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# Modeling the Dynamic Adsorption/Desorption of a NOM Mixture: Effects of Physical and Chemical Heterogeneity

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Because natural organic matter (NOM) can act as a carrier for contaminants, it is of great importance to understand its dynamic adsorption/desorption behavior. NOM is a mixture of organic molecules that vary both in chemical and physical properties. The adsorption/desorption behavior of a NOM mixture to the solid matrix cannot be adequately described using simple equilibrium sorption isotherms, like the Langmuir isotherm. Often adsorption/desorption hysteresis is found or "adsorption maxima" keep increasing slowly. In this paper a relatively simple model is developed to describe the kinetic adsorption/desorption of NOM. The model is calibrated using experimental data. Model simulations of experimental data show that adsorption/desorption hysteresis is an inherent property of a heterogeneous mixture of molecules. The composition and thus the properties of the mixture vary with the total amount of NOM added and with surface/volume ratios. Therefore the relationship between the overall adsorption and the overall solution concentration is nonunique and thus a nonthermodynamic isotherm. Although adsorption in terms of mass of carbon seems to reach equilibrium relatively fast, the distribution of individual components can still be far from equilibrium. This indicates that the composition of the NOM mixture may vary with time as well.

## Introduction

In groundwater and pore water of soils and sediments, natural organic matter (NOM) is present in variable concentrations. Organic carbon concentration ranges from less than 1 to more than 100 mg C/L (1–3). NOM can act as a carrier for solutes and may enhance transport of contaminants in soil and subsoil. Therefore, the understanding of the dynamic sorption behavior of NOM is of great importance for the understanding of carrier enhanced transport processes.

NOM is a mixture of different molecules, with sizes varying between 0.5 and about 400 nm and a molecular weight ranging from 200 to  $>10^5$  g·mol<sup>-1</sup>. Small NOM molecules can be well-defined weak organic polyacids such as e.g. citric acid, which has a molecular diameter of around 0.5 nm and a molecular mass of 349 g·mol<sup>-1</sup>. Low molecular weight humic molecules are more or less flexible cylinders (so-called "oblong" particles) or more compact globular particles or ellipsoids. The high molecular weight humic molecules are large enough to form random coils or gels (4). It is not easy to attribute a size to them as the conformation of these structures may easily change as a function of the environmental conditions. The diameter of high molecular weight humic molecules generally is estimated not higher than 5 nm (5, 6). However, Kim et al. (1) found humic colloids with diameters up to 400 nm in a saline aquifer system. Probably these colloids are aggregates of large humic molecules. NOM molecules contain functional groups such as carboxyl, alcohol, and quinone groups in variable concentrations and in general are negatively charged or neutral.

In soil, the main components for adsorption of NOM are iron- and aluminum(hydr)oxides. They can be present in crystalline form, as discrete particles or as amorphous oxide coatings on phyllosilicates (7). Under natural pH conditions (pH 3–8), pure iron and aluminum(hydr)oxides exhibit a positive charge, which decreases with increasing pH. Complexation of iron and aluminum(hydr)oxides with ligands such as phosphate and small organic acids is relatively well understood (8–12). Sorption of NOM on iron and aluminum(hydr)oxides is much more complicated. It is not likely that all reactive groups of NOM will interact in the same way with the surface due to steric effects, differences in the types of reactive groups, and differences in the "molecular environment" of the same type of groups. The hydrophobic nature of part of the NOM may influence the adsorption as well. Gu et al. (13) provided evidence for ligand exchange reactions between NOM and iron oxide surfaces. They concluded that the sorption mechanism of NOM on oxide surfaces probably is a combination of charge neutralization and ligand exchange reactions.

In this paper we focus on the effect of the physical and chemical heterogeneity of a NOM mixture on its dynamic adsorption and desorption behavior. Therefore, we only consider sorption of NOM as a function of concentration and time. It will be evident that understanding the sorption behavior is further complicated by the fact that sorption behavior is dependent on temperature and on properties of the soil solution like pH, ionic strength, and concentration of competing ions.

Studies of NOM adsorption to iron and aluminum(hydr)-oxides as a function of aqueous NOM concentrations (13–17) show that sorption of NOM is characterized by isotherms with initially a relatively steep slope which becomes less steep upon adsorption. Often, no distinct sorption maximum is reached, and a continuing slight increase of sorption density with increasing equilibrium NOM concentration is observed. Day et al. (14) found different sorption isotherms for the same NOM and oxide surface at different surface-to-volume ratios (SV). Gu et al. (13) found a profound hysteresis effect between adsorption and desorption. In contrast with adsorption data, desorption data showed high affinity behavior (a very steep initial slope followed by a plateau value).

To describe the sorption of NOM to iron oxides Tipping (16) and Day et al. (14) used the Langmuir isotherm. Part of their data could be described in an adequate way with this isotherm. Ochs et al. (18) used the Frumkin Fowler Gugen-

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heim (FFG) equation to describe sorption of humic acids to aluminum oxides in an adequate way. The FFG model takes into account lateral interaction of the adsorbed molecules. Gu et al. (13, 19) could describe adsorption of NOM in an adequate way with a so-called modified Langmuir isotherm, which is essentially the same as the FFG model. To describe desorption data, a modified version of the model was used in which a hysteresis coefficient was introduced.

