1   Running head: Review assemblage models

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1   The Use of Assemblage Models to Describe Trace Element Partitioning,

2   Speciation and Fate: A review

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ABSTRACT

The fate of trace elements in soils, sediments and surface waters is largely determined by their binding to reactive components of which organic matter, metal oxides and clays are considered most important. Assemblage models, combining separate mechanistic complexation models for each of the reactive components, can be used to predict the solid-solution partitioning and speciation of trace elements in natural environments. In this review we provide a short overview of advanced ion binding models for organic matter and oxides and their application to artificial and natural assemblages. Modeling of artificial assemblages of mineral components and organic matter indicate that the interactions between organic and mineral components are important for trace element binding, particularly for oxyanions. The modelling of solid-solution partitioning in natural systems is generally adequate for metal cations, but less so for oxyanions, probably due to the neglect of organic matter-oxide interactions in most assemblage models. The characterization of natural assemblages in terms of their components (active organic matter, reactive oxide surface) is key to successful model applications. Improved methods for characterization of reactive components *in situ* will enhance the applicability of assemblage models. Collection of compositional data for soil and water archetypes, or the development of relationships to estimate compositions from geospatially-available data, will further facilitate assemblage model use for predictive purposes.

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INTRODUCTION

The fate of trace elements in soils, sediments and surface waters is largely determined by their binding to reactive components of which organic matter, metal-oxides and clays are considered important. Over the last two decades, considerable progress has been made in the development and parameterisation of mechanistic models for ion binding to reactive components relevant for trace element behaviour in natural environments. These include models for ion binding to metal-(hydr)oxides [1], dissolved and particulate organic matter [2-4] and clay minerals [5]. Ion binding models have largely contributed to the scientific understanding of the behaviour and speciation of trace elements in surface waters [6, 7] groundwaters [8, 9] and soils [10-12], rare earth and radionuclide geochemistry [13, 14] and interactions of potential toxic trace elements with biota [15-17]. Combination of ion-binding models for the various components into "assemblage models" is a promising way to predict partitioning and speciation of metals and metalloids in natural environments [18-21] and waste materials and the dynamic behaviour of metals in soils, including transport to surface water [22, 23]. Concurrent with the increase in the number of mechanistic models of ion-binding has been an increase in the use of such models in environmental risk and hazard assessment of trace elements [24-26]. Increased use of assemblage models for these purposes requires confidence in and understanding of the possibilities, advantages and drawbacks associated with their use by stakeholders (e.g. environmental scientists and regulators) so that policy based on the outcomes of such modelling can be justified. To enhance and improve the use of assemblage models, there is a clear need to obtain a comprehensive overview of their conceptual underpinning, parameterisation and methods to assess site specific inputs. Furthermore, insight is needed on the consequences of choices of concepts, parameterisation, and site-specific inputs on the performance and utility of the models.

Assemblage model concept

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Assemblage models combine thermodynamic models for inorganic speciation and mineral equilibria with separate models for ion binding to various reactive components (oxides, clay, organic matter). The ion binding models are based on general thermodynamic principles. However, the complexity of ion binding to heterogeneous complexants requires simplifications in order to obtain practical models [27]. In this paper we will use the term surface complexation for the binding of ions to mineral surfaces and humic ion binding for binding to humics. In general we refer to these models as ion binding models. The models distinguish explicitly between electrostatic and ion-specific binding and account for competition among ions for binding. This allows the models to be applied across wide ranges of environmental conditions (e.g. pH, ionic strength); thus they are suitable in principle for predictions outside the parameterisation range [28]. The explicit consideration of the underlying ion binding equilibria distinguishes assemblage models from empirical approaches such as the distribution coefficient (K_d) [29] and empirical regression models [30].The modelling described here employs the component additivity approach, whereby the model is used to *predict* the total binding of elements to the assemblage by simulating binding to the individual seperate reactive components of the assemblage each with their unique sites for binding. Model parameters including binding constants and site densities for each component are determined a priori from adsorption experiments by the specific components. The total sorption is calculated as the sum of sorption by each specific component. Most component additivity models assume no interaction among components other than competition for ion binding. An alternative is the generalized composite approach, in which binding to the whole assemblage is simulated using a composite binding phase with generic surface sites. The generic surface sites represent average properties of the soil or sediment surface rather than specific minerals[31]. Binding constants and reaction stoichiometries are fit to experimental

data for the site specific assemblage [32], and are therefore not transferable to other sites. For an overview of applications of the general composite approach one is referred to[31, 33].

In this review we will discuss the ion-binding models which have been applied frequently to natural waters and soils: the NICA-Donnan model, WHAM-Models V,VI and VII and the Stockholm Humic Model (SHM) for ion binding to organic matter and the generalized two layer model (GTLM) of Dzombak and Morel, the CD-MUSIC model, and WHAM-SCAMP model for ion binding to oxide surfaces. Figure 1 shows a generalised scheme of an assemblage model setup, including submodels for the reactive components, (generic) parameterisation and site-specific inputs. Site specific inputs include the contents of the conceptual model components i.e. active humic substances, reactive metal-oxides and clays together with their active element contents. In the next sections we will describe model concepts and parameterisation, provide an overview of the setup, results and performance of assemblage model applications to artificial and natural assemblages over the last two decades, and evaluate the methods used to quantify site-specific inputs. Then we will discuss application of assemblage models to model the fate of trace metals in the context of risk assessment, before providing recommendations to improve their applications in future.

ION BINDING MODELS

Ion binding models for humic substances.

The importance of humic substances (HS) for binding ions has been long known [34, 35]. Humic substances are complex and heterogeneous macromolecular polyelectrolytes, presenting a significant challenge for modelling. They possess weakly acidic functional groups mainly carboxylic acids and phenols [36]. They also possess small amounts of N and S–based groups which may be significant for ion binding under natural conditions. Their chemical behaviour is to a large extent determined by their binding heterogeneity and their

ability to chelate metal ions at multidentate binding sites. Electrostatic effects modify the

strength of binding according to solution conditions, and need to be taken into account in

modelling. Development of molecular charge due to ion binding results in additional, non–

specific binding of counterions from solution, via accumulation adjacent to the humic

molecules. The first models of ion binding to HS appeared in the 1970s [37-39]. Further

development from the 1980s onwards has led to the models described here: Humic Ion–

Binding Models V/VI/VII, the Stockholm Humic Model (SHM) and the NICA–Donnan

model. The models are similar in that they all consider ion association to occur by specific

binding to functional groups and by electrostatic accumulation, but they differ in the manners

in which these processes are simulated.

Humic Ion–Binding Models V, VI and VII. Humic Ion–Binding (HIB) Model V [40,

41] is a discrete–site model for the binding of protons and metal cations to HS. The model is

best known as a component of the WHAM speciation model [3]. The discrete approach

represents the ion binding using an assemblage of binding sites at which solution ions bind

according to the law of mass action. The model uses a structured formulation of binding sites

to minimise the number of fitting parameters. Eight site types are considered: four

representing the carboxyl functionalities (type A), and four representing the phenolic

functionalities (Type B). The intrinsic acidity of each site type is described by a central value

pK_H and a spread factor ΔpK_H. Each site type is present in equal amount and the total number

of Type B sites is fixed to half the total number of Type A sites. Monodentate metal binding is

simulated by metal ion–proton exchange:

$$R\mathrm{H} + \mathrm{M}^{z+} = R\mathrm{M}^{(z\text{-}1)+} + \mathrm{H}^+ \tag{1}$$

and is described by two exchange constants, K_{MHA} for Type A sites and K_{MHB} for Type B

sites. Both the free ionic form and the first hydrolysis product of a metal can bind. A

proportion of the sites are paired to form bidentate metal binding sites. Intrinsic metal–proton

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exchange constants for the bidentate sites are given by the products of the K_{MH} values of the paired sites. The influence of molecular charge on binding strength is described by an electrostatic interaction factor of the form $\exp(2wzZ)$, where z is the change in charge of the humic site due to the binding, Z is the humic charge (mol g^{-1}) and w is given by a semi–empirical expression [42] related to the ionic strength. Non–specific accumulation of counter–ions is simulated assuming a diffuse layer (DL) of a given volume around the humic molecules, within which accumulation occurs. Concentrations of counter–ions in the DL are calculated using a Donnan expression, forcing the accumulated charge in the DL to balance the humic charge.

Tipping and Hurley [41] applied the model to fulvic acid–type materials, and Tipping [40] applied it to humic acid–type material. In both cases an emphasis was placed on deriving 'best average' parameters for ion binding to enable ready application of the model to natural humic–rich systems. In Model VI [43] the range of metal binding strengths was increased by allowing formation of tridentate sites and by broadening the range of binding strengths of the multidentate sites using an additional parameter ΔLK_2. The new model proved superior in fitting data, and derived values of ΔLK_2 showed a correlation with log Ks for metal binding to NH$_3$, tentatively suggesting a role for amino–type groups in forming small numbers of high affinity binding sites. Model VII [44] was a further development in which the numbers and types of the multidentate sites were adjusted to better fit the binding of Co, lanthanides and UO$_2$ at alkaline pH. Notably, better fits were obtained by preventing the formation of multidentate sites composed solely of phenolic groups.

The fixed-volume Donnan model (Model VI-FD) [45] was developed to describe the observed stronger salt effect on cation binding for solid phase humic matter as compared to dissolved humic acids. Essentially Model VI-FD is similar to Model VI except that the modelling of the electrostatic interaction which in Model VI-FD is described with a Donnan

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model with a fixed volume. The HIB models VI and VII are incorporated in the speciation

models WHAM6 and WHAM7 respectively. Model VI has also been incorporated in a

customised version of PHREEQC by defining the Model VI species and their stability

constants in PHREEQC's chemical database [46, 47].

The *Stockholm Humic Model (SHM)* [4] is a discrete site model with broad similarity

to the Humic Ion–Binding (HIB) Models. The formulation of proton binding site types is

similar to that for the HIB models, the difference being that instead of Type B sites having

half the abundance of Type A sites in both humic and fulvic acids, in SHM fulvic acid the

Type B sites have an abundance of 30% of the Type A sites. Both the free ionic form and the

first hydrolysis product of a metal can bind. Monodentate and bidentate binding of metals is

simulated, with six combinations of individual sites forming bidentate sites. Small numbers of

the sites have their strength increased using a parameter ΔLK_2, analogous to the parameter in

the HIB Models. The SHM differs primarily from the HIB models in its electrostatic

submodel. The humic molecules form a gel phase with a fraction g_f of binding sites outside

the gel and not subject to electrostatic influences on binding. Correction for electrostatic

effects within the gel phase is done using a Basic Stern model [48]. Dissolved HS are

assumed to have spherical geometry. Electrostatics of solid phase HS are described with

planar geometry, implying stronger electrostatic interaction between neighbouring charged

groups [49], to provide stronger ionic strength effects on proton binding in accordance with

observation. Charge due to dissociation of the acid groups is located at the o–plane of the

Stern layer (surface). The charge of specifically–binding ions is divided over the o–plane and

the d–plane, similar to the Charge Distribution model [50] (see section surface complexation

models for oxides). Humic charge is partly neutralised by counterion accumulation in the gel

phase. For dissolved HS, the remaining charge is neutralised by counterion in the fully

dissolved phase. For solid phase HS, the remaining charge is neutralized by diffuse

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accumulation of counterions [51], with selectivity of accumulation computed using the Gaines–Thomas equation. The SHM is incorporated in the Visual-MINTEQ package [52] which provides various database files with model parameters for proton binding, metal complexation and counterion accumulation.

