in presence of fulvic/humic substances have been discussed in details in chapter 6 and will not be repeated.
here. The influence of fulvics on the Cu(II) flux is discussed below, under conditions which have already been used with MHEDYN [17], to enable an easier comparison of the results of FLUXY with rigorous fluxes (MHEDYN). The conditions used for these computations (Table 8.7) are representative of typical environmental conditions.

8.6.2 Results

Figures 8.6a-b and 8.7a-b show the results of flux computations for two tested experimental conditions: pH = 6 and [Cu] = 10^{-6} M (Fig. 8.6, case A) and pH = 8 and [Cu] = 10^{-8} M (Fig. 8.7, case B). Since {FS} = 5 mg C/L for both cases A and B, [Cu]/{FS} is smaller for case B than for case A. This condition combined to higher pH leads to stronger complexes for case B than for case A. In each case, the value of $K^*$, obtained from eq. A2.1.3, is given as a reference value. The property of $K^*$ is such that the site $j$, for which $jK = K^*$, is half-saturated. Thus all sites for which $jK < K^*$ are such that $[jL] > [MjL]$ (excess of ligand), whereas for $jK > K^*$, $[jL] < [MjL]$ (non excess of ligand). It can thus be expected that FLUXY should work correctly at $K$ values lower than $K^*$ whereas errors in flux computation may occur at $jK > K^*$.

Figures 8.6a and 8.7a provide the individual fluxes due to each type of fulvic complex, $MjL$, as function of $log jK$, computed by MHEDYN ($J_{MHEDYN}$), FLUXY-RLA ($J_{RLA}$) and FLUXY-RS ($J_{RS}$). They also provide the ratio of the surface to bulk concentrations of the corresponding ligands $[L]$, $[L]^0/[L]^*$, computed by MHEDYN. Figures 8.6b and 8.7b gives the degree of lability of the $MjL$ complexes as function of $log jK$, computed by MHEDYN, FLUXY-RLA and FLUXY-RS.

Let’s first discuss the case A (Fig. 8.6a-b). As expected, Fig. 8.6a shows that $[L]^0/[L]^*$ becomes larger than 1 when $jK > K^*$. Nevertheless, $J_{RLA}$ and $J_{RS}$ correspond to $J_{MHEDYN}$ up to $log jK = log K^* + 1$. This is because under the conditions used, complexes are fully labile for $log jK < log K^* + 1$ (Fig. 8.7b). As we have seen in section 8.4.2.2., when complexes are fully labile, the flux is independent of chemical reactions and correct diffusion fluxes are computed by FLUXY-RLA and FLUXY-RS, irrespective of $[L]^0/[L]^*$. For $log jK > log K^* + 1$, the complexes $MjL$ become non labile (Fig. 8.6b, results of Mhedyn), but nevertheless sufficiently reactive to produce a large value of $[L]^0/[L]^*$ (Fig. 8.6a). Then the chemical reaction rates at interface, computed by FLUXY-RS or FLUXY-RLA, with the assumption...
[^L]_0 = [^L]^*, is not valid and wrong results are obtained for \(^1J_{RS}, \(^1J_{RLA} \) (Fig. 8.6a), \(^1J_{RS} \) and \(^1J_{RLA} \) (Fig. 8.6b). However it is important to note that, even though the errors on individual fluxes for \(\log K > \log K^*+1 \) are large, the error on the total flux of the whole of fulvic complexes remains small because the contributions of all the values of \(J \) for sites with \(\log K > \log K^*+1 \), is rather small (~10% of total flux).

In case B (Fig. 8.7a-b), the correct degree of lability of complexes (\(\xi_{MHDYN} \), Fig. 8.7b) is rather low (from \(10^{-7} \) to 0.2) in the whole range of \(\log K \) and very low (\(10^{-7} \) to \(10^{-8} \)) in the domain of \(\log K \) where \([^L]^* \) is not in excess. Thus, in this domain, only a small to very small fraction of each complex type is consumed at the interface, and \([^L]_0/[^L]^* \) ~1 for all sites (Fig. 8.7b). Under such conditions, the computations with FLUXY-RS provide the same results as with MHDYN (Fig. 8.7a) for all sites. FLUXY-RLA on the other hand gives wrong results, in the whole range of \(J \). The reason for this is discussed in [16]: in real solutions, when the test chemical system includes several complexes with reaction layer thicknesses close to each other, a coupling of the various chemical kinetics occurs and influences the overall flux. This effect is taken into account in the rigorous solution of FLUXY (FLUXY-RS), but not in the reaction layer approximation (FLUXY-RLA).

In conclusion, FLUXY-RS can be used to compute fluxes of metal in presence of fulvics, in particular when the degree of lability of all complexes is smaller than 0.1, even though the condition of ligand excess is not fulfilled for the strongest fulvic complexes. For larger degrees of lability, FLUXY can also be used, but with caution. In particular it is only applicable to fulvic complexes with \(\log K > \log K^*+1 \). In all cases FLUXY-RS is more appropriate than FLUXY-RLA for fulvic complexes.

8.7 Application of Fluxy to metal complexes with aggregates.

8.7.1 Simulation conditions.

Contrarily to complexes formed with simple and fulvic ligands, the low values of diffusion coefficients and the broad size distribution of metal complexes formed at the surface of natural solid particles or aggregates (Fig. 8.1) play crucial roles in the metal flux at the
consuming interface. It is worth noting that, even though these factors are irrelevant for computations of thermodynamic metal species distribution in solution, they are of major importance for flux computations. In addition, the effective chemical kinetics of metal complex formation/dissociation also depends on the particle/aggregate size, as explained in chapter 6:

\[
\frac{k_a}{k_{a,eff}} = \frac{k_a}{1 + \frac{[S]}{A_{n,t}} / \frac{\Delta A_j}{\Delta A_{i,j}}} = \frac{k_a}{1 + \frac{\Theta}{4\pi j r D_{M}^{-1} c_p}}
\]

(8.10)

where \( k_a \) is the inherent association rate constant, \([S]_t\) is the total site concentration, \( \Delta A_j/\Delta A_{i,j} \) is the surface area proportion of size class \( j \), \( j r \) is the radius of aggregates, \( D_{M} \) is the diffusion coefficient of free metal ion, \( j c_p \) is the number concentration of aggregates in size class \( j \). The size distribution functions of diffusion coefficients and chemical kinetics of particles/aggregates and their complexes are thus of key importance for flux computation. They can be evaluated as explained in details in chapter 6.

Aquatic ‘particles’ are often aggregates of inorganic colloids and organic biopolymers in various proportions. They can be seen as fractal aggregates (with fractal dimension \( D_f \)), including a major component (major in proportion), on which minor components may be adsorbed [18] (chapter 6). Below, it is supposed that only the minor component, \( X \), is complexing and that it is chemically homogeneous, i.e. with only one type of complexing sites forming 1/1 complexes [29] with the test trace metals (Cu(II), Zn(II) and Ni(II) (cases A, B and C below).

**Table 8.8.** Parameters used and computed total fluxes for metal flux simulations with particles/aggregates; \( T=25^\circ C \), \( I=0.01 \text{ M} \), \( \delta = 21 \mu \text{m} \). \( K' \) is the apparent stability constant at pH=8 and under the conditions used; it is expressed as \( K'=[ML]/[M][L] \). \( K' \) values correspond to those reported for metal complexes with river particles in [5]. \( \Psi = 0 \text{ mV} \). Due to the different diffusion coefficients of each size class, the intrinsic association rate constant, \( k_a \), computed with the generalized Eigen mechanism, slightly varies from class to class, for Cu(II) and Zn(II). So an average value of \( k_a \) is given in the table for cases A, and B. The ranges of \( k_a \) values are: \( 2.824 \times 10^8 \text{ to } 2.848 \times 10^8 \text{ M}^{-1}\cdot\text{s}^{-1} \) (case A) and \( 9.933 \times 10^6 \text{ to } 9.936 \times 10^6 \text{ M}^{-1}\cdot\text{s}^{-1} \) (case B).

<table>
<thead>
<tr>
<th>Input parameters</th>
<th>Case A (Cu)</th>
<th>Case B (Zn)</th>
<th>Case C (Ni)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([M]_{r,1}^\ast ) (M)</td>
<td>(10^8)</td>
<td>(10^8)</td>
<td>(10^8)</td>
</tr>
<tr>
<td>([L]_{r,1}^\ast ) (M)</td>
<td>(1.66 \times 10^{-6})</td>
<td>(1.66 \times 10^{-6})</td>
<td>(1.66 \times 10^{-6})</td>
</tr>
<tr>
<td>{X}^\ast_{r,1} (mg/L)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>{P}^\ast_{r,1} (mg/L)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>pH</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>( r_{\min} ) (nm)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>( r_{\max} ) (nm)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
</tr>
<tr>
<td>( \log K' )</td>
<td>9.43</td>
<td>6.45</td>
<td>6.35</td>
</tr>
<tr>
<td>( b ) (nm)</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>( \beta )</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>( D_f )</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>( k_a ) (M^{-1}.s^{-1})</td>
<td>2.836 \times 10^8</td>
<td>9.935 \times 10^6</td>
<td>9.97 \times 10^3</td>
</tr>
</tbody>
</table>
In the following simulation, the fluxes of Cu(II), Zn(II) and Ni(II) complexes with fractal aggregates of river suspended matter are considered. The width of class, \( \Delta \log D = \Delta \log r = 0.097 \) was chosen, corresponding to 26 size classes in the whole size range covered (3-1000 nm). Values of \( \log K' \) (Table 8.8) are taken from chapter 6. The other physicochemical conditions and parameters given in Table 8.8 are typical values, as discussed in chapter 6. Note that in all cases, there is an excess of ligand compared to metal.

### 8.7.2 Results

Figures 8.8, 8.9 and 8.10 show the changes of \( j \Theta \), of lability degree, \( j \xi \), and of the individual contribution of each complex to the total flux, \( j J/J_t \), for Cu(II) (Fig. 8.8), Zn(II) (Fig. 8.9) and Ni(II) (Fig. 8.10), as function of the size class \( j \). \( J_t \) is the total flux, i.e. the sum of all contributions including that of free metal ion. The curves of \( j J/J_t \) obtained both by MHEDYN and FLUXY-RS are given for comparison in the three cases. Very good agreement is obtained between the two codes, in all cases. The agreement between MHEDYN and FLUXY-RS was good for Zn(II) but not for Cu(II) and Ni(II) (Figs. 8.8b, 8.9b, 8.10b). The reason is the same as for computation with fulvic complexes. Zn(II) complexes are labile (all \( j \xi \) values are equal to 1), and under such conditions MHEDYN and FLUXY-RS give the same results. On the other hand, the Cu(II) and Ni(II) systems are not labile and include many complexes with similar reaction layer thicknesses. As discussed in [16] under such conditions, FLUXY-RLA can only provide rough approximations of the fluxes. The correct results given by FLUXY-RS (and MHEDYN) for the three complementary cases of Cu(II), Zn(II) and Ni(II) are discussed below.

**Cu(II)-aggregate complexes (Fig. 8.8a)**

In that case, \( j \Theta \) is much larger than 1 for all \( j \). This implies (chapter 6) that the chemical reaction of M with the aggregate site is not rate limiting (\( k_a \) cancels in eq. 8.10) and diffusion inside and outside the aggregate is the only limiting rate process for the formation/dissociation of the complexes. Thus diffusion inside and outside the aggregate imposes a very low value to the effective rate constant, \( k_a^{\text{eff}} \), as well as to the effective degree of lability of the complexes (\( j \xi \leq 1 \)).
In other words, the supply of Cu(II) at the consuming interface, by the release of Cu(II) from the Cu(II)-aggregate complexes is small. Indeed, the sum of the contributions of all aggregate complexes to the total flux \(2.15 \times 10^{-13} \text{ mol.m}^{-2}.\text{s}^{-1}\) is much lower than the corresponding flux which would be obtained if all complexes were fully labile \(5.82 \times 10^{-12} \text{ mol.m}^{-2}.\text{s}^{-1}\).

**Ni(II)-aggregate complexes (Fig. 8.9a)**

In that case, \(\Theta \ll 1 \forall j\), largely due to the fact (eq. 8.10) that, for this metal, \(k_a\) is small (Table 8.8). Thus \(k_a^{\text{eff}} = k_a\), and diffusion inside/outside the aggregate, does not play a role on the flux, as for simple ligands. The degree of lability, \(\xi\), of complexes is much lower than 1 due to the low value of \(k_a\). Interestingly, \(\xi\), increases with the aggregate size. This is due to the fact that, because of the slower diffusion coefficient of the aggregate, the number of formation/dissociation reactions of a given complex, during its diffusion towards the interface, increases. Thus, for small size aggregates, \(J\) is controlled by \(k_a^{\text{eff}} = k_a\) and is independent of size, while for larger sizes, \(\xi \rightarrow 1\), the complexes become labile and \(J\) is then controlled by the diffusion coefficient (i.e. the size) of these complexes.

**Zn(II)-aggregate complexes (Fig. 8.10a)**

This is an intermediate case, in the sense that \(\Theta\) takes values varying from much smaller than 1 for small size aggregates to much larger than 1 for large size aggregates. This implies that \(k_a^{\text{eff}}\) takes values equal to \(k_a\) (eq. 8.10) for small size aggregates, and values controlled by the diffusion around the aggregate, for large size aggregates. However, in all cases, both \(k_a^{\text{eff}}\), and the dissociation rate constant \(k_d = k_a^{\text{eff}}/K'; K' = \text{stability constant}\) are large enough for the degree of lability, \(\xi\), of all complexes at the consuming interface to be equal to 1. Thus all complexes are fully labile, and the individual fluxes, \(J\) are independent of \(k_a^{\text{eff}}\) and only controlled by the diffusion coefficient of the complex \(j\). Indeed, the sum of all contributions of Zn\(n\) L complexes \(3.87 \times 10^{-11} \text{ mol.m}^{-2}.\text{s}^{-1}\) is very close to the flux, \(J_{\text{lab}} = 4.54 \times 10^{-11} \text{ mol.m}^{-2}.\text{s}^{-1}\), which can be computed by assuming that all complexes are fully labile.
8.8 Flux comparison and general discussion.

Table 8.9 compares the total fluxes, computed in the case studies of sections 8.5 (modified AQUIL medium), 8.6 (fulvic complexes) and 8.7 (aggregate complexes), to the proportion of free M bulk concentration in each case and the contributions of free M and complexes to the total flux. In Table 8.9, \( J_{t}^{nc} \) is the total flux which would be obtained in absence of complexant. Note that both \( J_{t} \) and \( J_{t}^{nc} \) are maximum fluxes (see introduction), i.e. fluxes corresponding to very fast internalisation process of M (Fig. 8.1). Thus \( J_{t}/J_{t}^{nc} \) is a measure of the resistance to metal uptake due to the slower diffusion of metal complexes compared to M, and to slow dissociation kinetics of the complexes. For fully inert complexes, it is expected that \( J_{t}/J_{t}^{nc} \) should be equal to the bulk value of \([M]/[M]_{t}\).

### Table 8.9. Comparison of the total metal fluxes, \( J_{t} \), computed in the case studies presented in this paper, with the corresponding permeabilities, \( P = J_{t}/[M] \) (cm.s\(^{-1}\)), and the limiting fluxes obtained in non complexing medium, \( J_{t}^{nc} ([M] = [M]_{t}) \). All fluxes are in mol.cm\(^{-2}\).s\(^{-1}\). In the culture medium, \( J_{t}/J_{t}^{nc} \) is larger than 100% for Pb and Cd, because the diffusion coefficients of their chloro complexes are larger than that of free metal ion.

<table>
<thead>
<tr>
<th></th>
<th>[M](_{t}) (M)</th>
<th>( J_{t} ) (mol.cm(^{2}).s(^{-1}))</th>
<th>([M]/[M]_{t})</th>
<th>( J_{t}/J_{t}^{nc} )</th>
<th>( P ) (cm.s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Culture medium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>( 2 \times 10^{-9} )</td>
<td>( 9.00 \times 10^{-15} )</td>
<td>0.039</td>
<td>1.02</td>
<td>0.116</td>
</tr>
<tr>
<td>Cd</td>
<td>( 5 \times 10^{-10} )</td>
<td>( 2.67 \times 10^{-15} )</td>
<td>0.050</td>
<td>1.52</td>
<td>0.107</td>
</tr>
<tr>
<td>Zn</td>
<td>( 4 \times 10^{-9} )</td>
<td>( 1.47 \times 10^{-14} )</td>
<td>0.550</td>
<td>1.15</td>
<td>6.68 \times 10^{-4}</td>
</tr>
<tr>
<td><strong>Fulvic complexes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu pH6</td>
<td>( 1 \times 10^{-6} )</td>
<td>( 1.73 \times 10^{-12} )</td>
<td>0.263</td>
<td>0.518</td>
<td>6.58 \times 10^{-4}</td>
</tr>
<tr>
<td>Cu pH8</td>
<td>( 1 \times 10^{-8} )</td>
<td>( 4.53 \times 10^{-17} )</td>
<td>5.1 \times 10^{-6}</td>
<td>0.0014</td>
<td>0.890</td>
</tr>
<tr>
<td><strong>Aggregate complexes</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>( 1 \times 10^{-8} )</td>
<td>( 3.34 \times 10^{-17} )</td>
<td>2.1 \times 10^{-4}</td>
<td>0.0010</td>
<td>1.58 \times 10^{-2}</td>
</tr>
<tr>
<td>Ni</td>
<td>( 1 \times 10^{-8} )</td>
<td>( 6.97 \times 10^{-15} )</td>
<td>0.211</td>
<td>0.207</td>
<td>3.30 \times 10^{-4}</td>
</tr>
<tr>
<td>Zn</td>
<td>( 1 \times 10^{-8} )</td>
<td>( 6.15 \times 10^{-15} )</td>
<td>0.175</td>
<td>0.187</td>
<td>3.51 \times 10^{-4}</td>
</tr>
</tbody>
</table>
Table 8.9 also provides the values of the permeability, \( P = \frac{J_t}{[M]} \), which enables to perform simple comparisons with metal flux under FIAM conditions [6]. Since in our case, the membrane is not rate limiting, \( P \) is controlled only by diffusion and chemical reactions in solution. Then, for inert or immobile complexes at planar consuming interfaces, \( P = P_i = \frac{D_M}{\delta} \), i.e. under our conditions, \( P_i = 3.5 \times 10^{-3} \) cm.s\(^{-1}\) (using an average value of \( D_M = 7.10^{-6} \) cm\(^2\).s\(^{-1}\) for all cations); for labile or semi-labile complexes, \( P \) should be \( > P_i \). When membrane processes are rate limiting (FIAM or BLM models), \( P \) is much lower than \( 10^{-2} \) cm.s\(^{-1}\) [6] (often by a few orders of magnitude). Table 8.9 shows that indeed in our case \( P \geq P_i \) in all cases and consequently, the fluxes computed here are significantly larger than those which would be computed under FIAM or BLM conditions, as expected for maximum fluxes.

Table 8.9 enables to compare a few different types of metal complexes, representative of natural water conditions, with respect to their contribution to metal flux:

Pb and Cd in Aquil medium are strongly complexed by simple ligands, forming labile complexes (\( J_t/J_{tnc} \sim 1 \)), which all contribute to the flux (\( P >> P_i \)).

Zn in Aquil medium and Cu in fulvic solution at pH = 6, form labile but not very stable complexes, i.e. the proportion of free metal ion is large (55% and 26% respectively). In addition the diffusion of fulvic complexes is significantly slower than that of free M. Thus, in both cases, the contribution of free M play a major role on the total flux. The non negligible contribution of the complexes is reflected by the larger value of \( J_t/J_{tnc} \) with respect to \( [M]/[M]_t \), but the dominant role of free M explains a value of \( P \) close to \( P_i \).

Cu in fulvic solution at pH = 8 forms very stable, non labile complexes. As a consequence, the absolute contribution of these complexes to the flux is very small (\( J_t/J_{tnc} \ll 1 \)). On the other hand, the fact that \( P >> P_i \), shows that the relative contribution of the complexes to \( J_t \), is much larger than that of free M, whose proportion is indeed very low ([M]/[M] = 5 \times 10^{-6}).

For the aggregate complexes of Cu, Ni and Zn, \( J_t/J_{tnc} \ll 1 \) and \( J_t/J_{tnc} \sim [M]/[M]_t \). In addition, \( P \sim P_i \). All this indicates that these complexes behave as fully inert (close to fully inert for Cu) and/or immobile complexes, and that free M is the only (almost only for Cu) contributor to the total flux. The difference in \( J_t \) for Cu compared to Ni and Zn, is largely due to the larger stability of Cu complexes, i.e. its lower \([M]/[M]_t\) value. The reason for the non contribution of the complexes to the flux is however different for the three metals: Cu complexes are non labile because of slow diffusion inside/outside aggregates, Ni complexes are non labile because of the slow kinetics at the reactive sites, and Zn complexes are fully labile, but diffuse much too slowly compared to free M, to contribute significantly to the flux (immobile complexes; Note that in addition to their very low lability, the mobility of Cu(II) and Ni(II) complexes are also very low).

Finally, this chapter shows that in spite of the two assumptions made in FLUXY: i) the requirement of ligand excess compared to metal, and ii) the equilibrium between successive metal complexes, it is applicable in many environmental conditions and can be very useful to understand dynamic speciation in environmental systems. The code is readily applicable to solutions including simple ligands and/or particles/aggregates. FLUXY-RS can also be used with caution in presence of fulvic complexes. FLUXY-RLA is preferable in presence of simple ligands including successive complexes, while FLUXY-RS is preferable in presence of particle/aggregates. Because computations with FLUXY are easy and very quick, it is a useful complementary code to MHEDYN, which does not include any limiting assumption, but may be significantly more computer-time consuming.
8.9 References


[23] Martell, A.E.; Smith, R.M. *NIST Critically Selected Stability Constants of Metal Complexes*, Version 7 (NIST Standard Reference Data: Gaithersburg, MD 20889 USA)


**Chapter 9**

**Metal flux under natural freshwater conditions, at a planar consuming interface: the roles of physico-chemical properties of metals and complexants**

**9.1 Overview**

In this chapter, the fluxes of three metals, Pb(II), Zn(II) and Ni(II), at a planar consuming interface in natural waters, are studied. The system includes a) simple ligands (OH-, CO$_3^{2-}$); b) fulvics and c) aggregates, as complexants, i.e. those which play the major roles in controlling the metal flux in aquatic media. The above three metals are chosen because they participate respectively, to very fast, intermediate and very slow chemical reactions with complexing sites. The effects of the various physico-chemical factors, in particular, diffusion layer thickness, stability constants, complexing site distribution of fulvics and size distribution of aggregates, are studied in detail. Although most computations are performed under planar diffusion conditions, the results under planar and spherical diffusion are compared.

