Zerovalent Iron Nanoparticles for Treatment of Ground Water Contaminated by Hexachlorocyclohexanes

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Ground water and aquifer samples from a site contaminated by hexachlorocyclohexanes (HCHs; C₆H₆Cl₆) were exposed to nanoscale iron particles to evaluate the technology as a potential remediation method. The summed concentration of the HCH isomers in ground water was approximately 5.16 μmol L⁻¹ (1500 μg L⁻¹). Batch experiments with 2.2 to 27.0 g L⁻¹ iron nanoparticles showed that more than 95% of the HCHs were removed from solution within 48 h. Using a pseudo first-order kinetics model, the HCH isomers were removed in accordance with the trend γ > α > β > δ. This seems to be correlated with the orientation (axial vs. equatorial) of the chlorine atoms lost in the dihaloelimination steps. Although the reactivity of the HCH isomers has been investigated in the classical organic chemistry literature, the present study was the first in the environmental remediation arena. The rate of removal is directly correlated to the number of axial chlorines. The observed rate constant varied from 0.04 to 0.65 h⁻¹, and the rate constant normalized to the iron surface area concentration ranged from 5.4 × 10⁻⁴ to 8.8 × 10⁻⁴ L m⁻² h⁻¹. Post-test extractions of the reactor contents detected little HCH remaining in solution or on the iron surfaces, reinforcing the contention that reaction rather than sorption was the operative mechanism for the HCH removal. Together with previously published work on a wide variety of chlorinated organic solvents, this work further demonstrates the potential of zerovalent iron nanoparticles for treatment and remediation of persistent organic pollutants.

The hexachlorocyclohexanes (HCHs) are a well known group of persistent organic pollutants (POPs) and a widely studied class of organochlorine pesticides. First synthesized by Michael Faraday in 1825, the HCHs have garnered considerable research and regulatory attention over the years because of their toxicity, extensive global usage, and relative persistence in the environment (Kolpin et al., 1998; Willett et al., 1998; Walker et al., 1999). The highly toxic gamma isomer of HCH, better known as lindane, is regulated under the U.S. National Primary Drinking Water Standards with a maximum contaminant level of 0.2 μg L⁻¹ (USEPA, 2002). Although the HCHs are not generally regarded as major threats to surface and ground waters, past improper handling, storage, and disposal practices have resulted in contaminant plumes at some sites that exceed the maximum contaminant level by two or three orders of magnitude (Law et al., 2004). Considering that approximately 10 million tons of HCHs were consumed globally between 1948 and 1997, it is reasonable to assume that many HCH-contaminated sites exist throughout the world (Willett et al., 1998).

The synthesis of HCHs typically results in a mixture of isomers with an approximate composition as follows: 60 to 70% α-HCH, 10 to 12% γ-HCH, 5 to 12% β-HCH, 6 to 10% δ-HCH, and 3 to 4% ε-HCH (Slade, 1945; Willett et al., 1998). Of this mixture, generally referred to as technical grade HCH, all except the latter isomer are of major environmental significance. These isomers are depicted in Fig. 1. The principal difference among the HCH isomers concerns the orientation (e.g., axial vs. equatorial) of the chlorine substituents around the cyclohexane ring. The HCH isomers contain from three (γ) to six equatorial (β) chlorines and from zero (δ) to three (γ) axial chlorines (Fig. 1 and Table 1). In general, it is energetically more favorable for bulky substituents like chlorine to be located in the more spacious equatorial position (Morrison and Boyd, 1987). Stated another way, equatorial chlorine substituents contribute toward lower overall energy than their axial counterparts and therefore have greater stability (i.e., lower reactivity). Thus, isomers with the largest ratio of axial to
equatorial chlorines are expected to be more reactive toward iron nanoparticles. Theoretically, one would expect to observe progressively increasing reactivity along the series \( \beta < \delta < \alpha < \gamma \). Although the classical organic chemistry literature includes studies of the role of HCH structure on reactivity, the present work is, to our knowledge, the first such investigation in the environmental remediation arena (Cristol, 1947; Cristol et al., 1951). Moreover, it is the first assessment of the amenability of iron nanoparticles to degrade the HCHs. These structural differences contribute to the varying physical and chemical properties of the HCH isomers, which are summarized in Table 1.

