Polyfunctional description of metal complexation by natural organic matter: theory and practice

BUFFLE, Jacques, FILELLA, Montserrat, ALTMANN, Robert Scott
Polyfunctional Description of Metal Complexation by Natural Organic Matter: Theory and Practice

J. Buffle, M. Filella, R.S. Altmann
Department of Inorganic, Analytical and Applied Chemistry
Sciences II, 30 quai E.-Ansermet, CH-1211 Geneva 4, Switzerland

Abstract

The Differential Equilibrium Function (DEF) approach to metal complexation interpretation and prediction is compared to other models or approaches. The basic features of DEF are summarized, both from the experimental and theoretical points of view. The relation of DEF with key environmental concepts or parameters, in particular minor vs major complexing sites, the buffering intensity of natural organic matter (NOM), and their polyfunctional vs polyelectrolyte properties, is discussed. The relation between DEF and Freundlich isotherm is described quantitatively. The practical applications of DEF are discussed for i) interpretation of metal complexation by NOM, and ii) prediction of metal complexation by NOM. It is shown that DEF has the unique advantage of being able to make predictions with only two parameters, over several order of magnitudes of metal concentration, even outside the range explored to determine the DEF (i.e. sound extrapolation is possible with care). DEF can be readily incorporated in metal species distribution codes (e.g. MINEQL). DEF is not equivalent to a molecular complexation model which describes complexation at each individual site; DEF gives a rigorous representation of complexation by NOM as a whole chemical system.
I. Introduction

Various models have been proposed for interpreting metal complexation by natural organic matter, NOM (for a detailed comparison see ref.1), with the hope that they could also be used to predict metal complexation by NOM in unknown media. The most widely used models can be separated into two groups:

The discrete site distribution models. They include:

a- Single, two or three site models. (such as Scatchard plots). The complexation reaction at each site corresponds to the equation:

\[ K_i = \frac{[ML_i]}{[L_i][M]} \]  
(eq. 1)

where \( K_i \) is the equilibrium constant of metal M with site \( L_i \), and \([ML_i]\), \([L_i]\) and \([M]\) are the concentrations of species \( ML_i \), \( L_i \) and free metal ion. (Note that here, as in the rest of the paper, \( K_i \) is a conditional constant, valid at constant pH, ionic strength and temperature).

b- Discrete site models similar to those mentioned above, but considering in addition the polyelectrolyte properties of the NOM that result from their relatively large number of dissociated groups at natural pH. In such models, the \( K_i \) values depend on the surface charge of the NOM, which in turn depends in particular on pH and ionic strength.

c- Ion-exchange models, with or without consideration of the difference in osmotic pressure inside and outside the NOM (that is considered as a separate gel phase).

The descriptions of metal complexation by means of continuous site distribution functions. They include:

d- A priori imposed site distribution functions. Unimodal or bimodal gaussian distributions, and Sips distributions have been proposed in particular (20).

e- The Site Affinity Distribution Function (SADF) which allows computing the probability of finding a site type, \( L \), forming a complex \( ML \) with constant \( K \). Assuming that \( C_i \) is the total concentration of sites of NOM, the concentration, \( dC_L \), of sites having \( K \) values in the interval \( d\log K \), is given by (1, 2):

\[ dC_L = c(K) \cdot d(\log K) \]  
(eq. 2)

where \( c(K)/C_L = p(K) \), and \( p(K) \) is the corresponding probability density function. \( p(K) \) is also called SADF and may be a Gaussian, a Sips or any other function. The total concentration of metal bound to NOM, \([M]_b\), is related to SADF as follows. \([M]_b\), is the sum of the concentrations of all complex types, i.e.

\[ [M]_b = \sum_{i=1}^{n} \frac{K_i[M]}{1 + K_i[M]} \cdot C_{L,i} \]  
(eq. 3)

where \( C_{L,i} \) is the total concentration of type site \( i \). (Each term of eq. 3 corresponds to \([ML_i]\) obtained by combining eq. 1 with the condition \( C_{L,i} = [ML_i] + [L_i] \). Combining eqs. 2 and 3, by representing \( K_i \) as \( K \), and \( C_{L,i} \) as \( dC_L \), gives the relationship between \([M]_b\) and the SADF.
\[
[M]_b = \int \frac{K_i[M]}{1+K_i[M]} \cdot c(K_i) \cdot d\log K
\]  
(eq. 4)

