Sorption and Degradation of Alachlor and Metolachlor in Ground Water Using Green Sands

Taeyoon Lee and Craig H. Benson*

ABSTRACT

Reactive barriers are used for in situ treatment of contaminated ground water. Waste green sand, a by-product of gray-iron foundries, is used as a reactive medium. The findings in this study support the potential use of green sand iron to treat ground water contaminated with alachlor and metolachlor. A reactive barrier constructed with green sand iron can be expected to reduce alachlor and metolachlor concentrations below maximum contaminant levels (MCLs) in ground water. Laboratory studies conducted using transport parameters from the batch tests indicate that a 1-m-thick reactive barrier will result in a 10-fold reduction in concentrations of alachlor and metolachlor for seepage velocities less than 0.1 m/d provided the green sand contains at least 2% residual iron. This level of reduction generally is sufficient to reduce alachlor and metolachlor concentrations below maximum contaminant levels in the United States.

ALACHLOR AND METOLACHLOR are chlorinated herbicides that have been widely used in agriculture and are ubiquitous ground water contaminants in agricultural regions of the United States (Roux et al., 1991; Kolpin et al., 1996; Barbash et al., 1999; Spalding et al., 2003). Alachlor and metolachlor are mobile in ground water, and have been characterized as probable (alachlor) and possible (metolachlor) human carcinogens (Nowell and Resek, 1994). One potential method to remediate ground water contaminated with alachlor and metolachlor is to treat the ground water in a reactive barrier (RB) using zerovalent iron (ZVI). Laboratory studies conducted by Eykholt and Davenport (1998), Koppensteiner (1998), Comfort et al. (2001), Gaber et al. (2002), and Satapana-
Saturated hydraulic conductivity of each green sand was measured following the methods described in ASTM D 5886 (American Society for Testing and Materials, 2000). The constant head method was used and tap water was the permeant liquid. The green sands were tamped into the permeameter with a rod in three layers of equal thickness using 15 tamps per layer. The intent was to create a moderately compacted material that would simulate in situ placement of the sand by loose dumping followed by vibratory densification. Saturated hydraulic conductivities of the sands are summarized in Table 1. They range from 0.00079 to 23.3 m/d, but most are between 0.2 and 2.0 m/d. The saturated hydraulic conductivity is controlled primarily by the amount of clay in the green sand (i.e., green sands with a larger clay fraction typically have lower hydraulic conductivity). For example, Sand 11 has the lowest saturated hydraulic conductivity and the highest clay content of the sands that were tested, whereas Sand 9 has the smallest clay fraction and the highest hydraulic conductivity. This sensitivity to clay content is typical of mixtures of sand and bentonite, as described in Abichou et al. (2002).

The hydraulic conductivities of the green sands are lower than the hydraulic conductivity of granular ZVI, which typically is on the order of 10 m/d (Elder et al., 2002). Thus, green sands most likely would be used in permeable reactive barriers (PRBs) placed in less permeable aquifer materials (fine sands, silty sands) or in low-permeable reactive barriers (LPRBs) used in conjunction with ground water cutoff walls. Alternatively, the hydraulic conductivity of green sands can be increased to more conventional levels by mixing with coarse materials such as gravel, coarse sand, crushed glass, or tire chips (Lee and Benson, 2002).

Zerovalent Iron

Commercially available ZVI particles obtained from Peerless Metal Powders and Abrasives Co. (Detroit, MI) were used for comparative tests. Purity of the ZVI ranged from 92 to 95% (by weight), the total carbon content was 3.5% (by weight), the mean particle size was 0.7 mm, and the specific surface area was 0.87 m²/g (Koppensteiner, 1998). The Peerless ZVI particles are larger and have lower specific surface area than the iron in green sands, as will be discussed subsequently.

Chemicals

Alachlor (94% purity) and its dechlorination by-product acetyl alachlor (98% purity) were obtained from Monsanto.

Table 1. Properties of the green sands.

<table>
<thead>
<tr>
<th>Green sand</th>
<th>Particle size characteristics</th>
<th>USCS classification $\dagger$</th>
<th>Specific gravity of solids</th>
<th>TOC $\ddagger$</th>
<th>Total iron content</th>
<th>Saturated hydraulic conductivity $\S$</th>
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<tbody>
<tr>
<td></td>
<td>d$_{50}$†</td>
<td>Fines‡</td>
<td>2-$\mu$m Clay content</td>
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<td>%</td>
<td>%</td>
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<td>6.7</td>
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<td>9.3</td>
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<td>2.64</td>
<td>0.8</td>
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<td>SP–SM</td>
<td>2.73</td>
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<td>4.0</td>
</tr>
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<td>3.5</td>
<td>SP</td>
<td>2.73</td>
<td>2.4</td>
</tr>
</tbody>
</table>

