

Agent-based stochastic simulation of natural organic matter adsorption and mobility in soils

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ABSTRACT: Natural organic matter (NOM) is a heterogeneous mixture of organic molecules that is ubiquitous in terrestrial and aquatic ecosystems, and that plays a vital role in many biogeochemical processes. NOM represents an important component of complex biogeochemical systems that also contain minerals, metals, microorganisms, and other reactive entities. Such systems often demonstrate emergent properties; i.e. system properties not present in the individual components, but present in the whole. To better understand the behavior of NOM in complex systems, we developed a Web-based stochastic simulation of NOM interactions. Here, we focus on the effect of NOM molecular weight on NOM adsorption and mobility in soils. Experimental evidence suggests that relatively small NOM components adsorb quickly to soil minerals, and are gradually replaced by intermediate- to high-molecular weight components that form more stable adsorption complexes. Thus, different probabilities can be assigned for adsorption and desorption of different molecular-weight components. The simulation uses the Swarm and RePast agent-based modeling tools, and is configured, started, and viewed from Web browser pages.

1 INTRODUCTION

Computer models and simulations have been developed to understand quantitatively complex biogeochemical systems. These include, for example: equation-based models (EBM), agent-based models (ABM), deterministic models, and stochastic models. In ABM, different entities called 'agents' are defined, and specific attributes and probabilistic behaviors are assigned to the agents. Each agent carries its attributes and behaviors with it throughout the modeling exercise. In 1998, Parunak compared the effectiveness of EBMs versus ABMs for modeling complex systems, and he concluded that ABMs were more suitable for this purpose because ABMs are better at modeling overall behaviors of complex systems based on the interactions of behaviors of individual components (Parunak et al., 1998).

Complex systems are difficult to analyze and understand using traditional theoretical and mathematical methods. They are variable in scale and decentralized, are comprised of numerous heterogeneous individual components (i.e., 'agents'), and often change non-linearly with time. The interactions between natural organic matter (NOM) and other environmental components such as minerals, microorganisms, and metals constitute a complex system.

NOM is the refractory degradation product primarily of decaying plant material. It is a key component of natural waters and soils, and it plays an important role in a wide array of biogeochemical processes. NOM is a polydisperse and heterogeneous mixture of organic molecules. Thus, it consists of molecules that exhibit a range of molecular weights as well as different structures, chemical properties, and reactivities. Its polydispersity and heterogeneity make NOM difficult to characterize and analyze in the laboratory and the field. These same characteristics of NOM make its reactive behavior amenable to a biocomplexity approach that utilizes a computer simulation built on the principles of agent-based and stochastic modeling. Different components of NOM (i.e., different agents) can be assigned different probabilistic behaviors.

The objective of this project was to develop a Web-based ABM stochastic computer simulation that models laboratory batch and column experiments that focus on the adsorption of NOM to mineral surfaces and its mobility through porous media. To do this, we designed a hardware infrastructure and a Web platform to support the simulation, developed equations to define the probabilities of NOM adsorption and desorption as a function of

NOM molecular weight, defined initial NOM molecular weight distribution with a published equation, compared our results with laboratory data, and coupled our simulation to graphical visualization. This paper presents the resulting agent-based stochastic simulation model, NOMAdSIM.

2 PLATFORM AND ARCHITECTURE

Web-deployment of NOMAdSIM promotes its use as a "collaboratory" or a collaborative laboratory for geographically separated scientists and engineers. NOMAdSIM allows researchers to work together over the web, customizing their simulations. In building the model, we used middle-ware technologies, most notably Sun Microsystem's Java 2 Platform Enterprise Edition (J2EE). The main software components of the NOMAdSIM design include an intelligent Web interface, a core simulation engine, and a data analysis package. The Web interface offers a series of interactive screen displays that guide the user through simulation. The data analysis package allows online viewing of simulation results. Several computer servers are dedicated to performing specialized functions (Fig. 1). Some servers generate data reports while others are used for data mining. Users may access the NOMAdSIM simulation model via any standard Web browser. They log in, register if first-time users, and are able to select and adjust parameters listed in a series of screen displays in order to run customized simulations.