The *NICA–Donnan model* is a *continuous* distribution model where specific binding of ions is simulated using an isotherm incorporating humic heterogeneity and adsorbate (ion)–specific nonideality of binding. The NICA (Non–Ideal Competitive Adsorption) expression was derived by Koopal et al. [53], initially using the Langmuir equation with the distribution of binding affinities following the Sips distribution and allowing for the width of the binding affinity distribution to be binding ion–specific. They showed that in comparison with the classical isotherm, this equation provided a superior description of the pH dependence of Cd binding to FA. Benedetti et al. [54] extended NICA to account for the bimodal distribution of binding sites on HS and showed that it could describe very well H^+ binding to a peat humic acid, and binding of Ca^{2+}, Cu^{2+} and Cd^{2+} in competition with H^+, at constant ionic strength. Predicted $Cd^{2+}:H^+$ and $Ca^{2+}:H^+$ exchange ratios were within the experimental range, but the $Cu^{2+}:H^+$ ratio was underestimated. Benedetti et al. [55] added an electrostatic submodel by assuming the humic molecules to comprise a Donnan gel phase possessing charge neutrality and with concentrations of accumulated ions within the gel related to their concentrations in bulk solution using an empirical electrostatic correction factor. This model, was successful at describing the ionic strength dependence of proton binding to a range of humic and fulvic acids. Kinniburgh et al.[2] further developed the NICA model to be thermodynamically consistent and applied NICA–Donnan to $Ca^{2+}–Cd^{2+}$ and $Ca^{2+}–Cu^{2+}$ competition for binding to a peat HA following calibration with single metal binding datasets. Competition and metal proton exchange ratios were well described over a range of pH values and ionic strengths. Milne and co–workers [56, 57] used literature datasets to derive generic NICA–Donnan

parameters for the binding of protons and 23 metals to HA and FA. The NICA-Donnan model

is implemented in the chemical speciation codes ECOSAT [58], ORCHESTRA [59, 60] and

Visual MINTEQ [52].

Surface complexation models for oxides

Hydrous oxides of iron(III), aluminium, manganese and silica (further referred to as

FeO, AlO, MnO and SiO) have long been recognised as important sorbents of a host of

elements in soils, sediments and water. Hydrous oxides tend be finely dispersed and coat

other particles resulting in a large surface area for trace element binding. In aqueous systems

hydrous oxides possess amphoteric hydroxyl groups at their surfaces. These groups bind and

release protons, depending upon the solution pH, resulting in a net positive or negative

charge. Initial attempts to develop models for oxide surface chemistry were based on the

electrical double-layer theory of Gouy and Chapman and the extension by Stern and Grahame

[61]. In later models ion binding equilibria are described by complexation reactions with

surface functional groups. Binding is described with mass law equations analogous to those

for solution equilibria, with corrections for electrostatic effects due to the surface charging.

Based on this concept, a series of surface complexation models have been developed,

including the Constant Capacitance Model (CCM) [62, 63], the Diffuse Double Layer Model

(DLM) and the Generalized Two Layer Model (GTLM)[1, 64], the Triple Layer Model

(TLM) [65, 66] and the CD-MUSIC model [50]. The models differ in their structural

representation of the solid-solution interface, i.e. the location and hydration status of the

adsorbed ions [67], and in the description of electrostatic effects. For a comprehensive

overview of the models (except CD-MUSIC) refer to Goldberg [67] and Venema et al. [48].

The *Generalized Two Layer Model* (GTLM) of Dombak and Morel [1] has become a

standard in surface complexation modelling (Table 1) because of its comprehensive set of

model parameters for metal cation- and oxyanion- binding to hydrous ferric oxide (HFO). The

model is included in various model platforms: ECOSAT [58], MINTEQ [68], ORCHESTRA [59, 60], PHREEQC [69] and Visual MINTEQ [52]. The GTLM is based on the DLM [64] in which the oxide/water interface comprises two layers of charge: a surface layer and a diffuse layer of counterions. All specifically-sorbed ions are assigned to the surface layer. The model distinguishes two surface ionization reactions to account for the amphoteric behaviour of oxide surfaces, the 2-pK model:

$$\equiv XOH_2^+ = \equiv XOH^0 + H^+ \left(K_{a1}\right); \equiv XOH^0 = \equiv XO^- + H^+ \left(K_{a2}\right) \qquad (2)$$
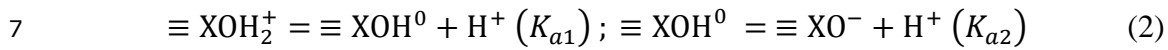
The model describes complexation reactions for cations and anions. For cations one surface species is considered i.e. $\equiv XOM^{(z-1)+}$, with M a metal cation with valence z^+, whereas for anions two to three surface species usually have to be considered, i.e. $\equiv XA^{2-}$ and/or $\equiv XHA^-$ and/or $\equiv XH_2A^0$. For cations, two surface sites with different affinities are distinguished, with the high affinity sites having the lowest abundance, whereas for anion reactions only one affinity is considered. The Gouy-Chapman relationship is used to calculate the surface potential, which corrects the intrinsic binding constants (K^{int}) for electrostatic effects according to the apparent constant : $K^{app} = K^{int} \exp\left(-\frac{\Delta Z \Psi}{RT}\right)$, where ΔZ is the change in the charge of the surface species, Ψ is the surface potential, R the gas constant and T the absolute temperature. The diffuse double layer is only used to correct for electrostatic effects; the model does not consider the accumulation of counterions in the double layer. The net charge at the surface is compensated by an equal but opposite charge in the solution. At high concentrations of trace elements, diffuse layer accumulation may contribute substantially to the total sorption, so neglecting this accumulation may lead to sorption underestimation. PHREEQC and Visual MINTEQ allow simulation of counterion accumulation which is, however, computationally intensive [70]. Since the generic constants in the GTLM were optimized without taking explicit account of diffuse layer accumulation, employing these parameters while allowing such accumulation is not completely correct. The GTLM also

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allows modelling of surface precipitation, which is important where high metal:oxide ratios are encountered. The model was generally well able to describe the experimental data used for parameterisation [1]. For elements lacking experimental data, binding constants were estimated using Linear Free Energy Relations (LFER), relating binding constants to the first hydrolysis product in solution. In addition to HFO, the GTLM has been extended with model parameter datasets for hydrous MnO [71] and gibbsite [72].

The *SCAMP oxide model* [19], which is implemented in the WHAM models (versions 6 and 7), describes cation binding to AlO, FeO, MnO and SiO using the same basic concept but with a different formulation of surface site heterogeneity and explicit consideration of non-specific binding. Proton binding is described with a two-pK model similar to the GTLM. Three binding strengths are used for metal cation binding, with the highest affinity for the least abundant sites and the lowest affinity for the most abundant. The spread of binding strengths is metal-independent, but specific to each oxide. The model considers adsorption of the free metal ion and its first hydrolysis product. Electrostatic effects are accounted for by an empirical relation similar to that used in the CCM but allowing the magnitude of the electrostatic correction to vary with solution ionic strength. Counterion accumulation is explicitly accounted for and is calculated using a Donnan model similar to that in Humic Ion-Binding Models V, VI and VII. This approach is far less computer intensive than modelling of the composition of the diffuse layer with the Gouy-Chapman approach as e.g. implemented in PHREEQC [69]. The model allows specification of ion-specific selectivity coefficients, however in the parameter optimisation the coefficient was set to unity for all ions. Various forms of the metal oxides were considered, assuming that variability in adsorption among forms can be attributed to variations in binding site densities.

Charge Distribution (CD) and Multi Site Ion Complexation model (MUSIC). The MUSIC model [73] distinguishes multiple surface sites as derived from the structure of the

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mineral by taking into account the coordination of the surface oxygen atoms. Proton affinity

constants of the various types of reactive groups (i.e. surface O(H) sites with different

coordination with the metal atoms) are predicted from the charge of the surface group and

bond length (surface-O metal), taking into account hydrogen binding [73]. Protonation is

described with a 1-pK model, which describes charging of the oxide surface using a single

equilibrium:

$$\equiv \text{XOH}^{-0.5} + \text{H}^+ = \equiv \text{XOH}_2^{+0.5} \ (K_{a1}) \tag{3}$$
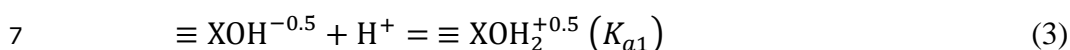
The decision to include one protonation step was motivated by the large differences in pK

between the first and second protonation step in the 2-pK model, which means that generally

only one protonation step is observed in the empirical pH window (typically pH 2-12) [74].

Using the 1-pK approach reduces the degrees of freedom in fitting data. The Charge

Distribution (CD) model [50] distinguishes three planes of charge: the surface plane, a mid-

plane and a second plane which is the head-end of the diffuse layer. The charge of specifically

adsorbing cations and anions (inner sphere complexes) is divided between the surface and

intermediate planes. Outer sphere complexes are positioned between the mid- and second

plane and the charge is divided over these two planes. The charge distribution is related to the

molecular structure of the surface complexes, information on which can be obtained from

surface spectroscopy e.g. EXAFS [75, 76]. Such molecular scale information can be used to

constrain surface reaction stoichiometry in fitting adsorption data. The CD-MUSIC model has

been implemented in various chemical speciation models including ECOSAT, ORCHESTRA

and Visual MINTEQ.

Model parameterisation of ion-binding models

Parameters for phase complexation models are generally obtained by fitting laboratory

data on ion binding to model systems (isolated HS, synthesized oxides). For the organic

matter models, largely similar laboratory data compilations have been used to obtain

comprehensive, internally consistent data sets for proton and metal binding constants to FA

and HA for HIB Models V,VI,VII [3, 43, 44], SHM [4] and NICA-Donnan [56, 57]. The most

recent and extensive compilation is that for Model VII, for which binding parameters are

available for 40 cationic metals. Additionally, parameters for the SHM have been obtained for

proton and metal sorption binding to solid phase organic matter (mor layer material) [51].

Comprehensive parameter sets for the GTLM are available for cation and anion binding to

HFO [1], MnO [71] and gibbsite [72]. For the SCAMP oxide model, comprehensive

parameter sets are available for cation binding to AlO, FeO, MnO and SiO [19]. As yet no

such comprehensive parameter set exists for the CD-MUSIC model, except for the binding of

Cd, Co, Cu, Ni, Pb, and Zn to goethite and HFO [76].