By using the Langmuir, modified Langmuir, and FFG model, equilibrium is assumed between the NOM in solution and sorbed on the solid phase. Moreover, possible preferent binding of certain fractions of the mixture of NOM molecules is not considered explicitly in these models. In fact one "average" NOM molecule is assumed with an "average" behavior. Sorption studies show that iron oxide and aluminum oxide adsorb different fractions of NOM with different affinity and capacity (18, 19). Also, UV-absorbance spectrometry observations of the NOM mixture in solution before and after adsorption differed, which indicates preferent adsorption of certain NOM fractions by iron oxides (20). Sorption data of NOM to aluminum oxide (18) show that different fractions of NOM (measured in the aqueous phase with UV/vis) respectively increase and decrease as a function of equilibration time at low SV. This indicates kinetic adsorption/desorption behavior and competition between the different NOM fractions. Equilibrium models assuming average behavior might describe sorption of NOM well under certain conditions. However, if sorption behavior is time dependent and not "average", a sorption model should take into account time dependence and the competition between the different NOM fractions.

For adsorption of polymers, it is theoretically and experimentally well established that (a) monodisperse polymers have a very high initial slope of the adsorption isotherm followed by a plateau (high affinity behavior), (b) the maximum amount adsorbed is a function of the molecular weight, and (c) large molecules adsorb preferentially over smaller ones (have a higher affinity). Thus in the equilibrium situation short chains will have been displaced by longer ones (21). Rates of diffusion and reformation will decrease with increasing molecular size, and thus the time required to exchange small polymer molecules for larger ones is governed by the rate of diffusion and reformation of the larger components (22).

For NOM the same phenomena may play a role. However with NOM the situation is more complicated than with synthetic polymers: the latter are a mixture of exactly the same type of molecules, differing only in size, whereas different NOM fractions differ in average molecular weight as well as in chemical composition and structure. Hence, a replacement of one class of molecules at the surface by another class could be caused by difference in molecular weight as well as difference in chemical composition of these classes (18). Vermeer (23) shows that using the advanced adsorption theory of Scheutjens and Fleer (24) for linear polyelectrolytes, the sorption of naturally occurring humic substances on iron oxide can be understood and that adsorbed humics can be described as a dynamic layer of polyelectrolytes, extending into the solution.

In this paper, the effect of the physical and chemical heterogeneity of NOM on its dynamic adsorption and desorption behavior is studied. The sorption of NOM is imagined as the sorption of a heterogeneous mixture of polyelectrolytes. The sorption behavior of the individual molecules is a function of the chemical characteristics and the molecular weight of the molecules. A relatively simple model is developed for time dependent sorption of a mixture of NOM. Model parameters (the number of NOM fractions, affinity, and maximum sorption capacity for each fraction) are determined using data and relations from literature. Using

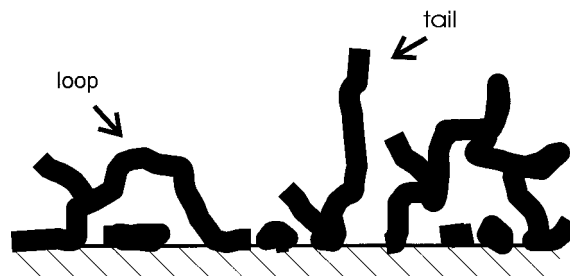


FIGURE 1. Sorption of a mixture of small and large NOM molecules on the solid matrix in 2-D.

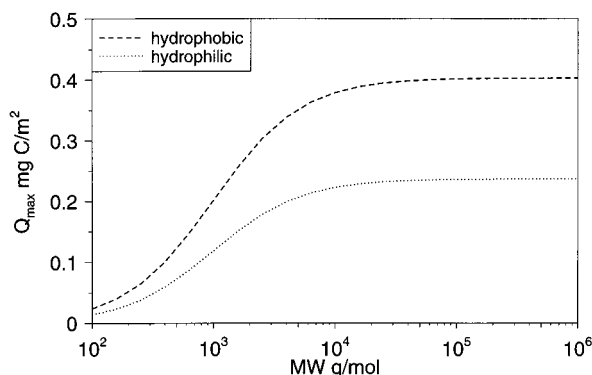


FIGURE 2. Relationship between molecular mass and sorption maximum for the hydrophobic (Hb) and Hydrophilic (Hl) fraction of NOM.

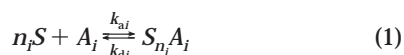
this model, experimental data are simulated, and the effect of dynamic competition between different fractions (MW and chemical characteristics) is shown.

### Adsorption/Desorption Model for a NOM Mixture

In our model we imagine the sorption of NOM as the sorption of a heterogeneous mixture of polyelectrolytes. The (hydr)-oxide surface is heterogeneous as well. However, we assume this heterogeneity to be negligible compared to the heterogeneity in the NOM mixture. Therefore, the solid matrix is treated as a reactive surface with only one type of sorption site to which the different molecules may adsorb. Occupation of surface sites may occur by direct binding of NOM functional groups. However, due to steric hindrance, more sites than those involved in direct binding may be blocked (occupied). Small molecules will only occupy one or a few sites that are located near or close to each other. The larger molecules, however, may cover a larger area of the surface. The occupied sites in this area are not necessarily neighboring. A fraction of the larger molecules extends in solution and may form so-called "loops" and "tails", parts attached to the surface at respectively two and one side. Figure 1 shows an example of sorption of a mixture of small and large molecules. For small, rigid molecules, the number of surface sites occupied per molecule will be a constant. As the larger molecules are flexible, they can bind in different conformations, which may vary in time. Due to this, the number of surface sites occupied may be variable and is dependent on the fraction of the molecule in direct contact with the surface. Despite this, we define an average number of surface sites occupied for every molecular weight fraction. The larger the molecule, the larger the part which is extended into the soil solution and the higher the sorption maximum expressed in mg C/m<sup>2</sup>. This is also observed in polymer chemistry. Cohen Stuart et al. (21) derived a relationship between molecular mass and the sorption maximum. Figure 2 shows a relationship between molecular mass and sorption maximum for the hydrophobic (Hb) and hydrophilic (Hl) fraction of NOM

