Kinetics of Mercury(II) Adsorption and Desorption on Soil

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Adsorption and desorption kinetics of Hg(II) on four soils at pH 6 were investigated to discern the mechanisms controlling the retention and release reaction rates of Hg(II) on soil. A stirred-flow method was employed to perform experiments. Apparent adsorption and desorption rate coefficients were determined by a one-site second-order kinetic model. Both adsorption and desorption were characterized by a biphasic pattern, a fast step followed by a slow step. After 2 min, the Hg(II) adsorbed for an 8 mg L⁻¹ influent accounted for 4–38% of the total Hg(II) adsorbed within 5 h. Of the Hg(II) released within 8 h, 62–81% was desorbed during the first 100 min. Both adsorption and desorption rate coefficients were inversely correlated with the soil organic C content. Not all adsorbed Hg(II) was readily released. The greater the soil organic C content, the higher the fraction of Hg(II) that was resistant to desorption. The diffusion of Hg(II) through intraparticle micropores of soil organic matter may be the principal factor responsible for the observed irreversibility. In addition, the binding of Hg(II) to high affinity sites on soil organic matter, such as the S-containing (-S) groups, may also be important to Hg(II) persistence in soils.

Introduction

Equilibrium reactions between Hg(II) and soils have been extensively studied (1–4). Little, however, has appeared in the literature concerning the kinetics of these reactions. Due to the mobility of soil solution, the retention and release reactions of soluble contaminants with soil, in most cases, are time-dependent rather than instantaneous equilibrium processes. A knowledge of the reaction rates is therefore necessary in order to predict the transport and fate of contaminants in soil and to provide cost-effective soil remediation strategies.

The reactions of contaminants with soil involve both chemical reaction and diffusion processes. Diffusion often has been reported to be the rate-limiting step (5). Both penetration into the mineral lattice (6–8) and diffusion through intraparticle pores (9, 10) have been suggested to be responsible for the slow reactions of metals with soil or soil components. These diffusion processes were often considered as the cause of the observed adsorption/desorption hysteresis, which increases with time of aging (11). Some researchers suggested that hysteresis resulted from the binding of metals to different sites. Di Toro et al. (12) modeled the adsorption—desorption of Co and Ni on montmorillonite and quartz by assuming the sorbed chemical to be the sum of a reversibly sorbed component and a resistant component. Amacher et al. (13, 14) proposed a multi-reaction model to describe the reactions of several metals with soil. They assumed that adsorption/desorption processes involved three concurrent reactions with three different kinds of sites on soil, i.e., a rapid and reversible reaction, a slow and reversible reaction, and an irreversible reaction.

In most cases, kinetic information has been obtained using either batch or miscible displacement techniques. Both methods suffer from pronounced diffusion effects (15). An alternative method, stirred-flow technique, has also been used to ascertain adsorption and desorption kinetics. The soil suspension in the reaction chamber is well-mixed by stirring (16), which significantly reduced diffusion limitations (17). With this method, the desorbed solute is continuously removed from the reactor; therefore, further release of solute was not prohibited by the released solute, as was observed in batch experiments (18). This method can also account for the dilution of incoming solution by the soil-retained solution. The stirred-flow method was employed in this study to perform experiments.

The purpose of this study was to examine the rates of Hg(II) retention to and release from soil and to understand the mechanisms controlling the reaction rates. We investigated Hg(II) adsorption and desorption kinetics on four soils with different properties. We also removed organic matter from soils to evaluate the importance of soil components and porosity in determining the reaction rates. Apparent rate coefficients for Hg(II) adsorption and desorption were determined using a one-site second-order kinetic model.

Materials and Methods

Soils. Four soils—Freehold sandy loam (fine-loamy, mixed, mesic Typic Hapludults), Sassafras sandy loam (fine-loamy, siliceous, mesic Typic Hapludults), Dunellen sandy loam (coarse-loamy, siliceous, mesic Typic Hapludults), and Rockaway stony loam (coarse-loamy, mixed, mesic Typic Fragudults)—collected from New Jersey were used to perform studies. All soils were collected from the A horizon. The soil samples were air-dried and sieved through a 2-mm screen. Soil aggregates were broken by hand and a wooden mallet before sieving. All experiments were conducted using the soil fraction of less than 2 mm, which was thoroughly mixed before use. Selected properties of the soils are listed in Table 1. The organic C content was determined using a Walkley-Black wet combustion method (19). The specific surface area was measured by a nitrogen adsorption BET method using a Quantasorb Model QS-7 sorption system (Quantachrome Corp., Greensville, NY).