† Median particle size.
‡ Percent finer than 75 $\mu$m.
§ Unified Soil Classification System. SP, poorly graded sand with little or no fines; SM, silty sand; SW, well-graded sand with little or no fines; SC, clayey sand.
¶ Total organic carbon.
# Dry density (Mg/m$^3$) of specimen tested for hydraulic conductivity is shown in parentheses.
Corporation (St. Louis, MO), Novartis Crop Protection (Greensboro, NC) provided the metolachlor (97.3% purity) and its dechlorination by-product (99% purity), which is known as “metolachlor by-product” or MBP. Deuterium oxide, which was used as a tracer, was obtained from Aldrich Chemical Co. (Milwaukee, WI).

**Analytical Methods**

**Herbicides and By-Products**

A Varian (Palo Alto, CA) 3400 gas chromatograph with a flame ionization detector (FID) and DB-5 column (30-m length × 0.25-mm i.d.) was used to analyze for alachlor, metolachlor, and their dechlorination by-products. A 1-μL sample was drawn using a 10-μL gas-tight syringe and manually injected into the gas chromatograph. The detector temperature was set at 300°C and the injector temperature was set at 210°C. Air was used as the carrier gas at a flow rate of 300 mL/min. Helium was used as the make-up gas using a flow rate of 30 mL/min. The column temperature was maintained at 110°C for 6 min and raised to 170°C at 20°C/min until 240°C was reached, at which the temperature was held for 2 min to remove any residuals. The total run time was 25 min. The detection limits for alachlor, acetyl alachlor, metolachlor, and MBP were 0.9, 1.1, 1.0, and 0.8 mg/L, respectively.

Samples were prepared for analysis using the method described in Koppensteiner (1998). A 2-mL sample of solution was extracted into 2 mL of methylene chloride and then mixed using a 5-mL gas-tight syringe, and then prepared for analysis. After tumbling, the vials were centrifuged at 8000 rpm (8200 × g) for 20 min. Samples were obtained from the vials using a 5-mL gas-tight syringe, and then prepared for analysis as described previously. Analyses were conducted for both the herbicides and their dechlorination by-products (acetyl alachlor and MBP). No dechlorination by-products were detected, which suggests that the iron removal process was successful and that dechlorination and degradation during the batch sorption tests were negligible.

**Batch Sorption Tests**

Batch sorption tests were conducted on green sands without iron so that reactivity and sorptivity could be evaluated separately. Sands 1 through 5 and 7 through 12 were tested. Sand 6 was not tested because insufficient quantities of Sand 6 remained after the hydraulic conductivity tests. A strong magnet was passed over the surface of a thin layer of green sand to remove the iron particles. The layer was mixed several times during removal to ensure that the iron particles could be removed from the magnet.

The batch tests were conducted by varying the mass (2–7 g) of green sand and holding the concentration of herbicide constant. Aqueous solutions and green sand were placed into 40-mL Teflon bottles sealed with Teflon caps. Aqueous solutions with no green sand were used as controls to estimate losses. Final concentrations of these controls were assumed to be the initial concentration of the mixtures to account for losses during the test (Zytner, 1992). All samples and controls were treated identically to maintain procedural similarities (Zytner, 1992). The vials were tumbled at 30 rpm.

A series of preliminary tests were conducted to determine the time required to achieve equilibrium. Results of these tests showed that the concentration ceased changing or was changing a very small amount after 24 h of tumbling. Thus, for practical purposes, a tumbling time of 24 h was used for the batch tests.

After tumbling, the vials were centrifuged at 8000 rpm (8200 × g) for 20 min. Samples were obtained from the vials using a 5-mL gas-tight syringe, and then prepared for analysis as described previously. Analyses were conducted for both the herbicides and their dechlorination by-products (acetyl alachlor and MBP). No dechlorination by-products were detected, which suggests that the iron removal process was successful and that dechlorination and degradation during the batch sorption tests were negligible.

**Batch Degradation Tests**

Batch tests were conducted to evaluate the rate of degradation of alachlor and metolachlor in the presence of green sand iron. Tests were also conducted with Peerless iron for comparison. Iron particles for the batch tests were extracted from the green sands using a magnet, washed with methanol, and then dried for 5 min with an external heater set at 40°C for 5 min. No brown oxides (i.e., iron oxyhydroxides) were visible on the washed particles. Iron particles extracted from the green sands were placed in 50-mL glass vials filled completely with solution (no headspace). Controls without iron were prepared in an identical manner. The vials were loaded on a tumbler and rotated at 30 rpm.

Vials were removed from the tumbler intermittently for analysis. The vial was allowed to sit for 5 min so the iron particles would settle, and then a 5-mL gas-tight syringe was used to collect a 2.5-mL sample. The sample was filtered through a 0.45-μm Teflon syringe filter and prepared for analysis as described previously.