as derived later in this paper, based on their work. We assume that it is always possible to saturate unoccupied sites with every molecular size. As the larger molecules are flexible, they can occupy sites that are not necessarily neighboring (see Figure 1). For simplicity, we assume that for all molecules the affinity is constant with surface coverage. However, lateral interaction may cause a variation of sorption affinity with surface coverage (13, 18, 19).

To model a NOM mixture, it is assumed that NOM consists of a number of discrete fractions (species) that may vary in their affinity for the surface,  $K$ , adsorption rate constant  $k_a$ , desorption rate constant  $k_d$ , maximum mass adsorbed  $Q_{\max}$ , and the average number of surface sites occupied per molecule  $n$ . All species are assumed to compete for the same sites, and their reaction with the surface may be simplified as in eq 1, where  $S$  is a free surface site,  $A_i$  is a molecule of species  $i$  in the aqueous phase, and  $S_n A_i$  is the surface complex formed.



The sorption of each individual species is described by a kinetic competitive Langmuir type equation of the form

$$\frac{d[S_{n_i} A_i]}{dt} = k_{ai}[A_i] \frac{S_t}{n_i} (1 - \Theta) - k_{di}[S_{n_i} A_i] \quad (2)$$

in which  $t$  (s) is time,  $[S_{n_i} A_i]$  ( $\text{mol} \cdot \text{m}^{-2}$ ) is the concentration of surface complexes with species  $i$ , and  $S_t$  ( $\text{mol} \cdot \text{m}^{-2}$ ) is the total number of surface sites  $S_t = [S] + \sum_{i=1}^{i=x} n_i [S_{n_i} A_i]$ .  $[A_i]$  ( $\text{mol} \cdot \text{L}^{-1}$ ) is the concentration of species  $i$ ,  $k_{ai}$  ( $\text{L} \cdot \text{mol}^{-1} \text{s}^{-1}$ ) and  $k_{di}$  ( $\text{s}^{-1}$ ) are the adsorption and desorption rate constant for species  $i$ , and  $\Theta$  (–) is the fraction of sorption sites which are occupied, given by

$$\Theta = \sum_{i=1}^{i=x} \Theta_i = \sum_{i=1}^{i=x} \frac{S_{n_i} A_i}{\frac{1}{n_i} S_t} = \sum_{i=1}^{i=x} \frac{n_i [S_{n_i} A_i]}{S_t} \quad (3)$$

where  $x$  is the number of species. Using Equation 3, Equation 2 can be rewritten in the following form:

$$\frac{d\Theta_i}{dt} = k_{ai}[A_i](1 - \Theta) - k_{di}\Theta_i \quad (4)$$

Note the difference between  $\Theta$  and  $\Theta_i$ .

For equilibrium, a thermodynamically consistent (25) competitive Langmuir equation can be derived

$$\frac{n_i [S_{n_i} A_i]}{S_t} = \Theta_i = \frac{K_i [A_i]}{1 + \sum_{i=1}^{i=x} K_i [A_i]} \quad (5)$$

in which the equilibrium constant  $K_i$  is given by

$$K_i = \frac{k_{ai}}{k_{di}} = \frac{[S_{n_i} A_i]}{\frac{1}{n_i} [S][A_i]} = \frac{[S_{n_i} A_i]}{\frac{1}{n_i} S_t (1 - \Theta) [A_i]} \quad (6)$$

It is not simple to derive forward and backward reaction rates for a mixture of polyelectrolytes consisting of large and small molecules. The reaction statistics are complicated. Larger molecules occupy more sites than small molecules, and the chance of finding these sites near each other is smaller. However, large molecules are flexible, and they may

reach sites in a large area. In contrast with standard Langmuir behavior, in eq 2 it is assumed that the adsorption reaction rate of a species is proportional with the number of free sites divided by the average number of sites occupied by this species. In accordance with standard Langmuir behavior we assume that the desorption reaction rate is proportional with the concentration of sorbed molecules, while the adsorption reaction rate is proportional with the aqueous concentration of the species.

As both the adsorbed and aqueous concentrations of NOM are usually given in mass of carbon, it is convenient to express the model equations in these terms.  $\Theta_i$  also can be written as

$$\Theta_i = \frac{[S_{n_i} A_i]}{\frac{1}{n_i} S_t} * \frac{M_{ci}}{M_{ci}} = \frac{Q_i}{Q_{\max i}} \quad (7)$$

where  $M_{ci}$  is the mass of carbon per mole of species  $i$  and  $Q_i$  and  $Q_{\max i}$  are the amount and the maximum amount of species  $i$  adsorbed ( $\text{g C} \cdot \text{m}^{-2}$ ). Note that  $n_i$  disappears by introducing  $Q_{\max i}$ . Expressing the aqueous concentration in mass per liter, the individual mass balance equation of the species and the overall mass balance equations for organic carbon adsorbed and in the aqueous phase respectively can be given by combining eqs 3, 4, and 7