1. the Differential Equilibrium Function (DEF) is based on the differential intensity parameter \(K^*\). \(K^*\) is a weighted arithmetic mean of the equilibrium constants \(K_i\), for all sites \(i\) present in NOM (3). The weighting factor depends on the mole fraction, \(\Delta X_i = C_{i-L} / C_{i-L_i}\), of each site \(i\) and their degree of occupation, \(\theta_i = [M]_{b,i}/C_{i-L}\):

\[
K^* = \frac{\sum_{i=1}^{n}K_i \cdot (1-\theta_i) \cdot \theta_i \cdot \Delta X_i}{\sum_{i=1}^{n}(1-\theta_i) \cdot \theta_i \cdot \Delta X_i}
\]  
(eq. 5)

There is therefore a direct relationship between \(K^*\) and the global degree of site occupation, \([M]_b/C_L\), which in turn depends on the site distribution function, \(c(K)\) (eq. 4). It has been shown (see below; refs. 1,3-5) that \(c(K)\) for trace metal complexation by NOM is such that, as a first approximation, DEF exhibits a linear relationship between \(\log([M]_b/C_L)\) and \(\log K^*\):

\[
\log([M]_b/C_L) = \text{const} - \Gamma \cdot \log K^*
\]  
(eq. 6)

where \(\Gamma\) is a constant whose value is between 0 and 1 (see below).

Approaches e- and f- are not "models" in the same sense as a- to d- approaches are, since, contrary to these latter, they do not impose any \textit{a priori} assumptions. This is preferable, since the large complexity of NOM nature and behaviour precludes \textit{a priori} guessing of the nature of the predominant factors which affect metal complexation reactions. Instead of imposing \textit{a priori} assumptions, approaches e- and f- allow the nature of these predominant factors to be determined by studying the change in SADF or DEF under varying experimental conditions.

It must be recognized however that none of the approaches e- or f- allows the exact structure of the site affinity distribution functions of NOM to be recovered by mathematical deconvolution of experimental complexation curves. In approach e- (SADF), \(c(K)\) is extracted from experimental data, by inversion of eq. 4. This can only be done by using simplifying assumptions but also requires sophisticated mathematics, rather sensitive to experimental errors. Mathematical "artifacts" may then be an important limitation to this approach, although progress have been made recently (6-8). Another basic characteristic of SADF is that the mathematical extraction procedure of the \(c(K)\) function is efficient for \textbf{major site types} (those representing the largest fraction of the complexing site population, see below), but not for the \textbf{minor sites} (those present in small proportion). These latter, although sometimes present in very small proportions, are often the most important sites for trace metal binding, because their complexion strength is much larger (see below).

\textbf{Approach f-} (DEF) is less convenient for extracting \(c(K)\) from experimental data and more difficult to apply to major sites. But it is particularly convenient for describing complexation of minor type sites. It is mathematically simpler than the SADF approach, and in most cases a linear relationship (eq. 6) is applicable to minor sites, which allows describing metal complexation in terms of only two parameters, sometimes over several order of magnitudes of metal concentrations. Since minor sites are the strongest binding sites and therefore the most important sites for trace metal complexation, discussion will be restricted below to DEF.
II. Experimental results

Equilibrium constants are generally determined experimentally by adding increasing total concentrations ($C_M$) of the metal of interest, M, to a solution of NOM (with total molar concentration of sites = $C_I$), and by measuring the free metal concentration at equilibrium, [M]. It has been shown (15) that $K^*$ can be computed at any point of such a titration curve, by the equation:

$$
K^* = -\frac{\alpha^2}{C_M} \left\{ \frac{1 - (\frac{\alpha - 1}{\alpha}) \frac{d\ln[\{S\}]}{d\alpha}}{\frac{d\ln(C_M/\{S\})}{d\alpha} + (\frac{\alpha - 1}{\alpha}) \frac{d\ln(C_M/\{S\})}{d\alpha}} \right\}
$$

(eq. 7)

where $\alpha = C_M / [M]$, and $\{S\}_I$ is the total site concentration expressed in any unit (grams of NOM per liter; number of surface sites per liter, etc). When $\{S\}_I$ units are mole/liter, then $\{S\}_I = C_I$. Often however, the total molar concentration of complexing sites is unknown and this is a limiting factor in most complexation interpretation models. The advantage of eq. 7 is that $K^*$ can be computed by knowing only $\{S\}_I$, without making any assumption concerning $C_I$. In such cases, eq. 6 becomes:

$$
\log([M]_L/[\{S\}_I]) = \Gamma \log K^*_o - \Gamma \log K^*
$$

(eq. 8)

where $K^*_o$ is a constant having no particular physical meaning.