A first-order decay model with instantaneous sorption was used to determine the bulk reaction rate constant ($K_{obs}$) and the iron-phase partition coefficient ($K_{p,H}$) for both herbicides. The model is (Koppensteiner, 1998):

$$C_{rH}(t) = C_{0}(t) = \frac{C_{0}}{K_{p,H}S_{0} + 1} \exp \left( \frac{-K_{obs}t}{K_{p,H}S_{0} + 1} \right)$$

where $C_{rH}$ is the concentration of herbicide in the batch reactor at time $t$ (mg/L), $C_{0}$ is the initial herbicide concentration (mg/L), $K_{obs}$ is the bulk first-order decay rate constant (h$^{-1}$), and $S_{0}$ is...
solid to solution ratio (kg/L). Equation [1] was fit to the data using a least-squares algorithm to obtain $K_{obs}$ and $K_p$. Typical fits of Eq. [1] are shown in Fig. 1 for batch tests conducted with iron particles from Sand 11.

Analyses were conducted to determine concentrations of the herbicides as well as their dechlorination by-products to confirm that dechlorination was occurring and to conduct mass balances. Dechlorination by-products were observed in all tests and mass balances of 94% (alachlor) and 96% (metolachlor) were obtained. Moreover, the rate of depletion of both herbicides agreed closely with the rate at which the dechlorination by-products accumulated (Lee and Benson, 2002).

**Column Tests**

Column tests were conducted to determine partition coefficients and rate constants for flow-through conditions. A schematic of the column test setup is shown in Fig. 2. A glass column (length = 450 mm, diameter = 25 mm) was used with Teflon adapters and porous ceramic disks attached to both ends. A glass fiber filter was placed between the porous disk and the reactive medium to prevent clogging. At least two pore volumes of Madison tap water were passed through the column initially. The influent solution was then switched to a herbicide solution for the column test. After finishing a test with herbicide solution, D$_2$O solution (10% by weight) was introduced as a conservative tracer to determine the effective porosity.

Solution was introduced into the columns at a constant flow rate (2.2 $\times$ 10$^{-4}$ L/min) using a peristaltic pump. All tests were conducted with upward flow. The influent was contained in a 2-L Teflon bag. All contact parts in the pump were made of Teflon, except for the tubing, which was Viton. Concentrations of alachlor or metolachlor in the influent ranging between 34 and 55 mg/L were used. A loss of approximately 3% occurred when the herbicides passed through the pump, but a constant influent concentration (+2.6% for alachlor, +3.5% for metolachlor) was maintained during testing (Lee and Benson, 2002).

Samples of the influent and effluent were collected from the sampling ports (Fig. 2) at regular intervals. Approximately 2 mL of solution was transferred to a 4-mL glass vial in less than 1 min, and was immediately prepared for analysis as described previously. Samples were stored in a refrigerator at 4°C before analysis and were manually injected into the gas chromatograph using a gas-tight syringe.

The bulk reaction rate constant ($K_{obs}$), partition coefficient ($K_p$), dispersivity ($\alpha_4$), and effective porosity ($n_e$) were determined for each column test by fitting the relative concentration ($C_e/C_0$) data to an analytical solution of the advection–dispersion–reaction equation (ADRE) with instantaneous sorption. Typical fits are shown in Fig. 3a. The solution to the ADRE that was used is (van Genuchten, 1981):

$$
\frac{C_e}{C_0} = \frac{1}{2} \exp \left( \frac{(v - u)L}{2D} \right) \text{erfc} \left( \frac{RL - ut}{2\sqrt{D}t} \right) + \frac{1}{2} \exp \left( \frac{(v + u)L}{2D} \right) \text{erfc} \left( \frac{RL + ut}{2\sqrt{D}t} \right) [2]
$$

where $C_e$ is the concentration at the effluent end of the column at time $t$, $C_0$ is the influent concentration, $L$ is the column length, $v$ is the seepage velocity (discharge velocity/effective porosity), $D$ is the effective dispersion coefficient, $R$ is the retardation factor, $\exp$ is the exponential function, and erfc is the complementary error function. This analytical solution is derived for the first-type initial and boundary conditions (i.e., background concentration is assumed to be zero, influent concentration is constant, and the concentration gradient is zero at great distance from the influent boundary). The variable $u$ in Eq. [2] is:

$$
u = v\left(1 + \frac{4K_{obs}D}{v^2}\right)^{1/2} [3]
$$

Use of Eq. [3] implicitly assumes that degradation of ad-
The dispersion coefficient ($D$) obtained by fitting Eq. [2] to the column test data is the sum of the mechanical dispersion coefficient ($D_m$) and the molecular diffusion coefficient ($D^*$). The dispersivity ($\alpha$) is related to the mechanical dispersion coefficient $D_m$ via (Freeze and Cherry, 1979):

$$\alpha_L = D_m/v$$  \hfill [6]