$$\frac{dQ_i}{dt} = k_{ai}^* C_i (1 - \Theta) Q_{\max i} - k_{di} Q_i \quad (8a)$$

$$\frac{dQ}{dt} = \frac{d \sum_{i=1}^{i=x} Q_i}{dt} = C(1 - \Theta) \sum_{i=1}^{i=x} k_{ai}^* f_i Q_{\max i} - \sum_{i=1}^{i=x} k_{di} Q_i \quad (8b)$$

$$\frac{dC_i}{dt} = -SV \frac{dQ_i}{dt} \quad (9a)$$

$$\frac{dC}{dt} = \frac{d \sum_{i=1}^{i=x} C_i}{dt} = -SV \frac{d \sum_{i=1}^{i=x} Q_i}{dt} = -SV \frac{dQ}{dt} \quad (9b)$$

where,  $Q$  ( $\text{g C} \cdot \text{m}^{-2}$ ) and  $C$  ( $\text{g C} \cdot \text{L}^{-1}$ ) are the overall concentration of NOM adsorbed and in the aqueous phase,  $f_i$  is the fraction of the aqueous phase carbon concentration consisting of species  $i$ ,  $C_i = f_i C$  is the aqueous concentration of species  $i$  ( $\text{g C} \cdot \text{L}^{-1}$ ),  $k_{ai}^*$  is the adsorption rate constant expressed in  $\text{L} \cdot \text{g C}^{-1} \text{s}^{-1}$ , and  $SV$  is the surface-to-volume ratio ( $\text{m}^2 \cdot \text{L}^{-1}$ ).

Combining eqs 3, 5, and 7 we obtain eq 10 for the equilibrium situation

$$Q = \sum_{i=1}^{i=x} Q_i = \sum_{i=1}^{i=x} \frac{C K_i^* f_i Q_{\max i}}{1 + C \sum_{i=1}^{i=x} K_i^* f_i} = \frac{C \sum_{i=1}^{i=x} K_i^* f_i Q_{\max i}}{1 + C \sum_{i=1}^{i=x} K_i^* f_i} \quad (10)$$

where  $K_i^*$  is the affinity expressed in  $\text{L} \cdot \text{g C}^{-1}$ . In situations where the amount sorbed substantially influences the composition of the aqueous phase (i.e. at low total amount of NOM added or high  $SV$ ) the fraction  $f_i$  of a species is not equal to the initial fraction of this species in solution due to preferential adsorption of certain fractions with high  $K_i^* Q_{\max i}$ . At high total amount of NOM added or low  $SV$ , however, the solution composition will be little influenced by the sorption and thus  $f_i$  will tend to a constant value. Using eqs 3, 7, and 10, for a system in equilibrium with constant mass fractions in solution,  $f_i$ , of the individual species, the following apparent



TABLE 1. Properties of the Discrete NOM Fractions Distinguished and Model Parameters Used for These Discrete Fractions<sup>a</sup>

fractions		MW (g·mol <sup>-1</sup> )	<i>f</i> (-)	<i>K</i> (L·mg C <sup>-1</sup> )	<i>k<sub>a</sub></i> ·10 <sup>2</sup> (L·mg C <sup>-1</sup> ·h <sup>-1</sup> )	<i>k<sub>d</sub></i> (h <sup>-1</sup> )	<i>Q<sub>max</sub></i> (mg C·m <sup>-2</sup> )
MW < 3 × 10 <sup>3</sup>	HI	1.5 × 10 <sup>3</sup>	0.24	9.0 × 10 <sup>-1</sup>	1.62	1.8 × 10 <sup>-2</sup>	178
	Hb		0.26	1.8 × 10 <sup>0</sup>	3.24		252
3 × 10 <sup>3</sup> < MW < 10 <sup>5</sup>	HI	5.0 × 10 <sup>4</sup>	0.11	3.0 × 10 <sup>1</sup>	1.62	5.4 × 10 <sup>-4</sup>	284
	Hb		0.31	6.0 × 10 <sup>1</sup>	3.24		403
MW > 10 <sup>5</sup>	HI	5.0 × 10 <sup>5</sup>	0.05	3.0 × 10 <sup>2</sup>	1.62	5.4 × 10 <sup>-5</sup>	287
	Hb		0.03	6.0 × 10 <sup>2</sup>	3.24		407
(d < 1 μm)							
	Hb		0.03	6.0 × 10 <sup>2</sup>	3.24		407

<sup>a</sup> Hb = hydrophobic, HI = hydrophilic, MW = molecular weight, and *d* = diameter.

monocomponent Langmuir equation, in terms of surface coverage can be derived

$$\Theta = \frac{\overline{CK^*}}{1 + \overline{CK^*}} \quad (11)$$

where  $\overline{K^*} = \sum_{i=1}^n f_i K_i^*$  is the weighted average of the affinities. Note that eq 11 is only valid under specific circumstances! Note further that Equation 11 cannot be transformed into an apparent monocomponent Langmuir equation in terms of mass adsorbed (*Q*) as the values of *Q<sub>max</sub>* *i* differ. Equations 8 and 10 simplify to the conventional kinetic Langmuir equation and its equilibrium form if the adsorption and desorption rate constant, the affinity, and the values of *Q<sub>max</sub>* are equal for the different species.