Although few studies have interpreted full NOM titration curves by reporting the corresponding change of $K^*$ with $[M]_L/C_I$ or $[M]_L/[\{S\}_I]$, (e.g. 9, 10), all the available information shows that plots of $\log K^*$ as function of $\log[M]_L/C_I$ (or $\log [M]_L/[\{S\}_I]$) are close to straight lines (11, 12), with $\Gamma$ values generally between 0.3 and 0.7 (13), for binding of both metals (11, 12) and organic pollutants (18). Fig. 1 shows an example of such a curve for the complexation of Pb(II) and Cd(II) by humic substances, determined by various voltammetric techniques. The results correspond to eq. 6 with $\Gamma = 0.69 \pm 0.02$ for Cd and $\Gamma = 0.43 \pm 0.01$ for Pb. The data dispersion of this figure is rather typical of any complexation data obtained by several analytical methods. It is therefore easy to understand that the fine structure of site distribution functions is very difficult to get, irrespective of the mathematical treatment.

Although relatively few single curves have been interpreted in terms of $K^*$ functions, the literature is abundant in NOM/metal titration curves interpreted in terms of single site or two site models. Such interpretations provide values for the so-called complexation capacity ($C_c$) of NOM for the test metal ($C_c$ is equivalent to complexing site concentration) and the corresponding average equilibrium quotient $\tilde{K}$ (equivalent to the complexation constant of these sites). It is now well established that the value of $C_c$ and $\tilde{K}$ depends on the analytical technique and the conditions used (1,5,14). But it has been shown (1, 5) that the couples ($\tilde{K}$, $C_c$) are analogues of the couples ($K^*$, $[M]_L/[\{S\}_I]$), with $(\tilde{K} \cdot K^*) \approx 0.5$, for $C_c = [M]_L/[\{S\}_I]$. Plots of $\log C_c$ vs $\log \tilde{K}$ for similar types of NOM and same conditions (ionic strength, pH, etc) should then give straight lines with slopes equal to $\Gamma$, as in eq. 8. All the data reported in the literature indeed confirm this prediction (Figs. 2-3). The fact that complexation properties of NOM closely follow linear DEF is therefore well documented.
III. Interpretation of DEF curves

As discussed in detail in refs. 3, 4, a DEF is a representation of a cumulative complexation site distribution, where the sum of concentrations of complexes with binding energy larger than a particular value of $\Delta G^\circ = -RT\ln K^*$ is plotted as function of $K^*$. In principle DEF may take any shape, depending on the nature of the underlying $p(K)$ function. In practice, roughly straight line log-log plots are always observed with chemically heterogeneous complexing agents, as shown above.

III.1. The various segments of a DEF curve

The chemical meaning of this straight line is understandable from Fig. 4. It represents only a segment (referred to hereafter as "the linear part") of the full DEF curve. The full curve has the global shape shown in Fig. 4, but in most cases, only part of it is visible experimentally because any experimental method used to measure metal complexation has a limited analytical window (3, 4). For compounds with small chemical heterogeneity (e.g. iron hydroxide in Fig. 5; Fig. 4, curve 2), the linear part is shorter, and $\Gamma$ is larger than for compounds with large heterogeneity. For both curves 1 and 2, the sites become stronger as one moves to the left side of the graph. In all cases there must be however a site which is stronger than any other; it corresponds to the vertical portion of the DEF. Because of experimental difficulties (related to the difficulty of measuring very low free M concentrations), such a vertical line is only visible for complexants with relatively small chemical heterogeneity (Fig. 5) but not for NOM (Figs. 1-3, 6). The right hand side of the graph (small $K^*$ values) corresponds to full saturation of the complexant and the curve tends toward an horizontal line ($[M]_b$ tends to a constant value, $[M]_{b, \text{max}}^\diamond$; Fig. 6). This part is also difficult to determine experimentally, because of the large experimental errors incurred on $[M]_b$. Indeed, in this region, $[M]_b$ is generally obtained as a small difference between two large numbers, $C_M$ and $[M]$.