A least squares algorithm was used for fitting Eq. [2] to the data (Lee and Benson, 2002). Equation [2] was fit to the relative concentrations of D$_2$O with $R = 1$ and $K_{oa} = 0$ to determine $\nu$ and $D$. The specific discharge (known from the pumping rate and the cross-sectional area of the test specimen) was divided by $v$ to obtain $n_c$ and $\alpha_L$ was computed from $D$ using Eq. [6]. The molecular diffusion coefficient ($D^*$) in Eq. [6] was obtained from Yaws (1995) and was reduced by a factor of 0.4 to account for tortuosity. However, the solution was not sensitive to $D^*$ because $D$ was dominated by $D_m$ at the flow rates that were used. Equation [2] was fit to the relative concentrations of alachlor and metolachlor to obtain $K_{oa}$ and $K_p$. During these fits, $u$ and $R$ were fitting parameters, $\nu$ was set at the value obtained from the tracer test, and $D_m$ was computed with Eq. [6] using $\alpha_L$ and $v$ from the tracer test. Equation [3] was used to compute $K_{oa}$ from $u$ and Eq. [4] was used to compute $K_p$ from $R$. The bulk reaction rate ($K_{oa}$) was also computed independently from the steady-state effluent concentration using Eq. [3] and [5]. The Fe-normalized rate constant ($K_{oa}$/Fe) was computed as $K_{oa}$/SSA, where SSA is the specific surface area of iron per volume of solution in the column.

Two control tests were conducted with Portage sand to assess the potential for sorption on the tubing and glass column. One test was conducted with alachlor and the other with metolachlor. Portage sand is a poorly graded silica sand from a sand deposit in Portage, WI. The sand has a median particle size of 1.8 mm, a uniformity coefficient of 2.0, a coefficient of curvature of 1.39, and a classification of SP in the Unified Soil Classification System. The sand was washed with deionized water until any visible impurities were removed, air-dried, and packed in the glass column. The control test was conducted in the same manner as all other column tests.

Breakthrough curves for alachlor and metolachlor from the control tests are shown in Fig. 3b. The relative concentration reaches steady state at unity, indicating that no continuous losses were occurring. Fitting Eq. [2] to the data yielded partition coefficients of 1.56 L/kg for alachlor and 0.23 L/kg for metolachlor. This modest partition coefficient is believed to be due in part to organic carbon in the sand. To assess this possibility, the partition coefficients for alachlor and metolachlor were estimated using the empirical equation from Briggs (1981):

$$K_p = \frac{f_w}{K_{oa}} \cdot 10^{A \log K_{oa} + B}$$  \hfill [7]

where $f_w$ is weight fraction of organic carbon in the Portage sand, $K_{oa}$ is the octanol–water partition coefficient, and $A$ and $B$ are empirical constants. The empirical constants $A$ and $B$ were set at 0.52 and 0.88, respectively, as reported by Briggs (1981). The $f_w$ for the Portage sand was determined using the same procedure used for the green sands and was found to be 0.2%. The $K_p$ values for alachlor and metolachlor estimated using this approach are 0.35 and 0.94 L/kg, respectively, which suggests the modest amount of partitioning observed in the control tests may have been due to the presence of organic carbon. Regardless, the $K_p$ obtained from the control tests are small relative to the $K_p$ obtained for most of the green sands. Thus, losses to the column materials are believed to have been negligible.

RESULTS AND DISCUSSION

Batch Tests

Batch Sorption Tests

Sorption isotherms for alachlor and metolachlor obtained from the batch tests on green sands without iron
are shown in Fig. 4 and 5 along with fits of the linear isotherm. Between 5 and 12 individual batch tests were conducted on each sand to develop an isotherm. No replicate tests were conducted, but each isotherm follows a well-defined trend without excessive scatter. Thus, the isotherms are believed to be reliable despite the lack of replication.

All of the isotherms are approximately linear within the range of concentrations that was tested. Partition coefficients for alachlor and metolachlor were obtained by fitting data from the batch tests to linear and Freundlich isotherm models using a least-squares algorithm. The parameters of the linear and Freundlich models are summarized in Table 2. Good fits were obtained with both isotherm models for the range of concentrations that were used.