A general issue with the models is to sufficiently constrain both the number of fitting

parameters and the possible stoichiometries of the ion binding reactions, in order to derive a

robust parameter set from multiple datasets of which few may cover a sufficient range of

conditions to allow a complete parameterization. Parameterization may be constrained using

formal relationships such as that in HIB Models VI and VII, where the value of the parameter

ΔLK_2 for a cation is *a priori* estimated from the equilibrium constant for its NH_3 complex.

Parameterisation is further constrained in Model VII by taking the approach of Carbonaro and

Di Toro [77], using a formal relationship among the parameter constants for various oxygen-

centred ligands for which the relative metal binding strengths parallel those of protons. The

use of such a structured approach constrains and improves the consistency of

parameterisation. Van Zomeren et al. [78] obtained structured the approach to obtain NICA-

Donnan parameters for proton binding to HS using a two-step procedure after de Wit et al

[79] in which parameters for intrinsic and electrostatic affinities were optimized separately.

Similarly Lenoir et al. [80] developed a three-step procedure for NICA-Donnan

parameterisation in which they separated electrostatic and intrinsic affinities to constrain

model fits toward chemically and physically realistic parameters. An important means to constrain parameterisation is the use of independent data on surface stoichiometries. Hiemstra and co-workers used structural data on oxide surfaces and information on bond lengths and adsorbing species to constrain parameterisation of the CD-MUSIC model [50]. Recently Gustafsson et al. [81] and Kleja et al. [82] used spectroscopic information (XAFS, XANES) to constrain parameterisation of Cr and Ag binding to HS in the SHM.

Discussion

The modelling of ion binding to organic matter and metal-oxides has developed to a stage where the most advanced models are shown to adequately describe ion binding over a wide range of element concentrations, pH and ionic strengths. The various ion-binding models for organic matter usually give similar overall goodness of fit to their parameterisation data which were predominantly single metal systems [43, 51, 57]. However, while the three models share many common features they also differ in their descriptions of electrostatic effects, reaction stoichiometry, the correlation between the proton and metal ion affinity distribution and the description of the affinity distribution (discrete, continuous). These differences may give rise to divergent predictions for the binding of metal ions in more complex natural systems [27] e.g. due to competition between trace metals and with Al and Fe. The relatively simple model descriptions for ion binding to oxides (GTLM, SCAMP) provide reasonable descriptions of adsorption data for various oxides but the more advanced CD-MUSIC approach is more likely to provide adequate predictions outside its calibration ranges. Specifically, the refined description of the electrostatics, which is important for the interactions among different adsorbing ions, may provide better results for the prediction of binding in systems where many ions interact simultaneously at the same surface, i.e. the typical situation encountered in natural systems. CD-MUSIC has been shown to adequately

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describe the interactions of a multicomponent system of As(III and V) oxy-anions with Ca^{2+}, Mg^{2+}, PO_4^{3-} and CO_3^{2-} ions on goethite [83].

A point of discussion is how representative isolated HS and synthesised oxides are for organic and oxide phases in natural environments. Natural oxide surfaces may e.g. differ from pure synthesized oxides due to metal substitution in and surface coating of the oxide surfaces. The harsh methods to isolate HS from soils and surface waters may potentially change their properties. The work by Ahmed et al. [84] using both traditionally and mildly isolated DOM, however, indicate that the isolation procedures traditionally used for HA and FA do not appreciably affect their binding characteristics.

MODELLING OF ARTIFICIAL ASSEMBLAGES

Modelling of artificial assemblages allows assessment of model performance for well– characterised systems under controlled chemical conditions. Since real environmental assemblages cannot be characterised as accurately as artificial systems, such work has a clear role in model development and testing.

Assemblages of mineral phases. Koretsky and co-workers [85-88] have studied Cd, Co(II) and Pb binding to assemblages of HFO, kaolinite, and quartz, and Cu binding to assemblages of HFO and kaolinite. Binding to HFO was simulated using the GTLM and either the parameters of Dzombak and Morel[1] , or by using the site density parameters of Sverjensky and Sahai [89] and fitting metal–binding parameters.

Binding to kaolinite was considered using a number of 1- or 2-site models (one variably charged site, one fixed charge site) based on the DLM, with variations in the nature of metal binding to the variably charged site (monodentate or bidentate binding) and in the handling of fixed charge sites (absent, binding H^+ and Na^+ only, or binding H^+, Na^+ and metal

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ions). Quartz binding was modelled with a single site DLM, using site density parameters

from Sverjensky and Sahai [89] and fitting metal binding parameters to the experimental data.

Metal binding to assemblages was predicted using combinations of the parameterised single–

phase models. Modelling of Co, Cd and Pb was done using one such combination, to create a

single assemblage model for each metal. For Cu, multiple assemblage models were

constructed, using all possible combinations of the parameterised single–phase models.

Deviations between observation and prediction of assemblage binding were largely

attributable to shortcomings in the single–phase models. For example, the models for Pb

binding to quartz and kaolinite were somewhat poor at reproducing the effects of ionic

strength or sorbent:sorbate ratio on binding, and this was clearly seen in the predictions of

binding to the assemblage. On the other hand, predictions of Cu binding to kaolinite/HFO

mixtures were reasonably well reproduced, reflecting good single–component model fits.

Generally, model fitting to HFO binding produced the most satisfactory single component fits

across the metals. Fits to kaolinite and quartz were reasonable for specific sets of conditions,

but in a number of cases (e.g. for Pb), the models were unable to fully reproduce the effects of

ionic strength and sorbent:sorbate ratio on the observed metal binding. In some cases the

authors suggested that site blocking or formation of metal precipitates may have influenced

results; for example, they suggested that blocking of kaolinite binding sites by quartz may

have been responsible for overestimation of Cd binding to kaolinite/quartz assemblages at

high kaolinite:quartz mass ratios [85].

Organic–mineral assemblages. In contrast to mineral–only assemblages, complexation

modelling studies of ion binding to assemblages containing organic matter frequently

demonstrate binding nonadditivity. Nonadditive binding has been observed by Vermeer et al.

[90] for Cd binding to HA and hematite, Christl and Kretschmar [91] for Cu binding to FA

and hematite, Heidmann et al. [92] for Pb binding to FA and kaolinite, Saito et al. [93] for Cu

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binding to HA and goethite, Weng et al. [94] for Ca binding to FA and goethite, Cu binding to

FA and goethite [95], and phosphate and arsenate binding to HA/FA and goethite [96, 97].

Generally, where nonadditive binding is found it is greater than additive for cations and less

than additive for anions. The extent of nonadditivity has been shown to vary according to the

experimental conditions; for example Saito et al. [93] found that Cu binding to HA−goethite

assemblages was consistently greater than additive, while Weng et al. [95] found that Cu

binding to FA−goethite assemblages was additive or close to additive, except at low Cu

surface loading in systems with a relatively high FA:goethite ratio, where it was greater than

additive. In all these cases binding to the individual components was well simulated, making

it unlikely that the nonadditivity was due to inadequate model formulation or

parameterisation. Vermeer et al. [90], Christl and Kretschmar [91] and Saito et al. [93] all

suggested that unmodelled interactions between the organic molecules and the mineral surface

were responsible for the observed behaviour. A minority of studies, e.g. Janot et al. [98, 99]

on Eu binding to assemblages of AlO (α−Al_2O_3) and HA, have observed only additive

behaviour.

  Sorption of humic substances to mineral surfaces is a well−attested phenomenon [100,

101]. Weng and co−workers have developed the Ligand and Charge Distribution (LCD)

model [102] to address the influence that humic−mineral interactions have upon ion binding

to their assemblages. The LCD model combines the CD−MUSIC and NICA−Donnan models

into a mechanistic framework to describe humic sorption to the mineral surface, and ion

binding to both. The model allows specific and electrostatic binding of humic functional

groups to the mineral surface, and distributes the humic charge across the planes of the diffuse

layer. To describe HA binding the CD model was extended with an additional Stern layer in

the double layer (the Extended Stern model) [103] to allow a realistic description of the

distribution of the charge of the relatively large HA molecules. The LCD model has been

successfully applied to a number of studies including Ca [94, 95] and Cu [95] adsorption to

FA–goethite assemblages, and phosphate [96] and arsenate [97] adsorption to FA– and HA–

goethite assemblages. In all these cases the LCD modelling was compared to a linear

additivity model, i.e. one assuming no interactions between FA and the oxide surface other

than the presence of an observed portion of the FA associated with the solid oxide phase. The

LCD model was generally able to account well, in some cases with modification, for

situations where the additive model underestimated or overestimated binding. The reasons for

observed nonadditivity were predicted to vary among binding cations, and between cations

and oxyanions. In the case of Ca [94, 95]a component additivity approach consistently

overestimated binding at acidic pH and underestimated binding at alkaline pH. Such

observations could in principle be attributed to a number of effects; for example, at low pH

FA adsorption to the oxide could reduce Ca adsorption by competition, while at high pH

increased binding of Ca to FA could cause increased adsorption of Ca–FA complexes to the

oxide. The LCD model attributed the nonadditive behaviour largely to electrostatic effects, in

particular the tendency for the charges of adsorbed FA and Ca to be co–located in the 1–plane

of the mineral diffuse layer due to the dominance of outer–sphere binding for Ca. Formation

of ternary complexes (i.e. Ca–FA–goethite, FA–Ca–goethite) was predicted to be of minor

importance for binding. The authors also suggested that increased adsorption of FA, due to Ca

adsorption to FA reducing the number of contacts between the FA molecules and the surface,

was of some importance but was not a major mechanism. Nonadditivity of Cu binding to FA–

goethite assemblages was observed at low Cu surface loading in systems with a relatively

high FA:goethite ratio (underestimation of Cu binding), and at very low pH (<4)

(overestimation of Cu binding). Simulations using the LCD model reduced the predicted Cu

binding at very low pH, but could not account for the situations where component additivity

underestimated binding. Addition of a ternary, bridging FA–Cu–goethite complex accounted

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for the binding underestimation. Nonadditive effects on phosphate [96] and arsenate [97]

binding to FA– and HA–goethite assemblages were attributed largely to electrostatic effects

of HS binding to the mineral surface. The LCD model interpreted the greater effects of FA

competition for binding, compared to HA, as being due to differences in the distributions of

adsorbed FA and HA charge across the mineral diffuse layer. Binding competition due to

specific HS functional group complexation was found to be a less significant influence on

oxyanion complexation to the mineral surface.