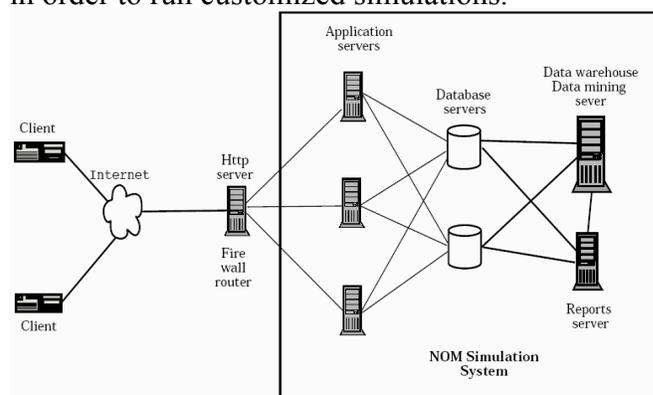


Figure 1. Overall architectural design of NOMAdSIM (Xiang et al., 2004).

3 NOMSIM ALGORITHM

NOMAdSIM is written in the Java programming language. It draws on Swarm and RePast toolkits. Swarm (Santa Fe Institute) software and libraries are designed for agent-based modeling. Swarm provides versatile random number generators and distributions, both essential to stochastic computer simula-

tions. RePast, a newer software package similar to Swarm, is used for its visualization features, and may eventually replace Swarm in NOMAdSIM.

NOMAdSIM is designed to operate in two different modes, the *no-flow mode* and the *flow mode*. They respectively model laboratory batch and column adsorption experiments. NOMAdSIM represents groups of NOM molecules as agents (different agents defined by different molecular-weight intervals) and defines them as objects that move, adsorb, and desorb according to a simple set of behavioral rules. The main difference between the *no-flow* and the *flow* modes involves the method of NOM input into each system. In the *no-flow mode*, NOM molecules are all added to the system at the same time and then begin to move, adsorb, and desorb. The initial number of entered NOM molecules remains fixed over time. The *flow mode* is characterized by the incremental input of NOM molecules over time. Molecules in the *flow mode* can flow into and out of the modeled column system, resulting in a continuously changing population of molecules in the system. The method for defining the initial molecular weight distribution of the inputted NOM mixtures is the same for both modes of operation and is described below.

4 NOM BEHAVIOR & REACTION PROBABILITY EQUATIONS

The simulation is based on the results of laboratory batch adsorption experiments. As described by Cabaniss et al. (2000), NOM molecular weight (MW) strongly correlates with its chemical properties and reactivities. The initial MW distribution of the NOM molecules is generally log-normal (e.g. Cabaniss et al. 2000, Zhou et al., 2001). When there is little or no competition for adsorption sites and NOM coverage of mineral surfaces is low, the adsorbed fraction mimics the original NOM distribution. When competition exists and NOM surface coverage is high, intermediate to high MW components adsorb preferentially. Additionally, kinetic batch experimental data show that lower MW molecules both adsorb and desorb quickly and are gradually replaced at surface sites by larger molecules that adsorb and desorb slowly (Zhou et al., 2001). It is this NOM behavior that we are modeling with NOMAdSIM.

NOMAdSIM is a probabilistic model based on Monte Carlo algorithms wherein the probabilities of NOM adsorption and desorption are defined as a function of molecular weight (x).

Case where molecule is currently in solution

$$P_{\text{adsorb}}(x) = 0.99 \left[\frac{1}{1 + e^{\frac{x-8000}{5000}}} \right] + 0.01 \quad (1)$$

$$P_{\text{no_adsorb}}(x) = 1 - P_{\text{adsorb}}(x) \quad (2)$$

Case where molecule is currently adsorbed

$$P_{\text{desorb}}(x) = 0.89e^{\frac{-x}{2000}} + 0.01 \quad (3)$$

$$P_{\text{no_desorb}}(x) = 1 - P_{\text{desorb}}(x). \quad (4)$$

These equations were optimized iteratively, by comparing the simulation results with laboratory experimental results, followed by adjustments to the equations. Partially based on these probability equations and on random number generation, the MW distribution of the original NOM mixture entered by the user randomly evolves temporally and spatially (i.e., down-column).

5 INITIAL NOM DISTRIBUTION

The equation used to define the initial NOM log-normal MW distribution is from Cabaniss et al. (2000):

$$f_i = \frac{1}{\sigma\sqrt{2\pi}} e^{-(\mu - \log M_i)^2 / 2\sigma^2} \quad (5)$$

The user needs to supply values for the mean molecular weight (μ) and the standard deviation of the molecular weight distribution (σ). These parameters can be obtained from HPSEC (high pressure size exclusion chromatography) data.

6 SIMULATION RESULTS

The batch kinetic data of Zhou et al. (2001) show that the average MW remaining in solution following adsorption decreases over time (Fig. 2). This indicates that higher MW components adsorb to the mineral surfaces over time. Output from NOMAdSIM captures this behavior (Fig. 3).