**Program.** An adsorption program for *NOM* adsorption, NOMADS, is developed that, given the initial composition of the sorption complex and the solution phase and the value of SV, calculates the distribution of species in a batch system at a certain time. Equations 8a and 9a for all species considered form the set of mass balance equations that describe the dynamic adsorption and desorption of the mixture of discrete fractions of NOM. These equations constitute a set of ordinary differential equations, which is solved using a standard fourth order Runge–Kutta method.

### Determination of Model Parameters

Ideally, one should determine model parameters from independent data. As every mixture of NOM is unique, it is not possible to determine model parameters for a mixture without considering properties of the mixture itself. In this paper we simulate data measured by Gu et al. (13). We try to determine model parameters as much as possible from properties that can be obtained independently from the adsorption/desorption data. However, not all parameters can be determined without fitting to these data. By finding relationships between model parameters and respectively MW and chemical composition of NOM, from theoretical consideration, literature, or other experiments, the number of degrees of freedom is minimized. When parameter values are obtained by fitting this will be mentioned explicitly. Table 1 shows the distinguished fractions, which will be treated as model species, together with their attributed MW and model parameters.

**Number of Fractions and Distribution of Mass Over Fractions.** McCarthy et al. (5) characterized the organic material used by Gu et al. (13). They give the distribution of carbon of the NOM over three chemical fractions and within these fractions over four MW fractions. It is assumed that sorption behavior of the hydrophobic acid and hydrophobic neutral fraction does not differ significantly (7). Further the largest MW fraction was not present in the NOM used in the adsorption/desorption experiment. Therefore, six fractions

(two chemical and three MW fractions) are distinguished. To each fraction an average MW is attributed.

**Maximum Mass Adsorbed, *Q<sub>max</sub>*.** In accordance with observations from polymer chemistry, it is assumed that *Q<sub>max</sub>* is a function of MW. For sorption of polymers, Cohen Stuart et al. (21) have derived an empirical equation relating *Q<sub>max</sub>* to molecular weight. For a good solvent this empirical equation can be simplified to

$$Q_{\max} = p / (1 + (M/M_0)^{-2b}) \quad (12)$$

where *M* is molecular weight, *M<sub>0</sub>* is the molecular weight at which the increase of *Q<sub>max</sub>* as a function of molecular weight is maximal, *p* is the maximum value of *Q<sub>max</sub>* to which eq 12 approaches at high MW. The value of *b* is chosen to be 0.6 (a value taken from ref 21). Equation 12 is valid for chemically homogeneous polymer solutions. Therefore, for both the hydrophobic (Hb) and the hydrophilic (HI) fraction *Q<sub>max</sub>* as a function of molecular weight is derived. Figure 2 shows the derived relationships. Gu et al. (19) derived *Q<sub>max</sub>* values for the Hb and HI fraction and the <3000 MW and >3000 MW fraction of Georgetown NOM at pH 4.3 (0.403, 0.284, 0.237, and 0.304 mg/m<sup>2</sup>, respectively). For *p*, the values of *Q<sub>max</sub>* for the Hb and HI NOM are taken. We assume that these values (measured at high NOM concentrations in a “chemically homogeneous” mixture of molecules of different MW) approach the *Q<sub>max</sub>* values for the largest MW. The value of *M<sub>0</sub>* is estimated by using the *Q<sub>max</sub>* values of the two MW fractions. Assuming that the measured *Q<sub>max</sub>* values (19) can be assigned to the MW at the upper boundary of the fraction (3000 and >100 000), *M<sub>0</sub>* is estimated to be 1000, and the *Q<sub>max</sub>* values for both MW fractions fall between the values found for the Hb and HI fraction determined at the “upper boundary MW” with eq 12 (see Figure 2).

**Adsorption and Desorption Rate Constants, *k<sub>a</sub>* and *k<sub>d</sub>*.** The values of *k<sub>a</sub>* and *k<sub>d</sub>* vary with the size of adsorbate molecules. Rates of diffusion and reformation will decrease with increasing molecular weight and size (22). Additionally, high MW polymer molecules adsorb preferentially over smaller ones at equilibrium (22), which means that their affinity, *K<sub>i</sub>* = *k<sub>a</sub>*/*k<sub>d</sub>*, is higher. Among others, this might be due to the fact that larger molecules adsorb with a larger number of functional groups. We assume that the affinity of sorption is proportional to molecular weight. Results from literature (7, 19) show that the affinity for Hb NOM is roughly a factor 2 higher than the affinity of HI NOM. This leads to the following relationships:

$$\begin{aligned} \text{HI NOM : } k_{a_i}/k_{d_i} &= \kappa MW \\ \text{Hb NOM : } k_{a_i}/k_{d_i} &= 2\kappa MW \end{aligned} \quad (13)$$

where  $\kappa$  is a coefficient relating the affinity for HI and Hb NOM to MW. Using the data of Gu et al. (13) its values is