Kinetic Experiments. The stirred-flow reaction chamber used was a modification of that developed by Carski and Sparks (20). It was made of Plexiglas and consisted of two units: a reaction cell (6.7 cm²) with an inlet side port near the bottom, and a cover with an outlet port on the top. The reaction cell was thread sealed by the cover. A 25 mm diameter, 0.45-µm pore size Nuclepore membrane filter (Costar, Cambridge, MA) was fitted just below the outlet port of the cover to retain the soil in the chamber. Both influent

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and effluent were transported by 0.89 mm i.d. Teflon tubing. For an adsorption study, a 0.3-g soil sample and a Teflon-coated magnetic stirrer were placed into the reaction chamber. The soil was wetted with 0.5 mL of 0.01 M NaNO₃ and allowed to hydrate for 1 h. The reaction cell was then quickly filled by adding 8 or 4 mg L⁻¹ Hg(II) solution (prepared in 0.01 M NaNO₃ at pH 6) using a 10-ml glass pipet (Fisher Scientific). Immediately after the addition of Hg(II) solution, the reaction chamber cell was sealed with the cover. The same influent solution was then pumped into the chamber using an Ismatec pump (Cole-Parmer, No. 7332) at a rate of 1 mL min⁻¹, and the effluent was collected with an automatic fraction collector after the first 2 min and then at 5-min intervals. Mercury(II) concentrations in the effluent samples were determined by a cold vapor Hg analyzer (Perkin Elmer MHS 10) coupled with an atomic absorption spectrophotometer (Perkin Elmer Zeeman Model 5000). The adsorption experiment was continued until equilibrium, which was judged by the equivalence of influent and effluent concentrations, was achieved. Following adsorption, desorption was initialized by passing 0.01 M NaNO₃ (pH 6) through the chamber.

To account for the dilution effect and the amount of Hg(II) adsorbed by the reaction chamber, we measured blank curves for adsorption and desorption without soil in the chamber following the same procedure as described above. Of the input Hg(II), 23% was initially adsorbed by the reactor for an influent Hg(II) concentration of 8 mg L⁻¹, and 38% was found for an influent concentration of 4 mg L⁻¹. The reactor was saturated in 30 and 60 min for an influent Hg(II) concentration of 8 and 4 mg L⁻¹, respectively. Duplicate experiments were run, and the variance of effluent concentrations at each time point was less than 6%.

The flow rate was monitored during the entire experiment, and the change of the flow rate was less than 5%. A magnetic stirrer was used to ensure adequate mixing in the reaction chamber. The stirring speed was maintained at a minimum to reduce abrasion of the soil, but still provided a good mixing of the soil suspension. After each run either with or without soil present, the transport tubing was washed by passing 15% HNO₃ followed by distilled deionized water, and the reaction chamber was cleaned by soaking in 15% HNO₃ overnight followed by washing with distilled deionized water.

**Data Analysis.** The amount of Hg(II) adsorbed or released from soil can be calculated from the difference in solution concentrations with and without soil in the reaction chamber (5, 21). The adsorbed or released quantity is the sum of the concentration differences in both effluents and the solutions in the chamber with and without soil. For adsorption, it can be expressed as

\[
q_a(t) = \frac{\sum \left( \left( C_{b,i} \right) - \left( C_{s,i} \right) \right) \frac{\Delta t}{V} + \left( C_{b} - C_s \right)}{W}
\]

(1)

in which \(q_a(t)\) is the cumulative adsorption at time \(t\), \(\mu g g^{-1}\); \(J\) is flow rate, \(L\) min⁻¹; \(\Delta t\) is sampling time interval, min; \(C_i\) is the influent concentration for the ith sampling period, \(\mu g L^{-1}\); \(C(t)\) is the concentration in the chamber at time \(t\), \(\mu g L^{-1}\); \(V\) is the volume of the reaction chamber, L; and \(W\) is the soil concentration in the chamber, g L⁻¹. Subscripts \(s\) and \(b\) refer to the cases with and without soil in the chamber, respectively.

The quantity desorbed is given by

\[
q_d(t) = \frac{\sum \left( \left( C_{b,i} \right) - \left( C_{s,i} \right) \right) \frac{\Delta t}{V} + \left( C_s - C_{b,i} \right)}{W}
\]

(2)

where \(q_d(t)\) is the cumulative desorption at time \(t\), \(\mu g g^{-1}\).