Partition coefficients obtained from the linear model range from 3.6 L/kg (Sand 9) to 50.2 L/kg (Sand 11) for alachlor and 1.0 L/kg (Sand 9) to 54.8 L/kg (Sand 11) for metolachlor and generally are within the range typically reported for soils with TOC similar to the green sands (Peter and Weber, 1985; Chesters et al., 1989; Johnson and Sims, 1993; Gaston and Locke, 1994; Seybold and Mersie, 1996; Clay et al., 1997; Wang et al., 1999; Patkioutas and Albanis, 2002). The fits with the Freundlich model confirm that the isotherms are essentially linear. Except for Sands 1, 3, and 4 (alachlor) and Sands 5 and 8 (metolachlor), the Freundlich parameter \(1/n\) is approximately 1. Similar values of \(1/n\) have been reported by Seybold and Mersie (1996), Wang et al. (1999), and Patkioutas and Albanis (2002) for organic soils, but slightly smaller values have been reported Clay et al. (1997).

The \(K_p\) values for alachlor and metolachlor are shown as a function of TOC and clay content in Fig. 6. The open circles are data points and the numbers in italics adjacent to the open circles are the measured \(K_p\). The contours were prepared with the minimum curvature algorithm in Surfer (Version 8.04; Golden Software, 2002). For both alachlor and metolachlor, \(K_p\) generally increases with TOC and clay content. For example, Sand 9 has the lowest \(K_p\) (3.6 L/kg for alachlor and 1.0 L/kg for metolachlor) as well as the lowest TOC and clay content of all sands. Similarly, Sand 11 has the highest \(K_p\) (50.2 L/kg for alachlor and 54.8 L/kg for metolachlor)
Table 2. Isotherm parameters from batch sorption tests.

<table>
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<tr>
<th>Green sand</th>
<th>Alachlor</th>
<th></th>
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<th>Metolachlor</th>
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<tr>
<td></td>
<td>Linear model</td>
<td></td>
<td>Freundlich model</td>
<td></td>
<td>Linear model</td>
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<tr>
<td></td>
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<td>$R^2$</td>
<td>$K_f$‡</td>
<td>$1/n$</td>
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<td>15.4</td>
</tr>
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</table>

† Partition coefficient.  
‡ Freundlich coefficient.

and the highest TOC and clay content. Both TOC and clay content are important because the herbicides have polar functional groups that permit hydrogen bonding to mineral surfaces (Chesters et al., 1989; Grundl and Small, 1993; Wang et al., 1999). For example, Sand 4 has relatively high $K_p$ (18.9 L/kg) because the sand has high clay content (10.5%) even though the TOC is low (0.5%).

A direct assessment of the relative contributions of the clay fraction and organic carbon in the green sands was not possible because the proportions of TOC, clay, and nonclay particles could not be determined with the data that were available. However, the relative contributions of mineral solids and organic carbon to the partition coefficient were estimated using the linear mixing model described in Grundl and Small (1993):

$$K_p = (1 - f_{oc})K_m + f_{oc}K_{oc}$$  \[8\]

where $f_{oc}$ is the fraction of organic carbon ($f_{oc} = \text{TOC}/100$), $K_m$ is the partition coefficient for the mineral solid, and $K_{oc}$ is the partition coefficient for the organic carbon. Least-squares regression was used to determine $K_m$ and $K_{oc}$ from the partition coefficients for the linear isotherms in Table 2. The regression yielded $K_m = 0.65$ L/kg and $K_{oc} = 809$ L/kg for alachlor and $K_m = 0.50$ L/kg and $K_{oc} = 854$ L/kg for metolachlor.

The $K_{oc}$ and $K_m$ values obtained from the regression analysis are similar to those reported by Grundl and Small (1993) for surficial organic soils having similar TOC as the green sands, but are larger than $K_{oc}$ reported for soils with low organic carbon content (<1.3%) by John-

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Fig. 6. Contours of partition coefficient (L/kg) as a function of total organic carbon (TOC) and 2-μm clay content for (a) alachlor and (b) metolachlor. Open circles represent data points. Numbers in italics next to data points are measured partition coefficients. Numbers in bold are contour intervals for the partition coefficient.
son and Sims (1993) and Seybold and Mersie (1996). The large $K_{oc}$ demonstrates the affinity of the organic carbon fraction for alachlor and metolachlor. However, sorption on the mineral fraction is also important. Even though $K_{oc}$ is much smaller than $K_{pi}$, the mass of mineral solid in green sands is much greater than the mass of organic carbon, making sorption on the mineral solid appreciable. The clay fraction likely is responsible for most of the sorption on mineral solids, as suggested by Peter and Weber (1985) and Wang et al. (1999). This inference is also consistent with the larger $K_{pi}$ associated with green sands having higher clay content (Table 2).