**9.2 Introduction**

As discussed in chapter 1, a natural water is a highly complicated system in which a metal may react with an almost infinite number of complexants whose nature is often highly physically and chemically heterogeneous. The computation of a metal flux, at a consuming interface, in such a complicated mixture, is a difficult task due to the many coupled dynamic physical and chemical processes. It is however possible to take all these processes into account, thanks to computer codes (FLUXY and MHEDYN) which have been developed recently for such purposes. It is the purpose of this chapter to use these codes, in particular MHEDYN which is not based on any a priori assumption, to determine the relative contributions of the various types of natural metal complexes, to its flux towards a consuming interface, such as a microorganism or a bioanalogical sensor.

As discussed in chapter 1, the major natural complexants can be classified into three categories: a) the ‘simple’, small size, organic or inorganic, ligands, such as OH-, CO$_3^{2-}$, citrate, aminoacids, which may form 1/n successive complexes with the metal M. They are often in excess with respect to trace metals; b) the organic macromolecules, often chemically heterogeneous with polyelectrolytic properties, in particular fulvic and humic substances. Their complexing sites usually form 1/1 complexes with metals, with a wide distribution of equilibrium and rate constants, influenced by the negative electric field often born by these macromolecules in circumneutral pH range. Some of these complexing sites are not necessarily in excess compared to trace metals; c) the natural particles or aggregates made of metal oxides (SiO$_2$, alumino-silicates, iron oxides) on which organic macromolecules may be adsorbed. The properties of their surface complexing sites can be modelled via the formation of 1/1 metal complexes also influenced by a surface electric field. The aquatic systems may include many ‘simple ligands’ and the fulvic substances and aggregates include many complexing sites. Thus the computations of this chapter are based on “model” natural waters comprising these three categories of complexants, in order to evaluate their relative importance on the metal flux. In addition, preliminary tests have shown that, under natural conditions, OH$^-$ and CO$_3^{2-}$ are the most important ligands to consider, in the group of simple ligands. Other complexes are usually not stable enough to play a significant role, even though
each specific case (e.g. Cd(II) chloro complexes in sea water) should be considered separately.

9.3 The physical model and the computation method

Flux computations are performed mainly under planar diffusion conditions, based on the computer code MHEDYN (chapter 1, section 1.5.2), which is not restricted by any limiting assumption. FLUXY (chap. 1, section 1.5.1, and chap. 8) is also used for the comparison of fluxes under planar and spherical conditions (section 9.7) For both codes, the mathematical formulation of metal flux at a planar consuming interface in multiligand systems is described in chapter 1 (section 1.4). In this chapter, the initial conditions of section 1.4.2 and the boundary conditions for a perfect sink are used (section 1.4.3.1, chapter 8, [1-3]). In addition, a constant value of the diffusion layer thickness is used (usually 20 μm unless otherwise stated). All the results of this chapter correspond to steady-state fluxes, except for Pb and δ > 100 μm. In these cases the results are close to steady state, but not exactly at steady-state. This reason is due to the fact that for large δ values the computer time required is very long.

The chemical composition of the test water (Table 9.1) is that of a typical freshwater. The trace metal concentrations, [M]t, given in the table are those used unless otherwise stated. It will be seen (section 9.7.1) that the overall degree of lability and metal flux depends on total metal concentration. In the case studies of sections 9.4 (Pb), 9.5 (Zn) and 9.6 (Ni), the typical freshwater concentrations of these metals are used (Table 9.1). It will be seen that under these conditions, the overall lability degrees are in the order Zn > Pb > Ni, even if complexation reaction rates of Pb are usually larger than for Zn. This is largely due to the fact that in these case studies, [Zn]t >> [Pb]t. The effect of [M]t is discussed in section 9.7.1. Other parameters of table 9.1 are the same in all simulations. {P} and {X} are the mass concentrations of the major (non complexing) and minor (complexing) components of the aggregates (see chapter 6, section 6.5 for details). P provides the structure (fractal dimension, Df, see below) and size distribution of the aggregates, while X (adsorbed on P) provides the complexing properties. The stability constants, K’, of the complexes MX, given in the following tables, correspond to those cited in the literature [3] for the three metals considered.

Table 9.1. Chemical composition of the test water used for the simulations. {FS} = C mass concentration of fulvic substances. {P} = mass concentration of the major (non complexing) component of the aggregates, {X} = mass concentration of the minor complexing component of the aggregates.

<table>
<thead>
<tr>
<th>pH</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CO3]t</td>
<td>2 × 10⁻³ M</td>
</tr>
<tr>
<td>{FS}</td>
<td>1.5 mgC/L</td>
</tr>
<tr>
<td>{P}</td>
<td>3 mg/L</td>
</tr>
<tr>
<td>{X}</td>
<td>0.3 mg/L</td>
</tr>
<tr>
<td>[M]t</td>
<td>3 × 10⁻⁹ M (Pb), 10⁻⁷ M (Zn), 5 × 10⁻⁷ M (Ni)</td>
</tr>
</tbody>
</table>

In order to perform flux computations, a large number of parameters related to the properties of the complexes and complexants must be provided to the computer codes. They include stability and association/dissociation rate constants for each complex, the diffusion coefficient of each species, as well as ‘secondary’ parameters, such as ligand electric charge density which influence the stability of complexes or the size distribution and fractal structure of aggregates which influence their diffusion coefficients and internal reactivity. These
parameters are linked to the physico-chemical properties of complexes and complexants through sometimes sophisticated models. The parameter values, or the corresponding computation models, used in this chapter are taken from chapter 6 and Appendix A.1, A.2 and A.3. They will not be described here again in details. We just remind the following key aspects.

- The values of kinetic and thermodynamic parameters correspond to T = 25°C and I = 0.01M
- The intrinsic formation rate constant, \( k_a^{MS} \), of a complex ML with a ligand or a complexing site of fulvics or aggregates is computed based on the generalized Eigen mechanism (section 6.3.3, [2]). The corresponding dissociation rate constant, \( k_d \), is obtained from \( k_d = k_a^{MS}/K \) where \( K \) is the thermodynamic stability constant of the complex.
- The fulvic complexing site distribution is computed from the Sips distribution derived from their Freundlich isotherm:
  \[
  \log \chi_j = \log (\Phi / \sigma) + \Gamma \log K_0^* - \Gamma \log K
  \]  
  (9.1)
  where \( \chi_j \) is the cumulative mole fraction of the site \( n \) of \( j \), \( K \) its stability constant, and \( \Gamma \) and \( K_0^* \) two constant parameters of the Freundlich isotherm. The dissociation rate constant of each site \( j \), \( k_d \), is obtained from \( k_d = k_a^{MS}/K \), where \( k_a^{MS} \) is defined as above (section 6.4.5, [2]).
- The size distribution of aggregates is described by the Pareto law:
  \[
  \frac{d c_p}{dr} = \lambda r^\beta 
  \]  
  (9.2)
  where \( c_p \) is the number concentration of particles/aggregates having an external radius, \( r \), in solution, and \( \lambda \) and \( \beta \) are constants. The diffusion coefficient of each aggregate is related to its radius via the Stokes-Einstein law (section 6.5.2 [3]). In addition, the formation rate constant of a complex with an aggregate site depends on the aggregate size via the equation:
  \[
  \frac{k_{a}^{MS}}{1 + k_a^{MS}[S]/A_{b,i}} = \frac{k_a^{MS}}{1 + \Theta} 
  \]  
  (9.3)
  where \( [S] \) is the total coarse-grained molar concentration of complexing sites, \( A_{b,t} \) is the total surface area of aggregates, \( \Delta A_b \) is the surface area in each size class and \( D_M \) is the diffusion coefficient of free metal ion M.

Below, we shall discriminate between different types of fluxes:
- the total flux, \( J_t \), is the computed metal flux through the interface, which takes into account the contributions of all metal species
- the individual flux, \( J_L \), is the contribution to the total flux, of the single species \( M^IL \), where \( L \) is one type of ligand (or complexing site for fulvics and aggregates)
- the complex type flux, (in general \( J_a \)), is the contribution to the total flux of a homologous group of complexes, namely all hydroxo-complexes, \( J_{OH} \), all carbonato-complexes, \( J_C \), all fulvic complexes, \( J_{FS} \), or all aggregate complexes, \( J_{agg} \)
- The “labile” flux, \( J_{lab} \), is the total flux which would be obtained if all complexes were fully labile, while keeping their own diffusion coefficient. It is readily computed by:
\[ J_{\text{lab}} = \frac{\overline{D}[M]}{\delta} \quad (9.4) \]

Where \( \overline{D} \) is the average diffusion coefficient of all metal species [4], and \([M]\) is the total concentration of M.

- The “inert” flux, \( J_{\text{in}} \), is the total flux which would be obtained if all complexes were fully inert. It is given by:

\[ J_{\text{in}} = \frac{D_M [M]}{\delta} \quad (9.5) \]

where \([M]\) is the bulk free M concentration.

\( J_{\text{in}} \) and \( J_{\text{lab}} \) are two useful reference values of flux, since they are the minimum and maximum possible fluxes which can be obtained under the test conditions, when all chemical reactions are infinitely slow, or infinitely fast respectively.

### 9.4 Pb fluxes in natural waters

#### 9.4.1 Simulation conditions

The definitions and values of parameters used for the simulations are listed in Table 9.2-9.4. For more explanation on the obtention of these values, see detailed discussions in chapter 6 and [2,3]. The values given in tables 9.2 – 9.4 are the default values which are used unless otherwise stated. For specific studies, a given parameter value is varied, while all the others constant, as indicated in the tables.

In Table 9.3, \( K^* \) is the rigorous average values of the stability constants of fulvics with the metal called differential equilibrium function, DEF. Mathematically it is the average value of the stability constants of all sites, \( K_j \), weighted by their mole fraction and degree of occupation (see section 6.4.5). It can be shown [5] that the site \( j \), for which \( K_j = K^* \), is half occupied by the metal, that sites for which \( K_j < K^* \) are little occupied and that those for which \( K_j >> K^* \) are saturated.

In Table 9.4, \( K' \) is the apparent stability constant of Pb with the complexing site of X. In practice, when \( K' \) values are determined experimentally with natural sediment or suspended colloidal matter, the exact nature of the complexing sites is unknown. The complexation reaction is usually treated as a single reaction: \( M + L \rightleftharpoons ML \), where only one (unknown) site is considered (section 6.5.4, [3]). The values of \( K' \) reported in compilations of such data, for river suspended particles, are used here.
Table 9.2. Parameters for simple ligands and complexes. Cumulative protonation constants of CO$_3^{2-}$ are $\log \beta_1 = 10.15$ and $\log \beta_2 = 16.41$.

<table>
<thead>
<tr>
<th>Species</th>
<th>$D$ ($10^{-10}$ m$^2$s$^{-1}$)</th>
<th>$k_a$ (M$^{-1}$s$^{-1}$)</th>
<th>$K$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>52.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_3$</td>
<td>9.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>9.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbOH</td>
<td>9.45</td>
<td>1.69 $10^{10}$</td>
<td>1.06 $10^{6}$</td>
</tr>
<tr>
<td>Pb(OH)$_2$</td>
<td>9.45</td>
<td>4.96 $10^{9}$</td>
<td>9.45 $10^{4}$</td>
</tr>
<tr>
<td>PbCO$_3$</td>
<td>9.45</td>
<td>3.08 $10^{10}$</td>
<td>4.35 $10^{6}$</td>
</tr>
<tr>
<td>Pb(CO$_3$)$_2$</td>
<td>9.45</td>
<td>1.34 $10^{9}$</td>
<td>99.7</td>
</tr>
</tbody>
</table>

Table 9.3. Parameters for fulvic substances and their Pb complexes.

<table>
<thead>
<tr>
<th>${FS}$ (mgC/L)</th>
<th>1.5</th>
<th>Concentration of fulvic substances</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Psi$ (mV)</td>
<td>-84.7</td>
<td>Average value of potential difference inside fulvic molecule at pH=8 and I=0.01</td>
</tr>
<tr>
<td>$D_{FS}$ ($10^{-10}$ m$^2$s$^{-1}$)</td>
<td>2.80</td>
<td>Diffusion coefficient of fulvic substances</td>
</tr>
<tr>
<td>log($K'/M^{-1}$)</td>
<td>10.9</td>
<td>DEF=An average of individual stability constants of all sites, weighted by their mole fraction and degree of occupation</td>
</tr>
<tr>
<td>$k_a$ (M$^{-1}$.s$^{-1}$)</td>
<td>3.00 $10^{10}$</td>
<td>Association rate constant of metal fulvic complexes</td>
</tr>
<tr>
<td>$\sigma$ (mol/kgC)</td>
<td>15</td>
<td>The total density of sites in the FS</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>0.60</td>
<td>The constant representative of the chemical heterogeneity in the linear Freundlich isotherms of Pb-FS complexes</td>
</tr>
<tr>
<td>log $K_0$*(M$^{-1}$)</td>
<td>8.0</td>
<td>The value of $K'$ for Pb-FS complexes, for $[\text{Pb}]/{{FS}}=1\text{mol/KgC}$</td>
</tr>
</tbody>
</table>

Table 9.4. Parameters of aggregates. P is the major component (assumed to be non complexing) of aggregates. It provides the structure and size distribution of aggregates. X is a minor complexing component (e.g. hydrous iron or manganese oxide). $K'$ is the corresponding apparent stability constant, defined as $K' = [ML]/[M][L]$, valid at the test pH (8), ionic strength (0.01 M) and temperature (25°C).

<table>
<thead>
<tr>
<th>${P}$ (mg/L)</th>
<th>3</th>
<th>Major component of aggregates</th>
</tr>
</thead>
<tbody>
<tr>
<td>${X}$ (mg/L)</td>
<td>0.3</td>
<td>Minor complexing component of aggregates</td>
</tr>
<tr>
<td>$r_{\min}$ (nm)</td>
<td>3</td>
<td>The minimum radius of aggregates</td>
</tr>
<tr>
<td>$r_{\max}$ (nm)</td>
<td>1000</td>
<td>The maximum radius of aggregates</td>
</tr>
<tr>
<td>$\beta$</td>
<td>3</td>
<td>Constant exponent in Pareto law</td>
</tr>
<tr>
<td>$D_f$</td>
<td>2</td>
<td>Fractal dimension of aggregates</td>
</tr>
<tr>
<td>$\Psi$ (mv)</td>
<td>pH=8</td>
<td>0</td>
</tr>
<tr>
<td>$\rho_p$ (kg/L)</td>
<td>2.5</td>
<td>Density of major component</td>
</tr>
<tr>
<td>$\rho_x$ (kg/L)</td>
<td>3</td>
<td>Density of minor complexing component</td>
</tr>
<tr>
<td>$n_x$</td>
<td>10</td>
<td>Number of sites per nm$^2$</td>
</tr>
<tr>
<td>$h_x$ (nm)</td>
<td>1</td>
<td>Thickness of minor complexing component</td>
</tr>
<tr>
<td>$b$ (nm)</td>
<td>3</td>
<td>Radius of basic subparticle</td>
</tr>
<tr>
<td>log($K'/M^{-1}$)</td>
<td>8.15</td>
<td>Apparent stability constant of metal with complexing site</td>
</tr>
<tr>
<td>log$k_{-w}$(s$^{-1}$)</td>
<td>9.8</td>
<td>Rate constant for elimination of a water molecule from the inner water shell of metal cations</td>
</tr>
</tbody>
</table>
The computation of Pb species distribution, by Minteq2 (Table 9.5), under the aforementioned conditions, shows that Pb(II) is mainly bound to carbonate, fulvics and aggregates. The proportions of free Pb(II) and hydroxo complexes are very low (< 1%) (Table 9.5). Thus the roles of carbonato-, fulvic and aggregate complexes on the total flux are the most interesting to study.

Table 9.5. Distribution of Pb complexes in typical freshwaters

<table>
<thead>
<tr>
<th>Componentsable</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>3.88e-12</td>
<td>0.13</td>
</tr>
<tr>
<td>PbOH+Pb(OH)₂</td>
<td>5.10e-12</td>
<td>0.17</td>
</tr>
<tr>
<td>PbCO₃+Pb(CO₃)₃</td>
<td>2.11e-10</td>
<td>7.23</td>
</tr>
<tr>
<td>PbFS</td>
<td>1.86e-9</td>
<td>62.00</td>
</tr>
<tr>
<td>Pbaggregates</td>
<td>9.20e-10</td>
<td>30.67</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
</tr>
</tbody>
</table>

9.4.2 Effects of the diffusion layer thickness on the fluxes and the degrees of lability of metal species

Figure 9.1 shows the influence of the diffusion layer thickness, \( \delta \), on the total flux, \( J_t \), and on the complex type fluxes, \( J_c \), in the range 5\( \mu \)m \( \leq \delta \leq 100\mu \)m. Because computer time becomes prohibitively large in systems combining many fast reactions (as with Pb(II)) with large diffusion layer thicknesses, \( \delta \) values larger than 100 \( \mu \)m could not be tested. Fig. 9.1 shows that the value of \( J_t \) is in between \( J_{lab} \) and \( J_{in} \); but, as expected for a metal forming fast complexation reactions, \( J_t \) is significantly closer to \( J_{lab} \). In addition it becomes closer and closer to \( J_{lab} \) when the diffusion layer thickness increases. This is expected, since by increasing \( \delta \), the diffusion time of complexes, inside the diffusion layer, increases. As a result Pb(II) complexes can form and dissociate more often during their diffusion towards the interface. Thus by definition, they become more labile, irrespective of their nature. Nevertheless, not all complex types behave in the same manner (Fig. 9.1), as discussed below.

The Pb(II) complexes with simple ligands (OH\(^-\) or CO\(_3^{2-}\)) are almost fully labile, in the whole range of diffusion layer thicknesses; thus their value of \( J_c \) decreases monotonously by increasing \( \delta \), with a slope very close to –1 in the log-log plot of Fig. 9.1 (eq. 9.4 applied to each considered complex type). Note that the flux of hydroxo complexes is negligible compared to \( J_t \), due to the very low proportion of these complexes in solution (Table 9.5).

For Pb-fulvic complexes, the complex type flux, \( J_{FS} \), decreases slowly when \( \delta \) increases. This is due to the fact that the degree of lability of the stronger complexes increases with \( \delta \), as shown in Figure 9.2a. In other words, the proportion of labile fulvic complexes increase with \( \delta \). This increase partly compensates for the decrease of \( J_{FS} \), due to the smaller concentration gradient (eq. 9.4 applied to labile fulvic complexes), as explained for the hydroxo and carbonato complexes.

For Pb-aggregates, \( J_{agg} \) first slightly increases and then decreases when \( \delta \) increases (Figs. 9.1 and 9.2b). The reason is more easily understood in Fig. 9.2b: at small \( \delta \) values, the Pb-aggregate complexes are non-labile \( (\xi \sim 0.1) \). When \( \delta \) increases, the degrees of lability of all complex aggregates tend to 1. This overcompensates for the decrease of flux due to smaller concentration gradients. At \( \delta \) values larger than 20 \( \mu \)m, almost all Pb-aggregates are fully labile (Fig. 9.2b) and the flux of \( J_{agg} \) tends to become inversely proportional to \( \delta \) (eq. 9.4 for
the group of aggregate complexes). In general, at sufficient large diffusion layer thickness, all the complexes are labile; thus all complex type flux, \( J_{ct} \), are proportional to \( 1/\delta \) and \( J_t = J_{lab} \).

**Figure 9.1.** Total and complex type flux as a function of \( \delta \) and comparison with \( J_{lab} \) and \( J_{in} \) (see section 9.3 for definition, and Tables 9.2-9.4 for parameters).

**Figure 9.2.** Degree of lability and individual fluxes of Pb-fulvic complexes (a) and Pb-aggregate complexes (b). Parameters: see tables 9.2-9.4.

Figure 9.3 is similar to Fig. 9.1, but points out the relative importance of the various complex type fluxes. It shows the change of the proportion of each \( J_{ct} \) with respect to \( J_t \), when \( \delta \) increases. The main contributions to \( J_t \) are from Pb-carbonate and Pb-fulvic complexes. All other contributions are smaller than 2%. At the smallest diffusion layer thickness which is the condition the closest to that at a voltammetric, PLM or microorganism interface (see section 9.7 for a more rigorous discussion), the major contributors to \( J_t \) are the Pb-carbonato-complexes. At the largest diffusion layer thicknesses, which correspond to DGT interfaces (\( \delta > 500 \mu m \)), it can be extrapolated that the major contributor will be the Pb-fulvic complexes.
This is due to the fact that the degree of lability of fulvic complexes increases with $\delta$, whereas, that of carbonato complexes is at its maximum, even at low $\delta$ values.

![Figure 9.3. Proportion of complex type fluxes as a function of $\delta$.](image)

### 9.4.3 Effects of the properties of fulvics on the fluxes and the degree of lability of metal species

The major parameters which control the complexation distribution of a metal by fulvics are $\Gamma$ and $\log K_o^*$ (eq. 9.1); in particular they determine the proportion of fulvic sites in each class of $\log j$. Thus studying the effect of $\Gamma$ and $K_o^*$ on the various metal fluxes is important because the values of these parameters are ill-known and associated to significant errors, and they may also vary from a fulvic sample to another. Studying their influence on metal fluxes thus serve as useful sensitivity analysis for these parameters. The proportion of each complex type (hydroxo-, carbonato-, fulvic and aggregate), in the test water, has first been computed with Minteq2, by using the parameters of Tables 9.2-9.4, but for different values of $\Gamma$ and $K_o^*$. The results (Tables A.5.1a-A.5.1c, A.5.2a-A.5.2c) show that by decreasing $\Gamma$ (at constant $K_o^*$ value) or increasing $\log K_o^*$ (at constant $\Gamma$ value), the proportion of Pb-fulvic complexes increases in the test water, and that the Pb-fulvic complexes are always present in significant proportion (20-100%). The increase of the Pb-fulvic complexes when $\Gamma$ decreases and $K_o^*$ increases is due to the fact that in both cases, the number of sites with large $\log j$ values increases (eq. 9.1). In all cases, the concentration of free Pb remains very low (< 0.26%). Thus, it can be expected that the total flux $J_t$ will be strongly dependent on $\Gamma$ and $\log K_o^*$.