The probability equations optimized for laboratory batch experiments (i.e., *no-flow mode*) are also

applied to column experiments via the *flow mode* of the simulation. The simulation results show both saturation (Fig. 4) and sorptive fractionation (Fig. 5)

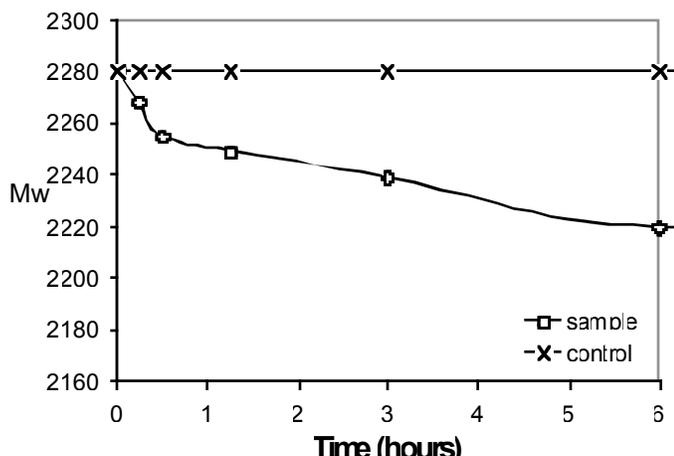


Figure 2. NOM adsorption batch kinetic data (from Zhou 1999). The weight-average molecular weight (Mw) remaining in solution decreases with time, suggesting increased adsorption of higher MW components over time.

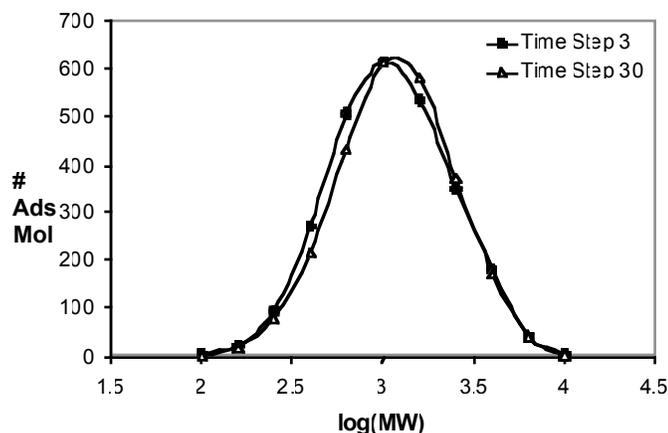


Figure 3. Results of NOM adsorption simulation from no-flow mode. The average MW of adsorbed molecules shifts slightly over time to higher MW.

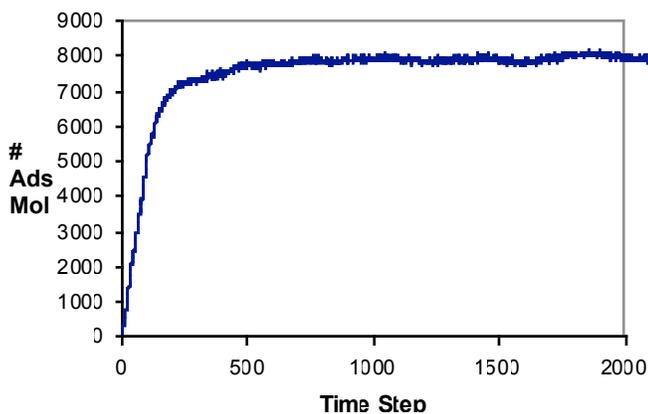


Figure 4. Results of simulation using flow mode. The number of molecules adsorbing to the column system increases with time and eventually plateaus, indicating that the system surfaces are fully saturated.

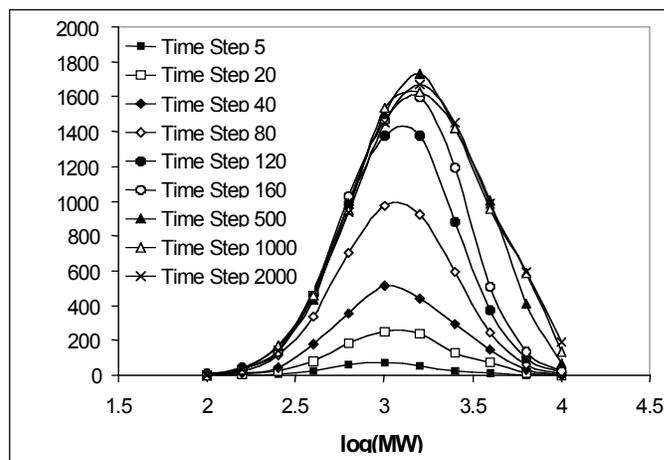


Figure 5. Results of NOM adsorption simulation from flow mode. The number of adsorbed molecules in the column system increases as a function of time. Also, a shift to increasingly more intermediate and high MW molecules is observed. Y-axis is total number of adsorbed molecules