**Batch Degradation Tests**

Batch degradation tests were conducted with iron from the green sands as well as Peerless ZVI for comparison. The parameters obtained from the model fits are summarized in Table 3. Rate constants and iron partition coefficients from tests conducted by Koppensteiner (1998) and Eykholt and Davenport (1998) using Peerless granular ZVI are also shown in Table 3. The rate constants in Table 3 ($K_{SA}$) are normalized by SSA (i.e., $K_{SA} = K_{pi}/SSA$).

The $K_{SA}$ obtained for the green sands iron is comparable with, but slightly larger (approximately 10%), than the $K_{SA}$ obtained for Peerless iron for both alachlor and metolachlor. The green sand $K_{pi}$ values are similar to the $K_{pi}$ values for Peerless iron. The $K_{SA}$ measured in this study also fall within the range reported by Eykholt and Davenport (1998) and Koppensteiner (1998) for Peerless ZVI ($K_{SA} = 3.9 \times 10^{-4}$ to $1.5 \times 10^{-3}$ L/m$^2$-h for alachlor and $3.3 \times 10^{-4}$ to $9.9 \times 10^{-4}$ L/m$^2$-h for metolachlor). However, the bulk reactivity of the green sand iron is higher than that of Peerless iron because the green sand has higher surface area than Peerless iron (2.45 vs. 0.87 m$^2$/g).

Although particle size analyses were not conducted on the green sand iron, visual comparison of green sand iron and Peerless iron showed that green sand iron consists of particles that are appreciably finer and more uniform than Peerless iron. The smaller particle size results in more surface area and greater reactivity per mass of iron. Green sands contain smaller iron particles because the particles are often derived from small pieces of flashing as well as residuals from grinding (the latter forming very fine particles), whereas commercial iron particles often are from recycled iron from machining operations.

**Column Tests**

The column tests differed from the batch tests in several important ways. Column tests simulate flow-through conditions where solid–liquid contact may be limited. Rate limitations may also exist or be exacerbated due to mass transfer restrictions between solutes in different pore spaces (e.g., pores active in flow and less accessible pores). Additionally, the batch tests were conducted to evaluate sorption and dechlorination separately, whereas both processes occur simultaneously during column tests. A key issue is whether transport parameters obtained from relatively simple batch tests (i.e., partition coefficients and rate constants) are comparable with those operative during flow-through conditions, which occur in column tests and the field.

Transport parameters obtained from the column tests are summarized in Table 4. Five green sands (1, 2, 4, 5, and 12) having a broad range of TOC, clay content, and iron content were used for the tests with alachlor. Tests with alachlor were also conducted with Sands 1 and 5 using admixtures of Peerless ZVI (10 and 20% by weight, respectively) to evaluate how elevated iron content affects reactivity of the green sand. Three green sands (1, 5, and 12) were used for the tests conducted with metolachlor. Two of the tests with Sands 1 and 5 contained an admixture of 20% Peerless iron (by weight). The tests with ZVI admixtures are reported in Table 4 for alachlor and 3.3 L/m$^2$-h for metolachlor. However, the bulk reactivity of the green sand has higher surface area than Peerless iron (2.45 vs. 0.87 m$^2$/g).

**Effective Porosity and Dispersivity**

The effective and total porosities are summarized in Table 4, along with the ratio of effective to total porosity. The ratio of effective to total porosity ranges from 0.82 to 1.0, which is comparable with ranges reported by others for compacted fine-textured soils (Kim et al., 1997; Bin-Shafique et al., 2002). The dispersions are

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**Table 3. Results of batch degradation tests for alachlor and metolachlor using foundry iron and Peerless granular zerovalent iron (ZVI).**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Iron source</th>
<th>Initial concentration</th>
<th>SSA†</th>
<th>$K_{SA}$$\dagger$</th>
<th>$K_{FA}$$\ddagger$</th>
<th>$K_{pi}$$\¶$</th>
<th>$K_{FA}$$\§$</th>
<th>$K_{pi}$$\¶$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alachlor</td>
<td>green sand</td>
<td>49 mg/L</td>
<td>186</td>
<td>1/8</td>
<td>0.148</td>
<td>7.9 $\times 10^{-4}$</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Alachlor</td>
<td>Peerless</td>
<td>49 mg/L</td>
<td>40</td>
<td>0.0029</td>
<td>7.1 $\times 10^{-4}$</td>
<td>3.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alachlor‡‡</td>
<td>Peerless</td>
<td>11 mg/L</td>
<td>308</td>
<td>0.12</td>
<td>3.9 $\times 10^{-4}$</td>
<td>3.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alachlor‡‡</td>
<td>Peerless</td>
<td>9 mg/L</td>
<td>28</td>
<td>0.042</td>
<td>1.5 $\times 10^{-3}$</td>
<td>3.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metolachlor</td>
<td>green sand</td>
<td>84 mg/L</td>
<td>186</td>
<td>0.10</td>
<td>5.5 $\times 10^{-4}$</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metolachlor</td>
<td>Peerless</td>
<td>38 mg/L</td>
<td>22</td>
<td>0.011</td>
<td>5.1 $\times 10^{-4}$</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metolachlor</td>
<td>Peerless</td>
<td>14 mg/L</td>
<td>308</td>
<td>0.10</td>
<td>3.3 $\times 10^{-4}$</td>
<td>8.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metolachlor‡‡</td>
<td>Peerless</td>
<td>9 mg/L</td>
<td>28</td>
<td>0.028</td>
<td>9.9 $\times 10^{-4}$</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