III.2. Major and minor sites

It is important to discriminate between the so-called major and minor sites. During a titration of the complexant by M (going over the DEF curves of Fig. 4 from left to right), the minor sites are titrated first and the major sites at last. The minor sites are the strongest but they only represent a small proportion of the total sites (they typically correspond to $[M]_b/[M]_{b, \text{max}} < 0.1$). The major sites correspond to the top of the DEF (corresponding to $[M]_b/[M]_{b, \text{max}} \geq 0.1$). In NOM, examples of minor sites are N- or S-containing groups; major sites are typically -COOH or phenolic groups. Because they form the largest proportion of dissociating groups, only the major sites play an important role on the polyelectrolytic properties of NOM. Consequently, at constant pH and ionic strength, the electric charge of NOM does not vary with metal complexation, when only the minor site occupation changes, i.e. when the linear part of DEF is studied. It is also important to note that, depending on their soft and hard character, different metals may bind preferably to major or minor sites: e.g. Cu(II) to minor sites and Ca(II) to major sites. Exchange reactions between metals may then be due to "secondary effects" related to the different properties of major and minor sites (e.g. change in electric charge of NOM by Ca(II)), rather than by simple competition of the two metals for the same site.

III.3. Buffering capacity

It has been shown in detail (4, 13), that the linear part of the DEF, between the vertical and horizontal sections, is directly related to the existence of a large number of site types $i$ with different $K_i$ values. In such case, it can be shown that:

- The binding equilibrium follows a Freundlich isotherm,

$$[M]_b/C_L = (K_M[M])^\Gamma$$

(eq. 9)
in conditions where $[M] \ll [M]_b$, i.e. in the titration region corresponding to the minor sites. In eq. 9, $\Gamma$ lies necessarily in the range $0 < \Gamma < 1$ and $K_m$ is a constant. It has been shown (4) that eqs. 8 can be derived from eq. 9, with the condition: 
$$K_m = K_0^{*} \frac{\Gamma - 1}{\Gamma} \left( \frac{[S]}{C_M} \right)^{1/\Gamma}.$$ 
Note however that the working conditions of eqs 8 and 9 are different; both are limited to regions where $[M] \ll [M]_b$, but contrarily to eq. 9, eq. 8 is also restricted to $[M]_b$ values larger than the region corresponding to the vertical portion of curves 1 and 2 in Fig. 4. This is due to a mathematical assumption made in deriving eq. 8 from eq. 9.

- In the linear part of the DEF, the system is chemically buffered in terms of $M$ complexation, over all the linear portion of the curve, i.e. the buffering capacity may exist over orders of magnitude of $[M]_b$. This is a unique characteristic of chemically heterogeneous complexants, which is at odds with simple ligands (like EDTA) for which buffering capacity only extends over one order of magnitude of $[M]_b$. The wide range of buffering capacity of heterogenous complexants play a key role in environmental processes (15).

- It can be shown (13) that the maximum buffering intensity of any chemically heterogeneous system is obtained when $\Gamma = 0.5$. This is often observed for NOM (Figs. 1-3), but not for synthetic metal oxides (Fig. 5). Although these latter show some heterogeneity, it is small since experimental values of $\Gamma$ are found to be $\Gamma > 1$ indicating that Freundlich isotherm does not apply here (13). For $\Gamma = 1$, eq. 9 corresponds to a linearized Langmuir isotherm, i.e. the system behaves as if only one ligand was present, in excess to $C_M$. This corresponds to the vertical part of curve 1 in Fig. 4; it is a condition for which buffer intensity is low. For $\Gamma = 0$, $[M]_b = \text{const.}$ (eq. 9); this corresponds to the horizontal part of curve 1 in Fig. 4 where all complexing sites have been saturated ($[M]_b = [M]_{b, \text{max}}$), and therefore where there is no buffering intensity.