For eqs 1 and 2, effluent Hg(II) concentrations can be determined directly. The concentration in the chamber at the end of a specific sampling period, however, needs to be estimated. This was approximated by averaging the effluent concentrations for that time period and the succeeding one. The use of eqs 1 and 2 to calculate the Hg(II) retained and released by soils accounts for both the effect of dilution and the amount of Hg(II) sorbed by the reaction chamber. It is assumed that the kinetics of Hg(II) sorption on the reaction chamber is not affected by the presence of soil in the chamber. In reality, the presence of soil in the chamber would likely slow down the adsorption of Hg(II) on the chamber by reducing the soluble Hg(II) concentration. The presence of soil in the chamber would reduce the desorption rate from the chamber as a consequence of an increase in the concentration of soluble Hg(II) resulting from desorption from the soil. Consequently, the initial adsorption and desorption of Hg(II) by soils could be underestimated. Since all adsorption sites of the chamber are outside sites on a planar surface, they are much easier to access than are most of the sites on soils, especially the intraparticle micro pores. It is expected that the adsorption of Hg(II) on the chamber is still fast, even in the presence of soil. Furthermore, after 10 min of adsorption, the quantity of Hg(II) adsorbed by the chamber without soil present is less than 10% of the total Hg(II) adsorbed by both soil and the chamber at each sampling interval for all experiments except for adsorption on the Freehold sandy loam at an 4 mg L⁻¹ influent. Therefore, the underestimation of Hg(II) adsorbed by soils would be small. Even for adsorption on the Freehold sandy loam, the results obtained for the two initial concentrations are consistent with those of the Dunellen sandy loam (for details see Figures 2a, b and 6a, b and related discussion) and other soils (Figure 1 and related discussion).

Since the amount of Hg(II) adsorbed by the reaction chamber is very small as compared to that adsorbed by the Sassafras sandy loam (43%) and the Dunellen sandy loam (1–7%), the adsorption of Hg(II) by the chamber would have a minor effect on Hg(II) desorption kinetics on these two

<table>
<thead>
<tr>
<th>soil no.</th>
<th>soil name</th>
<th>particle size distribution (g kg⁻¹)</th>
<th>organic C (g kg⁻¹)</th>
<th>surface area (m² kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Freehold sandy loam</td>
<td>920</td>
<td>5.22</td>
<td>2040</td>
</tr>
<tr>
<td>2</td>
<td>Sassafras sandy loam</td>
<td>450</td>
<td>5.78</td>
<td>5310</td>
</tr>
<tr>
<td>3</td>
<td>Dunellen sandy loam</td>
<td>560</td>
<td>5.57</td>
<td>5210</td>
</tr>
<tr>
<td>4</td>
<td>Rockaway stony loam</td>
<td>540</td>
<td>4.69</td>
<td>8620</td>
</tr>
</tbody>
</table>
The amount of Hg(II) adsorbed by the chamber was 23% of that adsorbed by the Freehold sandy loam for an influent of 8 mg L\(^{-1}\) and 28% for an influent of 4 mg L\(^{-1}\). Our calculation assumes that the desorption rate from the chamber is not affected by the presence of soil. When soil is present, however, the desorption rate from the chamber is probably slower than that when the soil is absent. The calculated values are therefore smaller than the actual desorption rates from the Freehold sandy loam.

### Results and Discussion

#### Adsorption Kinetics

Before running complete adsorption and desorption kinetic experiments, we conducted a preliminary study following the method of Bar-Tal et al. (22) to ascertain whether the reactions of Hg(II) with soil were instantaneous or kinetically controlled. The assumption of this method is that if a non-equilibrium condition exists in the reaction chamber, stopping the flow of adsorbate for a sufficient time period before equilibrium is established should result in a noticeable drop in effluent concentration when flow is restarted. If the reaction is instantaneous, the plot of effluent concentrations versus time should be continuous. Although not presented in this paper, a sharp drop (23%) in effluent Hg(II) concentration was observed after stopping the flow for 30 min. This indicated that the reaction of Hg(II) with soil was time dependent rather than instantaneous.

Kinetics of Hg(II) adsorption on four soils at an influent concentration of 8 mg L\(^{-1}\) are shown in Figure 1. Adsorption was initially very fast. At the end of the first 2 min, the Hg(II) adsorbed was 96 µg g\(^{-1}\) on the Freehold sandy loam, 153 µg g\(^{-1}\) on the Sassafras sandy loam, 180 µg g\(^{-1}\) on the Dunellen sandy loam, and 176 µg g\(^{-1}\) on the Rockaway stony loam, which respectively accounted for 38%, 12%, 5%, and 4% of the total Hg(II) adsorbed by these soils within 5 h. The time required to reach equilibrium depended on soil properties. Generally, the higher the soil organic matter content, the longer the time needed for a reaction to reach equilibrium. For example, the adsorption of Hg(II) on the Freehold sandy loam, which contained a very small amount of organic C, did not increase significantly after 60 min, while adsorption on the Dunellen sandy loam kept increasing until equilibrium was achieved at about 5 h. For the Rockaway stony loam, which had a similar particle size distribution as the Dunellen sandy loam, adsorption equilibrium was not achieved even within 5 h. This probably resulted from the higher organic C content of the Rockaway stony loam.