† Specific surface area of iron per unit volume of solution.
" Bulk first-order decay rate constant.
§ Normalized first-order rate constant.
¶ Iron-phase partition coefficient for herbicide.

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also summarized in Table 4, along with estimates made assuming the dispersivity equals 10% of the column length. The measured and estimated dispersivities are typically within a factor of 2, which suggests that the fits of Eq. [2] are reasonable.

**Rate Constants and Partition Coefficients**

The normalized first-order rate constants \( K_{SA} \) and partition coefficients are summarized in Table 4. Two \( K_{SA} \) are reported for each test. One of the \( K_{SA} \) values was obtained by fitting Eq. [2] to the entire breakthrough data set; the other was obtained by fitting Eq. [5] to the steady-state concentrations in the latter part of each test. Both methods yield essentially the same \( K_{SA} \), which suggests that the fits to Eq. [2] are reasonable. The similarity of the \( K_{SA} \) also suggests that assuming instantaneous sorption, which is implicit in Eq. [2], is reasonable for the relatively low flow rates that are characteristic of many ground water applications (and the column tests). Difficulties incurred when analyzing the effluent from Sand 12 prevented determination of the entire breakthrough curve. Thus, \( K_{obs} \) and \( K_{SA} \) were only computed from the steady-state portion of the breakthrough curve for Sand 12 (hyphens are shown in Table 4 for parameters obtained from Eq. [2]). Nevertheless, the \( K_{SA} \) for Sand 12 is comparable with the \( K_{SA} \) obtained for the other sands.

The bulk first-order rate constant \( K_{obs} \) for alachlor is shown as a function of SSA in Fig. 7. The slope of the trend line in Fig. 7, which was obtained by linear regression, equals the average \( K_{SA} \) for the green sands \((5.2 \times 10^{-4}\) L/m²-h). This average \( K_{SA} \) is similar to but slightly smaller than the \( K_{SA} \) obtained from the batch degradation tests \((7.9 \times 10^{-4}\) L/m²-h for Peerless iron). Moreover, the relationship between \( K_{obs} \) and SSA obtained from the column tests is essentially the same for the green sand iron and Peerless iron, suggesting that both materials have similar reactivity. The \( K_{SA} \) values for Sands 1 and 5 containing an admixture of Peerless iron also fall along the same trend line suggesting that the reactivities obtained from the batch and column tests for green sand and Peerless iron are comparable. A similar relationship was obtained between \( K_{obs} \) and SSA for metolachlor, but with more scatter (Lee and Benson, 2002). Regression of \( K_{obs} \) for metolachlor on SSA yielded \( K_{SA} = 3.8 \times 10^{-4}\) L/m²-h for Peerless iron.

Partition coefficients obtained from the fits to Eq. [2] are also summarized in Table 4. A partition coefficient
was not computed for Sand 12 due to the difficulty mentioned previously. A comparison of the partition coefficients from the batch tests (linear isotherm) and column tests for alachlor and metolachlor is shown in Fig. 8. The partition coefficients from the batch and column tests generally are within ±25%, but the column tests typically yielded lower partition coefficients for green sands exhibiting greater sorption. One possible reason for this difference may be the different solid to solution ratios in the batch and column tests. Solid concentrations in batch tests ranged between 50 and 175 g/L, whereas the solid concentration in the column tests was approximately 4250 g/L (i.e., the solid concentration for the column tests is about 38 times larger than that of the batch tests). The modest variation in solid to solution ratio during the batch tests may also have contributed to the differences in the partition coefficients. O’Connor and Connolly (1980) report that partition coefficients for organic compounds can be reduced as much as 38% when the solid concentration is increased by an order of magnitude because closer contact between the soil solids prevents organic compounds from accessing the solid surface. Doust and Huang (1992) also report that $K_p$ decreases as the solids concentration increases.