### III.4. Polyfunctional versus polyelectrolytic properties (Fig. 4)

For the reasons given above, the change of $K^*$ with $[M]_b/[S]_1$ in the linear part of the DEF is primarily due to the vast number of different minor site types, and not to the change of electric charge of NOM. Indeed in this domain $[M]_b$ is much smaller than the total concentration of the major sites which determine the electric charge of NOM. The polyelectrolytic effect therefore exists in the linear part of DEF, but does not change with $[M]_b/[S]_1$. It is only an additional constant factor influencing the conditional nature of $K$ or $K^*$ in this region. On the other hand, the top part of the DEF is dominantly influenced by change of the polyelectrolytic effect; indeed metal complexation in this region is dominated by the major site types whose electric charge is itself influenced by complexation. In addition, since major site types are few in number, the polyfunctionality effect may be small in this region compared to the polyelectrolytic effect. Nevertheless it must be recognized that the polyelectrolytic effect of fulvic is less important than that of synthetic polyelectrolytes like polyacrylic acid, because of a smaller dissociable site density (16, 17).

### IV. Practical usefulness of the DEF approach to metal complexation

A model may be used for two types of applications: i) for interpreting experimental data (e.g. the titration of NOM by a metal) in terms of sound physico-chemical parameters, or ii) for predicting metal complexation in a particular medium, based on the known values of its representative physico-chemical parameters.
IV.1. Interpretation of metal complexation experiments

The advantages of DEF for this purpose are the following:

- Its mathematical simplicity minimizes the introduction of mathematical artifacts in the transformation of raw data into sound physico-chemical parameters.

- Among the two parameters offered by DEF, \( \Gamma \) is strongly linked to the complexation buffer intensity, \( \beta = \frac{dC_M}{d\log[M]} \), of NOM, which is a key environmental parameter. For linear DEF, \( \Gamma = \beta/2.303, \ C_M \) (13).

- The other parameter provided by DEF is \( K^* \). Although \( K^* \) is an weighted average of all \( K_i \) values, the weighting factor is such (3,4) that \( \Delta G^* = -RT \log K^* \) represents the effective binding energy of M by the NOM for the corresponding \( [M]_b/[S]_l \) value. \( K^* \) therefore is also a key environmental parameter.

The main limitation of DEF for physico-chemical interpretation of complexation at the molecular level, is that \( K^* \) is an average of all \( K_i \). Even if it is a mathematically well defined average, extraction of individual values of \( K_i \) from DEF is more difficult than by using the SADF approach (eq. 4) (although this approach has its own limitations). In fact, it is of key importance to realize that DEF is not equivalent to a molecular complexation model which describes complexation at each individual site; \( \Gamma \) and \( K^* \) function describe and allow making predictions of the complexation behaviour of the system as a whole. This is a unique capability of DEF, particularly useful in the following cases:

- to study trace metal complexation with minor sites, where SADF is strongly limited due to the dominant role played by the major sites in the mathematical deconvolution procedures.

- as a first approach to determine the important factors affecting metal complexation, such as the role of pH, ionic strength, temperature, competition between metals etc. For instance Fig. 3 shows DEF curves for the same NOM at pH=8, for Cu, Zn and Mn. The points represent complexation interpretation by a two sites Scatchard plot. Comparison of the individual values of \( C_c \) and \( K \) for the three metals gives a very poor idea of their relative binding properties. On the other hand, comparison of their DEF curves allows them to be compared at constant \( C_c \) (or \( [M]_b/[S]_l \)) value which clearly shows that complexation increases in the order Mn>Zn>Cu, and even allows estimation of the difference in binding energy for these three metals (horizontal difference between the curves). This procedure also clearly shows that the three NOM samples behave in the same manner, which is not obvious by comparing the individual \( (C_c, K) \) couples.

IV.2. Prediction of metal complexation

DEF has two advantages over any other model, for making prediction of metal complexation by a particular type of NOM, thanks to the fact that most DEF are close to straight lines over several order of magnitudes:

i) the corresponding site distribution (and ultimately metal complexation) can be estimated by means of only two constant parameters: \( \Gamma \) and \( K^*_0 \)

ii) a reasonable estimation of complexation properties may be obtained outside the \( [M]_b/[S]_l \) range explored experimentally to determine \( K^* \) and \( \Gamma \), provided caution is used. Indeed, experimental evidence suggests that linear extrapolation of DEF is feasible. None of the other models allow such extrapolation.
IV.3. Incorporation of DEF into metal species distribution codes

Metal speciation codes (e.g. MINEQL, GEOCHEM, etc.) are based on Langmuir type relationships between the equilibrium constant and the concentrations of the metal complex, the free ligand and the free metal ion. Equation 8 does not fit with this standard representation. It can however be readily adapted to it, in the following manner (for details see ref. 4).