Discussion. There is a rather small literature on the application of assemblage models

to artificial assemblages. The available data do provide useful insights into deviations from

additive behaviour. The research of Koretsky and co–workers suggests that additivity

predominates in the absence of HS. There is a need to model binding to individual

components as well as possible to provide the best opportunity of detecting any deviations

from additivity, and a clear need to constrain parameterisation options for some solids, such

as kaolinite. Additionally, assemblage models require application over as wide a range of

realistic conditions as possible in order to fully test the additivity assumption; not doing so

may produce results contradictory to other studies. Research on mineral–HS assemblages has

frequently demonstrated deviations from additivity behaviour. The key finding here is that

cation binding frequently is more than additive, while anion binding is frequently less than

additive. The work of Weng and co–workers, particularly the development of the LCD model,

has made significant progress in explaining why such interactions occur, and increases

confidence that such interactions could be incorporated into models for application to natural

assemblages.

MODELLING OF NATURAL ASSEMBLAGES

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1   Table 1 summarises modelling studies of natural assemblages over the last two

2   decades. It gives an overview of the considered adsorbing components, corresponding ion

3   binding models, type of experiments, the binding elements and the

4   determination/quantification of the adsorbing components. The majority of reviewed

5   assemblage modelling (33 studies) is related to soils or sediments, with six studies studying

6   ion binding to particulate phases in surface waters. Most surface water speciation modelling

7   studies are limited to the speciation of the dissolved or filtered fraction, taking account only of

8   metal complexation by DOM and small inorganic ligands; these studies are not covered in this

9   review.

10   *Modelling metal cation binding*

11   An assemblage approach requires identification of the most significant binding

12   components. Organic matter is considered the most important sorbent for metal cations in the

13   slightly acid to neutral pH range. A number of studies have adequately described metal

14   solubility by considering only particulate (POM) and dissolved organic matter (DOM) as

15   binding phases, in systems where organic matter is expected to dominate binding and/or

16   where the metal(s) concerned have a known strong affinity for natural organic matter. Metals

17   simulated in this way have included Co, Sr and Am [14], Al [104], Cd [10, 105-107], Cu [10,

18   105, 107]. However, this approach has been shown to be inadequate in some cases, e.g. where

19   the metal appears to have a strong affinity for other binding phases even in organic-matter

20   rich soils (e.g. Cs in [14] and Pb in [10]), or where the assumption that other binding phases

21   are generally insignificant breaks down, e.g. in more mineral rich environments [10, 14].

22   Studies including mineral phases in the assemblage showed different emphases on

23   including particular phases; for example, 20 studies included FeO, while only eight included

24   AlO and/or MnO. This may be partly due to the GTLM model parameters only being

25   available as of 2004 for MnO [71] and 2010 for gibbsite [72]. To overcome such gaps in

23

parameters, some studies have considered AlO and FeO as a single composite phase when using the GTLM [18, 108-110] or CD-MUSIC model [111]. Binding to clays was considered in 14 studies, accounting for electrostatic accumulation in response to the permanent charge either using an electrostatic Donnan model [18, 19, 21, 108-110, 112, 113] or an ion exchange model [12, 114-118]. More advanced surface complexation models for clays, taking account specific binding to variable charge edge sites have been applied to pure clays e.g. [119, 120], and artificial mineral assemblages [85-88] but not yet to natural assemblages.

Some studies reported the contribution of the individual assemblage components to total binding in soils. Organic matter was consistently the dominant adsorbing component for Ba, Cd, Cr, Cu, Ni, Zn [18, 21, 108], Co and Sn [18]. In the near neutral pH range, about 90% of Cd and Zn [21, 109, 121] and Ni [21, 109] was predicted to be adsorbed to SOM. In addition to binding to OM, binding to clays is important at acidic to near neutral pH, whereas adsorption to FeO and AlO becomes increasingly important at pH 7 and above [109, 121-123]. Binding of Cu, Cr and Sn, i.e. metals with a very high affinity for OM, is however, almost entirely accounted for by SOM over a broad pH range(3<pH<8) [109]. Lead has a high affinity for both metal oxides and organic matter, with organic matter being the dominant phase at low pH (<6) and oxides at higher pH (>6) [109]. Although FeO and AlO usually have the highest contents in soils and sediments, MnO may be important because of their high cation affinity [19]. Cances et al. [124] demonstrated the importance of MnO for Pb binding, which was confirmed by EXAFS. According to Izquierdo [123], Pb binding is mainly to FeO and MnO, Cd to FeO, MnO and SOM whereas Zn binds mainly to SOM. Model predictions by Izquierdo et al. [123] and Marzouk et al. [121] indicate a profound effect of pH on the relative importance of Cd and Pb binding to MnO and FeO, with a dominant role of MnO in the acidic to near neutral pH range (pH<6) and dominance of binding to FeO at higher pH (pH>6).

Some studies considered the possibility of metal solubility control by mineral

equilibria in addition to surface adsorption [109, 110, 115, 116, 124, 125]. Dissolved Ba

appeared to be controlled by the solubility of barite in various soil samples [109, 110].

Furthermore Ni-, Zn- and Pb- hydroxides play a possible role at alkaline pH (pH$\geq$8) [18]and

dissolved Co is possibly controlled by the solubility of Co_3O_4 under strongly alkaline

condition [109]. In most cases however, inclusion of mineral equilibria did not necessarily

improve predictions of metal solubility. This is either due to soil waters being undersaturated

with respect to the considered minerals e.g. Cd-, Cu-, Zn-hydroxides and -carbonates and Zn-

Al double layered hydroxides (LDH) in contaminated soils near a Zn smelter [125]. Or

because thermodynamic data for many mineral phases are scarce or uncertain, even where

such minerals (e.g. Zn-Al-LDH) are known to be present in soils [124, 126].

In the solution phase, metals with a high affinity for organic matter (Cu, Cr, Pb, Sn)

are predicted to be largely present as complexes with DOM [109, 113]. Metals with a lower

affinity for organic matter (Ba, Co, Cd, Ni, Zn) are predicted to be mainly present as free

metal, or as inorganic ion-pairs with in the acid to neutral pH range and as organic complexes

at alkaline pH [109].

Nearly all the reviewed studies assess the models in terms of their ability to predict

measured total dissolved concentrations and one study [21] comparing predicted and

measured free ion concentrations. However, not all studies provided a quantitative measure of

model performance. Model performance in terms of the root mean squared error of the log

transformed concentration (logRMSE) was reported in nine studies [12, 18, 108-110, 114,

115, 121, 123]. Median values of the reported log RMSE were between 0.3 and 0.5 for Cd,

Cu, Ni and Zn, indicating rather good model performance. Predictions of Pb were poorer,

having a median logRMSE of 0.7. A number of studies attribute underestimation of Pb

binding to soil to an absence of MnO in the assemblage [108, 110, 113, 114]. Others

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considered shortcomings in parameterisation of Pb binding to HFO in the GTLM [109, 127, 128] and CD-MUSIC model [117, 129], or organic matter in the SHM [117, 129] to be a possible cause and adjusted parameters to optimise fits to measured solution concentrations. Xiong et al. recently published improved parameterisation of Pb binding to SOM for the NICA-Donnan model[121]. From the few studies on other metal cations, model performance appears to be reasonable for Co (median $RMSE_{log}$: 0.6) but less good for Ba, Cr, Sn and V ($RMSE_{log}$ 0.7-1.1). For the latter, binding constants were estimated by Linear Free Energy Relations (LFER), so confidence in the parameters is lower than for metals parameterised against measurements. Furthermore, there is considerable uncertainty about the prevalent redox species of V, which may either be present as cationic V(IV) or anionic V(V) species. Predictions assuming V to be vanadyl (VO^{2+}) gave the best results [109].

Weng et al. [21] used their assemblage model to predict Cd, Cu, Ni, Pb and Zn free metal ion activities in solution. Model inputs included reactive metal, organic matter, clay content and solution pH. DOM was, however, not used for input. Neglecting DOM is only justified when solution concentrations of the organic complexes of the considered elements are very low compared to total reactive concentrations, which may be valid for soils. The possibility of predicting the free metal without the need to quantify DOM can be of practical relevance as DOM concentrations are rarely if ever available in soil maps and databases. Predicted free metal ion activities compared favourably with measurements, except for Pb of which predictions were at least one order of magnitude greater than the measurements.

A small number of studies [104, 122, 125] have combined prediction of trace metal partitioning with simultaneous simulation of soil acid/base buffering. This typically requires model calibration by adjusting amounts of reactive phases to fit trends in pH in response to acid or base addition [104, 125].

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Another interesting example of assemblage modelling is its use to predict the solution and solid phase composition after mixing of acidic rock drainage with more alkaline surface waters [127, 128, 130]. Rather than specifying fixed concentrations of binding phases, the models accounted for the precipitation of mineral phases from solution in response pH changes, and the subsequent adsorption of various trace elements to these newly formed phases.

Reaction kinetics of metal cation (Cd, Ni, Cu, Pb and Zn) sorption to and desorption from organic matter in soils have been described with kinetic equations for metal adsorption and desorption in combination with Model V/ VI by Shi et al. [131, 132]. Metal cation binding including the short term (hours) kinetics thereof were successfully modelled by optimisation of the reactive organic matter content and two desorption constants, one for a fast reaction and the second for the slow reaction. The rate constant for the fast reaction was coupled with monodentate and electrostatic binding whereas the slower rate was assigned to bi- and tridentate binding. Buekers et al. [133] described the long term aging of Cd, Ni and Zn using an assemblage model combining equilibrium sorption to organic matter and clay with kinetic adsorption to FeO using Model VI for organic matter and the SCAMP models for oxide and clay. Aging is described with the transfer of geochemically active metal (see section quantification of reactive components of the natural assemblage) adsorbed to FeO to an inert metal pool using an empirical kinetic function. Rate constants for this function were derived from kinetic sorption experiments using synthetic Fe-oxides. With these parameters the model reasonable predicted geochemically active reactive metal contents, measured with isotopic dilution, in 28 metal spiked soils over an 850 days period.

Modelling oxyanion binding

There are relatively few (nine) studies considering oxyanion binding of which 7 are related to soil/sediment and two to surface water. All consider As [109-111, 115, 116, 128, 130, 134, 135] and four consider Mo, Sb [109, 110, 128, 130] and Se [109, 110, 128]. Oxyanion binding has been modelled exclusively to metal oxide surfaces. Binding to FeO was considered in all nine studies. Binding to AlO was considered in four studies. In the study of Tonkin et al. [128] (mixing acid rock drainage with surface water) AlO and FeO were modelled separately, using the GTLM with specific parameters for HFO [1] and AlO [121], whereas in the three other studies related to soils AlO and FeO were combined into a composite mineral using either the GTLM with parameters for HFO [109, 110] or CD-MUSIC with parameters for goethite [111]. Cui and Weng [111] found decreasing As sorption with increasing AlO contribution to the sum of AlO and FeO. The influence of AlO to the binding of As was much larger than its relative amount extracted from the soils which might be due to surface coating and substitution of FeO.