#### 9.4.3.1 Effect of $\Gamma$

As mentioned above, increasing $\Gamma$ at constant value of $K_o^*$ results in a smaller number of sites with large $\log j$ values, and thus with very small $l_{kd}$ values. In addition, a larger $\Gamma$ value also corresponds to a smaller average stability constant for the whole of Pb-fulvic complexes, $K^*$. Based on these two effects, it is expected that the lability of the whole of the fulvic complexes will increase with $\Gamma$. Figures 9.4 and 9.5 show that, when $\Gamma$ increases, $J_t$ is closer and closer
to its labile limit, $J_{\text{lab}}$. At the largest $\Gamma$ value, the $J_{t}$ is $\sim J_{\text{lab}}$. These results point out that the complexes of the test water become more labile. This is confirmed by Fig. 9.5 which shows the distribution of individual fluxes and lability degrees of the fulvic complexes for 3 values of $\Gamma$. For $\Gamma = 0.3$, the number of very strong, inert complexes is much larger than for $\Gamma$ equal to 0.5 or 0.8. Consequently the proportion of complexes in the low $J_{d}$ range (with sufficiently large $J_{d}$ values to provide a non negligible individual flux $J_{t}$) is much lower. In other words, the overall lability degree of fulvic complexes, and consequently their overall flux, $J_{FS}$, is much smaller for $\Gamma = 0.3$ than for the other two values. As a consequence, both $J_{FS}$ and $J_{t}$ increase strongly with $\Gamma$ (Figs. 9.4 and 9.5). The large difference between 0.3 and 0.6 and the small one between 0.6 and 0.8 are related to the respective values of $K^*$. At $\Gamma = 0.3$, log$K^*$=15.4, while for $\Gamma = 0.6$ and 0.8, log$K^*$ are 9.8 and 10.9 respectively which are very close.

**Figure 9.4.** Total flux of Pb, as a function of $\Gamma$ for the test water with parameters of tables 9.2 to 9.4, and comparison with $J_{\text{lab}}$ and $J_{\text{in}}$ $\delta \sim 20\mu$m.

**Figure 9.5.** Individual degrees of lability and fluxes of Pb fulvic species, as a function of log$J_{K}$ for different values of $\Gamma$. Parameters: see Tables 9.2-9.4, $\delta \sim 20\mu$m. The vertical dashed lines correspond to log$K^*$, from left to right: $\Gamma$=0.8, 0.6, 0.3.
The contributions of Pb-fulvics are significant in the whole range of $\Gamma$ as shown in Figure 9.6. In particular, at small $\Gamma$ value, their contribution is close to 100%. The increase of the fluxes of free Pb, aggregate complexes and hydroxo complexes, when $\Gamma$ increases, just reflect the fact that the average stability constant of Pb fulvic complexes, $K^*$, decreases, which implies that the Pb-fulvic complexes decreases, and thus the proportions of the other complexes increase.

**Figure 9.6.** The proportion of complex type fluxes as a function of $\Gamma$, for Pb in the test water. Parameters: see tables 9.2-9.4.

**9.4.3.2 Effect of $\log K_0^*$**

The influence of $K_0^*$ on metal fluxes is just analogous to that of $\Gamma$. Equation 9.1 points out that when the value of $K_0^*$ decreases, the number of sites with large $K$ values, and thus low $k_d$ values, becomes smaller. In addition, smaller $K_0^*$ values correspond to smaller $K^*$ values. Thus, it can be expected that the lability of the whole of Pb-fulvic complexes will decrease when $\log K_0^*$ increases. Figure 9.7 and 9.8 indeed confirm this prediction. The total flux $J_t$ becomes smaller and smaller compared to $J_{lab}$ when $\log K_0^*$ increases (Fig. 9.7), suggesting that the overall system becomes less labile. Fig. 9.8 confirms that this effect is due to the Pb-fulvic complexes.

**Figure 9.7.** Total flux $J_t$ as a function of $\log K_0^*$ and comparison with $J_{lab}$ and $J_{in}$ Parameters: see tables 9.2-9.4, $\delta \sim 20\mu m$. 
Figure 9.8. Individual fluxes and lability degrees of Pb-fulvic complexes, as a function as log\(K\). Parameters: see tables 9.2-9.4, \(\delta \sim 20\mu m\). Vertical dashed lines correspond to log\(K^*\), from left to right: log\(K^*_0 = 5.4, 6.4, 7.4\).

Figure 9.9 shows that the contribution of Pb-fulvic complexes (\(J_{FS}\)) to the total flux is significant in the whole range of log\(K^*_0\), and that its contribution is close to 100% at the largest log\(K^*_0\) values. The increase of \(J_{FS}/J_t\) and the corresponding decrease of \(J_C/J_t\) when log\(K^*_0\) increases largely reflects the changes of the proportions of Pb-fulvic and Pb-carbonato complexes, as shown in Table A.5.2a-c, even though the degree of lability of the Pb-fulvic complexes decreases a bit, but only slightly (Fig. 9.8).

Figure 9.9. Contributions of complex type fluxes (\(J_c\)) to the total flux \(J_t\) as a function of log\(K^*_0\). Parameters: see tables 9.2-9.4, \(\delta \sim 20\mu m\).
9.4.4 Effects of the properties of aggregates on the fluxes and the degrees of lability of Pb-complexes

The variability of the stability constant, \( K' \), of a metal with particles/aggregates is large, due to both experimental difficulties and variability of the nature of aggregates in the sample. The constant parameter \( \beta \) of the Pareto law (eq. 9.2) may also vary from sample to sample, between 2 and 4. The values of these parameters will influence the proportion and size distribution of Pb-aggregate complexes, and thus their complex type flux. In this section, we perform a sensitivity analysis of parameters \( K' \) and \( \beta \), to better understand their role on the Pb fluxes.

9.4.4.1 Effect of log\( K' \)

Figure 9.10 shows the proportion of the whole of Pb-aggregates as a function of log\( K' \), in the test water characterized in Tables 9.1 to 9.4. It shows that the proportion of Pb-aggregates is negligible at the lowest log\( K' \) value and is almost 100% at the largest log\( K' \) value. The change of log\( K' \) strongly affects the total flux, \( J_t \), since even if Pb-aggregates were fully labile, \( J_t \) would decrease when their proportion increases, due to their low mobility (low diffusion coefficient). Indeed Figure 9.11 shows that \( J_t \) decrease when log\( K' \) increases.

![Figure 9.10. Proportion of Pb-aggregate complexes in the test water, as a function of log\( K' \). Other parameters: see tables 9.2-9.4.](image)

Figure 9.11 also shows that the curve of \( J_t \) departs more and more from \( J_{lab} \) when \( K' \) increases. At the lowest \( K' \) value, Pb-aggregate complexes are negligible, and the difference between \( J_t \) and \( J_{lab} \) is mainly due to the fact that the Pb-fulvic complexes are not fully labile. With increasing \( K' \), the Pb-aggregate complexes become more and more important. The decrease of \( J_{lab} \) represents their decrease of mobility compared to the fulvic and carbonato complexes. But the increasing difference between \( J_t \) and \( J_{lab} \) is due to the fact that the Pb-aggregate complexes become less and less labile when \( K' \) increases.
Figure 9.11. Total Pb flux as a function of log\(K'\) and comparison with \(J_{lab}\) and \(J_{in}\). Parameters: see tables 9.2-9.4, \(\delta \sim 20\mu m\).

This is confirmed on Figure 9.12 which shows the individual degrees of lability and fluxes of Pb-aggregate complexes. For log\(K' = 6.15\) and 8.15, the Pb-aggregate complexes are almost fully labile (\(\xi \sim 1\)), while for log\(K' = 10.15\), all Pb aggregate complexes are non labile (\(\xi \leq 0.02\)).

The individual fluxes, \(J_{i}\), increase from log\(K' = 6.15\) to log\(K' = 8.15\), because the proportion of each Pb aggregate complex increases (Fig. 9.10). On the other hand, all \(J_{i}\) decreases again for log\(K' = 10.15\), because the decrease of degree of lability more than overcompensate the further increase of the proportion of Pb-complexes. The net result is a faster decrease of \(J_{i}\) compared to \(J_{lab}\) (Fig. 9.11).

Figure 9.12. Degrees of lability and individual fluxes of Pb-aggregate complexes, as a function of their diffusion coefficients. Parameters: see tables 9.2-9.4, \(\delta \sim 20\mu m\).
Anyway, even when the proportion of Pb-aggregates is large (close to 100% at \( \log K' = 10.15 \)), their contribution to the total flux, \( J_t \), is marginal and always less than 10%. This is visible on fig. 9.11 and confirmed by fig. 9.13 which gives the contribution to \( J_t \) of each complex type. This suggests that, under the conditions used, the contribution of Pb-aggregate complexes may be neglected in flux computations, in environmental system.

![Figure 9.13. Contribution of each complex type flux to \( J_t \) as function of \( \log K' \). Parameters: see tables 9.2-9.4, \( \delta \sim 20\mu m \).](image)

**9.4.4.2 Effect of \( \beta \)**

\( \beta \) does not affect the overall proportion of Pb bound to aggregates, but it influences the size distribution of aggregates and thus their distribution of diffusion coefficients. This may have an impact on the value of \( J_{agg} \) (Figure 9.14). The effect on the total flux is small since \( J_{agg} << J_t \). However, \( \beta \) greatly influences the overall flux of aggregate complexes: its proportion to \( J_t \) increases from 0.2% to 5.72% when \( \beta \) varies from 2 to 4 (Tables A.5.4a-c). As shown in Figure 9.15, \( \beta \) values do not influence the degree of lability, but it influences the proportion of Pb-aggregates in each size class. At \( \beta = 2 \), the proportion of complexes increases with the complex radius, \( r \). This effect compensates for the lower mobility of the larger size complexes, so \( J_t^i \) is independent of the radius, \( r \). For \( \beta = 4 \), the number of complexes in the smaller size classes is much larger than in the large size classes. Combined with the larger mobility of the small size complexes, this effect leads to individual fluxes which largely increase when \( r \) decreases. As a consequence, the overall aggregate flux, \( J_{agg} \), also increases.
Figure 9.14. Contributions of each complex type flux to $J_t$ as a function of $\beta$. Parameters: see tables 9.2-9.4, $\delta \sim 20\mu m$.

Figure 9.15. Individual fluxes and lability degrees of Pb-aggregate complexes as a function of log$D$ for different values of $\beta$. Parameters: see tables 9.2-9.4, $\delta \sim 20\mu m$.

9.5 Zn fluxes in natural waters

9.5.1 Simulation conditions

The definitions and values of parameters used for the simulations are listed in Table 9.6-9.8. For more explanation on the obtention of these values, see detailed discussions in chapter 6 and [2,3]. The values given in tables 9.6-9.8 are the default values which are used unless otherwise stated. For specific studies, a given parameter value is varied, while all the others constant, as indicated in the tables.
Table 9.6. Parameters for simple ligands and Zn complexes.

<table>
<thead>
<tr>
<th>Species</th>
<th>(D) ((10^{-10} m^2s^{-1}))</th>
<th>(k_a) ((M^{-1}s^{-1}))</th>
<th>(K) ((M^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>52.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₃</td>
<td>9.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>7.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnOH</td>
<td>7.03</td>
<td>1.15 (10^8)</td>
<td>6.61 (10^4)</td>
</tr>
<tr>
<td>Zn(OH)₂</td>
<td>7.03</td>
<td>2.83 (10^7)</td>
<td>1.02 (10^6)</td>
</tr>
<tr>
<td>ZnCO₃</td>
<td>7.03</td>
<td>1.32 (10^9)</td>
<td>2.51 (10^4)</td>
</tr>
<tr>
<td>Zn(CO₃)₂</td>
<td>7.03</td>
<td>8.31 (10^6)</td>
<td>346.7</td>
</tr>
</tbody>
</table>

Table 9.7. Parameters for fulvics and Zn-fulvic complexes.

| FS \((mgC/L)\) | 1.5 | \(\psi\) \((mV)\) | -84.7 | \(D_{FS}\) \((10^{-10} m^2s^{-1})\) | 2.80 | \(log(K' /M^{-1})\) | 7.2 | \(k_a\) \((M^{-1} s^{-1})\) | 5.65 \(10^9\) | \(\sigma\) \((mol/kgC)\) | 15 | \(\Gamma\) | 0.41 | \(log K_0^{*}(M^{-1})\) | 4.3 |

Table 9.8. Parameters for aggregates and Zn-aggregate complexes.

| P \((mg/L)\) | 3 | X \((mg/L)\) | 0.3 | \(r_{min}\) (nm) | 3 | \(r_{max}\) (nm) | 1000 | \(\beta\) | 3 | \(\Psi\) \((mv)\) | pH=8 | 0 | \(\rho_p\) \((kg/L)\) | 2.5 | \(\rho_x\) \((kg/L)\) | 3 | \(n_s\) \((\times)\) | 10 | \(h_x\) (nm) | 1 | b (nm) | 3 | \(log(K'/M^{-1})\) | 6.45 | \(log k_\psi (s^{-1})\) | 7.5 |

Table 9.9. Distribution of Zn complexes.

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1.03e-8</td>
<td>10.3</td>
</tr>
<tr>
<td>ZnOH+Zn(OH)₂</td>
<td>1.63e-9</td>
<td>1.63</td>
</tr>
<tr>
<td>ZnCO₃+Zn(CO₃)₂</td>
<td>3.24e-9</td>
<td>3.24</td>
</tr>
<tr>
<td>ZnFS</td>
<td>3.68e-8</td>
<td>36.8</td>
</tr>
<tr>
<td>Zn-aggregates</td>
<td>4.76e-8</td>
<td>47.6</td>
</tr>
<tr>
<td>Total</td>
<td>1e-7</td>
<td>100</td>
</tr>
</tbody>
</table>

The proportion of each complex has been computed by MINTEQ2, under the above conditions (Table 9.9). It appears that the proportion of free Zn\(^{2+}\) (~10\%) is significantly higher than that of Pb\(^{2+}\). The proportions of Zn-fulvic (37\%) and Zn-aggregate (47\%)
complexes are equivalent and dominant in the test water. The hydroxo and carbonato complexes are in similar but weak (a few %) proportions.

9.5.2 Effects of the diffusion layer thickness on the fluxes and the degrees of lability of Zn complexes

Figure 9.16 shows the influence of the diffusion layer thickness, \( \delta \), on the total and complex type fluxes. In the whole range of \( \delta \), from 5 \( \mu \)m to 800 \( \mu \)m, the total flux \( J_t \) locates in between \( J_{\text{lab}} \) and \( J_{\text{in}} \), but it is very close to \( J_{\text{lab}} \), particularly at the largest diffusion layer thicknesses (Fig. 9.16). This suggests that most complexes are fully labile or close to labile. Indeed, Fig. 9.16 confirms that for \( \delta \geq 20 \mu \)m, the fluxes of Zn(II) complexes with either simple ligands or aggregates are inversely proportional to \( \delta \) (slope of \(-1\) in the log-log plot of fig. 9.16), which is expected for labile complexes (eq. 9.1). On Fig. 9.16, the overall flux of Zn-fulvic complexes decreases with \( \delta \), with a slope smaller than \(-1\). This is due to the fact that the degrees of lability of Zn-FS complexes increase with \( \delta \), and thus partly compensate the decrease due to the build up of smaller concentration gradients, when \( \delta \) increases.

Figure 9.16. Total and complex type fluxes (a) as a function of diffusion layer thickness, \( \delta \), and comparison of \( J_t \) to \( J_{\text{lab}} \) and \( J_{\text{in}} \) (b). Parameters: see tables 9.6-9.8.

Figure 9.17. Individual lability degrees and fluxes of Zn-fulvic complexes as a function of their log \( \log K^\circ \) values, for different \( \delta \). Parameters: see tables 9.6-9.8.
Fig. 9.17, which shows the influence of $\delta$ on the individual degrees of lability and fluxes of each Zn-fulvic complex, clearly shows indeed that when $\delta$ increases, there are complexes with larger and larger $^{1}K$ values, for which $^{1}\xi \sim 1$. Thus the overall degree of lability of fulvic complexes increases with $\delta$.

The major contributions to the total flux, $J_t$, are those of free Zn$^{2+}$ and of Zn-fulvic complexes (Fig. 9.18). The contribution of each of them is larger than 30% in the whole range of $\delta$. Interestingly, the proportion of free Zn is only 10%, while its contribution to $J_t$ is 30-50%, and the contribution to $J_t$ of Zn complexes with simple ligands, is $\sim 20\%$ while their proportion of [Zn] is only a few %. On the opposite, The contribution to $J_t$ of Zn-aggregates is always less than 3%, whereas their proportion of [Zn] is 48%. These last results are mostly due to the much lower diffusion coefficient of Zn aggregates (even the smallest size ones) compared to those of free Zn or its simple complexes.

Figure 9.18. Proportion of the fluxes of each complex type as function of $\delta$. Parameters: see tables 9.6-9.8.

9.5.3 The contribution of Zn-aggregates

As shown in Figure 9.19, when $\delta \geq 20 \mu m$, the degree of lability of all the Zn-aggregates complexes is close to 1. Thus under natural conditions, Zn-aggregate complexes are labile: $^{1}\xi = 1$ and $^{1}J$ is inversely proportional to $\delta$ for any j value. However, due to their small mobility, they contribute little to the total flux. The cumulative flux, $J_{\text{cum}}$, of Zn-aggregates (starting the summation with the fluxes of the smallest size class) is shown on Fig. 9.20, for different $\delta$ values. $J_{\text{cum}}$ tends to a plateau when $^{1}D < 10^{-10.7} m^{2}.s^{-1}$, i.e. for a radius of aggregates $> 10 \mu m$. This points out that under natural conditions, the major contributors to $J_t$, amongst Zn-aggregate complexes, are the small-sized aggregates. But anyway, as discussed above, their contribution to $J_t$ is always small.
Figure 9.19. Degrees of lability and fluxes of individual Zn-aggregate complexes as a function of log $D$ under different $\delta$. Parameters: see tables 9.6-9.8.

Figure 9.20. Cumulative flux of Zn-aggregates as a function of log $D$ under different $\delta$. Parameters: see tables 9.6-9.8. $J_{\text{cum}}$ is computed by starting the summation with the fluxes of the smallest size class to the largest size class.
9.6 Ni fluxes in natural waters

9.6.1 Simulation conditions

Numerical simulations have been performed on the test water described in table 9.1. The parameters for Ni(II) complexes are listed in tables 9.10-9.12 below.

Table 9.10. Parameters for simple ligands and Ni complexes.

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<tr>
<th>Species</th>
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<th>$k_a$ (M$^{-1}$s$^{-1}$)</th>
<th>$K$ (M$^{-1}$)</th>
</tr>
</thead>
<tbody>
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<td>OH</td>
<td>52.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_3$</td>
<td>9.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>7.05</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiOH</td>
<td>7.05</td>
<td>1.16 $10^5$</td>
<td>8.29 $10^4$</td>
</tr>
<tr>
<td>Ni(OH)$_2$</td>
<td>7.05</td>
<td>2.83 $10^4$</td>
<td>6.43 $10^4$</td>
</tr>
<tr>
<td>NiCO$_3$</td>
<td>7.05</td>
<td>1.34 $10^6$</td>
<td>1.62 $10^4$</td>
</tr>
</tbody>
</table>

Table 9.11. Parameters for fulvics and Ni-fulvic complexes.

<table>
<thead>
<tr>
<th>{}FS{} (mgC/L)</th>
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</tr>
</thead>
<tbody>
<tr>
<td>$\Psi$ (mV)</td>
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</tr>
<tr>
<td>$D_{FS}$ ($10^{-10}$ m$^2$s$^{-1}$)</td>
<td>2.80</td>
</tr>
<tr>
<td>log($K'$/M$^{-1}$)</td>
<td>8.6</td>
</tr>
<tr>
<td>$k_a$ (M$^{-1}$s$^{-1}$)</td>
<td>7.34 $10^6$</td>
</tr>
<tr>
<td>$\sigma$ (mol/kgC)</td>
<td>15</td>
</tr>
<tr>
<td>$\Gamma$</td>
<td>0.57</td>
</tr>
<tr>
<td>log $K_0*(M^{-1})$</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Table 9.12. Parameters for aggregates and Ni-aggregate complexes.

| {}P{} (mg/L) | 3 |
| {}X{} (mg/L) | 0.3 |
| $r_{min}$ (nm) | 3 |
| $r_{max}$ (nm) | 1000 |
| $\beta$ | 3 |
| $D_T$ | 2 |
| $\Psi$ (mv) pH=8 | 0 |
| $\rho_0$ (kg/L) | 2.5 |
| $\rho_X$ (kg/L) | 3 |
| $n_x$ | 10 |
| $h_x$ (nm) | 1 |
| $b$ (nm) | 3 |
| log($K'/M^{-1})$ | 6.35 |
| log$k_w$(s$^{-1}$) | 4.5 |

Under the above conditions, the proportion of free Ni is significant (10%; Table 9.13 below). As for Zn(II), Ni-fulvic (49%) and Ni aggregate complexes (38%) are the dominant species. The simple complex with the largest proportion (2%) is NiCO$_3$. 

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>5.00E-10</td>
<td>10.0</td>
</tr>
<tr>
<td>NiOH+Ni(OH)₂</td>
<td>4.97E-12</td>
<td>0.0994</td>
</tr>
<tr>
<td>NiCO₃</td>
<td>1.01E-10</td>
<td>2.02</td>
</tr>
<tr>
<td>NiFS</td>
<td>2.44E-9</td>
<td>48.8</td>
</tr>
<tr>
<td>Ni-aggregates</td>
<td>1.88E-9</td>
<td>37.6</td>
</tr>
<tr>
<td>Total</td>
<td>5.00E-9</td>
<td>100</td>
</tr>
</tbody>
</table>

9.6.2 Effects of the diffusion layer thickness on the fluxes and the degrees of lability of Ni complexes

Due to the small dehydration rate of Ni²⁺, the formation/dissociation rates of complexes with this metal are much slower than with Pb(II) or even Zn(II). Thus it is expected that the diffusion layer thickness may have a significant influence on the lability of the Ni(II) complexes. This is indeed observed in Figure 9.21a. At small values of the diffusion layer thickness (5μm), \( J_t \sim J_{in} \), which implies that the only important contribution to \( J_t \) is due to free Ni²⁺ ion. When \( \delta \) increases, the diffusion time increases, and formation/dissociation of complexes may occur more often. Thus the degrees of lability of Ni(II) complexes increase, and \( J_t \) becomes closer and closer to \( J_{lab} \) (Fig. 9.21a). Fig. 9.21b shows the contributions of each complex type flux to \( J_t \), as function of \( \delta \). It is seen that indeed the total flux is largely due to free Ni. This is the reason why the contributions of complexes are smaller than \( J_{in} \) (Fig. 9.21a). In general these contributions increase with \( \delta \) (Fig. 9.21b), but nevertheless, they remain small in the whole range of \( \delta \). Only at the largest \( \delta \) values, the contribution of Ni-fulvic complexes to \( J_t \) is comparable to that of free Ni²⁺.

