EFFECT OF SOIL MOISTURE ON CHLORINE DEPOSITION (POSTPRINT)

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The effect of soil moisture on chlorine (Cl2) deposition was examined in laboratory chamber experiments at high Cl2 exposures by measuring the concentration of chloride (Cl-) in the soil columns. Soil mixtures with varying amounts of clay, sand, and organic matter and with moisture contents up to 20% (w/w) were exposed to Cl2. For low water content soils, additional water increased the reaction rate as evidenced by higher Cl- concentration at higher soil moisture content. Results also showed that the presence of water restricted transport of Cl2 into the soil columns and caused lower overall deposition of Cl2 in the top 0.48 cm layer of soil when water filled ≈ 60% or more of the void space in the column. Numerical solutions to partial differential equations of Fick’s law of diffusion and a simple rate law for Cl2 reaction corroborated conclusions derived from the data. For the soil mixtures and conditions of these experiments, moisture content that filled 30 -50% of the available void space yielded the maximum amount of Cl2 deposition in the top 0.48 cm of soil.
The effect of soil moisture on chlorine (Cl\textsubscript{2}) deposition was examined in laboratory chamber experiments at high Cl\textsubscript{2} exposures by measuring the concentration of chloride (Cl\textsuperscript{-}) in the soil columns. Soil mixtures with varying amounts of clay, sand, and organic matter and with moisture contents up to 20\% (w/w) were exposed to Cl\textsubscript{2}. For low water content soils, additional water increased the reaction rate as evidenced by higher Cl\textsuperscript{-} concentration at higher soil moisture content. Results also showed that the presence of water restricted transport of Cl\textsubscript{2} into the soil columns and caused lower overall deposition of Cl\textsubscript{2} in the top 0.48 cm layer of soil when water filled \approx 60\% or more of the void space in the column. Numerical solutions to partial differential equations of Fick's law of diffusion and a simple rate law for Cl\textsubscript{2} reaction corroborated conclusions derived from the data. For the soil mixtures and conditions of these experiments, moisture content that filled 30 -50\% of the available void space yielded the maximum amount of Cl\textsubscript{2} deposition in the top 0.48 cm of soil.
Effect of soil moisture on chlorine deposition

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HIGHLIGHTS

• Moisture increases chlorine’s reaction rate with soil constituents.
• Moisture decreases chlorine’s transport rate through the soil.
• Cl2 deposition rate is maximized when water filled 30–50% of the soil void space.

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ABSTRACT

The effect of soil moisture on chlorine (Cl2) deposition was examined in laboratory chamber experiments at high Cl2 exposures by measuring the concentration of chloride (Cl−) in soil columns. Soil mixtures with varying amounts of clay, sand, and organic matter and with moisture contents up to 20% (w/w) were exposed to ≈3 × 104 ppm Cl2 vapor. For low water content soils, additional water increased the reaction rate as evidenced by higher Cl− concentration at higher soil moisture content. Results also showed that the presence of water restricted transport of Cl2 into the soil columns and caused lower overall deposition of Cl2 in the top 0.48-cm layer of soil when water filled ≈60% or more of the void space in the column. Numerical solutions to partial differential equations of Fick’s law of diffusion and a simple rate law for Cl2 reaction corroborated conclusions derived from the data. For the soil mixtures and conditions of these experiments, moisture content that filled 30–50% of the available void space yielded the maximum amount of Cl2 deposition in the top 0.48 cm of soil.

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1. Introduction

For toxic chemical releases, consequence assessment models must account for source terms, meteorology, dispersion rates, and chemical degradation (e.g., photolysis and deposition) to accurately predict a hazard zone. Chlorine (Cl2) is a toxic industrial chemical that is of concern to the transportation and defense communities [1], but its fate is still not well characterized. Deposition has been mentioned as a potentially important factor in the fate of high-concentration Cl2 plumes when model results are compared with observations from actual releases [2,3], and one modeling study focusing on dense gas deposition found that deposition may be important for some conditions but additional experimental investigations were needed [4]. Experimental measurements of Cl2 uptake on aerosol particles [5,6], alfalfa grass [7], and soil [8] indicated that deposition is fast. In addition, measurements of Cl2 deposition during outdoor releases provided strong evidence that dry deposition is an important factor in the fate of a high-concentration Cl2 plume under calm conditions [9]. Thus, deposition must be included in consequence assessment models to accurately predict the hazard area resulting from a large-scale Cl2 release.

Previous laboratory [8] and field measurements [9] demonstrated that soil organic matter affected the Cl2 deposition rate, so a single deposition velocity would be inadequate to universally predict Cl2 deposition. An empirical relationship was derived to predict the deposition velocity from the fraction of soil organic matter and the Cl2 exposure, but this was accomplished for soil blends with constant moisture content. The field measurements showed a positive correlation between the Cl2 deposited and the moisture content; however, since there was also a positive correlation between organic matter and moisture content, the effect of moisture could not be resolved.