Higher organic C content (OC) also resulted in higher adsorption. For example, for an influent concentration of 8 mg L\(^{-1}\), the equilibrium adsorption was 257 µg g\(^{-1}\) for the Freehold sandy loam (A horizon) (OC: 1.2 g kg\(^{-1}\)), 1216 µg g\(^{-1}\) for the Sassafras sandy loam (OC: 3.5 g kg\(^{-1}\)), and 3610 µg g\(^{-1}\) for the Dunellen sandy loam (OC: 11.0 g kg\(^{-1}\)). Similar results were observed in a previous study (23), in which the soil adsorption capacity for Hg(II) was found to correlate to the organic C content.

We tested the importance of soil organic matter to the reaction rate by treatment of the Dunellen sandy loam by H\(_2\)O\(_2\) for removal of organic C. As shown in Figure 1, after H\(_2\)O\(_2\) treatment, adsorption on the Dunellen sandy loam reached equilibrium within about 1 h, which is much shorter than the time required for equilibrium attainment (5 h) before treatment of the soil by H\(_2\)O\(_2\). This suggests that soil organic matter is the most important component in determining Hg(II) adsorption rate.

After H\(_2\)O\(_2\) treatment, 1.3 g kg\(^{-1}\) residual organic C still remained on the Dunellen sandy loam. The amount of residual organic C on the Dunellen sandy loam is similar to that on the Freehold sandy loam (1.2 g kg\(^{-1}\)) without treatment with H\(_2\)O\(_2\); however, the H\(_2\)O\(_2\)-treated Dunellen sandy loam adsorbed more Hg(II) (390 µg g\(^{-1}\)) and required longer time (80 min) for the reaction to reach equilibrium than Freehold sandy loam did (adsorption: 254 g kg\(^{-1}\); time: 40 min). Comparing the inorganic constituents of the Dunellen sandy loam with those of the Freehold sandy loam, the former soil contains much more silt plus clay (44%) than does the latter (8%). The larger surface area of silt and clay and the diffusion of Hg(II) through the micropores of these minerals might contribute to the greater adsorption and longer equilibrium time of Hg(II) on the treated Dunellen sandy loam than on the Freehold sandy loam without treatment with H\(_2\)O\(_2\).

The effect of influent Hg(II) concentration on the reaction was tested for the Freehold sandy loam and the Dunellen sandy loam. The results are presented in Figure 2. A decrease in influent concentration decreased the quantity of Hg(II) adsorbed. This indicates that the reaction was reversible or partially reversible; otherwise, adsorption would have continued until all surface sites were saturated. The decrease in influent concentration also resulted in an increase in the equilibrium time. For the Freehold sandy loam, adsorption reached equilibrium at nearly 40 min for an 8 mg L\(^{-1}\) influent and at 80 min for a 4 mg L\(^{-1}\) influent. For the Dunellen sandy loam, at the end of 5-h adsorption, equilibrium was only attained for an influent of 8 mg L\(^{-1}\), but not 4 mg L\(^{-1}\).

The dependence of the adsorption rate on Hg(II) influent concentration suggested that diffusion was probably involved in the reaction. Diffusion has frequently been reported to be the rate-limiting step for metal adsorption and desorption (8, 10, 23). For very dilute suspensions, like those used in this study, diffusion-controlled processes for model adsorbs (rectangular or spherical) have been shown to result in a linear relationship between fractional adsorption (q/q\(_{\infty}\)) and time (24). Although not shown, plots of Hg(II) fractional adsorption versus t\(^{1/2}\) for all soils we studied are curvilinear. This probably resulted from the heterogeneous nature of soils and the continuous input of soluble Hg(II) to the reaction chamber. Involvement of more complex adsorption mechanisms could also contribute to the curvilinear relationship between q/q\(_{\infty}\) and t\(^{1/2}\).