The SADF (eq. 2) corresponding to eq. 9 can be derived theoretically (4) and corresponds to eq. 10:

\[
\frac{d\chi}{d\log K} = \rho(\log K) = \Theta K^\Gamma
\]  
\[\text{(eq. 10)}\]

with

\[
\Theta = 2.303.\sin\left\{\left(1 - \Gamma\right)\cdot \pi \right\} K^\Gamma m
\]  
\[\text{(eq. 11)}\]

where \(K_m\) is defined in eq. 9 and \(d\chi = dC_l/C_l\). As mentioned above, DEF is in reality a cumulative site distribution. Therefore it should be compared to the cumulative distribution (called CADF) corresponding to the SADF of eq. 10. A cumulative mole fraction of sites, \(\chi\), corresponding to the equilibrium constant \(K\), is the sum of the mole fractions of all sites whose equilibrium constant values are between \(\infty\) and \(K\). CADF is then obtained by the ad hoc integration of eq. 10, which gives (4):

\[
\log \chi = \log \left(\Theta / 2.303.\Gamma \right) - \Gamma \log K
\]  
\[\text{(eq. 12)}\]

The relation between the cumulative site occupation (DEF) and the cumulative site distribution (CADF) is obtained by comparing eqs. 8 and 12 which are the equations of two parallel straight lines. The cumulative mole fraction of sites, \(\chi\), corresponding to a particular site occupation, \([M]_b/[S]_i\) (i.e. also to a particular value of \(K^*\)), is obtained by subtracting eqs. 8 and 12 with \(K = K^*\):

\[
\log \chi = \log \left([M]_b/[S]_i\right) + \log \left([S]_i/C_l\right) + \log \left(\frac{\sin\left(\left(1 - \Gamma\right)\cdot \pi \right)}{\pi}\cdot \frac{\Gamma^{(\Gamma - 1)}}{\left(1 - \Gamma\right)\Gamma}\right)
\]  
\[\text{(eq. 13)}\]

In the vast majority of experimental cases, \(0.2 < \Gamma < 0.8\). It has been shown (4) that in such cases, the last term of eq. 13 takes values between -0.15 and -0.2. By using an average value of -0.174 irrespective of \(\Gamma\), the largest error occurred on \(\chi\) is 5%. Consequently, eq. 13 may be simplified into:

\[
\log \chi = \log \left([M]_b/[S]_i\right) - \log \left(C_l/[S]_i\right) - 0.174
\]  
\[\text{(eq. 14)}\]

Since \(C_l/[S]_i\) is a constant parameter for a particular type of NOM (e.g. total number of sites per gram of NOM), there is a very simple relation (eq. 14) between the cumulative mole fraction of site, \(\chi_j\), corresponding to any constant \(K_j\), and the corresponding site occupation (corresponding to \(K^* = K_j\)). An arbitrary number of \((\chi_j, K_j)\) couples can then be readily computed for any linear DEF. Each \(\log K_j\) value can be taken as a limit of a \(\Delta \log K\) interval (\(\Delta \log K = \log K_j - \log K_{j+1}\)). For each interval, the mole fraction of sites, \(\Delta \chi_j (\chi_j - \chi_{j+1})\) and a mean \(\log K\) value, \(\log K_j' = (\log K_j + \log K_{j+1})/2\) can be computed. This procedure defines a set of \((\Delta \chi_j, K_j')\) couples which represents the site affinity distribution function (SADF) corresponding to the DEF of interest. The set of couples \((\Delta \chi_j, K_j)\) can be introduced in any code like MINEQL, each couple being treated classically as for any other Langmuir type site. It has been shown (3) that, provided \(\Delta \log K \leq 0.1\), i) the set of couple \((\Delta \chi_j, \log K_j)\) is a close representation of SADF, and ii) the use of these sets of \(\Delta \chi_j, \log K_j\) couples in species distribution codes allow a correct evaluation of metal complexation by NOM.
V. Conclusion