![Fig. 1. Structures of the environmentally significant hexachlorocyclohexane (HCH) isomers, including the two \( \alpha \)-HCH enantiomers (Willett et al., 1998).](image)

Zero valent iron (ZVI) has been the subject of intense research interest over the past decade for its potential to remediate a wide variety of environmental contaminants in surface and ground water. The majority of the ZVI research has focused on the degradation of relatively simple one- and two-carbon chlorinated hydrocarbons using primarily granular or microscale iron (Gillham and O’Hannesin, 1994; Matheson and Tratnyek, 1994; Johnson et al., 1996; Arnold and Roberts, 2000). In recent years, the focus has expanded to include other potentially amenable contaminants and contaminant classes, including nitrate, pesticides, radionuclides, and toxic

<table>
<thead>
<tr>
<th>Isomer</th>
<th>Solubility</th>
<th>Vapor pressure</th>
<th>Henry’s law constant ( K_H )</th>
<th>( \log K_{ow} )</th>
<th>Axial vs. equatorial chlorine positions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma )-HCH</td>
<td>6–10 mg L(^{-1} )</td>
<td>( 3.5 \times 10^{-3} ) Pa</td>
<td>0.149</td>
<td>2.81–3.89</td>
<td>3 axial, 3 equatorial</td>
</tr>
<tr>
<td>( \alpha )-HCH</td>
<td>6–10 mg L(^{-1} )</td>
<td>( 4.4 \times 10^{-2} ) Pa</td>
<td>0.872</td>
<td>3.80–4.44</td>
<td>2 axial, 2 equatorial</td>
</tr>
<tr>
<td>( \beta )-HCH</td>
<td>&lt;1 mg L(^{-1} )</td>
<td>( 4.3 \times 10^{-5} ) Pa</td>
<td>0.116</td>
<td>3.78–4.15</td>
<td>0 axial, 6 equatorial</td>
</tr>
<tr>
<td>( \delta )-HCH</td>
<td>6–10 mg L(^{-1} )</td>
<td>( 2.0 \times 10^{-3} ) Pa</td>
<td>0.0825</td>
<td>4.14</td>
<td>1 axial, 5 equatorial</td>
</tr>
</tbody>
</table>

† The data represent an average of the range of values reported.
‡ The logarithm of the octanol-water partition coefficient \( K_{ow} \).
Table 2. Representative snapshot of site ground water quality.†

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Recent value</th>
<th>Type</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-HCH, μg L⁻¹</td>
<td>520</td>
<td>pesticide</td>
<td>no enantiomeric distinction</td>
</tr>
<tr>
<td>β-HCH, μg L⁻¹</td>
<td>138</td>
<td>pesticide</td>
<td></td>
</tr>
<tr>
<td>γ-HCH, μg L⁻¹</td>
<td>475</td>
<td>pesticide</td>
<td></td>
</tr>
<tr>
<td>δ-HCH, μg L⁻¹</td>
<td>390</td>
<td>pesticide</td>
<td></td>
</tr>
<tr>
<td>ε-HCHs, μg L⁻¹</td>
<td>1523</td>
<td>pesticide</td>
<td>summation of HCH§ isomers</td>
</tr>
<tr>
<td>Benzene, μg L⁻¹</td>
<td>75</td>
<td>volatile</td>
<td>organic</td>
</tr>
<tr>
<td>Xylenes, μg L⁻¹</td>
<td>75</td>
<td>volatile</td>
<td>organic</td>
</tr>
<tr>
<td>pH</td>
<td>2.4</td>
<td>conventional</td>
<td></td>
</tr>
<tr>
<td>Dissolved O₂, mg L⁻¹</td>
<td>&lt;1</td>
<td>conventional</td>
<td>near anaerobic conditions</td>
</tr>
<tr>
<td>Oxygen-reduction potential, mV</td>
<td>+50 – +150</td>
<td>conventional</td>
<td>moderately reducing conditions</td>
</tr>
<tr>
<td>Total dissolved solid, mg L⁻¹</td>
<td>2800</td>
<td>conventional</td>
<td></td>
</tr>
<tr>
<td>Sulfate, mg L⁻¹</td>
<td>2650</td>
<td>conventional</td>
<td></td>
</tr>
<tr>
<td>Chloride, mg L⁻¹</td>
<td>50</td>
<td>conventional</td>
<td></td>
</tr>
<tr>
<td>Iron, mg L⁻¹</td>
<td>239</td>
<td>conventional</td>
<td>total, unfiltered; exists as Fe²⁺</td>
</tr>
</tbody>
</table>

† The data reflect relatively recent site conditions and are representative of the ground water samples tested in this research.
‡ HCH, hexachlorocyclohexane.