The influence of \( \delta \) is different for each type of complex. For NiCO₃, the slope in Fig. 9.21a is almost –1, which shows that it behaves in a labile manner in almost the whole range of \( \delta \). The flux of Ni hydroxo complexes shows a maximum. This is due to the fact that their degrees of lability increase with \( \delta \) and compensates for the decrease of concentration gradient due to the increase of \( \delta \). At large \( \delta \) values (> 50μm), they are fully labile and a slope of -1 is indeed observed in Fig. 9.21a. The overall flux of Ni-fulvic complexes is almost constant or decreases very slightly in the whole range of \( \delta \). This reflects the fact that their lability increases (see below). This increase just compensates for the decrease of the concentration gradients due to the enlargement of \( \delta \) as mentioned above. Finally, the Ni-aggregate complexes follow a similar trend, but slightly shifted towards lower \( \delta \) values. As a consequence the Ni-aggregate complexes become labile for \( \delta > 500 \mu m \).
Figure 9.21. Changes of $J_t$ and the flux contributions of the various types of complexes (a), and their proportions to $J_t$ (b), as function of $\delta$. Parameters: see table 9.10-9.12.

Fig. 9.22 gives the degrees of lability and fluxes of individual Ni-fulvic complexes. When $\delta$ increases, there are more and more stronger complexes (larger $J_K$) which behave in a labile manner ($J_\xi \sim 1$). Thus the overall lability of Ni-fulvic complexes increases.
Figure 9.22. Degrees of lability and fluxes of individual Ni-fulvic complexes, as a function of $\log K^*$, for different $\delta$ values. Parameters: see tables 9.10-9.12.

Figure 9.23 clearly shows that at low value of $\delta$, the Ni-aggregate complexes are non labile, irrespective of their size. When $\delta$ increases, the degree of lability increases, starting with the largest aggregates. This is because their diffusion coefficient is lower, and therefore their diffusion time is large in the diffusion layer. As a consequence, formation/dissociation of complexes may occur more often and thus lability increases. Because all complexes are inert at $\delta = 5 \mu m$, the flux of the various complexes is independent of size. When $\delta$ increases, $J^*$ increases due to the increase of lability and it becomes dependant on size because $J^D$ becomes an important factor. However simultaneously, the concentration gradients decreases, and at large $\delta$ values, this effect is predominant, so that at a given $J^D$, $J^*$ decreases. The contribution of the different size classes of Ni-aggregate complexes can also be understood based on Figures 9.24a-b. At small $\delta$ value ($5 \mu m$), all Ni-aggregates are non-labile, the rate-limiting step is the chemical dissociation, and $J^*$ is independent of size as explained above. So $J_{\text{cum}}$ varies linearly with the aggregate radius $r$ (Fig. 9.24a), because all size classes have the same weight on $J_{\text{agg}}$. At large $\delta$ value ($800 \mu m$), all Ni-aggregate complexes are fully labile and only the small size complexes which are the most mobile (higher $J^D$ values) contribute significantly to $J_{\text{agg}}$ (Fig. 9.24b). $J_{\text{cum}}$ then tends to a plateau in the larger size range. Figure 9.24b shows that the flux from the small-sized aggregates (less than 20 microns) is the major contribution to $J_{\text{agg}}$ (which anyway remains at best 2% of $J_i$).
9.6.3 Effects of the properties of fulvics on the fluxes and the degrees of lability of metal complexes

9.6.3.1 Effect of $\Gamma$ and $\log K_0^*$

The parameters $\Gamma$ and $K_0^*$ have the same effects as for Pb, on the flux and lability of Ni fulvic complexes. When $\Gamma$ is smaller or $\log K_0^*$ is larger, there is more sites with large $\log j$, i.e. more sites with very small $k_d$. Also, smaller $\Gamma$ or larger $\log K_0^*$ corresponds to a larger $\log K^*$, i.e. a smaller value of free Ni concentration (see eq. 9.1). Thus, it is expected that both the lability degree of the whole system and $J_t$ will decrease when $\Gamma$ decreases or $\log K_0^*$ increases.
Figure 9.25 a-b indeed show that \( J_t \) follows the above predictions. They also show that \( J_t \) is very close to \( J_{in} \) for any value of \( \Gamma \) and \( K_0^* \), which suggests that the Ni-fulvic complexes are close to inert for any value of the above parameters.

![Graph](image)

**Figure 9.25 a-b.** The total flux of Ni species, as a function of \( \Gamma \)(a) and log \( K_0^* \)(b) and its comparison to \( J_{lab} \) and \( J_{in} \). Parameters: see tables 9.10-9.12. \( \delta \sim 20 \mu m \).

Figure 9.26 a-b indeed show that the curves of individual degrees of lability of Ni-fulvics complexes do not change with \( \Gamma \) or \( K_0^* \). However, because in all cases \( K^* \) is located in a domain of low \( j_\xi \) values, the vast majority of fulvics complexes behave in a non labile manner. When \( \Gamma \) decreases or \( K_0^* \) increases, \( K^* \) increases (Fig. 9.26a-b), and thus, on the average, the fulvic complexes become even more non-labile, and simultaneously, the free Ni
concentration decreases. This explains why $J_t$ remains very close to $J_m$ and both decrease (Fig. 9.25 a-b).

**Figure 9.26 ab.** Fluxes and degrees of lability of individual Ni fulvic complexes, as a function of $\log j K$, for different values of $\Gamma$ (a) and $\log K_o^*$(b). Vertical dashed lines: $\log K^*$, from left to right: (a) $\Gamma$=0.8, 0.57, 0.3; (b)$\log K_o^*$ =3.3, 4.3, 5.3. Parameters: see tables 9.10-9.12. $\delta \sim 20\mu m$.

Figure 9.27 shows the proportion of complex type flux as a function of $\Gamma$ or $\log K_o^*$. Under all conditions, the total flux is dominated by free Ni, but $J_{FS}$ is non negligible and comparable to the flux of Ni carbonato complexes. Each of them represent 5-30% of the total flux, depending on the values of $\Gamma$ and $K_o^*$.
9.6.4 Effects of the properties of aggregates on the fluxes and the degrees of lability of Ni complexes

9.6.4.1 Effect of $\log K'$

When the stability constant of Ni-aggregates, $K'$, is increased, the corresponding dissociation rate constant, $k_d'$, decreases, and thus a decrease of the degree of lability of the complexes is expected. This is indeed observed on Figure 9.28: at small $\log K'$ values, all the Ni-aggregates complexes are close to labile ($\zeta$ close to 1). Since, under our conditions, the proportions of all
Ni-aggregate complexes are equal, the individual flux, $iJ$, of each complex, only depends on its diffusion coefficient; so $iJ$ vary linearly with $\log D$. At larger $\log K'$ value, the degree of lability of Ni-aggregates becomes much smaller than 1 and the complexes tend to become non-labile. The chemical association and dissociation rates are the rate-limiting step, and $iJ$ is independent of $\log D$. This is confirmed by Fig. 9.29. For all the size class, $i\Theta$ (eq. 9.3) is much smaller than 1 which clearly shows that chemical association and dissociation are the rate-limiting steps.

![Figure 9.28. Degrees of lability and fluxes of individual Ni-aggregate complexes, as a function of $\log D$ for different $\log K'$ values. Parameters: see tables 9.10-9.12. $\delta \sim 20\mu m$.](image1)

![Figure 9.29. $\theta$ in eq 9.3 of Ni-aggregate. Parameters see table 9.12. It is valid for and $K'$ and $\beta$.](image2)
Table A.7.3a-e show the distribution of Ni species at equilibrium. The proportion of Ni-aggregates increases from almost 0 at small log\(K'\) value to almost 100% at large log\(K'\) value. However, due to the decrease of degree of lability with log\(K'\) and the low mobility of Ni-aggregates, a decrease of \(J_t\) is expected. Figure 9.30 indeed shows that both \(J_{in}\) and \(J_t\) decrease with \(K'\), because the bulk free Ni concentration also decreases. In addition, \(J_t\) becomes closer and closer to \(J_{in}\) because the corresponding complexes become more inert. Note that anyway the contribution of Ni-aggregates is very small (Fig. 9.31) for any log\(K'\) values: \(J_{agg}/J_t\) never exceeds 1%.

**Figure 9.30.** Total flux as a function of log\(K'\) and its comparison to \(J_{lab}\) and \(J_{in}\). Parameters: see tables 9.10-9.12. \(\delta \sim 20\mu m\).

**Figure 9.31.** Proportion of each complex type flux as a function of log\(K'\). Parameters: see tables 9.10-9.12. \(\delta \sim 20\mu m\).
9.6.4.2 Effect of $\beta$

As we have seen for Pb, $\beta$ only affects the size distribution of aggregates, but does not change the overall proportion of Ni bound to aggregates. Figures 9.32 and 9.33 show that $\beta$ has little effect on $J_{agg}$ and a fully negligible effect on $J_t$, since $J_{agg}$ itself is a small fraction of $J_t$. Fig. 9.34 also show that $\beta$ does not affect the degree of lability of the various Ni aggregate complexes. It influences $J_{agg}$, however, because the proportion of Ni-aggregates in each size class depends on it. At $\beta=2$, the proportions of Ni complexes in the large size classes are the largest and they are also the more labile complexes (Fig. 9.34). This combination of factors overcompensates the lower mobility of these complexes, and so $J_t$ increases with the radius, $r$ (or decreases with $D$). When $\beta$ increases, the proportion of complexes in small size classes, corresponding to larger mobility is more and more significant. Thus, at the largest $\beta$ values, $J_t$ strongly increases when $r$ decreases, even though the degree of lability of complexes decreases. This implies that the larger the $\beta$, the more important are the small size particles in $J_{agg}$.

**Figure 9.32.** Proportion of each complex type flux as a function of $\beta$. Parameters: see tables 9.10-9.12. $\delta \sim 20\mu m$.

**Figure 9.33.** Total flux as a function of $\beta$ and its comparison with $J_{lab}$ and $J_{in}$ Parameters: see tables 9.10-9.12. $\delta \sim 20\mu m$. 

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9.7 General discussion

9.7.1 Comparison of the behaviours of the three metals

By analogy to the degree of lability for the individual metal complex, we define the overall degree of lability for the whole system as follows:

$$\xi_o = \frac{J_{ia} - J_{iab}}{J_{iab}}$$

(9.6)

Figure 9.35 shows the overall degree of lability of the system for the 3 metals as a function of the total metal concentration. Two interesting observations can be done:

- For a given metal, the value of $\xi_o$ depends on [M], for the reasons given below. Thus the dynamic behaviour of various metals can only be compared at the same [M] value.
- At the same [M] value, the Pb system is the most labile, Ni is the less labile system and Zn has an intermediate behaviour. This really reflects the kinetic properties of the 3 metals: due to its biggest water dehydration rate, Pb forms complexes with the largest association rate constants. On the opposite, the water dehydration rate of Ni is the smallest and consequently the Ni system is the less labile.

It must be realized however, that this “logical” order results from the fact that the contribution of metal-aggregate complexes is negligible or small in all cases. Indeed we have seen that, under our (typical) conditions, the major contributions to the total flux are provided by carbonato complexes and fulvic complexes (sometimes the free metal ion), but never by hydroxo complexes or aggregate complexes. This has two consequences:
- the increase of overall lability with $[M]_t$ is largely due to the fulvics: when $[M]_t$ increases the weaker, more labile sites of fulvics are occupied. Since the fulvics often play an important role on $J_0$, this effect is reflected on $J_t$. Note that in a system including many ligands, the same effect will be observed, even if fulvics are not present. Indeed, the same process (the increase of the proportion of more and more labile complexes when $[M]_t$ increases) will always occur.

- under conditions where metal-aggregates would provide a major contribution to $J_0$, the order of overall lability of metal complexes based on their chemical kinetic properties (as discussed above and shown on Fig. 9.35) may not be respected. This is due to the fact that the metal-aggregate complexes may be non labile for two reasons: i) the slow formation/dissociation of the complex at the aggregate complexing site, but also ii) the slow diffusion of metal ion outside and inside the aggregates. When this is the slow step, the chemical reaction rates do not play a significant role on the lability (chap. 8, section 8.7.2).

![Figure 9.35](image_url)

**Figure 9.35.** Overall degree of lability of the metal complexes in the whole test water, for the 3 tested metals as a function of the total metal concentration. Parameters: see tables 9.2-9.4, 9.6-9.8, 9.10-9.12. $\delta \sim 20\mu$m.

### 9.7.2 Comparison of degrees of lability and total fluxes under planar and spherical diffusion

The fluxes and average degrees of lability of the various complex types computed above (planar diffusion) have been compared to those obtained under conditions of spherical diffusion. The code FLUXY has been used for that purpose. Due to the fact that hydroxo and carbonato $1/n$ ($n>1$) complexes are in low proportion compared to their $1/1$ complexes and because Mhedyn has shown that under our condition the fulvics concentration is constant in the diffusion layer, Fluxy could be used here.

The geometrical boundary conditions used were the following: for spherical diffusion the radius of the spherical interface was $r = 1\mu$m, and for planar and spherical diffusion, the diffusion layer thickness was $\delta = 20\mu$m. The results of simulations for Pb and Ni are shown in Table 9.14 and 9.15 and Figure 9.36 and 9.37.
The average degrees of lability of both Pb and Ni complexes are much decreased under spherical diffusion, as could be expected [6]. Those of Ni complexes however are significantly more decreased than those of Pb complexes. The increased diffusion under spherical conditions however, largely compensates for these decreases of lability. For the simple and fulvic complexes of Pb and all complexes of Ni, the second effect overcompensate the former, and the complex type fluxes of simples and fulvic complexes are larger under spherical than under planar diffusion. For the aggregate complexes of Pb, the decrease of degree of lability is not completely compensated and $J_{\text{agg}}$ slightly decreases under spherical diffusion. The net result is that,

i) overall the total flux, $J_t$, is significantly larger under spherical diffusion than under planar diffusion, in spite of the decrease of degree of lability of all complexes.

ii) The proportion of the contributions of $J_{\text{agg}}$ to the total flux, still decreases under spherical diffusion compared to planar diffusion for Pb. As we have seen that it is already very low under planar conditions, it is negligible under spherical conditions. The dominant contributors to $J_t$ are the carbonato complexes and fulvics for Pb, and the free metal ion for Ni, as it is also the case under planar diffusion.

Table 9.14. Degrees of lability and complex type fluxes of Pb species under planar and spherical diffusion.

<table>
<thead>
<tr>
<th></th>
<th>ξ, planar</th>
<th>ξ, spherical</th>
<th>Complex type flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1</td>
<td>1</td>
<td>1.67e-13, 3.85e-12</td>
</tr>
<tr>
<td>PbOH</td>
<td>0.847</td>
<td>0.294</td>
<td>1.86e-13, 1.35e-12</td>
</tr>
<tr>
<td>PbCO$_3$</td>
<td>0.834</td>
<td>0.240</td>
<td>7.57e-12, 5.03e-11</td>
</tr>
<tr>
<td>Pb-fulvics</td>
<td>See Fig. 9.36a</td>
<td>See fig. 9.36a</td>
<td>5.07e-12, 8.39e-12</td>
</tr>
<tr>
<td>Pb-aggregates</td>
<td>See Fig. 9.36b</td>
<td>See fig. 9.36b</td>
<td>2.75e-13, 2.18e-13</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1.33e-11, 6.41e-11</td>
</tr>
</tbody>
</table>

Figure 9.36a-b. Degrees of lability and fluxes of individual Pb-fulvics (a) and Pb-aggregates (b) complexes as a function of $\log K$ or $\log D$ under planar and spherical diffusion. Parameters: see tables 9.2-9.4, $\delta \sim 20 \mu$m.
Table 9.15. Degrees of lability and fluxes of the various complex types of Ni under planar and spherical diffusion conditions.

<table>
<thead>
<tr>
<th></th>
<th>planar</th>
<th>spherical</th>
<th>complex type flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1</td>
<td>1</td>
<td>1.65E-11</td>
</tr>
<tr>
<td>NiOH</td>
<td>0.650</td>
<td>0.0713</td>
<td>1.00E-13</td>
</tr>
<tr>
<td>NiCO₃</td>
<td>0.846</td>
<td>0.201</td>
<td>2.81E-12</td>
</tr>
<tr>
<td>Ni-fulvics</td>
<td>See Fig. 9.37a</td>
<td>See Fig. 9.37a</td>
<td>1.97E-12</td>
</tr>
<tr>
<td>Ni-aggregates</td>
<td>See Fig. 9.37b</td>
<td>See Fig. 9.37b</td>
<td>4.18E-14</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>2.14E-11</td>
</tr>
</tbody>
</table>

Figure 9.37 a-b. Degrees of lability and fluxes of Ni-fulvics (a) and Ni-aggregates (b) complexes as a function of log\(K\) or log\(D\) under planar and spherical diffusion. Parameters: see tables 9.10-9.12, \(\delta \sim 20\mu m\).

9.7.3 Summary

The change of the diffusion layer thickness greatly influences the overall lability of the system. At sufficient large \(\delta\) values (typically > 1 mm), all the complexes of the 3 metals are labile, even for metals with very slow kinetics, like Ni, while at small \(\delta\) values, in principle, only the contribution of free metal ion to the total flux is important. However, under realistic conditions where usually \(\delta > 5-10\ \mu m\), the complexes of some metals like Pb, may still be significantly labile.

The role of fulvics on the total flux may vary from very important for quickly reacting metals, at sufficiently large metal/fulvic ratio to negligible for slowly reacting metals at low metal to fulvic ratio. On the other hand, the metal aggregate complexes seem to play a very minor role on the total flux. \(\Gamma\) and \(K_{0^*}\) influence only the fluxes and lability of the fulvic complexes and little those of the other complex types. The same is true for the parameters of aggregate complexes, which makes interpretation of data less complicated.

For Pb, the labile complexes (carbonato complexes and fulvics) play an important role on the flux, and their physico-chemical parameters in the external medium should be considered. For Ni, only its free metal ion is important in the flux. While Zn is just an intermediate case.
9.8 References

[1] Zhang, Z.; Buffle, J.; Startchev, K.; Alemani D. *Environ. Chem.* accepted
Chapter 10

Conclusions and perspectives

10.1 Conclusions

In this thesis we first propose the basic theory for dynamic metal speciation in presence of one ligand. It is systematically validated by PLM experimental studies. Then we extend our studies to two ligands and multiligand systems in natural waters using the two flux computation codes: Fluxy and Mhedyn. The following developments have been performed.

1. We have compiled the dynamic parameter values for metals, complexants and their complexes in natural waters for the three main categories of complexants: ‘simple’ ligands, fulvics and aggregates. When such data are missing, especially for fulvics and aggregates, we propose models to compute these dynamic parameter values. It must be pointed out that some of the assumptions used in chapter 6 of this thesis require validation. The purpose of chapter 6 is to provide a quantitative framework enabling to model metal flux under variety of conditions, and compare the results with experimental observations. Hopefully this will lead to a better knowledge of structure and chemical composition of fulvics and aggregates, of complexation reaction mechanism, and of better values of rate and equilibrium constants.

2. a) Rigorous theories are first proposed for metal fluxes with one ligand and one complex for planar and spherical diffusion. Based on these theories, a more general definition of the reaction layer concept than the conventional one is proposed which considers both the association of metal M and ligand L and the dissociation of complex ML. This general reaction layer is combined in the flux computation code: Fluxy. A rigorous lability index and a well-defined criterium for inert complexes are also proposed based on this theory.

b) The above theories are validated by the studies of labile, semi-labile and non labile complexes with the dynamic metal speciation sensor PLM, which can well mimic the biouptake of metal by microorganisms. Systematic studies of the physicochemical parameters of the PLM membrane also show under which conditions the carrier concentrations, membrane thickness and diffusion coefficient of metal carrier complex in the membrane are rate limiting. By analogy with the plasma membrane of microorganisms, this enables to predict under which conditions the biouptake follows FIAM or BLM or depends on the physicochemical parameters of external medium of microorganisms.

3. We have studied systems with two ligands in natural waters with Mhedyn, Fluxy and a specific model based on the reaction layer approximation. We find that the more labile complex may increase the degree of lability of a less labile complex and its individual flux and thus the total flux. With the model proposed based on the reaction layer approximation, it is clearly shown that this phenomenon is due to the antagonistic role of the overall reaction layer thickness and the free metal ion concentration at the reaction layer boundary. This phenomenon may be universal in natural waters.

4. The two basic assumptions of Fluxy have been tested systematically: ligand excess and equilibrium between successive complexes. The results show that Fluxy-RLA is preferable in presence of simple ligands including successive complexes and that its error is small compared to rigorous solutions computed with Mhedyn. Fluxy-RS is preferable however when only 1/1 complexes are present. Fluxy-RS can be used with caution in presence of
fulvic complexes and it gives good results and is preferable to Fluxy-RLA in presence of particle/aggregates. Overall, Fluxy is an easy and quick flux computation method and a useful complementary code to Mhedyn.

5. The flux of various metals forming labile, semi-labile and non labile complexes at planar interface in environmental systems has been systematically studied with Mhedyn. The results show that: a) with the increase of diffusion layer thickness, all the complexes become more and more labile and the total flux is diffusion controlled in the external medium; b) the parameters of fulvics only influence the flux due to metal fulvic complexes themselves, and this is also true for metal aggregates complexes; c) the overall degree of lability of the system depends the nature of the test metal, i.e., Pb(II) forms the most labile system, while Ni(II) forms the less labile system. But it has also been shown that the overall lability also depends on the metal concentration; d) The main contributions to the total flux are from the complexes with ‘carbonate’ and fulvics for Pb(II) and Zn(II) and from free Ni(II), for Ni(II). The contributions from metal aggregates complexes are very low and may be neglected in flux computations.

10.2 Perspectives

The perspectives can be made in two directions: experimental validations and theory.