Predictions of oxyanion solubility were generally somewhat poorer than for metal cations, with median logRMSE of 0.5-0.6 for Mo and Se and 0.9-1.0 for As and Sb with concentrations of Sb overestimated one order of magnitude [109, 110]. A possible reason is competition from HS for binding of oxyanions to oxide surfaces. Modelling of oxyanion binding to soil have been improved considerably by competition from HS for binding. Gustafsson [134] simulated HS competition for arsenate binding to an oxide surface by introducing the irreversible binding of a hypothetical organic species RO^- to the surface, using CD-MUSIC. The sorbed amount of RO^- was optimized on a soil–by–soil basis to fit the observed As sorption. Hiemstra et al. [136, 137] employed a somewhat different approach, using the CD-MUSIC model in which OM binding to the oxide was modelled using a virtual OM-surface component which is only present in the adsorbed phase. Surface binding of OM is modelled using various surface OM species which can bind by inner-sphere and outer-

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sphere complexation. Phosphate solubility was well described across soils with a wide pH

range (3–7) following optimisation of the amount of adsorbed OM. The amount adsorbed OM

relative to the total of adsorbed OM and phosphate correlated well with the logarithm of the

SOM content (R^2=0.79). Recently, Cui and Weng [111] applied the LCD model (see section

modelling of artificial assemblages) to interpret the sorption behaviour of As and PO_4 in soil

samples over the pH range 4-8. The amount of OM adsorbed to the oxide surface was

optimized to fit the PO_4 solid/solution distribution at the original pH of the samples. The

optimized adsorbed OM was kept constant and further used in the modelling of the pH–

dependent solubility of As and PO_4

Aside from the appropriateness of the model structure, and the quality of the

parameterization, the final model performance depends largely on site–specific model inputs.

The various methods that have been used to quantify these inputs, together with possible

improvements, are discussed in the next two sections.

Quantification of reactive components of the natural assemblage

Oxides - Amounts of AlO, FeO and MnO available for ion binding are mostly

estimated by selective, but operationally defined, chemical extraction of Al, Fe or Mn (Table

1). Assumptions must be made regarding the mineral form of the oxide and its corresponding

specific surface area. The most common is the oxalate extraction to quantify amorphous FeO

and AlO [19, 21, 108, 110, 113, 122, 138]. Some studies distinguish between amorphous and

crystalline forms using various combinations of selective extractions [18, 21, 109, 113, 114,

122] (see also Table 1) for example using the difference between the dithionite-citrate-

bicarbonate (DCB) and oxalate extractions as a measure of crystalline oxides. The

distinguished mineral phases may be simulated either using by separate phase–specific

models, or by combination into a single composite oxide phase, assuming similar binding

affinities of the distinguished oxide surfaces. Dijkstra et al. [18, 109] used a single component

but distinguished between amorphous and crystalline FeO in calculating the total site density

by assigning different surface areas to the amorphous (600 m^2/g) and crystalline (50 m^2/g)

forms. Weng et al. [21] estimated FeO from oxalate–extracted Fe, correcting for the portion of

this extracted Fe bound to organic matter (10-29%) by estimating it with their assemblage

model.

Another approach is to simulate the amounts of (hydr)oxides from the total reactive

concentrations of Al, Fe and Mn and using mineral solubility equilibria to compute the

amounts from (hydr)oxides [18, 108, 109, 115, 116, 127, 128, 130]. Virtually no differences

were found in model performance either using the selective extraction data or modelled

amounts of AlO and FeO in soils [18, 21, 108]. In surface waters, oxide contents have been

determined by the difference between the acid available Al/Fe/Mn(including particulate

matter) minus filterable (0.45µm) concentrations of the elements [112, 139].

According to Hiemstra et al. [140] the ion binding affinities of the various Al and Fe

oxides are similar and can be modelled using a single oxide phase taking into account

differences in surface areas. Based on this assumption, an approach was developed to

determine the effective reactive surface area of oxides in soils using a probe anion (PO$_4^{3-}$)

[140]. With this method, an apparent reactive surface area of 630±470 m^2/g (HFO+HAlO)

was found, which is close to the surface area of 600 m^2/g frequently used for HFO [1], but

with substantial variation among soils. Dong et al. [141] determined the surface areas of

goethite and kaolinite in mineral assemblages using measured HA adsorption maxima on the

assemblage and the single constituents.

Organic matter - Ion binding models for OM are parameterized for isolated FA and

HA. Natural OM comprises, in addition to FA and HA, low molecular weight organic

molecules (acids, carbohydrates, lipids, amino acids) [142] with generally lower affinity for

metals. Therefore measured SOM and DOM have to be interpreted in concentrations of

30

"active" OM with equivalent binding properties to FA and/or HA. The composition of OM

and therefore its binding properties, varies both spatially and temporally [143].

Dissolved organic matter - In the reviewed studies assumed proportions of active

DOM range from 31-100% (Table 1). These proportions were chosen on the basis average

fractions in literature or were obtained by model optimisation or specific measurements.

Various studies have used the average active fraction of 65% from Bryan et al. [144] obtained

for freshwater DOM as an estimate for terrestrial DOM [21, 107, 121-123, 125]. Bryan et al.

estimated active DOM by optimizing the concentration of FA to fit copper binding data in

freshwaters, using Model VI. However, such optimization of the fraction of active OM

implicitly accounts also for variation in binding strengths amongst humics, which may vary

considerably [145], as well as any bias in the metal–humic binding strength. This explains

why the optimized active fraction can exceed 100% as was found for Ni [146], Cd and Zn and

can also vary among metals in the same sample [147]. Groenenberg et al. [145] specifically

measured the humic fraction (HS=FA + HA) of DOM in soil solution extracts (0.002 M

$CaCl_2$) according to the fractionation procedure of van Zomeren and Comans [148] and

reported fractions of HS between 14-63%. This fraction HS was used in their assemblage

model thereby neglecting the hydrophilic fraction. The role of the hydrophilic fraction in

metal binding is expected to be limited because most of its components have relatively low

affinity to bind metals relative to HS [145]. Croué et al. [149], however, measured substantial

binding of Cu to a nitrogen–rich hydrophilic DOM fraction using a different fractionation

protocol. Thus, more research is needed on the binding properties of the operationally–

defined organic matter fractions obtained with the various fractionation methods [148-150].

Some researchers have explored the relationships between spectroscopic and fluorescence

characteristics of DOM and its metal–binding affinity [147, 151, 152]. Mueller et al. [147]

derived empirical relationships between the Model VI–optimized active fraction of DOM and

fluorescence measurements. Such relationships could be of practical use to *a priori* estimate the active fraction of DOM from measurable data, if validated for waters of widely varying chemical composition.

Soil organic matter - The fraction of active SOM varies between 31-87% in the reviewed studies (Table 1). Active SOM can be estimated by measuring the concentrations of HS [20, 109, 145], assuming chemical activity to be solely due to this component. Lumsdon [20] quantified the amount of humic material in the soil using a scaled down version of the International Humic Substances Society method [153] and reported fractions of HS between 14-87% of SOM in 7 soil samples, with the lowest fractions in O-horizons of forest soils. Dijkstra et al. [109] measured fractions of HS in 8 sandy soils using the method of Van Zomeren and Comans in the range 25-67%. Groenenberg et al. [110] measured the fraction HS in a sandy soil profile, using the method of Van Zomeren and Comans, to be 81-87 % of SOM. Where data on HS concentrations have been absent, studies have estimated the active fraction by model optimisation [51, 104]. Tipping et al. [107] reported optimised active SOM in the range 9–86% of total SOM by fitting Model VI to the observed porewater pH in 98 UK upland soils. Gustafsson et al. [12] obtained fractions of active SOM in the range 17-84% by optimizing this fraction in the SHM to fit pH and soluble Al and Ca concentrations in 14 soil samples from O-, A- and B-horizons of various soil types.

Weng et al. [21] calculated the site density of SOM for a particular soil from its measured CEC, minus the CEC attributed to the clay fraction as calculated from the clay content of the soil and the assumed site density of the clay. With this method they estimated the average binding site density of SOM in a sandy soil, sampled at various depths, to be 16-46% (average 36%) relative to generic humic acid [57].

Geochemically reactive element contents

The geochemically reactive [107] or labile element content [29] is the elemental content in soil/sediment and surface water (including suspended particulate matter) available for interaction with the solution phase at short timescales through fast processes such as sorption/desorption and fast (surface)-precipitation reactions. The remaining inert fraction comprises element incorporated into crystal lattices of minerals or occluded in metal oxides or organic matter, due to its geogenic origin or to fixation processes [154]. Isotope exchange techniques are conceptually the most suitable technique to measure the geochemically reactive pool (E–value) [155, 156]. Isotopically exchangeable metal has only been used in three studies [121, 123, 133]. At present the method is not widely available for routine analysis and various chemical extractions have been used to determine reactive element contents. In the 39 studies summarized in Table 1, 11 distinct methods were used to determine the reactive metal content. Extractants are chosen for their perceived ability to select the reactive pool of metal, either by competing with the metal for solid–phase binding sites (e.g. dilute acids) or by competing with the binding sites to complex the metal (e.g. EDTA).

Metal cations - The use of Aqua Regia (AR) extracted metal has been shown to result in overestimation of dissolved concentrations in soil solution partitioning modelling for various metals i.e. Cd, Pb and particularly Ni and Zn [115, 116, 121]. Modelling using isotopically–exchangeable metal pools gave significantly better results for Cd, Pb and particularly Zn, than did the use of AR–extracted metal pools[121, 133]. Milder acid extracts of various strength have been used frequently to determine the reactive element content, such as 0.1M HCl [20], 0.22M HNO_3 [125], 0.43M HNO_3 [10] and 2M HNO_3 [21]. The strong ligand EDTA has been used in several applications e.g. [108, 114]. Good agreement between EDTA– and 0.43M HNO_3–extracted metal has been shown for organic soils (>10% SOM) [107] and forested and agricultural soils [157, 158]. Metal pools measured with both 0.43M HNO_3 and 0.05M EDTA extractions compared reasonably well with the E–values for Zn, Cd

33

and Pb in acidic organic soils, however, in calcareous soils the extractants overestimated E–values [159].