#### Desorption Kinetics

Desorption experiments were conducted following adsorption studies for which equilibrium was achieved within the experimental adsorption time period. As shown in Figure 3, Hg(II) removal rate profiles on all soils were characterized by two desorption regimes, a fast regime followed by a slow regime. The fast desorption regime occurred during the first 100 min. At the end of the first 100 min of desorption, 45% of the Hg(II) adsorbed from an 8 mg L\(^{-1}\) influent was desorbed from the Freehold sandy loam, 43% from the Sassafras sandy loam, and 27% from the

![Cumulative adsorption (µg g\(^{-1}\))](image-url)
Dunellen sandy loam. The amount of Hg(II) desorbed after the first 100 min accounted for 81% of the total Hg(II) desorbed within 8 h for the Freehold sandy loam, 68% for the Sassafras sandy loam, and 62% for the Dunellen sandy loam. A higher initial Hg(II) concentration in soil initially resulted in a higher desorption rate. After 8 h of desorption, the desorption rate was very small (<0.6 µg g⁻¹ min⁻¹) for all soils; however, 2000 µg g⁻¹ Hg(II) still remained on the Dunellen sandy loam, 446 µg g⁻¹ on the Sassafras sandy loam, and 50 µg g⁻¹ on the Freehold sandy loam (Figure 4). The fractional removal (q'/q₀) profiles for all soils are similar in shape, but the quantity is different (Figure 5). At the end of 8 h of desorption, 79% of the Hg(II) retained was released from the Freehold sandy loam, 62% was released from the Sassafras sandy loam, and 43% was released from the Dunellen sandy loam.

The fractional Hg(II) release from soils within 8 h in this study was much greater than that obtained for 96 h using a batch desorption method in a previous study (4). For example, after 96 h of batch desorption, 12–21% of the 2.42–3.66 µmol g⁻¹ adsorbed Hg(II) was released from the Freehold sandy loam. After 8 h of desorption using the stirred-flow technique, however, 79% of the adsorbed Hg(II) (1.29 µmol g⁻¹) was released from the same soil. For a higher initial concentration, a greater fraction of the Hg(II) is expected to be released using the stirred-flow method (details about the effect of the initial concentration on the fractional Hg(II) release will be discussed later in this section). The smaller fractional Hg(II) release in batch desorption experiments can be attributed to the backward reaction caused by the released Hg(II). Based on these results, it is obvious that a stirred-flow method is more appropriate than a batch method in obtaining information on the potential mobility of contaminants in soils.

One well-documented factor that can contribute to the persistence of metals in soil or soil components is diffusion into the mineral lattice (6–8) or through intraparticle pores (9, 10). Although few attempts have been made to study the
importance of soil organic matter to metal persistence in soil, it has been reported that restricted diffusion in organic matter was responsible for the persistence of many organic chemicals in soil (25–27). To understand the relative importance of soil components in determining Hg(II) persistence in soil, we compared Hg(II) desorption on the Sassafras sandy loam and the Dunellen sandy loam. As shown in Table 1, the Sassafras sandy loam has a similar surface area (5310 m² kg⁻¹), a greater silt plus clay content (550 g kg⁻¹), and a much smaller organic C content (3.5 g kg⁻¹) than does the Dunellen sandy loam (surface area: 5210 m² kg⁻¹; silt and clay: 440 g kg⁻¹; organic C: 11 g kg⁻¹). The fractional Hg(II) desorption from the former soil was much greater (62%) than that from the latter (42%) (Figure 4). This suggests that organic matter was the most important component responsible for Hg(II) persistence in soil. Similar results were observed in a previous batch desorption study (4).

We further ascertain the importance of organic matter for Hg(II) persistence in soil by removal of organic matter from the Freehold sandy loam and the Dunellen sandy loam. After treatment with H₂O₂ for removal of organic C, a very small amount of residual organic C (0.05 g kg⁻¹) still remained on the Freehold sandy loam. At the end of 8-h desorption, nearly all adsorbed Hg(II) was released (99%) from this soil. Since the Freehold sandy loam contains 92% sand, it is reasonable to assume that the Hg(II) retained by sand would eventually be leached out.

As indicated earlier, after H₂O₂ treatment, the residual organic C (1.3 g kg⁻¹) in the Dunellen sandy loam is similar to that in the Freehold sandy loam (1.2 g kg⁻¹) without treatment with H₂O₂; however, the fraction of the Hg(II) released (95%) at the end of 8-h desorption from the treated Dunellen sandy loam was much greater than that from the Freehold sandy loam without treatment with H₂O₂ (75%). It is possible that the treatment of the soil by H₂O₂ changed the nature of the residual organic matter in the Dunellen sandy loam and, consequently, resulted in a greater fraction of the retained Hg(II) being released. As indicated in Table 1, the Dunellen sandy loam contains a high fraction of silt plus clay (44%), but nearly all Hg(II) adsorbed by this soil after removal of organic C was released (95%). Again, this suggests that soil inorganic components were minor contributors to the observed persistence of Hg(II) in the soils.