Since 1996, we have actively investigated the ability of iron and bimetallic (e.g., Fe/Pd and Fe/Ag) nanoparticles to treat a wide variety of contaminants, including chlorinated solvents (Zhang et al., 1998; Lien and Zhang, 1999, 2001, 2005; Zhang, 2003), polychlorinated biphenyls (PCBs) (Wang and Zhang, 1997), chlorinated benzenes (Xu and Zhang, 2000), perchlorate (Cao et al., 2005), and heavy metals (Cao and Zhang, 2006; Li and Zhang, 2006, 2007) in laboratory studies and field applications. In these studies, the average particle diameter of the nanoscale iron was generally two orders of magnitude smaller than the commercially available iron powder (i.e., microscale iron) used in ZVI remediation studies. The much larger specific surface area of the nanoparticles translates into potentially significantly enhanced reactivity because the zero valent metal degradation reactions are surface mediated. Surface area normalized rate constants (kₐ) from experiments with nanoscale palladized iron are typically one to two orders of magnitude larger than those for microscale iron under similar conditions (Lien and Zhang, 2001). Lowry and Johnson (2004) indicated the capability of iron nanoparticles for degrading PCBs. The nanoparticle technology is considered well suited for in situ treatment of contaminant hot-spots given its high reactivity, portability, and flexible deployment in the field (Elliott and Zhang, 2001; Li et al., 2006b).

In this research, slurries of nanoscale iron (nZVI) were added to batch reactors containing HCH-contaminated ground water to evaluate its potential utility as a remediation tool. Process effectiveness was evaluated in terms of the extent of contaminant loss from solution and the rate (e.g., kinetics) of removal. Other key factors were the role of varying iron dose and the presence of indigenous aquifer solids on the contaminant removal process.

Materials and Methods

Site Overview and Ground Water Quality

The contaminated ground water and aquifer solids samples used in this study were obtained from an active pesticides manufacturing and formulating site in Jacksonville, Florida. The samples were collected within a contaminant source area affected by past waste disposal activities. Uncontaminated ground water from the area is of near-neutral pH, with calcium and bicarbonate being the dominant cation and anion, respectively. Major ground water contaminants in site ground water include the four HCH isomers, benzene, and xylene (Table 2). Using the gas chromatographic method described herein, the average initial concentration of the isomers was as follows: α-HCH = 520 μg L⁻¹, β-HCH = 138 μg L⁻¹, γ-HCH = 475 μg L⁻¹, and δ-HCH = 390 μg L⁻¹. The pH of the source area ground water was approximately 2.4 standard units, resulting from the historic disposal of sulfuric acid and other waste materials (Law et al., 2004). The low pH in this source area likely contributed to the persistence and extent of the HCH plume given the relative stability of the isomers under acidic conditions (Law et al., 2004). Dissolved oxygen levels were less than 1 mg L⁻¹. Measured values of the reduction potential relative to the standard hydrogen electrode were typically on the order of +50 to +150 mV, indicating mildly reducing conditions. The source area ground water also contains elevated levels of total dissolved solids, sulfate, chloride, and iron. In accordance with the prevailing standard hydrogen electrode, the vast majority of the total iron observed exists as ferrous (Fe²⁺) iron.