Comparison of measured metal solubility with modelling based on metal extractions can provide tentative information on the suitability of specific extractions. Predictions using the 0.43M HNO_3 extractable metal pool resulted in good results but with a slight overestimation of solution concentrations of Cu, Ni and Pb (with log mean error, logME <0.20), a somewhat more pronounced overestimation of Cd and Zn (logME 0.30 and 0.46 respectively) and a slight underestimation of Cr (logME -0.14) in the study by Dijkstra et al. [109] (J.J. Dijkstra, Energy research Centre of the Netherlands, The Netherlands, personal communication). The 0.43M HNO_3 extracted metal provided good predictions of Cd, Cr, Cu, Ni, and Zn concentrations in solution (-0.1 <logME<0.1) in the study by Groenenberg et al. [110]. Concentrations of Pb were, however, overestimated, most likely due to model failure as previously discussed. Bonten et al. [108] obtained good results using either 0.43 M HNO_3 or 0.05 M EDTA for Cu (ME= -0.02) and Zn (ME=0.19) and somewhat overestimated dissolved Cd (ME=0.41) but considerably overestimated dissolved Pb. Almas et al. [125] concluded that 0.22 M HNO_3 likely underestimates reactive Cu and Zn, whereas Cd was predicted very well. Extraction with 2M HNO_3 is likely too strong for Ni and Zn leading to an overestimation of solution concentrations in the study by Weng et al. [113]. Concentrations of Cd and Cu were predicted very well using 2M HNO_3 extraction. Bonten et al. [108] saw an overestimation of Zn solubility in some samples with high reactive zinc contents extracted with either 0.43M HNO_3 or 0.05M EDTA. They tentatively attributed this to the partial solubilisation of mineral (i.e. non–labile) Zn during the extractions, and thus to overestimation of the geochemically reactive pool. Given sufficient robust information on solid phase speciation, such artefacts can in principle be corrected for; Cances et al. [124] subtracted the

34

amount of Zn that is present as Zn/Al-hydrotalcites (20%) from the measured reactive Zn

content as input to their modelling.

Oxy-anions - Gustafsson extracted native As using ammonium oxalate, but

conclusions on its appropriateness to select for the reactive fraction are difficult because most

of the data from that study were from added As [134]. Schröder et al. [115] found that AR

digestion resulted in reasonable good predictions of soluble As in alkaline soils, but

overestimated As in soils with pH < 6.8. Interestingly, Dijkstra et al. [109] found that the use

of 0.43M HNO_3 resulted in an underestimation of As solubility at alkaline pH and fair

predictions in the acid to near neutral pH range. Using the 0.43 M HNO_3 extraction resulted in

good predictions of soluble As (except at pH>8) and Se, but overestimated Sb and

underestimated Mo solubility [109, 110].

Discussion

The reviewed studies show great potential for the use of component additivity assemblage

modelling using generic model parameters and plausible measurements or estimates of the

reactive element and active assemblage component concentrations. Model performance can be

potentially improved by (1) reducing the uncertainty in model parameters especially those

based solely on LFERs e.g.. Sn, Sb (Fe/Al-(hydr)oxides) and Ba, Cr, Sn and V(organic

matter) ; (2) taking account of interaction between organic and mineral components especially

the competitive binding of organic matter with respect to oxy-anion binding to Al/Fe-

(hydr)oxides; (3) improved methods to quantify the reactive element- and (4) active

assemblage component concentrations. Among the reviewed studies, the many differing

factors that affect model performance confound a systematic comparison of methods to

quantify the reactive element concentrations and reactive components. Therefore we

recommend a more thorough and systematic evaluation of methods to determine reactive

element concentrations and reactive components with respect to their effect on model

predictions, uncertainties and practical applicability.

FATE AND TRANSPORT MODELING

Modelling chemical transport in soils, aquifers, surface waters and sediments has great

importance for contamination assessment and management, for example in projecting changes

in chemical movement following remediation of contaminated soils and aquifers, predicting

potential for radionuclide migration from contaminated sites or waste repositories, or

predicting changes in contaminant pools in soils resulting from changes in environmental

conditions. Assemblage modelling has gradually assumed increasing importance, as

equilibrium chemical speciation modelling has been shown to be superior to the constant$-K_d$

approach for dynamic prediction of contaminant behaviour, e.g [160]. Despite this, the use of

component additivity models in groundwater transport modelling is relatively uncommon

compared to generalised composite modelling, e.g. [161, 162]. Some published work exists on

uranium transport using the component additivity approach. Bea and co–workers [163]

developed a two–dimensional reactive transport model coupling hydrodynamic processes with

solution speciation, solid precipitation and dissolution, and uranyl and H^+ adsorption onto the

aquifer solids using the component additivity model of Dong and co–workers [141]. The

model showed reasonable agreement with observed pH and Al, U and NO_3 concentrations in

groundwaters at the Savannah River Site (SC, U.S.A.).

Component additivity modelling has been applied in a number of instances in

predicting long-term dynamics of metals in soils, and transfers to surface waters. This work is

linked to assessing ecological and human health risks of such accumulation, and in a number

of cases is linked to the dynamic prediction of soil and surface water acidification. We here

describe a number of such applications, and then discuss the future potential for developing

such approaches.

The CHUM–AM model [164, 165] predicts long term changes in soil pH, S, N and

metal pools, in organic-rich soils and associated surface waters. The model couples

WHAM/Model VI with models for major ion and metal weathering in topsoils and S and N

cycling models. The model was used to predict present day soil pools and surface water

concentrations of Ni, Cu, Zn, Cd and Pb in several sub–catchments of the River Duddon,

northwest England. The default parameters for metal–humic substance binding were found to

provide good predictions (with a factor of three of the observations), with the exception of Pb,

for which the strength of binding to soil HA required increasing by 0.4 log units, largely to

provide reasonable agreement with the observed surface water concentrations.

Bonten and co-workers [22] developed the existing SMART dynamic model of soil

acidification to include equilibrium speciation and partitioning of metals. The developed

model includes NICA–Donnan for complexation to organic matter in the soil solids and

porewater, a non–specific Donnan model for ion exchange on clays, and the GTLM for

complexation to FeO and AlO. The model also simulates C and N cycling in soil and cycling

of elements through vegetation. When the model was applied to a forested site in Germany

with acidic soils, it was shown to successfully reproduce observed trends in porewater Cu, Zn,

Cd and Pb concentrations for 1980-2004, using default parameters, suggesting that the key

processes controlling metal solubility were well described. Porewater concentrations of Cu,

Zn and Cd were generally predicted within a factor of two of the observations. Porewater

concentrations of Pb were overestimated by up to a factor of four.

Bhavsar and co–workers developed TRANSPEC [24, 166], a coupled speciation and

transport model for surface waters. The model considers chemical movement and fate through

environmental compartments, using the MINEQL+ model to calculate speciation within each

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compartment. The model was used to simulate the dynamics of Zn in a lake subject to inputs from mining and smelting. The lake was simulated as two basins, each having surface water, surficial sediment and deep sediment compartments. Each compartment was assumed to contain dissolved, colloidal and particulate phases. Dissolved organic matter in the colloidal phase was simulated using a simple diprotic model while FeO present in the particulate phase under oxic conditions was assumed to be surface active, with complexation simulated using the GTLM [1]. The model was able to reproduce the year–round variability in Zn concentrations in the lake water column.

Farley and co–workers [26] have developed TICKET-UWM, a screening tool for assessing the hazards associated with metal inputs to lakes. The model uses a coupled kinetic/equilibrium/transport algorithm to simulate dissolution kinetics of solid metal forms and their subsequent transport and speciation, including complexation to dissolved and particulate organic matter in the water column and sediments (using HIB Model V). The latest version of the model [158] allows particulate and dissolved organic matter to be simulated using HIB Models VI or VII, and allows surface complexation to FeO and MnO in the surface water and sediment.

Ion binding and assemblage models have also been employed in the risk assessment of long-term metal loads to soils [167-169]. The critical loads approach considers the steady state fluxes of metals into and out of a topsoil that results in the soil metal concentration equalling a critical concentration for a given toxicological or human health endpoint. Hall and co–workers [169] calculated critical loads for semi–natural ecosystems in the U.K.. The approach considered the balance of inputs due to metal deposition from the atmosphere with leaching losses, and removal in harvested wood for forested ecosystems. Concentrations of metal in the soil solution at steady state, as a function of the reactive soil metal pool, were computed using a combination of a semi-empirical transfer function to relate the reactive pool

to the free metal ion, and a version of WHAM/Model VI to compute the total porewater metal from the free metal ion. De Vries and Groenenberg [167] extended the approach to consider metal cycling in forested ecosystems in more detail, and to consider the dynamics of metal accumulation and loss. In addition to critical loads, they considered the calculation of (i) stand-still loads, where the metal load that prevents further accumulation from the present day situation is computed, and (ii) target loads, where for soil exceeding the critical limit in the present day, a load is calculated based on a target future year for reducing the soil reactive metal to the critical limit.

Component additivity modelling has also been used to assess the leaching of potential contaminants from man–made materials. Verschoor et al. [170, 171] used a reactive transport model equipped with the model of Dijkstra et al. [109] to derive alternative emission limits for inorganic components in granular building materials. The model, together with scenarios for sand, clay and peat soil, is implemented in the decision support tool LeachXS [172].

Discussion The inclusion of assemblage models in models of contaminant transport and dynamics demonstrates their usefulness in providing a more realistic description of ion adsorption than approaches such as constant K_d values, particularly for groundwater reactive transport modelling. To date, component additivity models have been utilised less then generalised composite models, due to the difficulties in isolating and quantifying the surface reactive components of the field solid, as exemplified by the work of Davis and co–workers [32]. Clearly, for the wider acceptance of the component additivity approach, methods to improve such quantification are required. Additionally, for wider acceptance of the assemblage approach there remain few readily applicable, parameterised models and frameworks into which such models can be readily incorporated. Generic model frameworks such as TICKET-UWM or ORCHESTRA [55, 56] may be useful starting points, particularly if they can be made more user–friendly than at present.

The inclusion of assemblage modelling in tools such as TRANSPEC, the UWM and the critical loads and related models is linked to the need to take spatial and temporal variations in ion adsorption into account in hazard and risk assessment. Here, the generalised composite approach, with its reliance on parameterisation to the soil/aquifer/sediment of interest, is less useful than the component additivity approach. This is a key future area for development, particularly in relation to model evaluation where compositions of solid materials are required, and emphasises the need to further develop and evaluate analytical methods for quantifying reactive constituents and their surface areas in the environment, and to quantify the reactive (surface adsorbed) pools of metals in the field.

SYNTHESIS AND FUTURE PERSPECTIVES

The modelling of ion binding to metal oxides and organic matter has developed to a stage where the most advanced models can be readily applied to natural environments. Comprehensive datasets of default model parameters enable models to be applied predictively, given plausible measurements or estimates of the active assemblage component concentrations. Models for clays are underrepresented in assemblage models, with the exception of models that only simulate ion exchange. Development of generic models for clay minerals would further broaden the applicability of assemblage models.

The large number of parameters in surface and HS complexation models can hamper derivation of optimal binding parameters. Using spectroscopy to probe the ion binding environment and configuration has provided data useful for constraining parameterisation, and we recommend its further use for this purpose. Parameters based on LFERs should be replaced by experimentally-derived parameters when data becomes available. Several compilations of parameters, e.g. those of Dzombak and Morel for HFO in 1990, and Milne and co-workers for humics in 2003, could be usefully updated by incorporating more recent

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data. There is a need for a generic set of CD-MUSIC parameters, to facilitate wider uptake of this model.