We plotted the fraction of Hg(II) remaining ([q̄₂ − q̄₀]/q̄₀, where q̄₀ is the Hg(II) adsorbed at equilibrium and q̄₀ is the Hg(II) released at the end of the desorption) in the soil after 8 h of desorption versus the soil organic C (OC) content and found that the ([q̄₂ − q̄₀]/q̄₀) values exponentially increased with OC. Upon log transformation of OC values, a linear correlation between ([q̄₂ − q̄₀]/q̄₀) and log OC was obtained. The regression equation is ([q̄₂ − q̄₀]/q̄₀) = 0.179 + 0.374 log OC with a regression coefficient of 0.996.

We speculated that the slow release resulted from Hg(II) preferentially bonding to high energy sites. Because these high energy sites have limited adsorption capacity, lower concentration would result in higher fractional adsorption to these high energy sites and, consequently, cause lower fraction of release from soil. This hypothesis was tested using the Freehold sandy loam. As shown in Figure 6a, 60% of the Hg(II) retained was released within nearly 2 h for an initial concentration of 254 µg L⁻¹, whereas 55% of the Hg(II) retained was released for an initial concentration of 214 µg L⁻¹. Figure 6a also indicated that after 50 min of desorption, the Hg(II) remaining on the soil for two initial concentrations was almost the same. This can only be explained by the preferential distribution of adsorbed Hg(II) among soil sites. Although the initial concentrations were different, the amount of Hg(II) adsorbed on high energy sites could be similar. As a result, after the Hg(II) on the low energy sites was quickly released, the Hg(II) remaining on soil (high energy sites) was similar for different initial concentrations.

A similar result was observed for the Dunellen sandy loam. The desorption study was conducted following adsorption from 4 and 8 mg L⁻¹ influents. Since adsorption equilibrium was only reached for the 8 mg L⁻¹ influent but not for the 4 mg L⁻¹ influent within the experimental time period, the fractional desorption from the soil for the two initial concentrations (3611 vs 2825 µg g⁻¹) is not comparable. Comparison of Hg(II) remaining in the soil for the two initial concentrations as a function of time, however, allows us to understand the reaction processes involved. As shown in Figure 6b, after nearly 6 h of desorption, the Hg(II) remaining in the soil for the two initial concentrations was very close (2122 vs 2048 µg g⁻¹), although the initial concentration difference was large (786 µg g⁻¹).

**Modeling Adsorption and Desorption Kinetics.** A number of models have been postulated to describe metal adsorption and desorption kinetics. Early attempts mainly focused on one-site kinetic equations (28). The rate coefficient obtained using these equations is usually an apparent coefficient that changes with flow rate and the initial solute concentration. In some cases, a deviation of experimental data from the simple one-site kinetic equations was observed. Accordingly, two-site or two-region models, with two classes of sites either in series or parallel, were proposed to describe non-equilibrium sorption (26, 29). Selim and co-workers (14, 30) also proposed a multireaction model, with sorption sites ranging from three to five types, to simulate metal sorption on soil. Because this model involves so many adjustable parameters, its usefulness is limited.

In many cases, the reaction kinetics can be described equally well by different models (5). The model fitting alone...
therefore does not allow one to make a conclusion on the reaction mechanisms. Due to the heterogeneous nature of soil, there is a virtual continuum of sites on the soil. For simplicity, we assume that there is one type of sites on soil in this study. The apparent average rate coefficients for the reaction of Hg(II) with soil solids were calculated based on the model developed below.

The adsorption reaction between Hg(II) and soil surface sites can be expressed as

\[ \text{Hg} + S = \text{HgS} \]  

(3)

The reaction rate is defined by a second-order kinetic equation:

\[ \frac{dq_a}{dt} = k_a(q_a - q_{\text{aq}})C - k_{-a}q_a \]  

(4)

where \( dq_a/dt \) is the reaction rate (\( \mu g \text{ g}^{-1} \text{ min}^{-1} \)); \( k_a \) is the forward rate coefficient (\( L \mu g^{-1} \text{ min}^{-1} \)); \( q_a \) is the concentration of Hg(II) adsorbed by soil at time \( t (\mu g \text{ g}^{-1}) \); \( C \) is the soluble Hg(II) concentration in the reaction chamber at time \( t (\mu g \text{ L}^{-1}) \); \( k_{-a} \) is the reverse rate coefficient (\( \text{min}^{-1} \)); and \( q_{\text{aq}} \) is the concentration of Hg(II) adsorbed at equilibrium (\( \mu g \text{ g}^{-1} \)).