For the reasons given above, DEF is a useful tool both for the interpretation and prediction of metal complexation by chemically heterogeneous complexants. As for all other approaches, however, its application to practical cases is presently limited by the lack of sufficient information. In particular, more research is needed in the following areas:

- Improvement of the reliability and sensitivity of free metal ion concentration measurement methods. Accurate determination of DEF(or SADF) is presently strongly limited by the lack of available methods, even though progress has been made over the last years (21). In addition, most complexation measurements have been done, until now, under unrealistically large \([M]_0/\langle S \rangle_1\) conditions.

- In terms of metal complexation interpretation, there is very little information on
  * competition between metals,
  * mixed complex formation, in particular between M, NOM and OH\(^-\), or M, NOM and inorganic solid surfaces,
  * kinetics of complex formation/dissociation,
  * metal ions others than Cu, Pb and Zn.

- A sound environmentally relevant NOM classification should be developed. The present classification is empirically based on analytical procedures which are not environmentally relevant. For instance, discrimination between soil-derived and water-derived NOM is more useful than hydrophobic and hydrophilic acids based on XAD adsorption.

- Many metal complexation studies have been performed with "purified" NOM. Results obtained by high resolution TEM during the last decade (19) clearly show that NOM, in aquatic systems, is generally associated with inorganic colloidal material, in particular iron hydroxide, in the nm-\(\mu\)m size range. In this context, it is highly questionable whether a few discrete equilibrium constants obtained with "purified" NOM will be applicable for making useful predictions in real situations. DEF curves obtained with unperturbated material might be more useful.
References


Figure 1.
DEF plot for the complexation of Pb(II) (curve 1) and Cd(II) (curve 2) by humic acids extracted from Irish moss peat and separated from fulvic acids by acid precipitation. The various symbols correspond to various polarographic methods of complexation measurements. In the various experiments, $C_L$ varied between 0.15 and 0.54 mM, $pH = 5$; ionic strength $= 0.02 \text{ M}$; $T = 25 \, ^\circ \text{C}$. $[M]_b$ and $C_L$ are both in mole$\cdot$L$^{-1}$ (from 11).

Figure 2.
Change in the complexation capacity, $C_C$, of soil-derived (pedogenic) fulvic compounds as function of the corresponding average equilibrium constant, $K$ (from 1, 2). $C_C$ and $K$ values were obtained by 1-2 discrete site models. The various symbols were obtained with different fulvic samples and different methods of complexation measurements. $pH = 8.0-8.3$. Such plots show that individual $C_C$ and $K$ values have no particular meaning. Only a couple ($C_C, K$) is useful by defining one of the point of the DEF curve. The fact that a single curve is obtained for all data also shows that, in similar conditions, DEF plots are independent of fulvic samples and complexation methods.
Figure 3.
Change in the complexation capacity, $C_c$, with the corresponding equilibrium constant, $K$, for complexation of Mn, Zn and Cu by sediment organic matter. The various symbols correspond to different NOM samples. In each case, $C_c$ and $K$ values were derived by Scatchard method assuming two complexing sites (from 5).

Figure 4.
Schematic representation of complete DEF curves for a heterogeneous complexant with a vast number of different sites (curve 1; examples fulvics/humics, Figs. 1-3) and a heterogeneous complexant with a small number of different sites (curve 2; example FeOOH, Fig. 5). The drawing shows the relation between DEF curves and i) the analytical window of the complexation method used (central zone of the figure), ii) the regions where minor sites or major sites dominate complexation, and iii) the regions where changes in polyelectrolytic and polyfunctional effects affect predominantly the shape of DEF curve. Maximum values of $K^*$ and $[M]_{d}/[S]$ for curves 1 and 2 are arbitrarily chosen. $K^*$ and $[M]_{d,max}/[S]$ values, and limits between major and minor sites, and between polyfunctional and polyelectrolytic effects only refer to curve 1 (adapted from 4).
Figure 5.
Cd adsorption on amorphous Fe oxyhydroxide. Example of a case with little heterogeneity and for which the strongest site is visible within the analytical window (from 22). In this figure, $K^a$ represents the reaction $\text{FeOOH}_2 + M \rightarrow \text{FeOOM} + x H^+$. It has been found that $x = 1.8$. $K^a$ is an analogue of $K^a$ and has been computed for various values of $[\text{Cd}] / [\text{Si}]_1$ (expressed as mole of adsorbed Cd/mole of Fe).