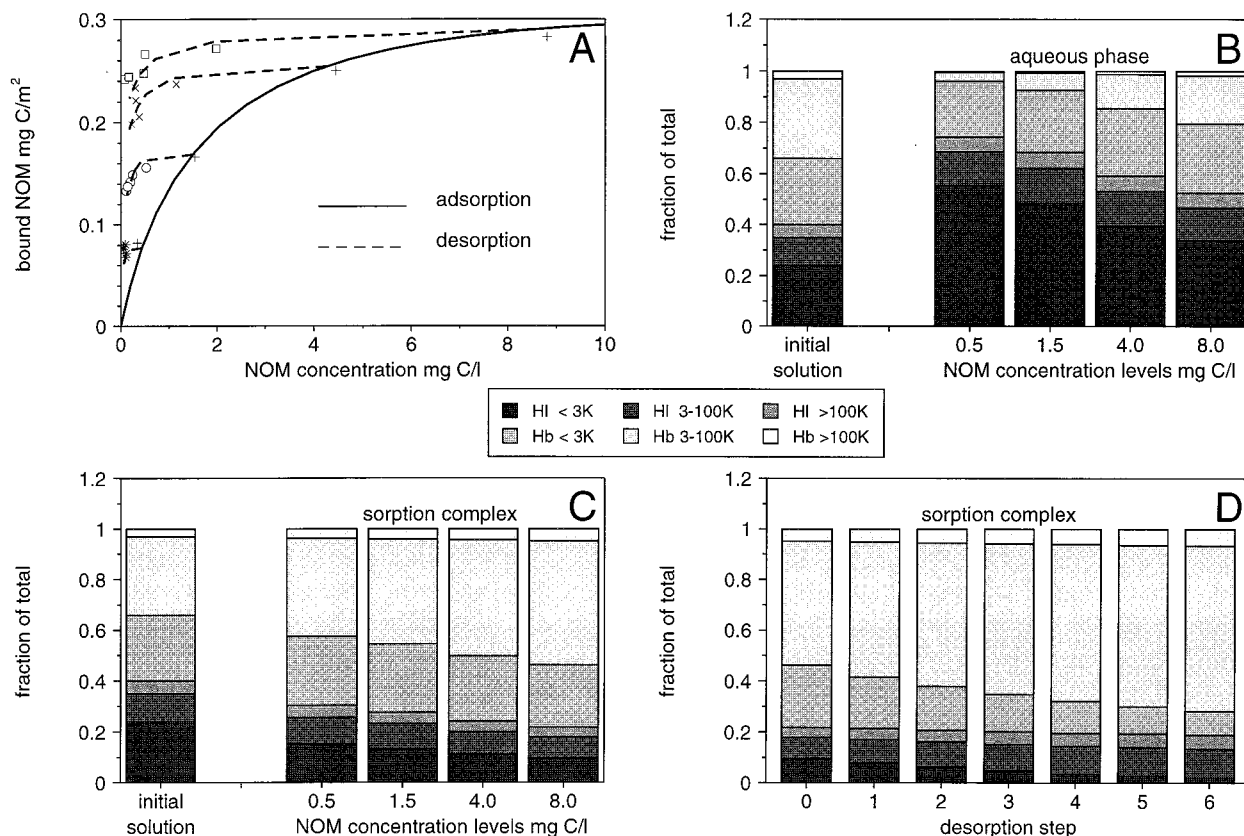


FIGURE 3. Simulation and experimental results of adsorption and desorption of NOM to iron oxide at pH 4.1 (data from Gu et al., 1994). (a) calculated adsorption and desorption curves together with experimental data of adsorption (+) and desorption experiments ( $\square$ ,  $\times$ ,  $\circ$ , \*). (b and c) Initial fractionation of the NOM solution together with calculated fractionation in the aqueous phase (b) and on the sorption complex (c) during the experiment at four NOM concentration levels representing roughly the adsorption data points in panel A. (d) Calculated fractionation of NOM on the sorption complex at a high NOM concentration level in the aqueous phase ( $\sim 8.0$  mg C/L, desorption step 0) and after the subsequent desorption steps, corresponding with the upper desorption curve in panel A. HI = hydrophilic, Hb = hydrophobic, K = 1 Kilodalton = 1000 g/mol.

fitted to be  $0.6 \cdot 10^{-3} \text{ L} \cdot \text{mg C}^{-1} \cdot \text{g}^{-1} \cdot \text{mol}$ . Both the affinity and the rate of diffusion and reformation of the molecules determine the absolute values of  $k_{ai}$  and  $k_{di}$ . To distinguish between both effects  $k_{ai}$  and  $k_{di}$  are divided in a part determined by the rate of diffusion and reformation,  $k_{aiD}$ ,  $k_{diD}$ , and a part determined by the affinity,  $k_{aiA}$ ,  $k_{diA}$ . The rate of diffusion and reformation is assumed to be inversely proportional with molecular weight. Further it is assumed that the diffusion related constants are equal during adsorption and desorption and equal for the Hb and HI fractions. This leads to the following relationships

$$\begin{aligned} k_{ai} &= k_{aiD} k_{aiA} \\ k_{di} &= k_{diD} k_{diA} \\ k_{aiD} &= k_{diD} = \gamma / MW \end{aligned} \quad (14)$$

where  $\gamma$  is a coefficient relating the rate of diffusion and reformation during adsorption and desorption to MW. Using the data of Gu et al. (13) its value is fitted to be  $27 \text{ g} \cdot \text{mol}^{-1} \cdot \text{h}^{-1}$ . Combining eqs 13 and 14, we then get the following relationships for the affinity:

$$\begin{aligned} \text{HI NOM: } \frac{k_{ai}}{k_{di}} &= \frac{k_{aiA}}{k_{diA}} = \kappa MW \\ \text{Hb NOM: } \frac{k_{ai}}{k_{di}} &= \frac{k_{aiA}}{k_{diA}} = 2\kappa MW \end{aligned} \quad (15)$$

The affinity might change due to changes in  $k_{aiA}$ ,  $k_{diA}$ , or both. We choose  $k_{aiA}$  to be equal to  $\kappa MW$  and  $2\kappa MW$  for HI and Hb NOM, respectively.  $k_{ai}$  HI and Hb then equals  $\kappa \gamma$  and  $2\kappa \gamma$ , respectively.  $k_{diA}$  then will be 1 and  $k_{di}$  will be  $\gamma / MW$  for both HI and Hb fractions.