In eq 4, the quantity of \( q_a \) and \( C \) are dependent each other, and each is a function of time. The correlation between \( q_a \) and \( C \) is unknown, which makes integration of eq 4 difficult.

A finite difference method (31) was therefore used to solve this equation. The derivatives in eq 4 can be replaced by the finite difference form:

\[ \frac{q(t + \Delta t) - q(t)}{\Delta t} = k_a(q_a - q_{\text{aq}})C - k_{-a}q_a \]  

(5)

where subscripts \( t \) and \( t + \Delta t \) indicate the quantities at time \( t \) and \( t + \Delta t \). Rearrangement of eq 5 gives

\[ q(t + \Delta t) = k_a(q_a - q_{\text{aq}})Ct + k_{-a}q_a\Delta t + q(t) \]  

(6)

The desorption reaction of Hg(II) from the soil can be expressed as

\[ \text{HgS} = \text{Hg} + S \]  

(7)

\[ \frac{d(q_b - q_d)}{dt} = -k_d(q_b - q_d) + k_{-d}q_dC \]  

(8)

where \( dq_b/dt \) is the desorption rate (\( \mu g \text{ g}^{-1} \text{ min}^{-1} \)); \( q_b \) is the concentration of Hg(II) released from the soil at time \( t (\mu g \text{ g}^{-1}) \); \( k_d \) is the desorption rate coefficient (\( \text{min}^{-1} \)); \( k_{-d} \) is the reverse rate coefficient (\( L \mu g^{-1} \text{ min}^{-1} \)); and \( q_d \) is the desorbable Hg(II) concentration on the soil at the beginning. At \( t = 0, q_b = 0 \), and the reverse reaction rate is zero.

Similarly, by applying finite difference method to eq 8, the following expression was obtained:

\[ \frac{q_{(t+\Delta t)} - q_{(t)}}{\Delta t} = -k_d(q_b - q_{\text{aq}}) + k_{-d}q_{\text{aq}}Ct \]  

(9)

where subscripts \( t \) and \( t + \Delta t \) indicate the quantities at time \( t \) and \( t + \Delta t \). Rearranging eq 9 to give

\[ q_{(t+\Delta t)} = q_{(t)} + k_d(q_b - q_{\text{aq}})\Delta t - k_{-d}q_{\text{aq}}Ct\Delta t \]  

(10)

Equations 6 and 10 were used to fit adsorption and desorption kinetic data, respectively. Parameters were determined with a nonlinear multivariate regression program (32). The fitting begins with an estimation of the values of the parameters and then keeps optimizing their values until the residual sum of squares no longer decreases significantly. A preliminary fitting exercise indicated that, under the experimental conditions, the reverse reactions during both adsorption and desorption experiments were insignificant. Equations 6 and 10 are therefore simplified as 11 and 12, respectively:

\[ q_{(t+\Delta t)} = k_a(q_a - q_{\text{aq}})Ct + q_{\text{aq}} \]  

(11)

\[ q_{(t+\Delta t)} = q_{(t)} + k_d(q_b - q_{\text{aq}})\Delta t \]  

(12)

We used eqs 11 and 12 to describe the kinetics of Hg(II) adsorption and desorption on soils. The model fitting results are summarized in Table 2. The small values of standard deviation (SE) for estimated parameters and the magnitude of root mean square (RMS) indicated that the fit of experimental data was good. An example is shown in Figure 7.

As indicated in Table 2, the amount of Hg(II) that could be released from soils \( (q_d) \) is much smaller than the total retained Hg(II) \( (q_a) \), suggesting that not all adsorbed Hg(II) can be readily desorbed. Both previous studies using a batch equilibrium method (3, 4) and this study using a stirred-flow technique indicated that organic matter had strong affinity for Hg(II) and was the principal component responsible for Hg(II) persistence in soils. The \( k_a \) and \( k_d \) values obtained for an influent concentration of 8 mg L\(^{-1}\) were also found to inversely correlate with the soil organic C content. By plotting log \( k_a \) and log \( k_d \) versus log OC, linear relationships were