1. The antagonistic role of the overall reaction layer thickness and the free metal ion concentration, predicted for the two ligands system should be tested with dynamic metal speciation sensors. This can be accomplished by PLM. The metal can be Pb(II) and two ligands might be: Diglycolic acid and NTA. The first one forms labile complex with Pb(II), while the latter forms non labile complex with Pb(II). By keeping constant NTA concentration and varying Diglycolic acid concentration, the above antagonistic role could be tested.

2. The conclusions of chapter 9 and the models proposed in chapter 6 need to be checked and validated by experimental studies in natural waters. PLM has been successfully applied in dynamic metal speciation in natural waters. It might be chosen for this aim. These tests can be assigned to be four steps:

   a) Tests with simple ligands. The system includes the modified Aquil culture medium in chapter 8 and Pb(II).
   b) Tests with fulvics. The system includes constant concentration of fulvics. By varying total Pb(II) concentration, the role of fulvics and the model proposed in chapter 6 can be tested.
   c) Tests with particles. The system includes constant concentration of Pb(II). By varying the total particle concentration, the role of particles and the model proposed in chapter 6 can be tested.
   d) Based on above results, the tests maybe extend to the mixture of simples ligands, fulvics and aggregates with Pb(II).

3. Theoretical predictions have shown that decreasing the radius of the consuming interface should cause a decrease of lability of metal complex. This should be validated by experiments. Due to the similarities between voltammetry and microorganims, voltammetry could be applied for these tests. In the past, CABE has developed microelectrodes whose size
can be as small as 100nm and meet the criteria of small spherical interface. Labile, semi-labile and non labile metal complexes could be tested.

4. Fluxy-RS is a time-saving analytical method for flux computations. However, it can only be applied to 1/1 metal complexes. It may be improved to be applied to 1/n metal complexes by adding the kinetic term of successive metal complexes in the conservation equations in chapter 1. The theoretical approach should be in this direction. Simutaneously Mhedyn could be developed for spherical geometry.
List of symbols

a  distance of closest approach between a metal ion and a complexing site
A  surface area of the membrane of PLM
A_b  surface area of the solid phase of the aggregates, per liter of solution
A_{b,t}  total surface area of solid phase of the aggregates, per liter of solution
A_{X,P}  surface area of the component X or P, in the aggregate, per liter of solution
b  radius of subparticles inside the aggregate
B(t)  Function of time relating the effective rate constant $k_a^{\text{eff}}$ to the chemical rate constant $k_a$
B_{ss}  value of B(t) under steady-state conditions.
c_p  the number concentration of particles/aggregates in solution
[C]  carrier concentration in the membrane of PLM
C_H  molar concentration of proton inside the aggregate
C_{M}^0  the initial molar concentration of free M inside the aggregate
C_{M}^{\text{in}}  the molar concentration of free M inside the aggregate
C_{M}^{\text{out}}  the molar concentration of free M in the surrounding of the aggregate
C_{MS}  the molar concentration of MS complexes inside the aggregate
C_{MS0}  the initial molar concentration of MS in the aggregate
C_{HS}  the molar concentration of protonated sites inside the aggregate
C_{SI}  the total molar concentration of sites inside the aggregate
C_{M}^{\text{(chapter 5) or } C_{M0}^{\text{(chapter 4)}}  total metal concentration in bulk source solution of PLM
C_L  total ligand concentration in bulk source solution of PLM
C_{M}^b  total metal concentration in bulk strip solution of PLM
C_{M}^s  total metal concentration in the strip solution of PLM
D  diffusion coefficient of the particles/aggregates in solution
D_{\text{min}, D_{\text{max}}}  values of D for particles/aggregates having minimum and maximum values of radii in the size distribution.
D_f  fractal dimension of the aggregates
D_M^a  diffusion coefficient of free M inside the aggregate
D_{MS}  diffusion coefficient of the metal-aggregate complex in solution
D_L  diffusion coefficient of ligand L
\bar{D}_L  average diffusion coefficient of protonated and unprotonated ligand L
D_M  diffusion coefficient of free metal ion M
D_{MC}  diffusion coefficient of metal-carrier complex in the membrane of PLM
D_{ML}  diffusion coefficient of complex ML
\bar{D}  average diffusion coefficient of M and ML in the source solution of PLM
\bar{D}_{so}  average diffusion coefficient of M and ML in the source solution of PLM
\bar{D}_{st}  average diffusion coefficient of M and ML in the strip solution of PLM
E  the relative difference between the fluxes or lability degrees computed by FLUXY and MHEDYN
F  preconcentration factor
H  proton
h_{so}  depth of the source channel of PLM
h_{st}  depth of the strip channel of PLM
h_X  thickness of a patch of component X on the subparticles of aggregates
I  ionic strength
$J$  metal flux

$j^0$  metal flux, at $t=0$

$k_a$  association rate constant

$k_{a,os}^+, k_{d,os}^-$  outer-sphere complex formation/dissociation rate constants of the complex (M,L)

$k_{a,os}^{in}, k_{d,os}^{in}$  inner-sphere complex formation/dissociation rate constants of the complex ML

$k_a^{MS}, k_d^{MS}$  effective formation/dissociation rate constant of the complex ML

$k_{a,n}, k_{d,n}$  formation/dissociation rate constants of the complex ML$_n$ from/to ML$_{n-1}$

$k_a^{L}, k_d^{L,exp}$  theoretical ($k_a^{L} = k_d^{MS}$) and experimental values of ML formation rate constant

$k_a^{HL}, k_a^{HK,exp}$  theoretical and experimental values of the rate constant for the reaction $M + HL \rightarrow ML + H$.

$k_a^{eff}$  effective rate constant for metal-aggregate complex formation between M and the fulvic site type $\nu^i$

$k_d$  overall association rate constant

$k_d'$  first-order (pH dependent) dissociation rate constant of MS.

$iK, iK^{MS}$  stability constant and dissociation rate constant of the complex $M'S$

$k_d^{eff}$  overall dissociation rate constant

$k_d^{eff}$  effective, pH-independent, rate constant for metal-aggregate complex dissociation.

$k_d^{eff}$  effective first-order, pH dependant, dissociation rate constant for the metal-aggregate complex

$k_{aw}$  rate constant for removal of a water molecule from the inner shell of the hydrated metal ion $M$

$K$  equilibrium constant

$K'$  apparent stability constants for metal complexation

$K_{a,ML}$  stepwise equilibrium stability constant of the complex ML$_n$

$K_{os}^{2}$ (chapter 6) or $K_{os}^{1}$ (chapter 3,4)  Equilibrium stability constant of the outer-sphere complex (M,L)

$K_D^*$  Constant parameter of the Freundlich isotherm

$K^*$  the differential equilibrium function (DEF) = the average of stability constants of all metal fulvic complexes weighted by the molar fraction and the degree of occupation of each site at the given value of [M]

$K_p$  partition coefficient of the metal between the solution and the membrane of PLM

$\ell$  thickness of the liquid membrane of PLM

$L$  lability index

$[L]^*$  bulk ligand concentration

$[LH]_t$  Total molar concentration of protonated and unprotonated ligand

$M$  free metal ion

$[M]^*$  bulk free metal concentration

$\text{ML}$  metal complex

$\text{[ML]}^*$  bulk complex concentration

$\text{MS}$  complex of M with complexing site S

$n_s^X$  number of complexing sites per surface area of compound X

$N_A$  Avogadro number

$N_b$  number of basic subparticles inside the aggregate

$P$  chapter 6: major component of particles/aggregates

$P$  chapter 4, 8: permeability

$P'$  chapter 5: permeability

$r$  chapter 3: distance from the centre of the spherical consuming interface
chapter 6: external radius of a particle/aggregate, 
$r_{\text{min}}, r_{\text{max}}$ minimum and maximum values of the radii of particle/aggregates in their size distribution.

$R_g$ gyration radius of a particle/aggregate

$R_h$ hydrodynamic radius of a particle/aggregate

$r_0$ radius of the spherical consuming interface

$S$ Complexing site

$[S]_t^n$ Total molar concentration of site type $n$ in the fulvics

$[S]_t^X, [S]_t^P$ total coarse-grained molar concentration of sites of complexants $X$ or $P$

$t$ time

$T_I$ threshold of inertia

$U(a)$ Coulombic energy between $M$ and the complexing site

$V_b$ volume of solid in the particles/aggregates, per volume of solution

$V_{b,t}$ total volume of solid in particles/aggregates, per liter of solution

$V_{st}$ volume of the strip solution of PLM

$x$ distance from the consuming interface

$[X]$ Molar concentration of $X$

$\{X\}$ Mass concentration of $X$

$X$ minor complexing component in the aggregates

$\{X\}_t, \{P\}_t$ total mass concentration of the components $X$ or $P$, per volume of solution

$Z_X$ Algebric number of electric charges of species $X$

$A$ prefactor of the Pareto law

$\alpha$ degree of complexation

$\beta$ exponent of the Pareto law

$\beta_i^H$ $i$-th cumulative acid-base constant of L

$\beta_{n ML}$ Cumulative stability constant of the complex $ML_n$

$\Gamma$ Heterogeneity parameter of the Freundlich isotherm

$\delta$ diffusion layer thickness

$\delta_{so}$ diffusion layer thickness in the source solution of PLM

$\delta_{st}$ diffusion layer thickness in the strip solution of PLM

$\varepsilon$ $D_{ML}/D_M$

$\lambda$ general reaction layer thickness

$\tilde{\lambda}$ composite reaction layer thickness

$\tilde{\lambda}$ overall reaction layer thickness

$\mu$ conventional diffusion layer thickness

$\xi$ degree of lability

$\xi_0$ overall degree of lability

$\pi$ permeability index

$\rho r/r_0$

$\rho_P$ density of the major solid component, $P$, of particles/aggregates

$\rho_X$ density of the component $X$ of particles/aggregates

$\sigma$ $\delta (\kappa/D_{ML})^{1/2}$, chapter 3

$\sigma^*$ chapter 6: total site density of the fulvics (in mole.kg$^{-1}$)

$\tau$ chapter 3: life time of free metal ion

$\tau_{1/2}$ chapter 7: resistance of flux in the diffusion layer

$\nu$ volume flow rate

$\chi$ $\varepsilon K[L]$
$\chi_i$  Cumulative mole fraction of site type n° i, in the fulvics

$\psi$  Average potential difference between the inside of a fulvic/humic molecule and the bulk solution.

$\psi$  the potential difference between the metal oxide surface and the solution far from the surface, inside the aggregate

$\omega$  dissociation reaction layer thickness
Appendix
A.1 Dynamic parameters of simple complexes

A.1.1 Diffusion coefficients

Whenever possible, values of diffusion coefficients at infinite dilution are given in Tables A.1.1-A.1.3. They are applicable to most natural waters. Usually values of diffusion coefficients, $D$, depart by more than a few % from the infinite dilution value, only when total salt concentration is larger than 0.1M. The difference with infinite dilution is largely due to changes in the viscosity, $\eta$, and can be corrected for by assuming an inverse relationship between $D$ and $\eta$, as in the Stokes-Einstein equation (p.108 in 46; 47).

The influence of temperature on diffusion coefficients is expressed by its temperature coefficient (in %/°K): $100.(dD/D)/dT$. Values of 2.78-2.99%/°K are obtained for most inorganic ions (p.89 in 46) and similar values are obtained for small organic molecules like amino acids (2.2 – 2.3 %/°K; Table A.1.2).

Table A.1.3 provides a few values of diffusion coefficients for peptides. Comparison of the $D$ values for EDTA (Table A.1.2a) and leucylglycylglycine (Table A.1.2c), whose molar mass, $M_m$, are similar, suggests that in this size range, branched or linear molecules have similar $D$ values. The relationship between $D$ and $M_m$ for macromolecules in the range 200-10^5 Daltons, is discussed in [84]. In this range, most macromolecules have spherical conformation and plots of experimental values of $\log D$ vs $\log M_m$ shows [39] that the following semi-empirical relationship can be used (with $D$ in m^2/s and $M_m$ in Daltons):

$$D = 2.84 \times 10^{-9}/M_m^{1/3} \quad (A.1.1)$$

$D$ values of several polysaccharides with $M_m$ values in the range 10^3- 10^6 Daltons are reported in [85].

$D$ values for specific metal complexes (Table A.1.3) are not easily available and should often be estimated. For very small ligands (e.g. inorganic anions), these latter replace water molecules in the inner hydration shell of the metal ion so that the net effect on $D$ may be rather small. In such a case, approximating the $D$ value of the complex with that of the hydrated ion is acceptable as a first approximation. Note however that when the hydration shell is completely replaced by small hydrophobic anions like Cl^- (HgCl in Table A.1.3), the diffusion coefficient of the complex may be significantly larger than that of the free hydrated ion. When the ligand size increases, the $D$ value of the complex tends towards that of the ligand. This seems to be the case when $M_m$ is larger than ~ 300.
Table A.1.1. Best values of diffusion coefficients of hydrated inorganic cations and anions in water, at T=298.15 °K and infinite dilution.

Most values are taken from [1]. Others refs are indicated as footnote

<table>
<thead>
<tr>
<th>Hydrated metal ion</th>
<th>a: Inorganic cations</th>
<th>Hydrated anion</th>
<th>b: Inorganic anions</th>
</tr>
</thead>
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<tr>
<td>H$_3$O$^+$</td>
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<tr>
<td>Al$^{3+}$</td>
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<td>Br$^-$</td>
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<td>Ba$^{2+}$</td>
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<td>CO$_3^{2-}$</td>
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$^a$ [2]; $^b$ [3]; $^c$ [4];
Table A.1.2. Best values of diffusion coefficients (in $10^{-10}$ m$^2$.s$^{-1}$) of some organic ligands in water, at T=298.15K and infinite dilution ($^a$,$^e$) or in dilute aqueous solution. When not otherwise stated, values are taken from [10]. Other refs. are given in the footnote. Units of 100.dlnD/dT are %/°K.

<table>
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<tr>
<th>Name</th>
<th>$D$</th>
<th>Name</th>
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<th>100.$\frac{d \ln D}{dT}$</th>
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<th>$D$</th>
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<tr>
<td>a: Carboxylic acids</td>
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</table>

$^a$ infinite dilution;  $^b$ [1];  $^c$ [6];  $^d$ [11];  $^e$ [12], values estimated by polynomial extrapolation of diffusion coefficient to zero concentration;  $^f$ [13];
**Table A.1.3.** Diffusion coefficients of metal complexes in water. Unless otherwise stated, T=298.15K and variable ionic strength. References corresponding to each value are given in footnotes. a value valid for both (+) and(±) compounds corrected for zero salt concentration. b T=293.15K

<table>
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<th>Ligand</th>
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<tr>
<td>OH⁻</td>
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<td>ML</td>
<td>5.4&lt;sup&gt;f,b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Tartrate&lt;sup&gt;a&lt;/sup&gt;</td>
<td>ML₂</td>
<td>4.14&lt;sup&gt;j,b&lt;/sup&gt;</td>
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</tbody>
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<sup>c</sup>[14]; <sup>d</sup>[15]; <sup>e</sup>[16a, 16b]; <sup>f</sup>[17]; <sup>g</sup>[18]; <sup>h</sup>[11,19a, 19b]; <sup>i</sup>[20]; <sup>j</sup>[21]; <sup>k</sup>[22]; <sup>l</sup>[23]; <sup>m</sup>[24]; <sup>n</sup>[11,24]; <sup>o</sup>[26]:

**A.1.2 Stability constants of simple complexes**

The values in Table A.1.4 are got by plotting the reported logK values found in the literature, as function of √ I (with I = ionic strength), at the temperature of interest. Polynomial curve fittings of such plots enable to get the value of logK at zero ionic strength, as well as the parameters for ionic strength correction, and the standard deviations on these parameters. Such data are listed in Table S6.8.4 for the complexes of a few bivalent metal ions with the inorganic anions the most relevant for aquatic chemistry. When required, corrections for temperature can be made from the enthalpy of formation of the complex (eg. 86 for theory and tables of values).
Table A.1.4. Logarithmic values of metal complexation equilibrium constants. For all ligands including OH\(^{-}\), they are expressed as M+nL⇌ML\(_n\), i.e. \(\beta_n=\frac{[ML_n]}{[M][L]^n}\). For MHCO\(_3\), \(K=\frac{[MHCO_3]}{[M][HCO_3]}\). Values collected for T=298.15°K in [27, 28, 29, 30] and fitted for ionic strength (I) dependence with the equation: \(\log \beta = \log \beta_{I=0} + A\sqrt{I} + B.I + C.I^{3/2}\).

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<td>log(\beta_{I=0})</td>
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<td>B</td>
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<td>-</td>
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<td>-</td>
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A.1.3 Rate constants of metal ion dehydration in aqueous solution

Table A.1.5. Values of the rate constants for elimination of a water molecule from the inner water shell of metal cations. T = 298.15°K. Data taken from refs \[a,b,c,d\], see footnote. Units: \( k_w = \text{s}^{-1}; \Delta H^\ddagger = \text{kJ.mol}^{-1}; \Delta S^\ddagger = \text{J.K}^{-1}\text{mol}^{-1} \). Values in parentheses are either ranges of reported values or additional reported values.

<table>
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<tr>
<th>Cation</th>
<th>Log ( k_w )^a</th>
<th>Cation</th>
<th>Log ( k_w )</th>
<th>( \Delta H^\ddagger )</th>
<th>( \Delta S^\ddagger )</th>
<th>Cation</th>
<th>Log ( k_w )</th>
<th>( \Delta H^\ddagger )</th>
<th>( \Delta S^\ddagger )</th>
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<td></td>
<td>Al</td>
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<td>112.9^c</td>
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<td>Be</td>
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<td></td>
<td></td>
<td>Bi</td>
<td>&gt;4^c</td>
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<tr>
<td>Li</td>
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<td>Ca</td>
<td>8.3^b</td>
<td></td>
<td></td>
<td>Cr</td>
<td>-5.6^b(-6.3^c)</td>
<td>109^b</td>
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<td></td>
<td>Fe</td>
<td>2.2^b</td>
<td>64^b</td>
<td>12^b</td>
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<td>In</td>
<td>~4.3^c(5.3)</td>
<td>~17^c</td>
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<td>7.3^c(8.0^d)</td>
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<td>7.5^c(7.3-7.8)</td>
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</tbody>
</table>

^a [31]; ^b [32]; ^c [33]; ^d [34];
A.1.4 Association rate constants of successive complexes, complexes with chelating agents or with protonated ligands

Formation of 1/1 ML complexes with unprot onated ligands is not the only type of reaction occurring in aquatic systems. A few other important cases are briefly discussed below.

**Successive complex formation**

In such cases, the relevant association and dissociation rate constants refer to each individual reaction step:

\[
\begin{align*}
ML_{n-1} + L & \rightleftharpoons ML_n \\
& \text{with the corresponding stability constant, } K_n = \frac{k_{a,n}}{k_{d,n}}.
\end{align*}
\]  

As a first step, the value of \( k_{a,n} \) can be estimated from eqs 6.8 or 6.10, where \( U(a) \) is computed from eq. 6.12, by replacing \( z_M \) by \( z_{ML} \). In addition, \( k_w \) should be modified to take into account that the number of water molecules which can be eliminated from the inner hydration shell of the metal (and replaced by a coordinating atom of \( L \)) is smaller in \( ML_{n-1} \) than in \( ML_{n-2} \), or in \( M \). The correct value of the rate constant can be estimated on a statistical basis [71], by considering that this number of water molecules is equal to the number \( \nu \) of “free” sites of \( M \) available for binding with \( L \). The probability of \( L \) to react with a coordinating site of \( M \) is thus given by the ratio of \( \nu \) to the maximum number of free sites, \( \nu_t \) (the latter for instance is equal to 6 for complexes of transition metals with octahedral configuration) and the dehydration rate constant of a successive complex, \( k^\nu_{\cdot w} \), is then computed from:

\[
k^\nu_{\cdot w} = \frac{k_w \cdot \nu}{\nu_t}
\]  

In many cases however, the value of \( k_{a,n} \) estimated by eq. A.1.3 should be considered as a lower limit of the real value. This is exemplified on fig. A.1.1b, where experimental values of \( k_{a,n} \) (\( k_{a,n}^{\exp} \)) and theoretical values computed from eq. 6.8 with \( k_a^{\text{in}} = k^\nu_{\cdot w} \) are plotted for a number of \( ML_n \) complexes, with variable \( n \) (see Table A.1.6b for list of numerical values). Indeed, the ligand(s) \( L \) already bound to \( M \) in \( ML_{n-1} \) may influence (usually decrease) the binding energy of the remaining water molecules in the inner hydration shell of \( M \), thus increasing the value of \( k^\nu_{\cdot w} \) [72,73]. This effect is the largest with donor ligands such as SCN\(^-\) or CN\(^-\). Carboxylate ligands have a negligible or weak influence. Fig. A.1.1b shows that experimental values of \( k_{a,n} \) can be up to 1 to 2 orders of magnitude larger than the theoretical ones.

**Complexes with organic chelating agents**

For a multidentate ligand \( L \), the mechanism of complex formation may be quite different from that depicted in eq. 6.3, and the value of the association rate constant should preferably be obtained from specific literature information. In absence of such data, the considerations of § 6.3.3 can be used, in particular when there is no steric constraint during the complex formation. In such a case, the formation of the first coordination bond (i.e. with a first arm of the chelating agent) is often slower than the formation of any other successive bond and is controlled, as for simple ligands, by the loss of a water molecule from the inner coordination...
shell of M. Thus eqs 6.10, 6.11 or 6.8, 6.13, 6.14 may be used, as a first approximation. It is often acceptable for bidentate (and some higher coordination) ligands (Fig A.1.1a). When steric constraints are important, the binding of the second, third or fourth coordinating atom may be the limiting step, and the overall rate constant is lower than that given by eq. 6.8 in which \( k_a^m \) is equated to \( k_w \). For many multidentate ligands an additional difficulty lays in the computation of \( U(a) \). Since multidentate ligands may bear several different charges, (e.g. –NH\(_3^+\) and –COO\(^-\) in amino-acids) at different locations, \( U(a) \) includes now the sum of all the electrostatic interactions between M and each charge of L, as well as the mutual intramolecular interactions between the different charged sites on L, in so far as they differ between the free L and the outer-sphere complex ML. The computation of \( U(a) \) is thus more involved than for spherical ligands with central charges and requires information of the geometrical configurations of the ligand and the complex. It is discussed in some details in [74]. Note that in Fig. A.1.1a the formal charge of the ligands are used.