Figure 6.
Comparison of the relative importance of polyelectrolytic and polyfunctional factors for the complexation of Cu(II) by pedogenic fulvic compounds (pH=8.0). Domain of total acidity (total complexing site concentration) estimated from general properties of fulvic compounds. Curve 1 corresponds to $K^a$ values of ligand sites of fulvics (23) obtained by computer simulation, without considering the polyelectrolyte effect (surface potential $= \psi = 0$). Curve 2 corresponds to experimental data of Fig. 2. Curve 1 shows that DEF tends to an horizontal line at large $[\text{M}]_2 / [\text{Si}]_1$ (or $C_2$) values. Horizontal difference between the linear parts of curves 1 and 2 gives an estimate of the $\Delta \log K (-2)$ corresponding to the constant polyelectrolyte effect affecting minor sites of real fulvics at pH 8.0. ($\Delta \log K -2$ corresponds to $\chi = -60 \text{mV}$ (from 2).
Binding Models Concerning Natural Organic Substances in Performance Assessment

Proceedings of an NEA Workshop organised in co-operation with the Paul Scherrer Institute

Bad Zurzach, Switzerland, 14-16 September 1994

The following texts are published in their original form to permit faster distribution at a lower cost. The views expressed are those of the authors, and do not necessarily reflect those of the Organisation or of its Member countries.
ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

Pursuant to Article 1 of the Convention signed in Paris on 14th December 1960, and which came into force on 30th September 1961, the Organisation for Economic Co-operation and Development (OECD) shall promote policies designed:

— to achieve the highest sustainable economic growth and employment and a rising standard of living in Member countries, while maintaining financial stability, and thus to contribute to the development of the world economy;
— to contribute to sound economic expansion in Member as well as non-member countries in the process of economic development; and
— to contribute to the expansion of world trade on a multilateral, non-discriminatory basis in accordance with international obligations.

The original Member countries of the OECD are Austria, Belgium, Canada, Denmark, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, the Netherlands, Norway, Portugal, Spain, Sweden, Switzerland, Turkey, the United Kingdom and the United States. The following countries became Members subsequently through accession at the dates indicated hereafter: Japan (28th April 1964), Finland (28th January 1969), Australia (7th June 1971), New Zealand (29th May 1973) and Mexico (18th May 1994). The Commission of the European Communities takes part in the work of the OECD (Article 13 of the OECD Convention).

NUCLEAR ENERGY AGENCY

The OECD Nuclear Energy Agency (NEA) was established on 1st February 1958 under the name of the OEEC European Nuclear Energy Agency. It received its present designation on 20th April 1972, when Japan became its first non-European full Member. NEA membership today consists of all European Member countries of OECD as well as Australia, Canada, Japan, Republic of Korea, Mexico and the United States. The Commission of the European Communities takes part in the work of the Agency.

The primary objective of NEA is to promote co-operation among the governments of its participating countries in furthering the development of nuclear power as a safe, environmentally acceptable and economic energy source.

This is achieved by:

— encouraging harmonization of national regulatory policies and practices, with particular reference to the safety of nuclear installations, protection of man against ionising radiation and preservation of the environment, radioactive waste management, and nuclear third party liability and insurance;
— assessing the contribution of nuclear power to the overall energy supply by keeping under review the technical and economic aspects of nuclear power growth and forecasting demand and supply for the different phases of the nuclear fuel cycle;
— developing exchanges of scientific and technical information particularly through participation in common services;
— setting up international research and development programmes and joint undertakings.

In these and related tasks, NEA works in close collaboration with the International Atomic Energy Agency in Vienna, with which it has concluded a Co-operation Agreement, as well as with other international organisations in the nuclear field.

© OECD 1995

Applications for permission to reproduce or translate all or part of this publication should be made to:
Head of Publications Service, OECD
2, rue André-Pascal, 75775 PARIS CEDEX 16, France.