over time. These results will be calibrated against future laboratory column experiments. They agree with field observations. Maurice et al. (2002) showed that dissolved NOM average MW decreases with depth through soils and into groundwater, suggesting adsorption of higher MW components, although other processes may also contribute.

7 NOMSIM VISUALIZATION

NOMAdSIM is coupled with a graphical user interface (GUI) (Fig. 6). The GUI provides visualization of a given simulation and animates the molecular behavior being modeled. It is written in Java and uses functions in the RePast toolkit. It visually displays the movement, adsorption, and desorption of NOM in NOMAdSIM's *no-flow mode* and *flow mode*. Current visualizations include a *NOM Display*, a display of the *Molecular Weight Distribution* inside the system, and a display of the *Input/Output Molecular Weight Distribution*. The *NOM Display* illustrates the algorithm behind the simulation model. It is comprised of two 2-D grids with the same dimensions and discrete space divisions (cells). The first is the *adsorption grid*. It is represented by a black background that models the batch and column matrices with broadly distributed surface sites. Each cell in the grid is capable of holding variable numbers of

molecules, such that the MW of the combined molecules does not exceed the MW of the largest molecule inputted into the associated simulation run. Superimposed over the *adsorption grid* is a transparent *solution grid* through which the NOM molecules flow. In the simulation algorithm, how the molecules adsorb and desorb as well as the nearest neighbor direction they move are defined by probability equations and random number generation, respectively. In the NOMAdSIM GUI, each molecule is represented by a circle and is assigned a color that corresponds to a particular molecular weight interval. Hollow circles represent molecules in solution, whereas solid circles represent adsorbed molecules. Combined, the GUI's adsorption and solution grids serve to represent what is happening at the mineral-water interface for a given simulation run. The *NOM Display* is accompanied by both a *Legend* and a *NOM Settings* display. The *NOM Settings* display allows the user to set the grid size, the specified NOM concentration (*Molecule Density*), and various other parameters. It also allows the user to choose whether a graph of MW distributions should accompany the *NOM Display*. The *Molecular Weight Distribution* display graphs the molecular weight distributions of the NOM fractions in solution and adsorbed in the system. The *Input/Output Molecular Weight Distributions* display plots the total number of molecules that enter and leave the system, according to molecular weight. Both graphs are periodically updated according to a user-defined time interval.

As currently written, NOMAdSIM can incorporate variable reactive surface site distributions. NOMAdSIM is currently designed to model adsorption at low pH (~3), where electrostatic interactions are minimized since NOM is largely protonated. We are working on refining our existing model. Model updates will incorporate the role of electrostatic interactions at higher pHs. Given the current model configuration, any reaction that can be expressed as a probabilistic function of NOM molecular weight, with appropriate consideration of factors such as pH, ionic strength, and other defined conditions, could easily be added. Future updates to the model will allow users to interactively add new parameters and equations.

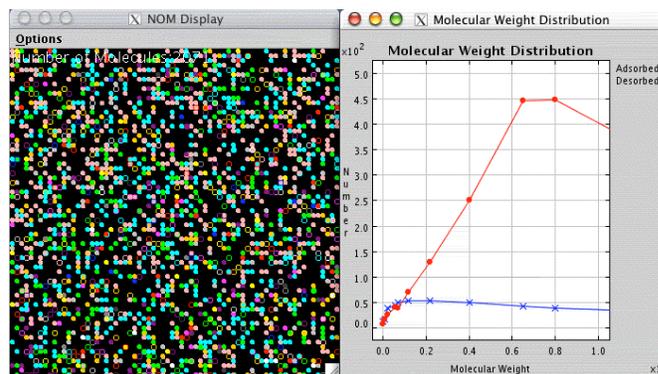


Figure 6. Example of a snapshot from a *flow mode* simulation. Left side displays molecules moving through the column; adsorbed (closed circles) or in solution (open circles). In a colored version, colors represent different MW intervals. Right side displays the corresponding MW distributions of adsorbed (higher peak) versus in-solution molecules. Adsorption is preferential to intermediate- to high MW components.

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