### Long-Term Tests

The column tests with Sand 12 and the Portage sand–iron mixture were continued over a longer time period to assess persistence of the reactivity. Nearly 1500 pore volumes passed through the test with Sand 12, and 600 pore volumes passed through the test with the Portage sand–iron mixture. The $K_{sa}$ values were computed using Eq. [5], and are shown in Fig. 9. A gradual reduction in $K_{sa}$ occurred between 300 and 400 pore volumes of flow for both tests, and the final $K_{sa}$ was two to three times lower than the initial $K_{sa}$. This slight reduction in $K_{sa}$ may have been due to oxide formation on the surface of the iron, although an analysis of the iron surface was not conducted.

### Practical Implications

Calculations were made with Eq. [5] to estimate the required thickness of RBs constructed with green sands having different iron contents. The dispersion coefficient was computed using Eq. [6] using a dispersivity equal to one-tenth of the barrier thickness. The aqueous diffusion coefficient was assumed to be $9 \times 10^{-6}$ cm$^2$/s, which is a typical value for common organic ground water contaminants (Yaws, 1995). The effective molecular diffusion coefficient was estimated as the aqueous diffusion coefficient multiplied by a tortuosity of 0.4. Iron content of the green sand was varied from 0.1 to 12%. Typical values were assumed for dry density (1.5 Mg/m$^3$) and specific gravity of solids (2.62) when calculating the SSA. The bulk first-order rate constant was calculated by multiplying the SSA for a given iron content by the average $K_{sa}$ for the green sands obtained from the column tests. Sorption was ignored, although it may be important if degradation can occur while the herbicide is adsorbed.

The seepage velocity was varied between 0.1 and 1.0 m/d, which is characteristic of field conditions (O’Hannesin and Gillham, 1998; McMahon et al., 1999; Mayer et al., 2001; Yabusaki et al., 2001). At these seepage velocities, the molecular diffusion coefficient only contributes 0.1% to the dispersion coefficient. Thus, the value assumed for the molecular diffusion coefficient has no appreciable effect on the computed barrier thickness. The influent concentration ($C_0$) was varied between 5 and 50 μg/L for alachlor.
may be feasible for RBs used to treat alachlor and metolachlor, there are other practical issues that need to be resolved before green sands can be used at full scale. For example, little is known about the long-term reactivity (i.e., over years or decades) of the iron in green sands. Other issues that need to be considered include in situ leaching characteristics, availability and fluctuations in the green sand supply, transportation costs to the project site, and variability in the properties of green sands (e.g., due to variations in foundry operations). Some of these issues can be inferred using existing data from full-scale RBs using ZVI. Others need to be evaluated by additional study or on a site-specific basis. Examples of site-specific issues include the potential for additional costs incurred by constructing a thicker barrier using green sands (relative to a barrier constructed with granular iron) and regulatory hurdles associated with using an industrial by-product in an application below the ground water table.

CONCLUSIONS

The objective of this study was to evaluate the potential of using waste green sands from gray-iron foundries as inexpensive media for reactive barriers (RBs) used to treat ground water contaminated with alachlor or metolachlor. Batch and column tests were conducted to evaluate the reactivity and sorptive capacity of 11 green sands. Results of the tests showed that green sands have a high sorption capacity for alachlor and metolachlor, with partition coefficients ranging from 3.6 to 50.2 L/kg for alachlor and 1.0 to 54.8 L/kg for metolachlor. A linear sorption model can be used to describe the sorption isotherms. Partition coefficients obtained from the batch and column tests generally were within ±25%, although the partition coefficients from the column tests tended to be lower than those from the batch tests for more sorptive sands. Differences in the solid to solution ratios may be responsible for these differences in the partition coefficients.

Normalized degradation rate constants obtained from the batch tests were similar for green-sand iron and conventional granular ZVI, which suggests that the iron in the green sands has comparable reactivity as conventional granular ZVIs used in RBs. Column tests conducted with green sands also yielded similar normalized rate constants regardless of the sand source, and the rate constants obtained from the column tests were also similar to those from batch tests.

Normalized concentrations for alachlor and metolachlor are shown in Fig. 10 for various zerovalent iron contents and barrier thicknesses. The horizontal lines on each graph correspond to the $C/C_0$ needed to meet the MCL for the range of influent concentrations being considered. For seepage velocities less than 0.1 m/d, a 1-m-thick RB will reduce concentrations below the MCL for typical concentrations found in ground water if the iron content exceeds 1%. When the seepage velocity is 1.0 m/d and the barrier thickness is 1.0 m, iron contents on the order of 6 to 8% are required.

Although these calculations indicate that green sands and 150 to 1500 µg/L for metolachlor, which bounds most conditions observed in the field (Spalding et al., 2003). Maximum contaminant levels (MCLs) for alachlor and metolachlor in the United States are 0.5 and 15 µg/L, respectively (Chesers et al., 1989). Accordingly, the normalized concentration required to meet the MCL (i.e., MCL/$C_0$) ranges between 0.1 and 0.01 for the $C_0$ that were used.

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