Nanoparticle Synthesis

The nZVI particles were synthesized by mixing equal volumes of 0.50 mol L⁻¹ sodium borohydride (98.5%) (Finnish Chemicals OY, Aetsa, Finland) and 0.28 mol L⁻¹ ferrous sulfate heptahydrate (VWR Scientific, West Chester, PA) solutions. The borohydride solution was metered into the ferrous sulfate solution at approximately 0.15 L min⁻¹, forming nanoscale zerovalent iron according to the following stoichiometry:

\[ 2\text{Fe}^{2+} + \text{BH}_4^- + 3\text{H}_2\text{O} \rightarrow 2\text{Fe}^{0} + \text{H}_2\text{BO}_3^- + 4\text{H}^+ + 2\text{H}_2 \text{O} \]  [1]

The synthesis was conducted in a fume hood in 5-gallon polyethylene containers fitted with variable-speed, explosion-resistant mixers (Heindorf) set at 700 ± 50 rpm. No attempt was made to exclude air from the reaction mixture. After 1 h of settling, the jet-black nanoparticle aggregates were recovered by vacuum filtration. The finished nanoparticles...
were then washed with ethanol, purged with nitrogen, and refrigerated in a sealed polyethylene container under ethanol until use. The residual moisture content of the nanoparticles as used typically varied between 45 and 55%. The moisture content refers to the percent of water and ethanol remaining in the iron nanoparticle slurry relative to its dry weight and is found by dividing the weight of water/ethanol in the slurry by the weight of dry particles. Figure 2 shows an image of iron nanoparticles comprised of spherical particles assembled in chains taken with a Philips EM 400T transmission electron microscope (Philips Electronics Co., Eindhoven, The Netherlands) operated at 100 kV. Detailed procedures for the imaging have been previously reported (Sun et al., 2006).

Although detailed surface characterizations were not performed as part of this research, many studies have confirmed the presence of ZVI and crystalline iron oxide (FeO) phases on freshly synthesized nZVI by using the sodium borohydride method (Nurmi et al., 2005; Sun et al., 2006; Li et al., 2006a). Although the nitrogen gas–dried Brunauer–Emmett–Teller surface area for freshly synthesized nZVI has been determined to be 33.5 m² g⁻¹, it may not be reflective of conditions in aqueous solution given the strong aggregation potential and reactivity of nZVI (Wang and Zhang, 2001). However, the nZVI loadings in more recent applications have been on the order of 15 to 20 g L⁻¹, similar to the higher end of concentrations in this study. The sealed reactors were placed on a rotating platform shaker at 325 rpm and 30°C and sampled at regular intervals. Although the controls were used in duplicate, the reactors containing variable iron and fill concentrations were not set up as replicates given limitations in the availability of aquifer materials and ground water. Hence, error bars are shown only for the control reactors. However, quantification was based on triplicate injections of sample into the GC.

At each interval, 2 mL of sample withdrawn by a gastight syringe was passed through a 0.20-μm syringe filter and added to 2 mL of 2,2,4-trimethylpentane in a 5-mL vial (Wheaton, Millville, NJ) fitted with an aluminum crimp cap and Teflon-lined septa. The samples were extracted for a minimum of 30 min before GC analysis. Resolution of the individual HCH isomers was accomplished on the basis of gas chromatographic elution times. Quantification was achieved by retention time comparison and a calibration curve over the anticipated concentration range. The detection limit for the HCH isomers was on the order of 1 to 5 μg L⁻¹. The data reported for all analyses are the result of triplicate injections from each reactor at the appropriate time interval. At the conclusion of the test, some reactors were extracted with 20 mL of TMP for 24 h to evaluate the role of sorption in the HCH removal process. These “whole reactor” extractions afforded a qualitative means of identifying possible surface-associated degradation products. Moreover, it helped to ascertain whether the loss of HCHs from solution could be attributed exclusively to sorption or to some combination of sorptive- and reaction-based processes.

**Analytical Procedures**

A Hewlett-Packard 5890 gas chromatograph (Hewlett-Packard, Santa Clara, CA) equipped with an electron capture detector and an Econocap EC-5 (Altech, Nicholasville, KY) low-polarity capillary column was used to quantify the aqueous concentrations of the HCH isomers and degradation products. The column specifications were 30 m length by 0.25 mm internal diameter by...
Results and Discussion

Effectiveness of Nanoscale Iron in Removing Hexachlorocyclohexanes from Ground Water

