Supplemental Material:

Transport and Retention of Molybdenum(VI) in Soils: Kinetic Modeling

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Ten pages of supporting information are provided, including one Table and six Figures.

Section 1 Soil characterization

Webster loam formed in glacial till or local alluvium derived from the till on uplands and was collected from Story County, Iowa. Windsor sand was a fine sandy loam formed on glacial outwash plains, and deltas of the U.S northeast region and was sampled near Lebanon, New Hampshire. Soil properties for these benchmark soils, such as, pH, TOC, CEC, and particle size distribution, were determined earlier in our laboratory by Buchter et al. (1989). Both citratebi-carbonate-dithionite (CBD) and ammonium oxalate extractions were conducted on these soils by shaking duplicate 50-mL centrifuge tubes containing 0.50 g of soil in 25 mL of extractant for 24 h according to method of Chao and Zhou (1983) and Mehra and Jackson (1960), respectively.
During adsorption as well as desorption experiments, pH of the supernatant was measured and reported in Fig. S1 and Fig. S2 and the pH of the effluent solution during the miscible displacement experiments was provided Fig. S3. The volume of each Mo(VI) and \(^{3}H_{2}O\) pulse along with soil parameters associated with each column (e.g., \(\theta\), \(\rho\), and \(\upsilon\)) are given in Table S1.

Reference:

Buchter, B.; Davidoff, B.; Amacher, C.; Hinz, C.; Iskandar, I. K.; Selim, H. M.  
Correlation of Freundlich \(K_d\) and \(n\) retention parameters with soils and elements.  


Fig. S1. Solution pH for different initial concentrations during adsorption for Webster and Windsor soils.
Fig. S2. Change of solution pH during adsorption of Mo(VI) on Webster and Windsor Soils. The pH of input concentrations are 6.86 (5 mg/L), 6.83 (10 mg/L) and 6.76 (20 mg/L), respectively. The pH of background solution (Ca(NO₃)₂) is 7.67.
Fig. S3. Variation of solution pH for Webster and Windsor columns
Fig. S4. Isotherms of Mo(VI) adsorption on different soils. Solid lines depict results of curve-fitting with the Langmuir equation.
Table S1. Soil physical parameters for the miscible displacement experiments*

<table>
<thead>
<tr>
<th>Soil</th>
<th>Bulk density (g cm$^{-3}$)</th>
<th>Water content (cm$^3$ cm$^{-3}$)</th>
<th>Porosity (%)</th>
<th>Dispersion coefficient (cm$^2$ h$^{-1}$)</th>
<th>Retardation factor</th>
<th>Darcy flux (cm h$^{-1}$)</th>
<th>Pore volume (cm$^3$ cm$^{-3}$)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Webster</td>
<td>1.18</td>
<td>0.50</td>
<td>55.6</td>
<td>0.73±0.15</td>
<td>0.98±0.23</td>
<td>0.37</td>
<td>9.49</td>
<td>87.4</td>
</tr>
<tr>
<td>Windsor</td>
<td>1.54</td>
<td>0.45</td>
<td>41.8</td>
<td>0.48±0.05</td>
<td>1.1±0.09</td>
<td>0.32</td>
<td>11.01</td>
<td>69.1</td>
</tr>
</tbody>
</table>

* Values of the dispersion coefficient and retardation factor were estimated from tritium breakthrough results
Section 2 Second order Model

This kinetic model assumes that a fraction of the total sorption sites is rate limited whereas the remaining fractions interact rapidly or instantaneously with Mo(VI) in solution. The model also accounts for reversible as well as irreversible sorption of the concurrent and consecutive type (Selim and Ma, 2001). In this study, three model versions were derived from the general model and the required model parameters are dependent on the formulation of the SOM used. A fully reversible two-phase SOM formulation requires 4 parameters ($S_{\text{max}}$, $K_e$, $k_1$ and $k_2$) and three-phase reversible-irreversible (consecutive or concurrent) SOM formulations require 5 parameters ($S_{\text{max}}$, $K_e$, $k_1$, $k_2$ and $k_3$ or $k_i$). Retention mechanisms associated with equilibrium and kinetic sorption sites ($S_e$ and $S_k$) include the formation of outer-sphere complexes, inner-sphere complexes, and diffuse ions in electrical double layers (Sposito, 1989). The reactions on the consecutive and concurrent irreversible sites ($S_s$ and $S_i$) include different types of surface precipitation that account for the formation of metal polymers, solid solution or co-precipitates, as well as homogeneous mineral precipitates. Note that in eq 4, the concurrent irreversible sites ($S_i$) are conceptual representation of direct precipitation from solution.

Reference:
Fig. S5. A schematic diagram of the second order model (SOM). Here $C$ is concentration in solution, $S_e$, $S_k$, $S_s$ and $S_i$ are the amounts sorbed on equilibrium, kinetic, and irreversible sites, respectively, where $K_e, k_1, k_2, k_3$ and $k_i$ are the respective rates of reactions.
Fig. S6. Vertical distribution of Mo(VI) among total sorbed sites ($S$), equilibrium sites ($S_e$) and kinetic sites ($S_k$) for Webster and Windsor soils. These modeling data are from Two-Phase (reversible equilibrium-kinetic sites) SOM approach.