NOM site binding heterogeneity in natural waters: Discrete approaches

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ABSTRACT

Nowadays it is commonly accepted that natural organic matter (NOM) plays a key role as a complexing agent for trace metals in natural systems (surface and groundwaters, soils). However, significant limitations are imposed on the measurement and interpretation of the complexation equilibria where NOM participates because of the fact that it is ill-defined in nature. As a consequence, a real mix of NOM binding models can be found in the literature. The purpose of this article is to discuss how one of the main features of NOM, the heterogeneity of their binding sites, is taken into account in existing discrete models. A better understanding of this aspect should help the potential user to decide which strategy could be used to solve a particular problem.

1. Introduction

In natural waters, trace element reactions with natural organic matter (NOM) have been shown to play a decisive role in trace element chemistry. However, our ability to measure and interpret the complexation equilibria of NOM is severely constrained both by the fact that their nature is ill-defined and the fact that they possess certain complex characteristics. This limits the type of information that can be obtained experimentally and, ultimately, determines which method is most effective in representing and interpreting their complexation properties. The purpose of this article is to discuss the implications of one of the main features of NOM, the heterogeneity of their binding sites, and how this is taken into account in existing models. Most of the ideas presented in this article are not new and can be found in various published articles and book chapters. However, some of the original publications are hard to read, some fundamental work is not easily accessible on-line (which nowadays often means that it is overlooked), and it is difficult to integrate all the fragments into a common conceptual framework. This may explain why both 'pure' physico-chemists and environmental practitioners often ignore some very basic ideas in this field. Both consider it too complicated, the former choosing not to bother with, and the latter not to attempt to find an alternative to the unquestioning application of recipes. Only discrete models are discussed in this article as continuous models will be the subject of a future article. Very little in the way of mathematical formulae has been included in order to focus on conceptual discussion. Should the reader be interested in exploring the subject further, a wide range of reviews published over the years is available [1–8].

2. The causes

2.1. 'Simple' versus heterogeneous ligands

Great differences exist in the binding properties among the ligands that are present in aqueous environments. They can be roughly divided into two groups which have been defined by Buffle and co-workers [9] as 'simple' and 'heterogeneous' complexing agents, on the basis of both differences in structural complexity and our current ability (or limitations thereof) to describe both the compounds themselves and their metal complexation chemistry.

'Simple' compounds are those for which: (i) the molecular structure (composition and geometry) of the compound is well-defined for any solution condition; (ii) the concentration (or activity) of the compound and its complexes can be expressed in molar concentration (or activity) units; (iii) the stoichiometry of each complex formed with any metal ion is (or can be) known; (iv) the free energy of formation of each metal-ligand complex has a unique value and is (or can be) known.

'Heterogeneous' complexing agents, on the other hand, include those ligand-containing structures found in aqueous systems that do not satisfy all the 'simple' compound criteria listed above. Heterogeneous complexing agents cannot be isolated from environmental samples in a pure state (i.e., consisting of a single molecular structure). They can, however, often be either separated or identified from such samples into groups of compounds with similar operationally defined physico-chemical characteristics. Typically this is the case for humic-type substances. Please note that the concept of heterogeneity as used here

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differs from its usual use in chemistry, i.e. "composed of two or more different phases (as solid–solid phases, solid–liquid phases, or solid–liquid–vapour phases)", rather it refers to an object "consisting of dissimilar ingredients or constituents".

All 'heterogeneous' compounds exhibit, to varying degrees, four major properties: (i) polyfunctionality, due to the existence of a variety of functional groups and a broad range of functional reactivity; (ii) high electric charge density due to the presence of a large number of dissociated functional groups; (iii) structural lability, understood as the capacity to associate intermolecularly and to change molecular conformation in response to changes in pH, pE, ionic strength, trace metal binding, etc.; (iv) size polydispersity. All these properties are exhibited to varying degrees by all biopolymers present in natural waters: proteins, polysaccharides, and humic substances. However, while in proteins and carbohydrates they reflect the behaviour of structurally well-defined, single macromolecules; in humics these properties reflect the behaviour of a heterogeneous mixture of polymeric molecules.

2.2. What type of NOM?

The term "natural organic matter" (NOM) is normally used to designate all the organic matter in a reservoir or natural ecosystem other than living organisms and compounds of man-made origin. The NOM found in natural waters is composed of an extremely complex mixture of compounds with different degradabilities, physico-chemical and binding properties. Studies of NOM have been often concerned with groups of compounds separated from the initial mixture or observed by means of different techniques. The names applied to the different groups vary enormously depending on the type of methodology applied and background of the investigator. The result is a complicated patchwork of names and fractions. A recent, comprehensive review of the terminology used can be found in [10]. Traditionally, only the so-called humic and fulvic acids have been considered in trace metal binding studies on the grounds that they are "the most chemically significant fraction of NOM" [8] or "widely believed to be representatives of NOM behaviour" [11]. The binding properties of other NOM fractions have not been studied as much. The terms humic and fulvic acids refer to organic materials defined operationally as a function of a well-established fractionation procedure. Fulvic acids are soluble in both acidic and alkaline conditions and humic acids are soluble in alkaline conditions. As the standard methods of isolation used are rather extreme, concerns exist about the representativeness of the isolated material [12,13]. Moreover, differences in the isolation procedure used in soils and freshwaters result in fractions that are given the same name having different compositions (humics from natural waters contain only hydrophobic organic acids which is not the case for soils). In this article, the term humic will be used to refer to both fulvic and humic fractions without distinction.