The HCHs were rapidly removed from the ground water in batch reactors containing the nanoscale iron (Fig. 3). The data in Fig. 3 are reported in normalized fashion, C/C0, in which the concentration at any time (t) is divided by the initial concentration (C0). For the two higher dosages, 8.3 and 16.5 g L−1, more than 95% of the summed HCHs initially present were removed within 24 h. The lowest nZVI dose, 2.2 g L−1, still removed 74% of the total HCHs from the aqueous phase after a reaction period of 24 h. After 100 h, all three doses performed equally well, having removed 98% or more of the HCHs. In addition, the solution pH increased from about 2.4 to 6.0–6.5 standard units. In batch aqueous (distilled water) nZVI systems, the maximum pH observed tends to be in the range of 8.5 to 9.5 standard units, depending on the iron dose. As shown in Eq. [2], the increasing solution pH reflects the generation of hydroxide resulting from the corrosion of iron by water under anaerobic conditions (Matheson and Tratnyek, 1994):

\[
\text{Fe}^{0} + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 2\text{OH}^- + 2\text{H}^+.
\]

Figure 4 depicts the removal curves for the individual HCH isomers. The curves are similar to Fig. 3, indicating that all four isomers exhibit roughly equivalent reactivity toward nanoscale iron, particularly at the two higher dosage levels. At the lowest dosage (2.2 g L−1), some reactivity differentiation is evident because the beta and delta isomers seem to be more recalcitrant than the gamma and delta isomers. After 24 h, an appreciable fraction of the beta and delta isomers (38 and 39%, respectively) remained apparently unreacted in the aqueous phase. In contrast, only 16 and 23% of the alpha and gamma isomers remained over the same period. Thus, when the iron dose is low enough, a reactivity differentiation is apparent in the data. \(\delta\)- and \(\beta\)-HCH with five and six equatorial chlorines, respectively, exhibited greater stability over the initial 24 to 48 h than gamma (three) and alpha (four) isomers.

The control reactors showed a roughly 25% loss in the total HCH concentration over the initial 48 h of the experiment, although normalized concentrations (C/C0) were more than 0.80 thereafter. This may reflect HCH partitioning to the headspace during the early stages of the experiment. \(\alpha\)-HCH exhibits a surprisingly robust vapor pressure for an organochlorine pesticide (approximately 4.4 \times 10^{-3} \text{ Pa} at 25°C), which is an order of magnitude larger than the \(\gamma\) and \(\delta\) isomers and three orders of magnitude larger than \(\beta\)-HCH (Table 1). The apparent losses of the alpha isomer were slightly larger given its vapor pressure. Given its relative stability and low vapor pressure, control losses for the beta isomer were lower than those for the other isomers. The 80% overall mass balance observed in the control reactors in this work was considered reasonable (Fig. 4a–4d).

In comparison to the modest initial concentrations of the HCH isomers (100–550 \text{ pg L}^{−1}), the substantial nZVI loadings (i.e., 2.2–27.0 \text{ g L}^{-1}) likely contributed to the lack of significant levels of intermediates or degradation products observed during the experiment. Other factors included the greater volatility and loss tendencies of probable degradation products, including benzene. However, in other studies with comparable nZVI dosages and significantly higher (e.g., 300–600 \text{ mg L}^{-1}) lindane (i.e., \(\gamma\)-HCH) concentrations in ethanol, gamma-tetrachlorocyclohexadiene (\(\gamma\)-TeCCH) was detected by GC/MS at concentrations of up to 5 to 15% of the initial HCH dosage (Elliott, 2005). Moreover, because of their hydrophobic nature, many POPs (e.g., PCBs) exhibit a high adsorption affinity toward zerovalent iron (Lowry and Johnson, 2004). Reaction with the iron surface could result in some portion of the contaminant mass being lost from solution. There is a need to develop better experimental procedures for further investigation of the reaction products and mass balance for HCHs degradation with iron nanoparticles.

Assessment of HCH Degradation Kinetics

In the literature, iron-mediated contaminant degradation is often characterized in terms of simplified pseudo first-order kinetics (e.g., Johnson et al., 1996; Lien and Zhang, 1999). As applied to HCH, the appropriate equation is as follows:
\[
\frac{d[HCH]}{dt} = -k_{obs}[HCH]
\]

where \([HCH]\) is the concentration of HCH in \(\mu\text{mol L}^{-1}\), and \(k_{obs}\) is the observed pseudo-first-order rate constant (h\(^{-1}\)). The rate of contaminant transformation is directly proportional to the amount of available iron surface (Johnson et al., 1996). To achieve this, \(k_{obs}\) can be expanded as follows:

\[
k_{obs} = k_{SA}[Fe_0]a_{Fe}
\]

where \(k_{SA}\) is the rate constant normalized to the iron surface area concentration (L m\(^{-2}\) h\(^{-1}\)), \([Fe_0]\) is the concentration of iron (g L\(^{-1}\)), and \(a_{Fe}\) is the specific surface area of the iron (m\(^2\) g\(^{-1}\)). A representative specific surface area of 33.5 m\(^2\) g\(^{-1}\) for dry iron nanoparticles was used in this study. Although more complex kinetics approaches, such as the mixed order (e.g., combined zero and first-order) model from Wüst et al. (1999), have been reported in the literature, the simple pseudo first-order model described by Eq. [3] and [4] was used herein.

Table 3 summarizes the relevant rate constants from the experiments with the nZVI. All four HCH isomers exhibited similar reactivity toward the nZVI with the following trend observed: \(\alpha > \gamma > \beta > \delta\) at the iron dosage of 2.2 g L\(^{-1}\). The \(k_{obs}\) values observed ranged from 0.065 to 0.04 h\(^{-1}\), and the corresponding \(k_{SA}\) values ranged from \(8.8 \times 10^{-4}\) to 5.4 \(\times 10^{-4}\) L m\(^{-2}\) h\(^{-1}\). The \(k_{SA}\) data are comparable to data observed in the experiments with lindane (\(\gamma\)-HCH) at the relatively low nZVI dosage (0.015–0.39 g L\(^{-1}\)) (Table 3). However, the normalized rate constants are approximately one order of magnitude smaller. This can be partly explained in terms of the effect of iron dosages. Larger iron dosages may cause aggregation-related reductions in surface area, which has the effect of decreasing the observed rate constants. Because the \(a_{Fe}\) value used in Eq. [4] is assumed to be constant, the calculated values of \(k_{SA}\) may be underestimated due to the effect of aggregation. The reactors were shaken during the experiments, but the effect of aggregation was not thoroughly investigated.

**Effect of Aquifer Solids on HCH Degradation**

In these experiments, the role of fill materials on the overall HCH removal process was investigated. The uncontaminated fill samples were collected at a depth of between approximately 1.5 and 2.27 m below ground surface in the vicinity of the former waste disposal area. The fill was used “as is” without additional testing or characterization. The sole intent of this experiment was to preliminarily evaluate the effects of the fill in the nZVI-HCH system insofar as the relative rates and extent of removal observed. Additional focused batch and column experiments, which were beyond the scope of this “first-cut” assessment, are needed to examine the sorp-
tive potential of the HCHs on this material and the other major lithologic units at the site and to fully characterize their effects on the iron-mediated degradation reactions.

The HCHs are reasonably hydrophobic compounds, with log \( K_w \) values on the order of 2.81 to 4.14 (Mackay et al., 1997) (Table 1). Figure 5 depicts the effect of 100 g L\(^{-1}\) fill on HCH loss in the aqueous phase in the presence of 0.0 to 27.0 g L\(^{-1}\) nZVI. The moderately hydrophobic HCHs exhibit an affinity for the fill solids as the approximate half-life for the summed isomers is on the order of 125 h (Fig. 5). Although 77% of the summed HCHs remained in solution after 24 h in the reactor containing only fill (i.e., 0 g L\(^{-1}\) nZVI), only 2 and 27%, respectively, remained in parallel reactors containing 27.0 and 8.3 g L\(^{-1}\) nZVI. The presence of such aquifer materials would reasonably be expected to deter or prolong the iron-mediated degradation process. This effect can be confirmed by comparison with the HCH removal in the absence of fill materials shown in Fig. 3. For example, without fill materials, over 99% of HCHs were removed by 8.3 g L\(^{-1}\) nZVI within 24 h. By comparison, it took 96 h to remove 99% of HCHs in the presence of fill materials at the same iron dose. However, to the extent that the sorption of HCHs onto aquifer materials is reversible, nanoscale iron in the system can function as a reactive sink for these and other redox-amenable contaminants as they partition into the aqueous phase.