The accuracy of assemblage model predictions for metal cations is generally good, especially for those metals with a moderate to high affinity for binding to organic matter. An exception is Pb, for which binding is frequently underestimated. This may be attributed to various factors including the parameterisation of Pb binding to humic substances and oxides, the exclusion of MnO from some assemblage models, or significant non-additive effects on binding. Model performance is generally inferior for elements whose parameters are based on LFER, such as Cr and Sb. Oxyanion binding, of which there are relatively few studies, generally shows good prediction of trends but with relatively high scatter. Competition between oxyanions and humic substances for sorption, which is not considered in most models, is likely to be an important reason for this. Recent advances to include the effects of organic matter interaction with the oxide surface, as have been applied to both artificial and natural assemblages, need optimisation of the adsorbed surface OM to fit the data. The methods should be further developed and tested, particularly with natural assemblages, in order to be used for predictive purposes.

Assemblage modelling is a powerful scientific tool to develop knowledge and understanding about the processes controlling partitioning and speciation of trace elements in natural systems. Ion-binding models contribute to the interpretation of experimental data by allowing competing hypotheses regarding surface speciation to be tested quantitatively. Assemblage modelling of ion sorption to artificial phase assemblages has a clear role to play in model assessment and development, providing well-characterised and quantified systems against which to test models. The LCD model is proving highly useful in developing understanding of the complex interactions of combined mineral and organic assemblages, moving beyond the concept of strict additivity to take the interactions among the assemblage

components into account. It would be useful to extend the model concept to more realistic and natural systems by including submodels for clay minerals and soil organic matter not associated with oxides.

Assemblage model prediction of ion sorption to natural assemblages is less accurate than for artificial assemblages, given the inherent uncertainties in characterisation of natural systems. Nonadditivity effects need to be more important than in artificial composites in order to be detected robustly. To advance the science, we recommend top down study of assemblage systems, by firstly identifying discrepancies between experimental results and model predictions for natural assemblages. Targeted experiments with artificial assemblages can then be used to study such discrepancies in more detail and to provide data to develop models that account for non-additivity. Quantifying uncertainties in model predictions is important in assessing to what degree discrepancies can be attributed to non-additivity. Therefore, we recommend that calculation of uncertainty in predictions, as has been done for the NICA-Donnan [145] and HIB Model VII [173], be incorporated into assemblage models. Uncertainty analysis can also be employed to identify the most important sources of the uncertainty in model outputs and thus to guide research on model development and methods to determine parameters and site specific inputs.

The present review reveals a multitude of methods to determine the active contents of humics and mineral surfaces available for ion binding, and to determine geochemically reactive element contents in natural systems. Because of variations in model setups, experimental designs and the systems under investigation, it is challenging to provide general guidance on the most suitable methods to improve such determinations. We therefore recommend systematic evaluation of a selection of methods on a set of soils with a wide variation in soil characteristics and element contents by evaluation of the model performance using the various model inputs.

Assemblage models have proven useful for prediction of metal transport in soils and sediments, long term accumulation of metals in soils and prediction of concentrations in groundwaters and surface waters. Generally models are applied predictively, with the aim of hazard and/or risk assessment. At present, uncertainties in adequately quantifying natural systems somewhat restrict further use of the models for these purposes. Therefore, the improvements already recommended should increase confidence and uptake of the models for this purpose. For generic risk assessment, inputs should be available at the geographic scale of interest. It is however not to be expected that such detailed information will become readily available at national, regional or global scale. This data gap may be tackled by the use of pedotransfer functions (predictive functions of certain soil properties using data available from soil surveys) to relate the desired model inputs to soil information generally available at the desired scales.

A surface complexation-type approach could possibly be used to derive a more mechanistic approach to metal uptake by and toxicity to biota. Some promising results have been obtained using humic acid sorption as an analogue for uptake by plants [15] and aquatic biota [174]. Such an approach could be incorporated into an assemblage model to create a combined speciation and uptake/toxicity model for the field.

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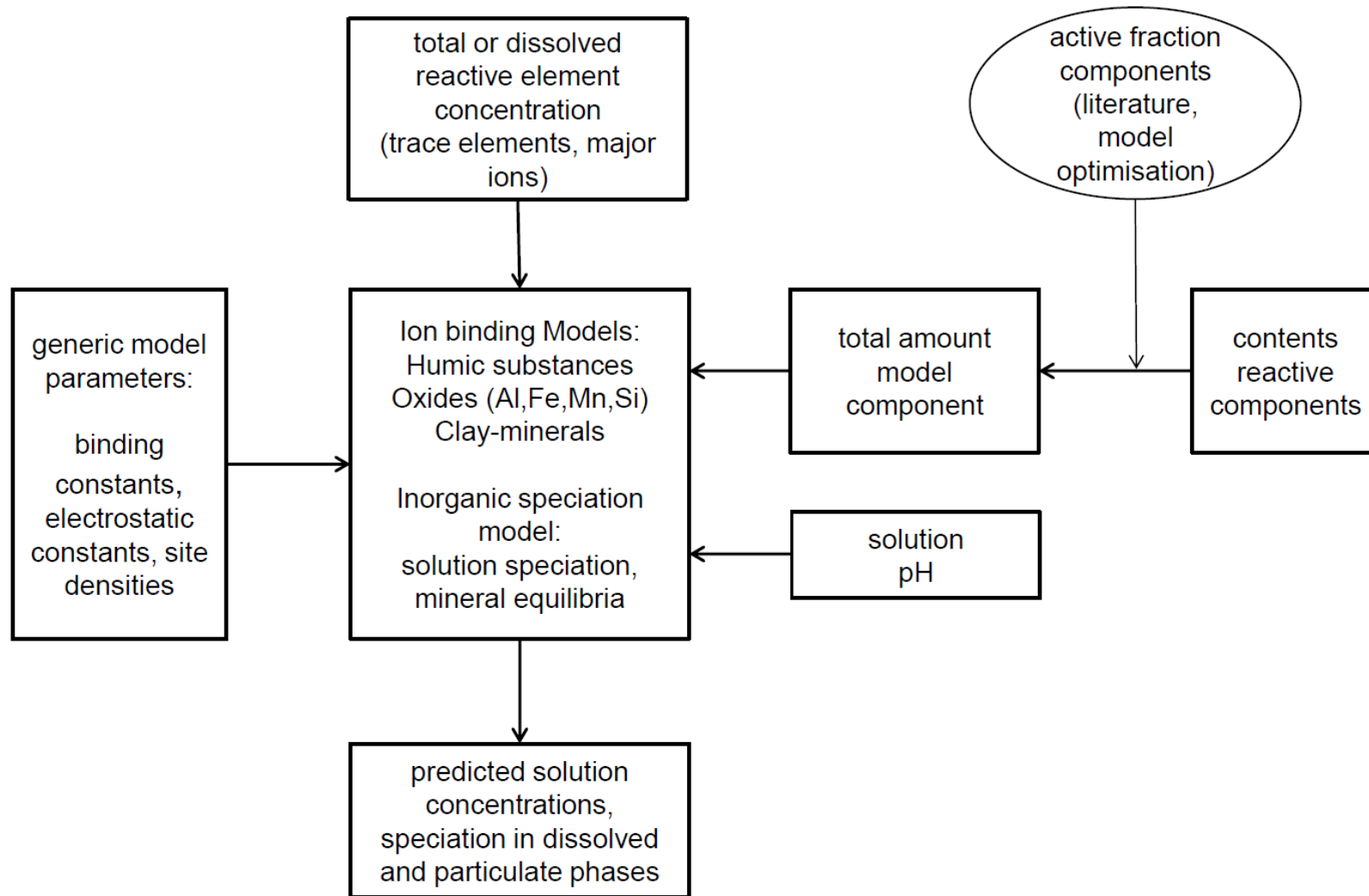
Figure captions:

Figure caption: Figure 1. Schematic overview of an assemblage model setup to predict trace element speciation and solid-solution partitioning from total reactive element contents. The assemblage model contains several sub models for the various model components. Inputs include model parameters (fixed), contents of the reactive components: particulate and dissolved organic matter, metal-oxides, clays, trace elements, major ions, and pH in the solution phase. Inputs of reactive components to the model may require adjustment relative to measured amounts of the model components (humic substances, hydrous ferric oxides, goethite etc.), using literature information and/or by optimisation of the model.

1 Table 1 Summary of reviewed studies with modelling of natural assemblages in chronological order.

	Reactive components and *models*	modelled system	elements	reactive element concentration	active organic matter	oxide surface / clay	reference
1	SOM, DOM: *Model V*	batch adsorption study organic rich acid soils	Co, Sr, Cs, Am	added metal	optimized to fit pH and dissolved Al	not considered	Tipping [14]
2	SOM, DOM: *NICA-D*	lake water, soil solution extracts	Cd, Cu (FMI in lake water, total concentration in soils)	0.43 M HNO_3 (soils)	optimized to fit proton titration data	not considered	Benedetti et al. [10]
3	POM, DOM: *Model V*; FeO, AlO, MnO, SiO: *SCAMP*; clay: *Donnan*	batch adsorption suspended particulate matter in river water	Co, Ni, Cu, Zn, Sr, Cd, Cs, Eu, Pb	added metal	soluble OM 50% FA, 50% HA	oxalate Fe; Al and Si by electron probe analysis (all Al present in alluminosillicates); hydroxylamine Mn	Lofts and Tipping [19]
4	FeO, AlO: *GTLM*	batch adsorption experiments sediments	Zn	added metal	not considered	Al, Fe various extractions	Davis et al. [32]
5	FeO, AlO: GTLM POM, DOM: empirical ligand complexation model	mixing of acidic groundwater with surface water	Cd, Cu, Pb, Zn	total solution concentration before mixing	POM= DOM adsorbed to FeO and AlO (Langmuir model)	precipitated Al and Fe	Paulson and Balistrieri [104]
6	POM, DOM: *Model V*; FeO,MnO *SCAMP*; clay: *Donnan*	river water	Co, Ni, Cu, Zn, Pb	1% v/v HNO_3 (=0.24 M)	DOM:50% FA, 50% inert; POM 50% FA, 50% HA	oxide: non filterable Fe and Mn	Lofts and Tipping [105]
7	SOM, DOM: *Model V*	titrations of soil with acid and base 3≤pH≤6	H, Al	0.1 M $CuCl_2$	adjusted fraction active HS to fit the observed pH and dissolved Al	not considered	Lofts et al. [106]
8	SOM:*NICA-D*; HFO: *GTLM*, Goethite: *CD-MUSIC*, clay: *Donnan*	soil column DMT	Cd, Cu, Ni, Pb, Zn (prediction FMI)	2 M HNO_3	SOM as HA with estimated site density from CEC DOM: not considered	HFO = oxalate Fe – org. bound; goethite = DCB – oxalate Fe; clay fraction	Weng et al. [21]
9	SOM: *NICA-D* clay: *Gaines Thomas*	soil batch adsorption and column leaching experiment	Cd, Ni, Zn	added metal	HA 50% of measured SOM, DOM not considered	oxides not considered; clay: size fraction	Voegelin et al. [107]
10	HFO: *GTLM*	batch titrations soil with acid/base (pH 3-10)	As	XRF	not considered	HFO = 1.7 * oxalate Fe	Lumsdon et al. [108]
11	FeO, AlO: GTLM	mixing acid rock dranaige with surface water	As, Cu, Mo, Pb, Sb	total solution concentration prior to mixing	not considered	precipitated Al and Fe	Tonkin et al. [109]
12	SOM, DOM: *NICA-D*, HFO: *GTLM*; Goethite: *CD-MUSIC*; Clay: *Donnan*	soil column DMT	Cd, Cu, Ni, Pb, Zn total concentrations	2 M HNO_3	SOM as in [21]; DOM as 30%FA +30%HA or as 65% FA	HFO = oxalate Fe – org. bound; goethite = DCB – oxalate Fe; clay: size fraction	Weng et al. [110]