The NOM present in surface waters will mostly be a combination of NOM refractory to degradation either from terrestrial or aquatic sources (the so-called humics) and of non-degraded biota material (bacteria, phytoplankton and their exudates). The relative contribution of each source to metal complexation will depend on the particular system involved and on the spatial scale considered. For instance, the direct influence of freshly-derived biota compounds is expected to be more local in scale than the effects of the more refractory NOM and biota complexation will be more significant in productive freshwaters poor in humics and in seawater. Interestingly, complexing substances such as alga and bacteria exudates and cell walls can also be considered to be heterogeneous complexants. Although a number of studies have been published on their binding properties towards trace elements, they have still been studied a great deal less than the so-called humic substances. Even if rarely acknowledged, the interpretation of complexation data by these substances has much in common with the interpretation of humic binding data. Although this article focuses mainly on humic substances, most of the topics discussed are applicable to biota-derived material.

2.3. Isolated fractions and heterogeneity

The application of fractionation procedures in order to 'break-up' the complexity of NOM is inherent to the scientific method where breaking an observation or theory down into simpler concepts in order to understand them is a common practice. There is, however, a growing interest in the study of cases where novel and coherent structures, patterns and properties arise during the process of self-organization in complex systems [14]. In such cases, the whole cannot be predicted from the properties of the parts. Emergent behaviour is hard to predict because the number of interactions between a system's components increases combinatorially with the number of components, thus potentially allowing for many new and subtle types of behaviour to emerge. NOM, formed by an infinite number of possible different structures, could well be an example of emergent behaviour. Moreover, NOM is not present alone in natural systems; microscopic investigations [15–18] have shown that different types of NOM and inorganic colloids form intimate structures in natural waters. It remains to be proved whether the binding properties of such structures can be predicted from the binding properties of its fractionated constituents, heterogeneous in themselves, provided that they can be known.

2.4. Binding site heterogeneity

Results of elemental analysis (C, H, O, N, S) of humic-type compounds are widely available in the literature. Obviously, such values can only give an estimation of the maximum values of the functional groups containing oxygen, nitrogen or sulphur donor-groups because a significant percentage of the atoms will probably be present in non-complexing groups. The main functional groups in humic substances have been characterized relatively well. They include, in decreasing order of typical content: carboxyl, phenolic and alcoholic hydroxyl, quinone and ketonic carbonyl, nitrogen- and sulphur-containing groups. The prevalence of carboxyl and phenolic hydroxyl groups is responsible for the significant acidity of humic substances and for their net negative charge in natural waters.

Following the reasoning of Hummel [6], it can be estimated that a fulvic molecule (i) contains on average 5.5 mmoles of carboxyl groups per gram, which corresponds to one carboxylic group per six carbon atoms, or one group per aromatic ring, if distributed evenly; (ii) the average phenolic content group is 1.2 mole per gram, this is one phenolic group per 30 carbon atoms, or only two phenolic groups per fulvic molecule; (iii) hydroxyl and carbonyl groups, put together, are as abundant as carboxyl groups (5–7 mmol g^{-1}). Thus, an average fulvic acid molecule (molecular weight 2000 g mol^{-1}) would have one carboxylic, hydroxyl or carbonyl group every three carbon atoms. Strictly speaking, such a molecule cannot be considered to be a large, complex molecule. However, what makes the difference when compared to a 'simple' molecule or to biomolecules such as proteins is the fact that, for instance, 1 litre of a 1 mmolar solution of a fulvic acid will not contain 6.02×10^{20} identical molecules, as would be the case for an equivalent solution of a 'simple' ligand, but 6.02×10^{20} potentially different molecules with the properties mentioned above. The same considerations apply to humic acids, which are larger in size and show slightly different compositional features (fewer carboxyl groups and a somewhat larger phenolic content) [1]. Moreover, as is well-understood, both in fulvic and humic compounds not all functional groups of the same type (e.g., carboxylates, phenolates) will be exactly equivalent because they are heavily dependent on their environment in the molecule.

Much less is known about the nitrogen- and sulphur-containing functional groups. Until recently, their presence could mainly be inferred from elemental analysis results. Now, S-XANES have shown that sulphur