The effect depicted for the summed HCHs was also observed for the individual isomers but to varying degrees. Figures 6a and 6b show the plots for the gamma and beta isomers, respectively. The differences are most obvious for the reactors containing 0 g L\(^{-1}\) and 8.3 g L\(^{-1}\) nZVI. With respect to the former, only slightly more than 60% of the gamma isomer remained in solution after 48 h, and about 40% remained after 175 h. By comparison, 77 and 60% of the beta isomer remained in solution at 48 and 175 h, respectively, for the reactor containing no nZVI. Although these data may suggest that the observed sorption potential of \( \beta \)-HCH was slightly less than that of \( \gamma \)-HCH, they may reflect the greater degradability of the gamma isomer to other reactive components of the fill. Regarding the 8.3 g L\(^{-1}\) nZVI dose, only 21 and 12% of the gamma isomer remained in solution after 24 and 48 h of reaction, respectively. The fraction of the beta isomer remaining at these two time intervals was observed to be 40 and 17%. This reflects their differing reactivity toward the nanoscale iron particularly during the early period of the experiments. At the higher nZVI doses, virtually no beta isomer remained in solution, while trace levels (<5%) of \( \gamma \)-HCH were observed. Post-test extraction revealed low levels of all isomers except \( \beta \)-HCH (Fig. 7).

### Comparison of Microscale vs. Nanoscale Iron

As we have previously reported, the particle size of the iron strongly influences observed reactivity in the iron-mediated degradation process (Zhang, 2003). The 8.8 g L\(^{-1}\) nanoscale iron dose performed considerably better than the 49.0 g L\(^{-1}\) microscale iron dose (Fig. 8). After 24 h, approximately 47% of the summed HCHs remained in solution in the reactor containing microscale iron, whereas only 1% remained in the nanoscale iron reactor. The \( k_{\text{obs}} \) value of microscale iron was about 0.013 h\(^{-1}\), whereas the limited dataset precluded determination of the rate constant for the nanoscale iron reactor. The \( k_{\text{SA}} \) value of microscale iron was 2.65 \( \times \) 10\(^{-4}\) L m\(^{-2}\) h\(^{-1}\), which is one to two orders of magnitude lower than that of nanoscale iron (Table 3). The larger available surface area associated with the nanoscale iron would be expected to translate into a faster reaction and greater adsorption potential with respect to the contaminants. However, the specific surface area of the nZVI is not a static property and varies over time. All other factors being equal, the specific surface area would be expected to decrease over time as a result of nanoparticle aggregation and loss of reactivity. Although the data for the individual isomers is not shown here, the effect of iron type and the general reactivity trends observed were similar to that depicted in Fig. 8.

### Alternative HCH Degradation Pathways

The disappearance of the HCHs from solution observed in these experiments strongly suggests the occurrence of iron-mediated degradation as opposed to other processes. The HCHs

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**Table 3. Comparison of rate constants for all four hexachlorocyclohexane (HCH) isomers and lindane.**

<table>
<thead>
<tr>
<th>Iron dose (g L(^{-1}))</th>
<th>( k_{\text{obs}} )</th>
<th>( k_{\text{SA}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \alpha )-HCH</td>
<td>( \gamma )-HCH</td>
</tr>
<tr>
<td>0.015</td>
<td>3.62 ( \times ) 10(^{-2})</td>
<td>7.20 ( \times ) 10(^{-2})</td>
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<tr>
<td>0.10</td>
<td>1.49 ( \times ) 10(^{-1})</td>
<td>8.8 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>0.39</td>
<td>1.38 ( \times ) 10(^{-1})</td>
<td>8.8 ( \times ) 10(^{-4})</td>
</tr>
<tr>
<td>2.2</td>
<td>6.5 ( \times ) 10(^{-2})</td>
<td>5.0 ( \times ) 10(^{-2})</td>
</tr>
</tbody>
</table>

\( k_{\text{obs}} \) observed pseudo first-order rate constant; \( k_{\text{SA}} \) surface area normalized rate constant.