**Fig. A.1.1a**: Plot of \( \log k_a^{1,\text{exp}} \) vs \( \log k_a^{MS} \) corresponding to the reaction \( M + L \rightarrow ML \). Theoretical values = \( k_a^{MS} \). eqs 6.8, 6.13, 6.14. Ionic strength and temperature: see Table A.1.6a. The symbols represent different ligands (the corresponding figures refer to those of Table A.1.6a).

**Fig. A.1.1b**: Plot of \( \log k_{a,n}^{\text{exp}} \) vs \( k_{a,n}^{MS} \) (eq. A.1.2) for successive complexes: \( ML_{n-1} + L \rightarrow ML_n \). Theoretical values = \( k_{a,n}^{MS} \); see text. Ionic strength and temperature: see table A.1.6b. Each symbols represents a different ligand (the corresponding figures refer to those of Table A.1.6b). For a given ligand, the difference between experimental and theoretical values increases with \( n \).
Fig. A.1.1c. Plot of log $k_a^{HK, exp}$ vs log $k_a^{HL}$ (eq. A.1.4) corresponding to the reaction: $M + HL \rightarrow ML + H$. Theoretical values = $k_a^{HL}$; see text. Ionic strength and temperature: see Table A.1.6a. Each symbols represents a different ligand (the corresponding figures refer to those of Table A.1.6a).
Table A.1.6a
Reported values of the rate constants $k_{a,\text{L,exp}}$ and $k_{a,\text{HL,exp}}$ (eq. A.1.4) for the reactions:
\[ \text{M} + \text{L} \rightarrow \text{ML} , \quad \text{and} \quad \text{M} + \text{HL} \rightarrow \text{ML} + \text{H} \]
respectively. The \( n^o \) of each complex refers to Fig A.1.1a,c

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<th>Number</th>
<th>Ligand</th>
<th>Metal</th>
<th>( T ) (°C)</th>
<th>( I ) (M)</th>
<th>$\log k_{a,\text{L,exp}}$ (M(^{-1}).s(^{-1}))</th>
<th>$\log k_{a,\text{HL,exp}}$ (s(^{-1}))</th>
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Table A.1.6b
Reported values of the rate constant $k_{a,n}^{\exp}$ for the reaction: $ML_{n-1} + L \rightarrow ML_n$.

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<tbody>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>ML$^2$</td>
<td>ML$^3$</td>
</tr>
<tr>
<td>1</td>
<td>Acetate</td>
<td>Hg</td>
<td>30</td>
<td>1.0</td>
<td>9.89</td>
<td>[68]</td>
</tr>
<tr>
<td>2</td>
<td>Ammonia</td>
<td>Co</td>
<td>25</td>
<td>5.53</td>
<td>5.74</td>
<td>6.32</td>
</tr>
<tr>
<td>3</td>
<td>Chloride</td>
<td>Hg</td>
<td>25</td>
<td>0</td>
<td>9.88</td>
<td>[69]</td>
</tr>
<tr>
<td>4</td>
<td>Cyanide</td>
<td>Cd</td>
<td>25</td>
<td>0.1</td>
<td>10.53</td>
<td>[70]</td>
</tr>
<tr>
<td>5</td>
<td>Glycinate</td>
<td>Co</td>
<td>25</td>
<td>6.30</td>
<td>5.90</td>
<td>[54]</td>
</tr>
<tr>
<td>6</td>
<td>Glycinate</td>
<td>Cu</td>
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<td>8.60</td>
<td>[55]</td>
</tr>
<tr>
<td>7</td>
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<td>4.75</td>
<td>4.63</td>
<td>[54]</td>
</tr>
<tr>
<td>8</td>
<td>Thiocyanate</td>
<td>Zn</td>
<td>25</td>
<td>8.17</td>
<td>8.73</td>
<td>8.60</td>
</tr>
</tbody>
</table>
Metal complexes with protonated ligands

Most ligands can be protonated. Two parallel reactions may then lead to the formation of ML, by reaction of M with either L or the protonated ligand HL. Again specific reactions may occur, and whenever possible the relevant literature data should be used. However it has been shown experimentally [73] that for many simple mono and bidentate ligands, as well as for a few multidentate ligands, the overall formation rate constant can be written as:

\[ k_a = k_a^L + k_a^{HL} \beta H[H] \]  

(A.1.4)

where \( k_a^L \) (≡ \( k_a^{MS} \) section 6.3.3) and \( k_a^{HL} \) are the rate constants for the reaction of M with L (\( M + L \rightarrow ML \)) and HL (\( M + HL \rightarrow ML + H \)) respectively. The experimental values reported in the literature for \( k_a^{HL} \) are compiled in Table A.1.6a. In absence of such data, an estimation of \( k_a^{HL} \) can be obtained as follows, for monoprotonated ligands, by assuming that the classical Eigen mechanism is operative [74]. Extension to multiprotonated ligand and/or to the more general eq. 6.8 is straightforward.

The two paths for ML formation are linked as follows:

\[
\begin{align*}
M + L & \rightleftharpoons (M,L) \rightarrow ML \\
M + HL & \rightleftharpoons (M,HL) \rightarrow ML + H \\
K_{os,ML} & = k_{w,ML} \\
K_{os,MHL} & = k_{w,MHL}
\end{align*}
\]

The overall formation rate, R, is thus:

\[ R = k_{w,ML} [(M,L)] + k_{w,MHL} [(M,HL)] = k_a [M][L] \]  

(A.1.5)

where \( k_a \) is the effective, overall rate constant for the formation of ML. Since, for 1/1 complexes, the dehydration rate constant can be assumed to be independent of the nature of the ligand and thus of its degree of protonation, \( k_a^{ML} = k_a^{MHL} = k_a \). By assuming that equilibrium is always reached for the formation of both outer-sphere complexes (classical Eigen mechanism), their concentrations can be computed from their complexation constants, \( K_{os,ML} \) and \( K_{os,MHL} \). Then, eq. (A.1.5) can be expressed as:

\[ R = k_a [M] ( K_{os,MHL} [HL] + K_{os,ML} [L] ) = k_a [M][L] ( K_{os,MHL} \beta H[H] + K_{os,ML} ) \]  

(A.1.6)

where \( \beta H = [HL]/[L][H] \). The effective, overall rate constant is thus:

\[ k_a = k_a \left( K_{os,MHL} \beta H[H] + K_{os,ML} \right) \]  

(A.1.7)

Comparing eqs. (A.1.4) and (A.1.7) shows that \( k_a^L = k_a^{MS} = k_a^{os,ML} \), while \( k_a^{HL} = k_a^{HL,K_{os,MHL}} \). Therefore, according to this theory, the only difference between \( k_a^L \) and \( k_a^{HL} \) is their respective values of \( K_{os} \). Since \( z_{HL} \) is less negative than \( z_L \), it is expected that \( K_{os,MHL} < K_{os,ML} \) (eq. 6.11). At low pH however, \( \beta H[H] > 1 \) which may compensate for the lower value of \( K_{os,MHL} \). In general, the path through (M,HL) formation will predominate when:

\[ [H] >> \frac{K_{os,ML}}{K_{os,MHL}} \beta H[H] \]  

(A.1.8)
Interestingly, \(\log(K_{os}^{ML}/K_{os}^{MHL})\) varies little (from 1.2 to 0.8 when ionic strength varies from 0 to 0.1 M, irrespective of \(z_L\)). Thus as a good approximation, eq. A.1.8 reduces to \([H] \gg 10/\beta_{HL}\).

Figure S6.8.1c shows a plot of experimentally determined values of \(k_a^{HL}\) for a number of complexes (Table A.1.6a for numerical values), as function of their theoretical values \((= k_a K_{os,MHL})\). It is seen that for a number of complexes, experimental values are close (although a bit lower) than experimental ones. However the difference may be up to 2-3 orders of magnitude for some complexes, often with multidentate ligands. Several explanations have been given. An important one is that, in HL, two or several arms may form through hydrogen bonding, rings which are difficult to break down during ML formation [75].

Figure A.1.1a shows a plot of experimentally determined values of \(k_a^{MS}\) (listed in Table A.1.6a), as function of \(k_a^{MS}\) values computed theoretically from eqs 6.8, 6.13 and 6.14. It shows that indeed a quite good agreement is observed over a very large range of values, even for bidendate and some multidentate ligands. The figure also enables to evaluate the variability of the points around the straight line of slope 1.0, and thus the general validity of this theory.
A.2 Dynamic parameters of fulvic and humic substances

A.2.1 Diffusion coefficients

Figure A.2.1. A. Diffusion coefficient ($D$) and hydrodynamic radius ($r_{FS}$) of Suwanee river fulvic substances (SRFS) as function of pH, for 2 ionic strengths (5 mM: white circles; 50 mM: black squares). $D$ and $r_{FS}$ are related by the Stokes Einstein equation. SRFS = 10 mg/l. Modified from (35). B. Diffusion coefficient ($D$) and hydrodynamic radius ($r_{HS}$) of Suwanee river humic substances (SRHS) as function of pH, for 2 ionic strength (5 mM: white circles; 50 mM: black squares). SRFS = 10 mg/l. $D$ and $r_{HS}$ are related by the Stokes Einstein equation. Modified from [35].
The following linear relationships (units in mV) are observed between \( \bar{\psi} \) and \( \psi_c \) or \( \bar{\psi} \) and \( \psi_0 \), at variable ionic strengths:

\[
\begin{align*}
\text{at pH 10.7:} & \quad \bar{\psi} = 0.65 \psi_c - 8.95 \\
& \quad \bar{\psi} = 1.05 \psi_0 - 16.7 \\
\text{at pH 4:} & \quad \bar{\psi} = 0.71 \psi_c + 0.62 \\
& \quad \bar{\psi} = 1.15 \psi_0 - 3.01
\end{align*}
\]
Below the relationship \( \overline{\psi} = 0.68 \psi_c + a \) will be used, where the coefficient 0.68 is an average of those of eqs A.2.2 and A.2.4, and \( a \) is a parameter which depends on pH, but not on ionic strength. By assuming that \( a \) is a linear function of pH in the pH range 4-10.7, one gets, for any pH and ionic strength:

\[
\overline{\psi} = 0.68 \psi_c - 1.43 \text{pH} + 6.34 \tag{A.2.6}
\]

This relationship is used below to get an empirical equation enabling to compute values of \( \overline{\psi} \) at any pH and ionic strength.

---

**Figure A.2.3-1.** Equilibrium potential distribution inside and outside Suwanee river fulvic molecules, at pH = 10.7 and various ionic strengths indicated on the curves (in mM). \( r_{FS} = 0.88 \text{ nm} \) = radius of fulvic substances. Modified from [41].

**Figure A.2.3-2.** Equilibrium potential distribution inside and outside Suwanee river fulvic molecules, at pH = 4 and various ionic strengths, indicated on the curves (in mM). \( r_{FS} = 0.83 \text{ nm} \) = radius of fulvic substances. Modified from [41].
From the change of $\psi_c$ with ionic strength, in figures A.2.3-1, A.2.3-2 and A.2.3-3, the following empirical relationship is obtained for fulvics:

$$\psi_c = b + c \log I$$  \hspace{1cm} (A.2.7)

where $I$ is ionic strength, and $b$ and $c$ are constant parameters which only vary with pH. The parameter $c$ varies little with pH and this variation is assumed to be linear in the range $4 < \text{pH} < 10.7$. With the data of Figs A.2.3-1 to A.2.3-3, we get:

$$c = -5.37 + 4.64 \text{pH}$$  \hspace{1cm} (A.2.8)
The parameter \( b \) in eq. A.2.7 for fulvics is obtained by fitting the corresponding curve of Fig. A.2.3-4 with a polynomial function of pH:

\[
b = -328.9 + 190.2 \text{ pH} - 41.60 \text{ pH}^2 + 3.670 \text{ pH}^3 - 0.1130 \text{ pH}^4 \tag{A.2.9}
\]

By combining eqs A.2.6-A.2.9, one gets the general empirical expression:

\[
\overline{\psi} = -217.4 + 127.9 \text{ pH} - 28.29 \text{ pH}^2 + 2.496 \text{ pH}^3 - 0.07685 \text{ pH}^4 + 3.159 \text{ pH} \log I - 3.654 \log I \tag{A.2.10}
\]

Equation A.2.10 enables to compute \( \overline{\psi} \) values at any pH or ionic strength in the domains \( 4 < \text{pH} < 11 \) and \( 0.005 \text{ M} < I < 0.15 \text{ M} \). The difference with experimental data used to find eq. A.2.10 is less than 1 mV.

A.2.3 Site distribution of fulvic and humic substances related to the Differential Equilibrium Function

The concept of Differential Equilibrium Function (DEF) is applicable to any metal complexation in a mixture of a large number of different ligands, each site type, \( \text{S} \), forming a 1:1 complex, \( \text{MS}, \) with \( \text{M} \), with a stability constant \( \text{iK} \). DEF does not make any assumption on the driving force for the complexation reaction. Qualitatively, the titration curve of a chemically heterogeneous complexant, like FS (Fig. A.2.4A), can be thought of as resulting from the successive saturation of a large number of different ligands, each one being present in very small concentration. According to this picture, the curve of \( \log ([\text{MS}]_t/\text{[FS]}) = f(\log [\text{M}] \) should show a large number of jumps of very small amplitude [36]. In practice, this is not so because the \( \text{iK} \) values of the successive complexes are too close to each other for each ligand \( \text{i} \) to be titrated separately. Consequently a continuous curve, devoid of jump is observed (Figs. A.2.4-A,C) and the effective equilibrium “constant”, \( K^* \), decreases along the titration curves since weaker and weaker sites are titrated.

At a given point, \( j \), of the titration of FS by M, where the free metal concentration is \( j[M] \), the strongest site types are saturated, the weakest site types are free, and intermediate site types are partially occupied. A value of the effective equilibrium constant at point \( j \), for the reaction of \( \text{M} \) with the whole of the site types at this point, is given by [50]:

\[
j[K^*] = - \frac{d^j[\text{MS}]_t}{j[M]} d^j[S]_t \tag{A.2.11}
\]

where \( [\text{MS}]_t = \Sigma [\text{M'S}] \) and \( [S]_t = \Sigma [\text{S}] \) are the total molar concentrations of the complexes and of free sites respectively, at point \( j \). \( ^j[K^*] \) decreases when \( j[M] \) increases along the titration curve, and the corresponding ensemble of points forms the so-called DEF, \( K^* \). Its interesting features are the following: i) it is readily computed experimentally [38, 40, 78], ii) it is simply related to the parameters of each complexing site type \( \text{i} \) (i.e., \( \text{iK}; \text{iχ} = \text{mole fraction of site type i }; \text{θ} = \text{degree of site occupation by M}; \) see Figure S4-C-F and related discussion), and iii) it is simply related to \( [\text{M}] \) [36,37] by:

\[
K^* = (1-\Gamma)/\Gamma [\text{M}] \tag{A.2.12}
\]

Combining eqs. 29 and A.2.12 leads to:
\[
\log \left[ \frac{[MS]_t}{[FS]} \right] = \Gamma \log K^*_o - \Gamma \log K^* 
\] (A.2.13)

**Figure A.2.4 A,B**  Examples of experimental relationship between the values of \( K^* \) (eq. S14-S15) and the ratio of the metal bound to fulvic substances (expressed as \([MS]_s\) = molar concentration of bound metal, over the fulvic concentration, expressed as dissolved organic carbon concentration, DOC, in kg/dm\(^3\) of solution). Note that \([FS] \sim 2 \text{ DOC}\). T = 25°C, I = 0.1M. A: Titration of a humic sample by Cu(II) (38). B: Results obtained for a large number of different water fulvic samples. Each point corresponds to the \( K^* \) of a different sample at the corresponding value of \([MS]_t/\text{DOC}\). Modified from [39] and [79].

Where \( K^*_o \) is a constant characteristic of M under the experimental conditions used (pH, T, ionic strength). It has been found (Figure A.2.4A) that this equation is valid for fulvic or humic minor sites, over at least 3–5 orders of magnitudes of \( \log K^* \) depending on metal, and no limit to its validity has yet been found in the low \([MS]_t/\{FS\} \) range (corresponding to large \( K \) values). Equation A.2.13 is applicable both to laboratory titration of individual fulvic samples (38, 80-82; Fig. A.2.4A) and for the comparison of the complexing properties of fulvic of various origins (39, 82,83; Fig. A.2.4B). Interestingly, the latter results show that both \( \Gamma \) and \( K^*_o \) depend on the nature of the metal ion, but can be considered as rather independent from the origin of the fulvic.

Note that \( K^*_o \) is only a reference parameter equal to \( K^* \) when the ordinate of Fig. A.2.4 is nil. Its value (in dm\(^3\)/mol) depends on the parameter and units used on the ordinate, e.g. \([M]/\{FS\}\) (in mol/kg of fulvics) or \([MS]_t/\text{DOC}\) (in mol/kg of C) and should be selected coherently with the latter.

It has been shown that \( K^* \) is an average of all the stability constants \( ^iK \), weighted by the degree of occupation \( i(\theta) \) and the mole fraction, \( \Delta^i\chi \), of each site type, \( i \) [37,38,39,40].

\[
K^* = \frac{\sum_{i=1}^{n} iK^i \theta(1 - i\theta) \Delta^i \chi}{\sum_{i=1}^{n} i\theta(1 - i\theta) \Delta^i \chi} 
\] (A.2.14)

where \( \Delta^i\chi = [iS]/\Sigma[iS] \), \([iS] \) = total concentration of site type \( i \), and \( i\theta = [M^iS]/[iS] \). \( K^* \) is related to [M] through eq. (A.2.15) valid for all sites:

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As it is discussed below, for any [M] value (e.g. at any titration point of FS by M), the relative contribution of a site i to the $K^*$ value is maximum if $iK = 1/[M]$ and about negligible ($\leq 1\%$) if either $\log iK \geq -\log[M] + 2$ or $\log iK \leq -\log[M] - 2$.

Figure A.2.4-C gives a schematic representation of a typical titration curve for the minor sites of a chemically heterogeneous complexant. The horizontal axis coincides with the direction of the titration, from left to right. The increase in [MS] or in [M] corresponds to the successive saturation of weaker and weaker sites and in turn to a decrease in the $\log iK$ of the sites effectively active at each titration point. Figures A.2.4-DEF give a quantitative description of a complexant whose site distribution ($\Delta_i \chi = f(\log iK)$; fig. A.2.4-D, curve 2) corresponds to a linear DEF (eq. A.2.13) with $\Gamma = 0.5$, i.e. a case often found in natural systems (Table 6.2). Such a site distribution can be simulated by the Sips distribution function [37, 38]. Figures A.2.4-DEF show the contributions of each individual site to the various terms of eq. S17, at a given titration point corresponding to $[M] = 10^{-10}$ M. The horizontal axis is drawn with decreasing values of $iK$, to allow comparison with fig. A.2.4C.

At each titration point, three classes of site types may be discriminated on the bases on their value of $i\theta$ (Fig. A.2.4-D): class I includes the sites for which values of $iK$ are so large that they are fully saturated (i.e. $i\theta \sim 1$ in this class); class II includes the sites whose $iK$ values are not as high as those of class I, but high enough to form stable complexes; in this class, $0.01 < i\theta < 0.99$; class III includes the sites for which $iK$ is so low that $i\theta \sim 0$. The contribution of any site in controlling [M] (and $K^*$) depends on a) $i\theta$ (most effective control being achieved when $i\theta = 0.5$), and b) $iK$ (eq. A.1.6).

$i\theta.(1-i\theta)$ (Fig. A.2.4-E) is one of the weighting factors of eq. A.2.14. It is a measure of effect a) above: $i\theta.(1-i\theta)$ is zero when the sites I are either saturated ($i\theta = 1$) or totally free ($i\theta = 0$) and it passes through a maximum at $i\theta = 0.5$, for sites with $iK$ close to $iK = 1/[M]$ (= $10^{10}$ M$^{-1}$ in fig. A.2.4-CDEF). Clearly, with respect to this property, sites having $-2 - \log[M] < \log iK < 2 - \log[M]$ are the only important ones controlling [M] in the whole system (note that the above limits for $iK$ depends somewhat on $\Gamma$). The term $i\theta.(1-i\theta)$ however is not sufficient to compare the relative importance of the various sites to control [M]; the influence of their relative concentrations on the buffering action should also be considered. The latter increases with the mole fraction of occupied + unoccupied sites, $\Delta\chi$. The relationship between $\Delta\chi$ and $\log K$ is shown in fig. A.2.4-D (curve 2). The actual contribution of each site to the buffering action is obtained by multiplying $i\theta.(1-i\theta)$ by $\Delta\chi$. This yields curve 1 in fig. A.2.4-F, which, when compared with fig. A.2.4-E reflects the dissymmetry of the $\Delta\chi$ distribution, giving more importance to the sites present in large concentrations.

The role of $\log iK$ (effect b) above) is shown in fig. A.2.4-F (curve 2) which reflects a bias in the contributions of the sites, favoring large $iK$ values. Thus $K^*$ (eq. A.2.14) is an average of the $iK$'s of all sites, weighted for their buffering action. Graphically it is represented by the ratio of the surface areas under curves 1 and 2 of fig. A.2.4-F. $K^* = 10^{10} = 1/[M]$ is obtained from the figure.
Figure A.2.4-C. Definition of the strong (I), intermediate (II) and weak (III) site classes amongst the minor sites, at any particular titration point (corresponding to the free metal ion concentration [M]) of fulvic/humic complexants by M. Calculations are based on the assumption that the system follows eq. 6.22, with the same conditions as in figures A.2.4-DEF. Tabulated numerical values are the percentages of the summation terms of eq. A.2.14 corresponding to each site type class, with respect to that for all three classes. In the numerators, when no subscript is given under the symbol Σ, summation is done over site type class I, II or III, as indicated in the column of the table. Modified from [36].

The important point is that, although dissymmetric site distribution (Δiχ= f(logiK)) has a “spreading” effect on the sites which play an important role on K* (compare figs A.2.4-E and A.2.4-F), this effect is not large, since site type of class II (10^{12} > log_iK > 10^8) account for 88% of both the numerator and denominator of eq. A.2.14 (fig. A.2.4-C). It is also important
to note that the width of class II sites may be affected by the value of \( \Gamma \), but it does not depend on \([M]\).