<table>
<thead>
<tr>
<th>soil no.</th>
<th>influent Hg concn (( \mu g \text{ L}^{-1} ))</th>
<th>( q_a (\mu g \text{ g}^{-1}) )</th>
<th>SE (( \mu g \text{ g}^{-1} ))</th>
<th>( k_a (L \mu g^{-1} \text{ min}^{-1}) )</th>
<th>SE (( L \mu g^{-1} \text{ min}^{-1}) )</th>
<th>RMS (( \mu g \text{ g}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8000</td>
<td>1176</td>
<td>11</td>
<td>6.09e-6</td>
<td>4.97e-7</td>
<td>0.46</td>
</tr>
<tr>
<td>6</td>
<td>4000</td>
<td>210</td>
<td>2</td>
<td>2.57e-5</td>
<td>2.74e-6</td>
<td>0.46</td>
</tr>
<tr>
<td>6</td>
<td>8000</td>
<td>255</td>
<td>1</td>
<td>1.99e-5</td>
<td>4.05e-7</td>
<td>0.09</td>
</tr>
<tr>
<td>8</td>
<td>8000</td>
<td>5100</td>
<td>64</td>
<td>3.06e-6</td>
<td>3.22e-7</td>
<td>1.64</td>
</tr>
<tr>
<td>12</td>
<td>4000</td>
<td>2930</td>
<td>32</td>
<td>1.06e-5</td>
<td>1.22e-6</td>
<td>1.40</td>
</tr>
<tr>
<td>12</td>
<td>8000</td>
<td>3610</td>
<td>50</td>
<td>5.56e-6</td>
<td>7.47e-7</td>
<td>1.85</td>
</tr>
</tbody>
</table>

\(^a\) SE is standard deviation of the estimated parameter. \(^b\) RMS is the root mean square, which is defined by \([\text{RSS}((n - p))^2]\), where RSS is the residual sum of squares; \( n \) is the number of data points; and \( p \) is the number of parameters.
TABLE 3. Relationships between Rate Coefficients Obtained for an 8 mg L\(^{-1}\) Hg(II) Influent and Soil Organic C (OC) Content

<table>
<thead>
<tr>
<th>log (k_d) (L mg(^{-1}) min(^{-1}))</th>
<th>log (k_a) (min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{intercept}</td>
<td>\text{slope}</td>
</tr>
<tr>
<td>log OC (g kg(^{-1}))</td>
<td>-4.76</td>
</tr>
</tbody>
</table>

\(^a\) Standard deviation of predicted values.

obtained as indicated in Table 3. The regression coefficients (\(r^2\)) for both regressions are \(\geq 0.88\).

The irreversibility of Hg(II) adsorption/desorption on soils could involve complex mechanisms. First of all, interparticle (or film) diffusion limitation is significantly reduced by stirring (33), but intraparticle diffusion may still be an important rate-limiting step. The diffusion of Hg(II) through intraparticle micropores of soil organic matter may be the principal factor responsible for the observed irreversibility; thus, a greater organic C content resulted in slow reaction rates and a higher fraction of Hg(II) that were resistant to desorption. A similar mechanism has been proposed to explain the persistence of the binding of Hg(II) to high affinity sites on soil organic matter such as the S-containing (-S) groups, which might also contribute to the observed adsorption/desorption hysteresis because the binding of -S with Hg(II) is very strong (34).

The influent concentrations (4 and 8 mg L\(^{-1}\)) used in this study were relatively high, and the resultant Hg(II) retention levels (210–5100 mg kg\(^{-1}\)) by soils are higher than those found in uncontaminated agricultural soils (\(\leq 4.6\) mg kg\(^{-1}\)) (35). The Hg(II) levels retained by soils of this study, however, are within the concentration range of contaminated sites, which could range from up to 75 mg kg\(^{-1}\) in slightly contaminated sites like golf courses (36), to as high as 123 000 mg kg\(^{-1}\) in seriously contaminated sites, such as Berry’s Creek in New Jersey (37).

An implication of the results of this study is that the contamination of any soils with high concentrations of Hg(II) could result in groundwater contamination because a large fraction of Hg(II) could eventually be leached out. The application of a small concentration of Hg(II) to a high organic matter soil may not pose groundwater problems because Hg(II) has strong affinity to organic matter and the sorption rate is sufficient fast compared to that of groundwater flow. The decontamination of Hg-contaminated sites using some methods, such as in-situ washing with water, may not be effective due to slow desorption. On the other hand, the contamination of a low organic matter sandy soil with Hg(II) may pose a serious groundwater problem because the retained Hg(II) by sand could eventually be leached out. These contaminated sites, however, could be easily remediated by the cost effective method—in-situ washing with water.

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