	Reactive components and *models*	modelled system	elements	reactive element concentration	active organic matter	oxide surface / clay	reference
13	SOM, DOM: *NICA-D*; FeO, MnO: *CD-MUSIC*, mineral equilibria (Zn/Al)	soil solution extract	Cd, Cu, Pb, Zn total concentrations and FMI	0.43 M HNO_3	SOM as 50% HA; DOM as 50% FA and 50% HA	HFO: 15% of Fe-tot, HMnO: 50% of Mn-tot	Cances et al. [111]
14	SOM, DOM: *WHAM Model VI*	porewater organic rich soils	Cd, Cu, Pb, Zn	0.43 M HNO_3	SOM: HS optimized to fit measured pH ; DOM as 65% FA	not considered	Tipping et al. [112]
15	SOM, DOM: *SHM;* clay: *Gaines-Thomas*	batch titrations	Cd, Cu, Pb, Zn	added metal	% HA and FA by optimization to fit pH, Al and Ca concentrations	oxides not considered; clay: size fraction	Gustafsson et al. [12]
16	DOM: *organic ligand model MINTEQ2*; FeO, AlO: *GTLM,*	mixing of anoxic pore water with oxic surface water	As, Cd, Co, Cr, Cu, Mo, Ni, Sb, Se, Pb, Zn	total solution concentration prior to mixing	DOC 100% active	predicted from solubility of FeO and AlO	Ballistrieri et al. [113]
17	SOM, DOM: *NICA-D,*; FeO,AlO: *GTLM*; clay: *Donnan,* mineral equilibria	batch titrations of soils with acid/base (pH 2-12)	Cd, Cu, Ni, Pb, Zn	0.43 M HNO_3	SOM: as HA from measured HS; DOM as 100% HA	crystalline Fe = ascorbate; HFO = dithionite-asc; HAlO = oxalate; clay: size fraction	Dijkstra et al. [18]
18	SOM, DOM: *NICA-D*: HFO: *GTLM*	soil solution extracts	DOM, Al, Cd	0.1 M HCl (Al); Cd added	SOM: as HA from measured HS (14-87%); DOM as HA (DOM predicted with model)	HFO = 1.7 * oxalate Fe	Lumsdon [20]
19	SOM, DOM: *NICA-D;* HFO: GTLM: crystalline FeO: *CD-MUSIC*	titration soils with acid (pH 3-6)	H, Al, Ca, Mg, Cd, Cu, Ni, Zn	0.43 M HNO_3	SOM as HA with 31% site density of generic HA; DOM as 65% FA	HFO = oxalate Fe; crystalline = DCB – oxalate Fe	Fest et al. [114]
20	SOM, DOM: *NICA-D,* FeO: *CD-MUSIC;* MnO: *GTLM[1];* clay: *exchange model* (Ca, Mn, Zn); mineral equilibria	Soil solution extracts river floodplain soils	Cd, Cu, Zn, Pb, As, Fe, Mn	Aqua regia	SOM as 50% HA, DOM as 40% FA	HFO and MnO predicted from solubility; clay: size fraction	Schröder et al. [115]
21	SOM, DOM: *NICA-D /SHM*	batch adsorption experiments forest floors	Cd, Cu, Pb, Zn	0.1 M HCl	SOM: HA and FA by optimization to fit pH, Al	not considered	MacDonald and Hendershot [116]

	Reactive components and *models*	modelled system	elements	reactive element concentration	active organic matter	oxide surface / clay	reference
22	HFO, allophane: *CD-MUSIC*	batch adsorption experiments soils	As	native oxalate As + added metal	not considered	HFO: oxalate Fe, allophane oxalate extractable Si	Gustafsson [117]
23	SOM, DOM: *Model VI*	titrations soils with acid/base (pH 4-8)	H, Al, Ca, Mg, Cd, Cu, Zn	0.22 M HNO₃	SOM: 50% HA + 50% FA; DOM 65% FA	not considered	Almas et al. [118]
24	SOM/DOM: *SHM*, HFO: *GTLM*	column studies	Cd, Cr, Cu, Hg, Ni, Pb, Zn	sequential extraction including EDTA	SOM different estimates for different soils based on literature; DOM as 87% FA	HFO oxalate extractable Fe	Linde et al. [119]
25	SOM/DOM: *Model VI*	batch adsorption	Cd	added metal	reactive SOM optimised to fit the data; DOM not considered	not considered	Shi et al. [120]
26	SOM: *Model V*	kinetic adsorption experiments soils	Zn	added metal	reactive SOM optimised to fit the data; DOM not considered	not considered	Shi et al. [121]
27	SOM/DOM: *NICA-D*; HFO/AlO: *GTLM*; clay: *Donnan*	soil solution extracts	Cd, Cu, Pb, Zn	0.43 M HNO₃/ EDTA	SOM as HA with 31% site density of generic HA, DOM as 30% FA+ 30% HA	HFO and HAlO: oxalate Al and Fe or calculated from solubility; clay (illite): size fraction	Bonten et al. [122]
28	SOM/DOM: *NICA-D/ SHM*, HFO, crystalline FeO: *GTLM*, clay: *Gaines-Thomas*	batch titrations pH 2.5-8.5	Cd, Cr Cu, Mn, Pb, Zn	EDTA	DOM as 43.5% FA and 43.5% HA, SOM as HA and FA fitted to measured CEC	crystalline Fe = ascorbate; HFO = dithionite-asc; AlO = oxalate; clay: size fraction	Khai et al. [123]
29	DOM: *NICA-D/ SHM* FeO, MnO: *GTLM*[1]	surface water acid mine drainage impacted stream	Cu, Zn	total acid soluble	POM DOM as 71% FA	HFO and MnO as difference between total acid-soluble and dissolved Fe and Mn	Butler et al. [124]
30	SOM, DOM: *NICA-D*, Goethite: *CD-MUSIC*; MnO: *GTLM*[1]; clay: *exchange model* (Ca, Mn, Zn) mineral equilibria	pore water river flood plain soils	Cd, Cu, Zn, Pb, As, Fe, Mn	Aqua Regia	SOM: 30% HA DOM: 50% FA	goethite, magnetite and MnO calculated from total contents and mineral solubility; clay size fraction	Schröder et al. [125]
31	SOM, DOM: *Model VI*	0.01 M CaCl₂ soil solution extracts from spiked metal soils after 1-850 days	Cd, Ni, Zn	isotopic dilution + added metal	SOM 50% HA; DOM 65% FA;	FeO: dithionite ; clay: size fraction or calculated from CEC	Buekers et al. [126]

	Reactive components and *models*	modelled system	elements	reactive element concentration	active organic matter	oxide surface / clay	reference
32	SOM,DOM: *NICA-D*, HFO, crystalline FeO, AlO: *GTLM*; clay: *Donnan*, mineral equilibria	batch titrations soils with acid/base (pH 2-12)	Cd, Cu, Ni, Pb, Zn, Sn, Cr, Co, Ba, S, As, Se, Sb, Mo, V	0.43 M HNO$_3$	SOM: as HA from measured HS; DOM as 50% HA	crystalline Fe = ascorbate; HFO = dithionite-asc; HAlO = oxalate; clay: size fraction	Dijkstra et al. [127]
33	SOM, DOM: *SHM*; Fe-oxide: *CD-MUSIC*	batch titrations soils pH 2.5-8.5	Pb	EDTA	not described	crystalline Fe = ascorbate; HFO = dithionite-asc; HAlO = oxalate	Gustafsson et al. [128]
34	SOM, DOM: *NICA-Donnan*, HFO, AlO *GTLM*; clay: *Donnan,* mineral equilibria	soil solution extracts, centrifuged pore waters and batch titrations soils with acid/base (pH 2-12)	Cd, Cu, Ni, Pb, Zn, Sn, Cr, Co, Ba, S, As, Se, Sb, Mo, V	0.43 M HNO$_3$	SOM: 50% HA or measured HS DOM: 50% HA or measured HS	HFO and AlO :oxalate or crystalline FeO = ascorbate; HFO = dithionite-asc; clay: size fraction	Groenenberg et al. [129]
35	SOM, DOM: *Model VII,* FeO, AlO, MnO: *SCAMP*	centrifuged pore waters	Cd, Pb, Zn	isotopic dilution / 0.05 M EDTA/	SOM: measured HA and FA DOM: 65% FA	Fe, Al and Mn with citrate-dithionite extraction	Izquierdo et al. [130]
36	SOM, DOM *Model VI/VII*, FeO, AlO, MnO: *SCAMP*	0.01 M Ca(NO$_3$)$_2$ soil solution extracts	Cd, Pb, Zn	isotopic dilution	SOM: 50% HA DOM: 65% FA	Fe, Al and Mn with a Na-citrate-bicarbonate-ascorbic acid extraction	Marzouk et al. [131]
37	SOM, DOM: *Model VI*	kinetic adsorption experiments soils	Cd, Cu, Ni,Pb, Zn	added metal	reactive SOM optimised to fit the data; DOM = 65% FA	not considered	Shi et al. [132]
38	SOM, DOM *SHM* crystalline and amorphous FeO: *CD-MUSIC* AlO: GTLM[1] clay	batch adsorption: adsorption edge pH 3-8 adsorption isotherm pH 4.5, 6	Pb	added metal	active OM according to empirical relation with total SOM; active OM modeled as 75% HA, 25% FA	amorphous FeO and AlO: oxalate; crystalline FeO: DCB-oxalate clay: size fraction	Shi et al. [133]
39	DOM: *NICA-D* FeO, AlO: *CD-MUSIC*	batch adsorption pH 4-8	As, PO$_4$	As: added metal; PO$_4$: oxalate extraction	DOM: 100% FA	amorphous AlO, FeO: oxalate extraction; crystaline AlO, FeO: DCB-oxalate	Cui and Weng [134]

NICA-D = NICA-Donnan model , GTLM = generalized two layer model , Model V/VI/VII = Humic Ion Binding model V/VI/VII, SHM = Stockholm Humic Model, CD-MUSIC = charge distribution multiple site ion complexation model, DLM = diffuse layer model, DCB = dithionite citrate bicarbonate extraction, POM = particulate organic matter.
[1] With parameters from [71] ; [2]With parameters from [72]

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