![Figure A.2.4-D,E,F: Changes in the various terms of eq. A.2.14, corresponding to each site type \( i \), as a function of their stability constant \( \mathcal{K} \) (for explanations, see text). Curves calculated under the following conditions: \([M] = \text{constant} = 10^{-10}M\); for each site, \( \mathcal{K} = \mathcal{K}_0/[M](1-\theta) \) with \( \theta = [M^iS]/[iS] \) and \( \Delta \chi = [iS]/\Sigma [iS] \). The overall complexation follows eq. A.2.13, i.e. it obeys the Freundlich isotherm, and \( \Delta \chi \) values are given by a Sips distribution (eq. 6.27) with \( \Gamma = 0.5 \) and \( \log K_{o}^* = 8.5 \) and \( \Delta \log K = 0.1 \). (Modified from 36; for calculation details, see 38).
A.3 Dynamic parameters of particles

A.3.1 Aggregate structure and size distribution (Pareto law)

Typical values of the exponent $\beta$ of Pareto law, valid for aquatic particle/aggregates, are given in Table A.3.1.

<table>
<thead>
<tr>
<th>Aquatic system</th>
<th>Dominant component in aggregates</th>
<th>$\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake Bret</td>
<td>am-FeOOH</td>
<td>3.0</td>
</tr>
<tr>
<td>Rhine river (CH)</td>
<td>alumino silicate</td>
<td>3.0</td>
</tr>
<tr>
<td>Alpine river (CH)</td>
<td>silica</td>
<td>2.7</td>
</tr>
<tr>
<td>Groundwater Noiraigue (CH)</td>
<td>Calcite, FeOOH</td>
<td>2.8</td>
</tr>
<tr>
<td>Groundwater Grimsel (CH)</td>
<td>silica</td>
<td>3.0</td>
</tr>
<tr>
<td>Groundwater Wallenberg (CH)</td>
<td>silica</td>
<td>4.0</td>
</tr>
<tr>
<td>Groundwater Markham Clinton (UK)</td>
<td></td>
<td>2.7</td>
</tr>
<tr>
<td>Lac Leman hypolimnion (CH)</td>
<td>Organic matter</td>
<td>4.0</td>
</tr>
<tr>
<td>Gulf Mexico</td>
<td>Organic matter</td>
<td>2.65</td>
</tr>
</tbody>
</table>

A.3.2 Surface area and coarse-grained concentrations of the complexing sites

The minor components, $X$

The minor complexants (e.g. am-FeOOH), adsorbed on the basic subparticles (e.g. aluminosilicates), may form the strongest complexes with metal ions inside the aggregates, even though their proportions in the aggregate are very small. A minor component is denoted below by $X$, whereas the major component constituting the basic subparticles is denoted by $P$.

The surface area of a patch of $X$, with thickness $h_X$, per unit volume of solution, is:

$$A_X = \frac{\{X\}_t}{h_X \rho_X}$$  \hspace{1cm} (A.3.1)

where $\{X\}_t$ is the total mass concentration of the component $X$ in kg.dm$^{-3}$, and $\rho_X$ is its density. On the other hand, the total surface area of the aggregates per unit volume of solution, $A_{b,t}$, is obtained by combining the volume of the major component, $V_{b,t} = \{P\}_t/\rho_P$, the integration of eq. 6.32 between $r_{min}$ and $r_{max}$, and eqs (6.34) and (6.35). One gets:

$$A_{b,t} = \frac{3\{P\}_t}{b\rho_P}$$  \hspace{1cm} (A.3.2)

where $\{P\}_t$ is the total mass concentration of the major component of the aggregate, in kg.dm$^{-3}$, and $b$ is the radius of the basic subparticles. Thus:
The total coarse-grained molar concentration of sites of X is given by:

\[
[S]^X_t = \frac{n_s^X}{N_A} \frac{A_X}{\rho_X} \quad (A.3.4)
\]

where \(n_s^X\) is the number of complexing sites per surface area of compound X (Table A.3.2), and \(N_A\) is the Avogadro number. Combination of eqs (A.3.1) and (A.3.4) gives:

\[
[S]^X_t = \frac{n_s^X}{N_A} \frac{A_X}{\rho_X} \quad (A.3.5)
\]

The major component, P.

The surface area of the major component non covered by X, \(A_P\) is:

\[
A_P = A_{b,t} - \sum A_X \quad (A.3.6)
\]

By combination with eq. A.3.3:

\[
A_P = A_{b,t} \left(1 - \frac{b \{X\}_{t} \rho_P}{3h_X \{P\}_{t} \rho_X} \right) \quad (A.3.7)
\]

The total coarse-grained molar site concentration, \([S]^P_t\), is given by:

\[
[S]^P_t = \frac{n_s^P}{A_P/N_A} \quad (A.3.8)
\]

where \(n_s^P\) is the number of complexing sites per surface area of compound P (Table A.3.3). By combination with eq. A.3.7, one gets:

\[
[S]^P_t = \frac{3n_s^P \{P\}_{t}}{b \rho_P N_A} - \frac{n_s^P}{N_A} \frac{\{X\}_{t}}{h_X \rho_X} \sum \frac{n_s^X}{h_X \rho_X} \quad (A.3.9)
\]

When the surface occupied by the minor components is small compared to \(A_{b,t}\), the second terms of eqs. (A.3.6, A.3.7, A.3.9) are negligible.
Table A.3.2. Values of fractal dimensions, $D_f$, reported for natural aggregates in aquatic systems (Selected from [43]).

<table>
<thead>
<tr>
<th>Aquatic medium (nature of aggregate components)</th>
<th>$D_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil (mostly alumino-silicate, quartz)</td>
<td>2.29</td>
</tr>
<tr>
<td>River sediment</td>
<td>2.75</td>
</tr>
<tr>
<td>Lacustrine aggregates</td>
<td>1.39-1.69</td>
</tr>
<tr>
<td>Estuarine aggregates</td>
<td>1.78-2.06</td>
</tr>
<tr>
<td>Oceanic aggregates</td>
<td>1.9-2.1</td>
</tr>
<tr>
<td>Marine snow (mostly organic)</td>
<td>1.3-1.7</td>
</tr>
<tr>
<td>Flocs of activated sludge (mostly organic)</td>
<td>1.4-2.0</td>
</tr>
</tbody>
</table>

A.3.3 Stoichiometric and thermodynamic complexation parameters

Table A.3.3. Density and surface properties of metal oxides relevant in natural waters. Am = amorphous. \(^{a}\) Values for Geothite and Lepidocrocite are 3.3-4.3 and 4.05-4.31 respectively; \(^{b}\) values for Opal and Tridymite are 1.73-2.16 and 2.27 respectively; \(^{c}\) Value for Pyrolusite is 5.04-5.08. Density: taken from [44]; Other parameters, from [39].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Density</th>
<th>$A_s$ (m$^2$/g)</th>
<th>$n_s$=number of sites per nm$^2$</th>
<th>pH$_{ZPC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Am-FeOOH</td>
<td>2.44-3.60(^{a})</td>
<td>700</td>
<td>10</td>
<td>7.9-8.1</td>
</tr>
<tr>
<td>Am-SiO$_2$</td>
<td>~ 2(^{b})</td>
<td>260</td>
<td>5</td>
<td>3.0-3.5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>3.97</td>
<td>100</td>
<td>10</td>
<td>8.4</td>
</tr>
<tr>
<td>Am-MnO$_2$</td>
<td>~ 5.06(^{c})</td>
<td>260</td>
<td>10</td>
<td>2.25</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>2-3</td>
<td>800</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

Values of the logarithm of stability constants for proton and metal ion binding with metal oxides and natural particles/aggregates. Complexation constants for SiO$_2$, Al$_2$O$_3$ and natural particles/aggregates are apparent constants, $K$, (eq 6.45), not corrected for surface charge and ionic strength. Complexation constants for am-FeOOH, $K_{int}$, and all acid-base constants, $K_{H1}^{int}$, $K_{H2}^{int}$ (eqs. below) are intrinsic constants, valid at I=0, and $\psi = 0$. (x/y) indicates the range of published values, from x to y. The variability depends largely on the chemical composition of aggregates of the test samples. Isolated values are averages of literature data. s.m. = suspended matter. T = 25°C; unless otherwise stated, I = 0.01M; \(^{a}\) : I = 1.0M; \(^{b}\) : I=0.1M; \(^{c}\) values recomputed from reported values of $Q = n_gK$, by using arbitrarily $n_g = 1$ mol.kg$^{-1}$; they should be considered as indicative only. Q is defined as K in eq. 6.47, but with [HS] expressed in kg.dm$^{-3}$; in most cases, the total site density of aggregates, $n_g$, is between 0.1 and 10 mol.kg$^{-1}$.

\[
K_{H1}^{int} = \frac{[MS][H]}{[S][H]^{2}} \exp(F\psi/RT); \quad K_{H2}^{int} = \frac{[H_2S]}{[HS][H]} \exp(F\psi/RT); \quad K_{int} = \frac{[MS][H]}{[HS][M]} \exp(F\psi/RT)
\]

[MS], [S], [HS] and [H$_2$S] are the coarse-grained concentrations of the surface complex, MS, of the free site, S, and of the protonated surface sites HS and H$_2$S$^+$ (Similar but slightly different expressions are used in the so-called 1-pK model [76]). $K_{H1}^{int}$, $K_{H2}^{int}$ and $K_{int}$ do not depend on surface electric charge and surface potential, $\psi$. K and $K_{int}$ have no unit and in their expressions, the coarse-grained concentrations,[MS] and [HS], may be expressed in mol.dm$^{-3}$, kg.dm$^{-3}$, or kg/m$^2$ provided the same units are used for both. Acid-base and complexation reactions of MnO$_2$ with a number of divalent metals are discussed in details in [77].
<table>
<thead>
<tr>
<th>Solid</th>
<th>Complexation constant</th>
<th>Acid-base constant</th>
<th>log$K_1^H$</th>
<th>log$K_2^H$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
<td>Co</td>
<td>Cu</td>
<td>Hg</td>
</tr>
<tr>
<td>am-FeOOH [45]</td>
<td>0.47</td>
<td>0.46</td>
<td>2.89</td>
<td>7.76</td>
</tr>
<tr>
<td>γ-Al$_2$O$_3$ [39]</td>
<td>-</td>
<td>-3.7$^b$</td>
<td>-2.1$^b$</td>
<td>-</td>
</tr>
<tr>
<td>am-SiO$_2$ [39]</td>
<td>-6.1$^a$</td>
<td>-7.3$^a$</td>
<td>-5.5$^a$</td>
<td>-</td>
</tr>
<tr>
<td>River s.m. [46$^c$, $^{47b,c,48,49,75}$]</td>
<td>-3.9/+0.4</td>
<td>-</td>
<td>-1.8/+1.5</td>
<td>-</td>
</tr>
<tr>
<td>Estuarine s.m. [46$^c$, $^{47b,c,49}$]</td>
<td>-2.2</td>
<td>-0.5</td>
<td>+0.2</td>
<td>-</td>
</tr>
<tr>
<td>Marine s.m. [48]</td>
<td>-3.9/-1.5</td>
<td>-1.6/-0.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Marine sediment [48]</td>
<td>-3.1</td>
<td>-1.4</td>
<td>-0.6</td>
<td>1.6</td>
</tr>
<tr>
<td>River sediments [48,75]</td>
<td>+0.2/+1.0</td>
<td>+1.7/+2.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Marine sediment [48]</td>
<td>-3.7/+1.0</td>
<td>-1.8/+1.7</td>
<td>-3.8</td>
<td>-1.7</td>
</tr>
<tr>
<td></td>
<td>- 0.6</td>
<td>1.6</td>
<td>+1.4</td>
<td>-2.2/-0.2</td>
</tr>
</tbody>
</table>
A.3.4 Electrostatic potential profiles at alumina- and iron oxide- solution interface

![Graph showing electrostatic potential profiles at different pH values and ionic strengths.](image)

Figure A.3.1 Change with pH of ψ potential at the surface of aluminum oxide, for 2 different ionic strengths. T = 25°C. Modified from [51].
Figure A.3.2 A Change with pH of $\psi$ potential at the surface of amorphous iron oxide, for different values of ionic strength. 1:1 electrolyte. T = 25°C. Recomputed from values in [45].  B Change with pH of $\psi$ potential at the surface of amorphous iron oxide, for different values of ionic strength. 2:2 electrolyte. T = 25°C. Recomputed from values in [45].
A.4 The average rate constants of CuCO_3 and Cu(CO_3)_2

Let's consider the following successive reactions of Cu with CO_3, in which the slow step is the rate of formation/dissociation of CuCO_3 from Cu and CO_3, while CuCO_3 and Cu(CO_3)_2 are always at equilibrium:

\[
Cu + CO_3 \rightleftharpoons k_d CuCO_3 + CO_3 \rightleftharpoons k_a Cu(CO_3)_2
\]  
(A.4.1)

At a consuming interface, the kinetic flux is:

\[
J_{kin} = k_d \mu_{CO_3} [CuCO_3]
\]  
(A.4.2)

where

\[
\mu_{CO_3} = \frac{D^{1/2}_{Cu}}{(k_d[CO_3])^{1/2}}
\]  
(A.4.3)

Here we use \(\mu\) instead of \(\lambda\), since \(K_{CO_3}>>1\), the term with \(k_{d1}\) can be omitted. Now we want to express the kinetic flux, as function of the whole of the Cu-carbonato complexes. This can be done by using average values of of \(k_a\), \(k_d\) and \(\mu\), namely \(\bar{k}_a\), \(\bar{k}_d\) and \(\bar{\mu}\). We get:

\[
J_{kin} = \bar{k}_d \bar{\mu} ([CuCO_3] + [Cu(CO_3)_2]) = \bar{k}_d \bar{\mu} [Cu]_c
\]  
(A.4.4)

where \([Cu]_c\) is the sum of the concentrations of the Cu carbonato complexes, and

\[
\bar{\mu} = \frac{D^{1/2}_{Cu}}{(\bar{k}_a[CO_3])^{1/2}}
\]  
(A.4.5)

Since only the first step of eq. A.4.1 is rate limiting \((k_{d1}=9333s \text{ and } k_{d2}=8.71.10^6s)\), the reaction layer thickness is fixed by \(k_{d1}\), i.e. eqs A.4.3 and A.4.5 are equal, with:

\[
\bar{k}_a = k_{d1}
\]  
(A.4.6)

In addition, the degree of complexation of Cu(II) must be conserved, i.e.:

\[
[Cu]_c/[Cu] = [CuCO_3]/[Cu] + [Cu(CO_3)_2]/[Cu]
\]  
(A.4.7)

By expressing \([Cu]_c/[Cu]\) as \(\bar{K}[CO_3]\), and the right hand side of eq. A.4.7 via the thermodynamic stability constants of the 1/1 and 1/2 complexes, one gets:

\[
\bar{k}_d = \frac{\bar{k}_a[CO_3]}{K_1 \bar{K}_2[CO_3] + K_1[CO_3]}
\]  
(A.4.8)

where \(\bar{K} = \frac{\bar{k}_a}{\bar{k}_d}\). By combining eqs A.4.8, and A.4.6, on gets the relationship between \(\bar{k}_d\) and \(k_{d1}\):
\[ \bar{k}_d = \frac{k_{d1}}{1 + K_2[CO_3]} \] (A.4.9)
A.5 Lists of results of simulations of Pb(II) in natural freshwaters

A.5.1 Sensitivity analysis by changing $\Gamma$ of fulvics

Table A.5.1a $\Gamma=0.3$

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1.18e-15</td>
<td>3.93e-5</td>
<td>5.08e-17</td>
<td>0.54</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>1.55e-15</td>
<td>5.17e-5</td>
<td>4.27e-17</td>
<td>0.45</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>6.40e-14</td>
<td>2.13e-3</td>
<td>1.69e-15</td>
<td>17.94</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>3.00e-9</td>
<td>100</td>
<td>7.59e-15</td>
<td>80.57</td>
</tr>
<tr>
<td>Total</td>
<td>3.00e-9</td>
<td>100</td>
<td>9.42e-15</td>
<td>100</td>
</tr>
</tbody>
</table>

Table A.5.1b $\Gamma=0.60$

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>3.88e-12</td>
<td>0.13</td>
<td>1.67e-13</td>
<td>1.26</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>5.10e-12</td>
<td>0.17</td>
<td>1.86e-13</td>
<td>1.40</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>2.11e-10</td>
<td>7.23</td>
<td>7.57e-12</td>
<td>56.92</td>
</tr>
<tr>
<td>PbFA</td>
<td>1.86e-9</td>
<td>62.00</td>
<td>5.07e-12</td>
<td>38.12</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>9.20e-10</td>
<td>30.67</td>
<td>2.75e-13</td>
<td>2.07</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
<td>1.33e-11</td>
<td>100</td>
</tr>
</tbody>
</table>

Table A.5.1c $\Gamma=0.8$

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>7.75e-12</td>
<td>0.26</td>
<td>3.33e-13</td>
<td>1.56</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>1.02e-11</td>
<td>0.34</td>
<td>3.85e-13</td>
<td>1.81</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>4.21e-10</td>
<td>14.03</td>
<td>1.57e-11</td>
<td>73.71</td>
</tr>
<tr>
<td>PbFA</td>
<td>7.15e-10</td>
<td>23.83</td>
<td>4.28e-12</td>
<td>20.09</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>1.84e-9</td>
<td>61.33</td>
<td>5.95e-13</td>
<td>2.79</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
<td>2.13e-11</td>
<td>100</td>
</tr>
</tbody>
</table>
A.5.2 Sensitivity analysis by changing log$K_0^*$ of fulvics

Table A.5.2a log$K_0^*$ = 5.4

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>7.77e-12</td>
<td>0.26</td>
<td>3.34e-13</td>
<td>1.70</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>1.02e-11</td>
<td>0.34</td>
<td>3.87e-13</td>
<td>1.96</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>4.22e-10</td>
<td>14.07</td>
<td>1.58e-11</td>
<td>80.20</td>
</tr>
<tr>
<td>PbFA</td>
<td>7.10e-10</td>
<td>23.67</td>
<td>2.58e-12</td>
<td>13.10</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>1.84e-9</td>
<td>61.33</td>
<td>5.99e-13</td>
<td>3.04</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
<td>1.97e-11</td>
<td>100</td>
</tr>
</tbody>
</table>

Table A.5.2b log$K_0^*$ = 6.4

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>3.88e-12</td>
<td>0.13</td>
<td>1.67e-13</td>
<td>1.26</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>5.10e-12</td>
<td>0.17</td>
<td>1.86e-13</td>
<td>1.40</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>2.11e-10</td>
<td>7.23</td>
<td>7.57e-12</td>
<td>56.92</td>
</tr>
<tr>
<td>PbFA</td>
<td>1.86e-9</td>
<td>62.00</td>
<td>5.07e-12</td>
<td>38.12</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>9.20e-10</td>
<td>30.67</td>
<td>2.75e-13</td>
<td>2.07</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
<td>1.33e-11</td>
<td>100</td>
</tr>
</tbody>
</table>

Table A.5.2c log$K_0^*$ = 7.4

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>7.52e-13</td>
<td>0.025</td>
<td>3.23e-14</td>
<td>0.67</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>9.88e-13</td>
<td>0.033</td>
<td>3.18e-14</td>
<td>0.66</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>4.08e-11</td>
<td>1.36</td>
<td>1.28e-12</td>
<td>26.50</td>
</tr>
<tr>
<td>PbFA</td>
<td>2.80e-9</td>
<td>93.33</td>
<td>3.44e-12</td>
<td>71.22</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>1.78e-10</td>
<td>5.93</td>
<td>4.19e-14</td>
<td>0.87</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
<td>4.83e-13</td>
<td>100</td>
</tr>
</tbody>
</table>
## A.5.3 Sensitivity analysis by changing log$K$' of aggregates

### Table A.5.3a log$K$' = 6.15

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>6.75e-12</td>
<td>0.23</td>
<td>2.90e-13</td>
<td>1.29</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>8.86e-12</td>
<td>0.30</td>
<td>3.25e-13</td>
<td>1.45</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>3.67e-10</td>
<td>12.23</td>
<td>1.33e-11</td>
<td>59.38</td>
</tr>
<tr>
<td>PbFA</td>
<td>2.62e-9</td>
<td>87.33</td>
<td>8.46e-12</td>
<td>37.77</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>1.60e-11</td>
<td>0.53</td>
<td>7.25e-15</td>
<td>0.032</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>3e-9</strong></td>
<td><strong>100</strong></td>
<td><strong>2.24e-11</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

### Table A.5.3b log$K$' = 7.15

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>6.30e-12</td>
<td>0.21</td>
<td>2.71e-13</td>
<td>1.30</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>8.26e-12</td>
<td>0.28</td>
<td>3.03e-13</td>
<td>1.45</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>3.42e-10</td>
<td>11.40</td>
<td>1.23e-11</td>
<td>58.85</td>
</tr>
<tr>
<td>PbFA</td>
<td>2.49e-9</td>
<td>83.00</td>
<td>7.94e-12</td>
<td>37.99</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>1.49e-10</td>
<td>4.97</td>
<td>6.11e-14</td>
<td>0.29</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>3e-9</strong></td>
<td><strong>100</strong></td>
<td><strong>2.09e-11</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

### Table A.5.3c log$K$' = 8.15

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>3.88e-12</td>
<td>0.13</td>
<td>1.67e-13</td>
<td>1.26</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>5.10e-12</td>
<td>0.17</td>
<td>1.86e-13</td>
<td>1.40</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>2.11e-10</td>
<td>7.23</td>
<td>7.57e-12</td>
<td>56.92</td>
</tr>
<tr>
<td>PbFA</td>
<td>1.86e-9</td>
<td>62.00</td>
<td>5.07e-12</td>
<td>38.12</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>9.20e-10</td>
<td>30.67</td>
<td>2.75e-13</td>
<td>2.07</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>3e-9</strong></td>
<td><strong>100</strong></td>
<td><strong>1.33e-11</strong></td>
<td><strong>100</strong></td>
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</table>

### Table A.5.3d log$K$' = 9.15

<table>
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<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>9.20e-13</td>
<td>0.031</td>
<td>3.96e-14</td>
<td>1.18</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>1.21e-12</td>
<td>0.040</td>
<td>4.34e-14</td>
<td>1.30</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>4.99e-11</td>
<td>1.66</td>
<td>1.77e-12</td>
<td>52.84</td>
</tr>
<tr>
<td>PbFA</td>
<td>7.68e-10</td>
<td>25.6</td>
<td>1.28e-12</td>
<td>38.21</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>2.18e-9</td>
<td>72.67</td>
<td>2.13e-13</td>
<td>6.36</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>3e-9</strong></td>
<td><strong>100</strong></td>
<td><strong>3.35e-12</strong></td>
<td><strong>100</strong></td>
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### Table A.5.3e log$K$' = 10.15