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**Fig. 5. Effect of 100 g L\(^{-1}\) fill on the disappearance of hexachlorocyclohexanes (HCHs) from solution in the presence of 0.0 to 27.0 g L\(^{-1}\) nanoscale iron (nZVI) particles. Error bars depict the SE from the duplicate control reactors (0 g L\(^{-1}\) nZVI, 0 g L\(^{-1}\) fill).**
are known to be susceptible to attack by anaerobic microorganisms that exist in sewage sludge, in river or lake sediments, or in the soil of flooded fields (Hill and McCarty, 1967; Tsukano and Kobayashi, 1972; Jagnow et al., 1977; Ohisa et al., 1980; Middledorp et al., 1996). Hill and McCarty (1967) measured the half-life of lindane, under anaerobic conditions, to be approximately 1 d in reactors containing non-acclimated sewage sludge. Buser and Müller (1995) found that the anaerobic degradation rates by sewage sludge microorganisms followed the sequence $\gamma > \alpha > \delta > \beta$, with half-lives between 20 and 178 h for gamma and beta, respectively. The conditions existent in our reactors were sufficiently anaerobic because typical redox potential values at 24 h were between $-40$ and $-160$ mV. However, the presence of sodium azide (50 mg L$^{-1}$) should prevent the growth of microorganisms, and the observed HCH removal is far faster than that which would occur through biodegradative pathways.

The HCHs can also be abiotically degraded under alkaline conditions to yield a mixture of trichlorobenzenes, particularly the 1,2,4 isomer (Cristol, 1947; Cristol et al., 1951; Ngabe et al., 1993). These abiotic dehydrodehalogenations (e.g., loss of HCl) progress through pentachlorocyclohexene and tetrachlorocyclohexadiene intermediates before forming the stable aromatic ring. The reactivity trend for these reactions mirrors that observed for anaerobic biodegradation: $\gamma > \alpha > \gamma > \beta$. Unlike the previous case, however, the beta isomer exhibited virtually no reaction even after 3 d at a pH of 12.6, which is considerably more basic than the conditions in our reactors (e.g., maximum pH reached approximately 9.5). Ngabe et al. (1993) determined that the half-life of lindane in aqueous solution at pH 9.0 and 30°C is approximately 3 to 4 d. The observed disappearance rates in our experiments were much faster than could be accounted for by base-catalyzed dehydrohalogenation. Although very low levels of pentachlorocyclohexene (e.g., 20 $\mu$g L$^{-1}$ or less) were frequently observed in the $t = 0$ samples before addition of the nanoscale iron slurry, none was generally detected in the $t = 24$ h samples and beyond. These considerations and the fact that none of the terminal products (i.e., the trichlorobenzenes) was detected in any of our reactors suggest that the dehydrohalogenation pathway did not play a major role in our experiments.
The HCHs have been reported to be relatively stable under acidic conditions (Law et al., 2004). In the present work, the pH of the control reactors was as low as 2.4 standard units, and the relative loss of the HCHs was generally less than 25% over timescales in excess of 250 h. This suggested that acid-catalyzed hydrolyzation of HCHs should be negligible in this study.

Conclusions
In this work, reactors containing HCH-contaminated groundwater and fill materials were treated by varying dosages of nZVI. In filtered ground water containing 2.2 to 27.0 g L⁻¹ nZVI, typically greater than 95% of the HCHs were removed from solution within 48 h. The presence of fillence of 8.3 g L⁻¹ nZVI increased from 24 to 96 h for the reaction. The time required to remove 99% of the HCHs in the presence of fill materials significantly retarded the HCH removal process. The time required to remove 99% of the HCHs in the presence of 8.3 g L⁻¹ nZVI increased from 24 to 96 h for the reactors containing 0 and 100 g L⁻¹ fill, respectively.

The trend $\gamma > \alpha > \beta > \delta$ was observed in terms of the rate of disappearance from solution. This trend seems to be correlated with the orientation (axial vs. equatorial) of the chlorine atoms lost in the dihaloelimination steps. Rate constants obtained from this work were comparable to previously determined values for lindane ($\gamma$-HCH). Little HCH remained in solution or was detected on the solid surfaces after the reaction, indicating that sorption was the principal removal mechanism.

Acknowledgments
The work was supported by a grant from the Pennsylvania Infrastructure Technology Alliance (PITA) and by USEPA STAR grants R829624 and GR832225. We thank a confidential colleague for supplying the contaminated ground water and aquifer materials used in this study. Mr. Stephen T. Spear also provided valuable assistance in the laboratory and design of the experiments.

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