### Simulation Results and Comparison with Experimental Data

Figure 3 shows adsorption and desorption data measured by Gu et al. at pH 4.1 (13) together with simulation results using NOMADS. Model parameters are summarized in Table 1. Adsorption data are obtained by adding an iron oxide suspension to a series of Georgetown NOM solutions with different concentrations. After about 18 h of shaking, the supernatant was separated, and the NOM concentration was measured in this separated supernatant. After the adsorption phase of the experiment, desorption was initiated by replacing 4/5 of the supernatant volume by water with the same pH and ionic composition. The suspensions were shaken for 24 h. The desorption equilibration process was repeated five times for each sample. The NOM concentration was measured in the separated supernatant. For all adsorption and desorption experiments SV was  $20.2 \text{ m}^2/\text{L}$ .

From the adsorption and desorption data in Figure 3a it is clear that adsorption and desorption occurs via a different pathway. The desorption isotherms exhibit more high affinity behavior than the adsorption isotherm; the slope at low concentration is steeper, and a plateau is reached at much lower concentrations than in the adsorption isotherm. Simulation results show a good agreement with the adsorp-

tion and desorption data, suggesting that both adsorption and desorption data can be described with the same model, NOMADS, without changing any of the parameters. Figure 3a shows the overall adsorption and desorption, while Figure 3b–d shows the calculated contribution of the different species to the organic carbon concentration in the aqueous phase and on the solid matrix during adsorption and desorption. The calculated composition of the NOM in the aqueous phase and the adsorption complex differ significantly as was also suggested by measurements of Gu et al. (20). The high molecular weight (HMW) and hydrophobic (Hb) fractions are overrepresented on the adsorption complex, and the low molecular weight (LMW) and hydrophilic (Hl) fractions are overrepresented in solution. Figure 3b,c shows that during adsorption, the composition of the NOM in solution resembles more and more the initial composition of NOM as the solution concentration increases. On the sorption complex however, the Hb and the HMW fractions are overrepresented more and more with increasing concentration. During desorption (Figure 3d) the HMW and intermediate MW (IMW) fractions remain sorbed on the surface, and the LMW fractions are removed selectively. During the adsorption and desorption phase of the experiment, the composition of the NOM mixture in solution changes, which is one of the reasons for the different shapes of the isotherms measured for adsorption and desorption (Figure 3a).

## Discussion

NOMADS is a relatively simple mechanistic model that describe the competitive kinetic adsorption behavior of a heterogeneous mixture of natural organic molecules. In this paper, NOM is described using six discrete fractions. The choice of fractions is based on experimental fractionation studies that have been done with this NOM. For every fraction we need values for  $k_a$ ,  $k_d$ , and  $Q_{\max}$ , leading to 18 model parameters for the simulations. However, the number of adjustable parameters is reduced to 2 by using relations between molecular weight and model parameters and values from literature. The relation between  $Q_{\max}$  and molecular weight is derived from polymer chemistry (21). The other assumed simple linear relationships between the affinity and the rate of diffusion and reformation and molecular weight represent trends described in the literature (21, 22). The model concept and the relations between physical and chemical properties of the NOM molecules and model parameters can be refined, once more detailed knowledge of these complex systems becomes available.

Only the values of  $\gamma$  and  $\kappa$ , which are coefficients that relate respectively the affinity and the rate of diffusion and reformation to the molecular weight, are fitted using the adsorption and desorption data from Gu et al (13). Although only six fractions are used, experimental results, indicating a different pathway for adsorption and desorption can be described well. This gives confidence that the here defined model concepts and ideas are reasonable at least in a semiquantitative manner. The physical and chemical heterogeneity of the NOM mixture appears to be an essential element in understanding the dynamic adsorption and desorption behavior of NOM on mineral surfaces.

During the adsorption experiment the mass fractions of the individual NOM species in the whole system (sorbed and in solution) are constant because the proportions in which the species are added to the system are constant. Simulations show, however, that the individual mass fractions in solution and on the sorption complex change, both as function of time and total amount of NOM added to the system (loading). This is due to differences in affinity and rate constants of the species. During desorption experiments performed according to Gu et al. (13) the individual mass fractions for the whole

system may change as well due to selective removal of certain species from the system.

During the experiments, the composition and thus the properties of the NOM mixture change, and, therefore, adsorption and desorption cannot be described using average properties of the mixture. The use of adsorption isotherms to describe adsorption and desorption of a mixture of NOM molecules therefore easily leads to confusion.

In adsorption isotherms usually the amount adsorbed of a certain species per unit mass or area of solid matrix is plotted against the activity of this species in solution. Other experimental conditions such as pH, ionic strength, temperature, and concentration of competing species will be kept constant. If adsorption of a species is given in this way, and the system is in equilibrium, the slope of the isotherm at low surface loading is a measure of the affinity. Different values of SV will not affect the thermodynamic adsorption isotherms, and adsorption and desorption experiments will result in the same curve.