<table>
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<tr>
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<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>1.18e-13</td>
<td>0.0039</td>
<td>5.08e-15</td>
<td>1.15</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>1.55e-13</td>
<td>0.0052</td>
<td>5.45e-15</td>
<td>1.25</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>6.39e-12</td>
<td>0.21</td>
<td>2.25e-13</td>
<td>50.90</td>
</tr>
<tr>
<td></td>
<td>PbFA</td>
<td>Pb aggregates</td>
<td>Total</td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>------------</td>
<td>---------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.06e-10</td>
<td>2.78e-9</td>
<td>3e-9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.87</td>
<td>92.67</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.70e-13</td>
<td>3.57e-14</td>
<td>4.42e-13</td>
<td></td>
</tr>
<tr>
<td></td>
<td>38.46</td>
<td>8.08</td>
<td>100</td>
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</table>
### A.5.4 Sensitivity analysis by changing $\beta$ of aggregates

#### Table A.5.4a $\beta=2$

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>3.88e-12</td>
<td>0.13</td>
<td>1.67e-13</td>
<td>1.27</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>5.10e-12</td>
<td>0.17</td>
<td>1.86e-13</td>
<td>1.42</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>2.11e-10</td>
<td>7.23</td>
<td>7.59e-12</td>
<td>57.94</td>
</tr>
<tr>
<td>PbFA</td>
<td>1.86e-9</td>
<td>62.00</td>
<td>5.07e-12</td>
<td>38.70</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>9.20e-10</td>
<td>30.67</td>
<td>2.63e-14</td>
<td>0.20</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
<td>1.31e-11</td>
<td>100</td>
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</tbody>
</table>

#### Table A.5.4b $\beta=3$

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>3.88e-12</td>
<td>0.13</td>
<td>1.67e-13</td>
<td>1.26</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>5.10e-12</td>
<td>0.17</td>
<td>1.86e-13</td>
<td>1.40</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>2.11e-10</td>
<td>7.23</td>
<td>7.57e-12</td>
<td>56.92</td>
</tr>
<tr>
<td>PbFA</td>
<td>1.86e-9</td>
<td>62.00</td>
<td>5.07e-12</td>
<td>38.12</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>9.20e-10</td>
<td>30.67</td>
<td>2.75e-13</td>
<td>2.07</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
<td>1.33e-11</td>
<td>100</td>
</tr>
</tbody>
</table>

#### Table A.5.4c $\beta=4$

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>3.88e-12</td>
<td>0.13</td>
<td>1.67e-13</td>
<td>1.22</td>
</tr>
<tr>
<td>PbOH+Pb(OH)$_2$</td>
<td>5.10e-12</td>
<td>0.17</td>
<td>1.85e-13</td>
<td>1.35</td>
</tr>
<tr>
<td>PbCO$_3$+Pb(CO$_3$)$_3$</td>
<td>2.11e-10</td>
<td>7.23</td>
<td>7.53e-12</td>
<td>54.96</td>
</tr>
<tr>
<td>PbFA</td>
<td>1.86e-9</td>
<td>62.00</td>
<td>5.07e-12</td>
<td>37.01</td>
</tr>
<tr>
<td>Pb aggregates</td>
<td>9.20e-10</td>
<td>30.67</td>
<td>7.84e-13</td>
<td>5.72</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
<td>1.37e-11</td>
<td>100</td>
</tr>
</tbody>
</table>
### A.5.5 Effect of total Pb(II) concentration

#### Table A.5.5a \([\text{Pb}]_t = 3e-9\text{M}\)

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m(^{-2}).s(^{-1}))</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>3.88e-12</td>
<td>0.13</td>
<td>1.67e-13</td>
<td>1.26</td>
</tr>
<tr>
<td>PbOH+Pb(OH)(_2)</td>
<td>5.10e-12</td>
<td>0.17</td>
<td>1.86e-13</td>
<td>1.40</td>
</tr>
<tr>
<td>PbCO(_3)+Pb(CO(_3))(_3)</td>
<td>2.11e-10</td>
<td>7.23</td>
<td>7.57e-12</td>
<td>56.92</td>
</tr>
<tr>
<td>PbFA</td>
<td>1.86e-9</td>
<td>62.00</td>
<td>5.07e-12</td>
<td>38.12</td>
</tr>
<tr>
<td>Pbaggregates</td>
<td>9.20e-10</td>
<td>30.67</td>
<td>2.75e-13</td>
<td>2.07</td>
</tr>
<tr>
<td>Total</td>
<td>3e-9</td>
<td>100</td>
<td>1.33e-11</td>
<td>100</td>
</tr>
</tbody>
</table>

#### Table A.5.5b \([\text{Pb}]_t = 3e-8\text{M}\)

<table>
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<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m(^{-2}).s(^{-1}))</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>6.73e-11</td>
<td>0.22</td>
<td>2.90e-12</td>
<td>1.42</td>
</tr>
<tr>
<td>PbOH+Pb(OH)(_2)</td>
<td>8.84e-11</td>
<td>0.29</td>
<td>3.28e-12</td>
<td>1.61</td>
</tr>
<tr>
<td>PbCO(_3)+Pb(CO(_3))(_3)</td>
<td>3.65e-9</td>
<td>12.17</td>
<td>1.34e-10</td>
<td>65.69</td>
</tr>
<tr>
<td>PbFA</td>
<td>1.03e-8</td>
<td>34.33</td>
<td>5.83e-11</td>
<td>28.58</td>
</tr>
<tr>
<td>Pbaggregates</td>
<td>1.58e-8</td>
<td>52.67</td>
<td>4.96e-12</td>
<td>2.43</td>
</tr>
<tr>
<td>Total</td>
<td>3e-8</td>
<td>100</td>
<td>2.04e-10</td>
<td>100</td>
</tr>
</tbody>
</table>
A.6 Lists of results of simulations of Zn(II) in natural freshwaters: effect of total Zn(II) concentration

Table A.6.1a [Zn] = 1e-6M

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m^{-2}.s^{-1})</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1.90e-7</td>
<td>19.0</td>
<td>6.38e-9</td>
<td>59.1</td>
</tr>
<tr>
<td>ZnOH+Zn(OH)_2</td>
<td>3.00e-8</td>
<td>3.00</td>
<td>8.60e-10</td>
<td>7.96</td>
</tr>
<tr>
<td>ZnCO_3+Zn(CO_3)_2</td>
<td>5.96e-8</td>
<td>5.96</td>
<td>1.99e-9</td>
<td>18.4</td>
</tr>
<tr>
<td>ZnFA</td>
<td>5.82e-7</td>
<td>13.0</td>
<td>1.26e-9</td>
<td>11.7</td>
</tr>
<tr>
<td>Znaggregates</td>
<td>1.30e-7</td>
<td>58.2</td>
<td>2.72e-10</td>
<td>2.52</td>
</tr>
<tr>
<td>Total</td>
<td>1.00e-6</td>
<td>100</td>
<td>1.08e-8</td>
<td>100</td>
</tr>
</tbody>
</table>

Table A.6.1b [Zn] = 1e-7M

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m^{-2}.s^{-1})</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>1.03e-8</td>
<td>10.3</td>
<td>3.46e-10</td>
<td>41.7</td>
</tr>
<tr>
<td>ZnOH+Zn(OH)_2</td>
<td>1.63e-9</td>
<td>1.63</td>
<td>4.62e-11</td>
<td>5.57</td>
</tr>
<tr>
<td>ZnCO_3+Zn(CO_3)_2</td>
<td>3.24e-9</td>
<td>3.24</td>
<td>1.07e-10</td>
<td>12.9</td>
</tr>
<tr>
<td>ZnFA</td>
<td>3.68e-8</td>
<td>36.8</td>
<td>3.07e-10</td>
<td>37.0</td>
</tr>
<tr>
<td>Znaggregates</td>
<td>4.76e-8</td>
<td>47.6</td>
<td>2.30e-11</td>
<td>2.77</td>
</tr>
<tr>
<td>Total</td>
<td>1e-7</td>
<td>100</td>
<td>3.46e-10</td>
<td>100</td>
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</tbody>
</table>

Table A.6.1c [Zn] = 1e-8M

<table>
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<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m^{-2}.s^{-1})</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>2.54e-10</td>
<td>2.54</td>
<td>8.53e-12</td>
<td>19.4</td>
</tr>
<tr>
<td>ZnOH+Zn(OH)_2</td>
<td>4.01e-11</td>
<td>0.401</td>
<td>1.02e-12</td>
<td>2.32</td>
</tr>
<tr>
<td>ZnCO_3+Zn(CO_3)_2</td>
<td>7.91e-11</td>
<td>0.791</td>
<td>2.61e-12</td>
<td>5.93</td>
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<tr>
<td>ZnFA</td>
<td>8.41e-9</td>
<td>84.1</td>
<td>3.13e-11</td>
<td>71.1</td>
</tr>
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<td>Znaggregates</td>
<td>1.20e-9</td>
<td>12.0</td>
<td>5.10e-13</td>
<td>1.16</td>
</tr>
<tr>
<td>Total</td>
<td>1.00e-8</td>
<td>100</td>
<td>4.40e-11</td>
<td>100</td>
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</table>
A.7 Lists of results of simulations of Ni(II) in natural freshwaters

A.7.1 Sensitivity analysis by changing $\Gamma$ of fulvics

Table A.7.1a $\Gamma=0.3$

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>8.09E-13</td>
<td>0.0162</td>
<td>2.67E-14</td>
<td>66.6</td>
</tr>
<tr>
<td>NiOH+Ni(OH)$_2$</td>
<td>8.04E-15</td>
<td>0.000161</td>
<td>1.57E-16</td>
<td>0.392</td>
</tr>
<tr>
<td>NICO$_3$</td>
<td>1.63E-13</td>
<td>0.00326</td>
<td>4.45E-15</td>
<td>11.1</td>
</tr>
<tr>
<td>NiFA</td>
<td>4.99E-9</td>
<td>99.8</td>
<td>8.80E-15</td>
<td>21.9</td>
</tr>
<tr>
<td>Ni aggregates</td>
<td>3.04E-12</td>
<td>0.0608</td>
<td>6.52E-17</td>
<td>0.163</td>
</tr>
<tr>
<td>Total</td>
<td>5.00E-9</td>
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<td>4.01E-14</td>
<td>100</td>
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Table A.7.1b $\Gamma=0.57$

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<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>5.00E-10</td>
<td>10.0</td>
<td>1.65E-11</td>
<td>77.1</td>
</tr>
<tr>
<td>NiOH+Ni(OH)$_2$</td>
<td>4.97E-12</td>
<td>0.0994</td>
<td>1.00E-13</td>
<td>0.467</td>
</tr>
<tr>
<td>NICO$_3$</td>
<td>1.01E-10</td>
<td>2.02</td>
<td>2.81E-12</td>
<td>13.1</td>
</tr>
<tr>
<td>NiFA</td>
<td>2.44E-9</td>
<td>48.8</td>
<td>1.97E-12</td>
<td>9.21</td>
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<td>Ni aggregates</td>
<td>1.88E-9</td>
<td>37.6</td>
<td>4.18E-14</td>
<td>0.195</td>
</tr>
<tr>
<td>Total</td>
<td>5.00E-9</td>
<td>100</td>
<td>2.14E-11</td>
<td>100</td>
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</table>

Table A.7.1c $\Gamma=0.8$

<table>
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<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>8.49E-10</td>
<td>17.0</td>
<td>2.80E-11</td>
<td>79.8</td>
</tr>
<tr>
<td>NiOH+Ni(OH)$_2$</td>
<td>8.45E-12</td>
<td>0.169</td>
<td>1.70E-13</td>
<td>0.484</td>
</tr>
<tr>
<td>NICO$_3$</td>
<td>1.71E-10</td>
<td>3.42</td>
<td>4.79E-12</td>
<td>13.6</td>
</tr>
<tr>
<td>NiFA</td>
<td>6.52E-10</td>
<td>13.0</td>
<td>2.14E-12</td>
<td>6.10</td>
</tr>
<tr>
<td>Ni aggregates</td>
<td>3.17E-9</td>
<td>63.4</td>
<td>7.16E-14</td>
<td>0.204</td>
</tr>
<tr>
<td>Total</td>
<td>5.00E-9</td>
<td>100</td>
<td>3.51E-11</td>
<td>100</td>
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</table>
A.7.2 Sensitivity analysis by changing $\log K_0^*$ of fulvics

### Table A.7.2a $\log K_0^* = 3.3$

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration (M)</th>
<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>8.07E-10</td>
<td>16.1</td>
<td>2.66E-11</td>
<td>82.6</td>
</tr>
<tr>
<td>NiOH+Ni(OH)$_2$</td>
<td>8.03E-12</td>
<td>0.161</td>
<td>1.63E-13</td>
<td>0.506</td>
</tr>
<tr>
<td>NICO$_3$</td>
<td>1.63E-10</td>
<td>3.26</td>
<td>4.57E-12</td>
<td>14.2</td>
</tr>
<tr>
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### Table A.7.2b $\log K_0^* = 4.3$

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<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>5.00E-10</td>
<td>10.0</td>
<td>1.65E-11</td>
<td>77.1</td>
</tr>
<tr>
<td>NiOH+Ni(OH)$_2$</td>
<td>4.97E-12</td>
<td>0.0994</td>
<td>1.00E-13</td>
<td>0.467</td>
</tr>
<tr>
<td>NICO$_3$</td>
<td>1.01E-10</td>
<td>2.02</td>
<td>2.81E-12</td>
<td>13.1</td>
</tr>
<tr>
<td>NiFA</td>
<td>2.44E-9</td>
<td>48.8</td>
<td>1.97E-12</td>
<td>9.21</td>
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<td>1.88E-9</td>
<td>37.6</td>
<td>4.18E-14</td>
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</tr>
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<td>5.00E-9</td>
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<td>2.14E-11</td>
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### Table A.7.2c $\log K_0^* = 5.3$

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<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.34E-10</td>
<td>2.68</td>
<td>4.41E-12</td>
<td>62.3</td>
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<tr>
<td>NiOH+Ni(OH)$_2$</td>
<td>1.33E-12</td>
<td>0.0266</td>
<td>2.59E-14</td>
<td>0.366</td>
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<tr>
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<td>2.70E-11</td>
<td>0.540</td>
<td>7.36E-13</td>
<td>10.4</td>
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<td>4.31E-9</td>
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<td>1.08E-14</td>
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<td>2.14E-11</td>
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### A.7.3 Sensitivity analysis by changing log\(K^\prime\) of aggregates

#### Table A.7.3a \(\text{log}K^\prime=4.35\)

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<th>Components</th>
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<th>Flux (mol.m(^{-2}).s(^{-1}))</th>
<th>Percentage (%)</th>
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</thead>
<tbody>
<tr>
<td>Ni</td>
<td>9.75E-10</td>
<td>19.5</td>
<td>3.21E-11</td>
<td>77.2</td>
</tr>
<tr>
<td>(\text{NiOH}+\text{Ni(OH)}_2)</td>
<td>9.69E-12</td>
<td>0.194</td>
<td>1.95E-13</td>
<td>0.469</td>
</tr>
<tr>
<td>(\text{NICO}_3)</td>
<td>1.97E-10</td>
<td>3.94</td>
<td>5.49E-12</td>
<td>13.2</td>
</tr>
<tr>
<td>NiFA</td>
<td>3.63E-9</td>
<td>72.6</td>
<td>3.79E-12</td>
<td>9.11</td>
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<tr>
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<td>3.67E-11</td>
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<td>1.25E-14</td>
<td>0.0305</td>
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<td>Total</td>
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<td>100</td>
<td>4.16E-11</td>
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#### Table A.7.3b \(\text{log}K^\prime=5.35\)

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<th>Percentage (%)</th>
<th>Flux (mol.m(^{-2}).s(^{-1}))</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>8.90E-10</td>
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<td>2.93E-11</td>
<td>77.1</td>
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<tr>
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<td>8.86E-12</td>
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<tr>
<td>(\text{NICO}_3)</td>
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#### Table A.7.3c \(\text{log}K^\prime=6.35\)

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<th>Flux (mol.m(^{-2}).s(^{-1}))</th>
<th>Percentage (%)</th>
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<tbody>
<tr>
<td>Ni</td>
<td>5.00E-10</td>
<td>10.0</td>
<td>1.65E-11</td>
<td>77.1</td>
</tr>
<tr>
<td>(\text{NiOH}+\text{Ni(OH)}_2)</td>
<td>4.97E-12</td>
<td>0.0994</td>
<td>1.00E-13</td>
<td>0.467</td>
</tr>
<tr>
<td>(\text{NICO}_3)</td>
<td>1.01E-10</td>
<td>2.02</td>
<td>2.81E-12</td>
<td>13.1</td>
</tr>
<tr>
<td>NiFA</td>
<td>2.44E-9</td>
<td>48.8</td>
<td>1.97E-12</td>
<td>9.20</td>
</tr>
<tr>
<td>Ni aggregates</td>
<td>1.88E-9</td>
<td>37.6</td>
<td>4.18E-14</td>
<td>0.195</td>
</tr>
<tr>
<td>Total</td>
<td>5.00E-9</td>
<td>100</td>
<td>2.14E-11</td>
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#### Table A.7.3d \(\text{log}K^\prime=7.35\)

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<th>Flux (mol.m(^{-2}).s(^{-1}))</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1.03E-10</td>
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<td>3.39E-12</td>
<td>76.7</td>
</tr>
<tr>
<td>(\text{NiOH}+\text{Ni(OH)}_2)</td>
<td>1.02E-12</td>
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<tr>
<td>(\text{NICO}_3)</td>
<td>2.08E-11</td>
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<td>NiFA</td>
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#### Table A.7.3e \(\text{log}K^\prime=8.35\)

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<th>Percentage (%)</th>
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<tr>
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</tr>
<tr>
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<td>2.52E-12</td>
<td>0.0504</td>
<td>7.02E-14</td>
<td>13.1</td>
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<td>Value 2</td>
<td>Value 3</td>
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<td>5.36E-13</td>
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A.7.4 Sensitivity analysis by changing $\beta$ of aggregates

Table A.7.4a $\beta=2$

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<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>5.00E-10</td>
<td>10.0</td>
<td>1.65E-11</td>
<td>77.1</td>
</tr>
<tr>
<td>NiOH+Ni(OH)$_2$</td>
<td>4.97E-12</td>
<td>0.0994</td>
<td>1.00E-13</td>
<td>0.467</td>
</tr>
<tr>
<td>NiCO$_3$</td>
<td>1.01E-10</td>
<td>2.02</td>
<td>2.81E-12</td>
<td>13.1</td>
</tr>
<tr>
<td>NiFA</td>
<td>2.44E-9</td>
<td>48.8</td>
<td>1.97E-12</td>
<td>9.21</td>
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<td>37.6</td>
<td>2.34E-14</td>
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<tr>
<td>Total</td>
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Table A.7.4b $\beta=3$

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<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>5.00E-10</td>
<td>10.0</td>
<td>1.65E-11</td>
<td>77.1</td>
</tr>
<tr>
<td>NiOH+Ni(OH)$_2$</td>
<td>4.97E-12</td>
<td>0.0994</td>
<td>1.00E-13</td>
<td>0.467</td>
</tr>
<tr>
<td>NiCO$_3$</td>
<td>1.01E-10</td>
<td>2.02</td>
<td>2.81E-12</td>
<td>13.1</td>
</tr>
<tr>
<td>NiFA</td>
<td>2.44E-9</td>
<td>48.8</td>
<td>1.97E-12</td>
<td>9.21</td>
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<tr>
<td>Ni aggregates</td>
<td>1.88E-9</td>
<td>37.6</td>
<td>4.18E-14</td>
<td>0.195</td>
</tr>
<tr>
<td>Total</td>
<td>5.00E-9</td>
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<td>2.14E-11</td>
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Table A.7.4c $\beta=4$

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<th>Percentage (%)</th>
<th>Flux (mol.m$^{-2}$.s$^{-1}$)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>5.00E-10</td>
<td>10.0</td>
<td>1.65E-11</td>
<td>77.1</td>
</tr>
<tr>
<td>NiOH+Ni(OH)$_2$</td>
<td>4.97E-12</td>
<td>0.0994</td>
<td>1.00E-13</td>
<td>0.467</td>
</tr>
<tr>
<td>NiCO$_3$</td>
<td>1.01E-10</td>
<td>2.02</td>
<td>2.81E-12</td>
<td>13.1</td>
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<tr>
<td>NiFA</td>
<td>2.44E-9</td>
<td>48.8</td>
<td>1.97E-12</td>
<td>9.21</td>
</tr>
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<td>2.14E-11</td>
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A.7.5 Effect of total Ni(II) concentration

Table A.7.5a [Ni] = 3E-7M

<table>
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<tr>
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<th>Concentration (M)</th>
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<th>Flux (mol.m².s⁻¹)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1.84E-9</td>
<td>78.6</td>
</tr>
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<td>5.58E-10</td>
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<tr>
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<td>1.63E-10</td>
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<td>1.87E-7</td>
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Table A.7.5b [Ni] = 5E-8M

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<th>Flux (mol.m².s⁻¹)</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>15.2</td>
<td>2.50E-10</td>
<td>77.6</td>
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<tr>
<td>NiOH+Ni(OH)₂</td>
<td>7.55E-11</td>
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<td>1.53E-9</td>
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<td>Total</td>
<td>5.00E-8</td>
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Table A.7.5c [Ni] = 5E-9M

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<th>Percentage (%)</th>
<th>Flux (mol.m².s⁻¹)</th>
<th>Percentage (%)</th>
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</thead>
<tbody>
<tr>
<td>Ni</td>
<td>5.00E-10</td>
<td>10.0</td>
<td>1.65E-11</td>
<td>77.1</td>
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<tr>
<td>NiOH+Ni(OH)₂</td>
<td>4.97E-12</td>
<td>0.0994</td>
<td>1.00E-13</td>
<td>0.467</td>
</tr>
<tr>
<td>NICO₃</td>
<td>1.01E-10</td>
<td>2.02</td>
<td>2.81E-12</td>
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</tr>
<tr>
<td>NiFA</td>
<td>2.44E-9</td>
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<td>1.97E-12</td>
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<td>Total</td>
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<td>100</td>
<td>2.14E-11</td>
<td>100</td>
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A.8 References of Appendix


[33] Burgess J. *Metal ions in solution*, Ellis Horwood, Chichester, **1978**.


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