In adsorption isotherms for NOM generally the mass of organic carbon per unit area or weight of solid matrix is plotted as a function of the mass of organic carbon in solutions. In fact the total adsorption of a mixture of competing species is plotted against the total concentrations of all species. In contrast with an adsorption isotherm for one species under constant conditions, sorption isotherms for a mixture are not unique. Changes in SV may affect the mass fractions of different NOM species in solution. In this way, the overall adsorption is affected and thus the adsorption isotherm of the mixture (see eq 10 and the explanation after it). At low surface loading, the slope of the adsorption isotherm can vary strongly because differences in SV affect the composition of the mixture strongly under these conditions. It is impossible to construct desorption experiments for a mixture of molecules without either changing SV or allowing selective removal of certain species. Both will affect the sorption isotherms of a mixture of molecules. Therefore it is almost unavoidable that adsorption and desorption experiments will result in different "sorption isotherms" for such systems. These types of isotherms are therefore from a thermodynamic point of view not meaningful.

We deal with a mixture of NOM molecules which may result in different curves for adsorption and desorption experiments: hysteresis. However, these phenomena may also occur if reactions are not in equilibrium. In the model simulation, using the "best fit" parameters, overall equilibrium is not reached in the time frame of the adsorption and desorption experiments. However, the mixture effect is the major reason for the observed hysteresis, because simulations with increased reaction time reaching full equilibrium show that the curves change somewhat but the hysteresis is still present (results not shown).

In accordance with observations of Gu et al. (13) simulations show only little increase of the amount of NOM sorbed (in terms of gC) after 18 h (results not shown). However, this does not mean that equilibrium has been reached for the individual NOM species in the mixture. Redistribution of the different species may still occur. From eq 8a we can derive that for the individual species at equilibrium we have

$$\frac{Q_i}{C_i(1 - \Theta)} = \frac{k_{ai}^* Q_{\max i}}{k_{di}} \quad (16)$$

The quotient at the right-hand side (RHS) of eq 16 is a constant, meaning that also the quotient at the left-hand side (LHS) should be a constant at equilibrium. If equilibrium is not reached yet, the LHS quotient will vary with time. Dividing this quotient by the RHS quotient gives a good measure of the degree of equilibrium of the individual NOM



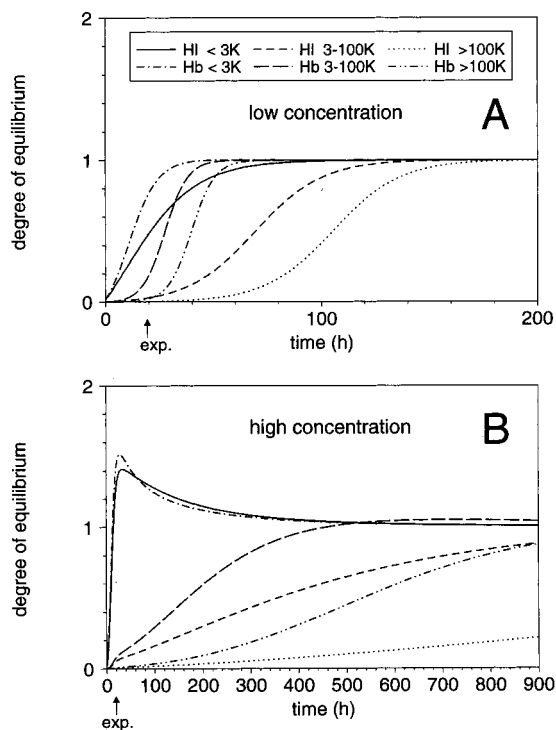


FIGURE 4. Simulated degree of equilibrium of the individual species in the NOM mixture as a function of time at two NOM concentration levels. The initial concentration in the system was 2.0 mg/L (a) and 14.4 mg/L (b) (corresponding roughly to the initial concentrations at lower and upper point of the adsorption isotherm in Figure 3a). The arrows indicate the duration of the adsorption experiments of Gu et al. (1994). The degree of equilibrium is given by the quotient of the LHS and RHS of eq 16.

species in the system that can be calculated easily. Note that the degree of equilibrium of a NOM species is influenced by its concentration in solution, its amount adsorbed, and the total sorption of all species ( $\Theta$ ). Values higher and lower than 1 indicate more respectively less adsorption than at equilibrium. Figure 4 shows the simulated degree of equilibrium against time for all species at two points of the adsorption isotherm. Results show that depending on the amount of NOM added to the system (the point on the adsorption isotherm) and on the particular NOM species, the degree of equilibrium varies (if full equilibrium has not yet been reached). At low concentrations total equilibrium is reached within about a week (168 h). At high concentrations however, even after a month (720 h) equilibrium is not reached and redistribution still occurs. At high concentration we see that the smallest fractions are initially overrepresented on the surface and will exchange with the larger fractions in course of time. At low concentration we see that Hb fractions reach equilibrium earlier than the HI fractions. For a mixture of NOM, the fact that the amount sorbed in time is almost constant is not a good indication for approaching equilibrium. Although the occupation of sites ( $\Theta$ ) will hardly change, the redistribution will lead to more high affinity species (with a higher  $Q_{\max}$  and more carbon per site occupied) on the sorption complex. This will lead to a slow increase of the amount sorbed in terms of g of C/m<sup>2</sup> with progressing contact time.

In this paper we have shown that adsorption and desorption data showing hysteresis can be described well with a relatively simple model integrating knowledge from polymer chemistry and environmental chemistry. The model describes all reported data without changing model parameters. It allows illustrating and quantifying important features of dynamic sorption of a mixture of NOM molecules, which are not easily understood without such a model concept.

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