Water affects both the chemistry of Cl2 deposition and gas-phase transport. Cl2 reacts reversibly with water to produce HOCl and OCI−, which oxidize organic molecules, providing an irreversible mechanism for Cl2 deposition [10]. HCl is also formed, which can react with carbonate minerals, providing another
mechanism for irreversible deposition. Thus, regarding the chemistry of \( \text{Cl}_2 \) deposition, higher water content should act to accelerate the observed rate of reaction. However, partitioning into an immobile phase (in this case, water) is also known to slow transport through a porous bed of soil particles [11]. The effective diffusion coefficient for vapor transport is reduced by a tortuosity factor that is related to the void space and water content [12,13].

Therefore, the dependence of \( \text{Cl}_2 \) deposition on soil moisture content may not be a simple linear correlation. Here we examine \( \text{Cl}_2 \) deposition into soils with moisture contents from 0 to 0.2 (w/w) and with varying organic matter contents. We use the chloride ion (\( \text{Cl}^- \)) as a tracer for \( \text{Cl}_2 \) deposition to measure the depth of penetration of \( \text{Cl}_2 \) into the soil columns with the same nominal \( \text{Cl}_2 \) exposure. We expect to see evidence showing that water increases the effective reaction rate of \( \text{Cl}_2 \) but decreases the transport rate. These competing factors should yield a soil moisture of maximum \( \text{Cl}_2 \) deposition, below which \( \text{Cl}_2 \) deposition increases with increasing moisture and above which \( \text{Cl}_2 \) deposition decreases with increasing moisture.

2. Materials and methods

2.1. Synthetic soil characterization and preparation

Synthetic soils were made by mixing basalt clay (Welch Tennis Courts, Inc., Sun City, FL) with sand and compost (the latter two purchased from a local hardware store, Home Depot, Panama City, FL). Basalt clay and sand were used as received. Compost was sieved (\#8 mesh, <2.56 mm particle size) to remove large particles. Mineral content and mass fraction of organic matter of starting materials were determined previously [8] and are listed in Table 1.

All soil constituents were dried in a 90 °C oven overnight to remove moisture. Dried starting materials were mixed and then water was added back into the mixtures at the indicated mass loadings (0–0.2). Soil types are named for the relative mass fractions of the three starting materials in this order: compost:clay:sand. Thus, soil type 4:1:1 contains (by mass) 4 parts compost and 1 part each of clay and sand. All samples were stored in sealed containers to minimize water loss prior to \( \text{Cl}_2 \) exposure. Synthetic soil blends were \( \text{Cl}_2 \) exposed in nominally 5 cm \( \times \) 10 cm (diameter \( \times \) length) stainless steel columns. The columns were packed by adding a small amount of soil to the column, compacting the soil layer with a hand plunger, and repeating until the column was full. The total volume of a packed soil column was 163 cm\(^3\), and columns were weighed to obtain bulk soil density (\( \rho_{\text{bulk}} \)).

Column void fractions (\( \phi \)) were determined from measured bulk soil densities (\( \rho_{\text{bulk}} \)) and estimated densities for soils with a void fraction of zero (\( \rho_{\text{solid}} \)). \( \rho_{\text{solid}} \) was calculated from the measured abundances of the mineral and organic content of the starting materials using 0.9 g/cm\(^3\) as the density of the organic content and published mineral densities [14] (see Table 1). Mass-weighted averages of the starting material densities were used as \( \rho_{\text{solid}} \) for the soil mixtures. \( \phi \) was then calculated using Eq. (1).

\[
\phi = 1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{solid}}} \quad (1)
\]

Table 2 shows soil parameters \( \phi, \rho_{\text{bulk}}, \rho_{\text{solid}}, \) organic content normalized to the soil column volume, and the maximum water content (\( \theta_{\text{max}} \)).

2.2. Chlorine exposure

Six soil samples were exposed simultaneously in each experiment. The six samples were either different soil mixtures with the same moisture loading or the same soil mixture with different moisture loadings. For experiments with the same soil, one moisture loading was run in duplicate (i.e., 5 different water contents were used). The soil mixtures are denoted in the first column of Table 2 according to the notation described in Section 2.1. Six packed soil columns were exposed to vapor-phase \( \text{Cl}_2 \) (chemical purity grade, Airgas USA, LLC, Atlanta, GA) at ambient laboratory temperature (≈20 °C) in the deposition chamber described previously [8]. The assembled apparatus was purged with 0.5 L/min zero-grade compressed air (Airgas USA, LLC) for one hour prior to introduction of \( \text{Cl}_2 \). \( \text{Cl}_2 \) and air were introduced through separate ports approximately 10 cm from the base plate. The \( \text{Cl}_2 \) flow rate was initially set high to quickly reach a \( \text{Cl}_2 \) concentration ([\( \text{Cl}_2 \)]) of \( \approx 3 \times 10^4 \) ppm in the chamber and then adjusted to maintain the [\( \text{Cl}_2 \)]. [\( \text{Cl}_2 \)] was measured in real time by a UV absorption cell described previously [8]. [\( \text{Cl}_2 \)] was

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Chemical formula</th>
<th>Compost (%)</th>
<th>Clay (%)</th>
<th>Sand (%)</th>
<th>Density(^a) (g/cm(^3))</th>
</tr>
</thead>
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<td>Organic content</td>
<td>N/A</td>
<td>10.2</td>
<td>2.3</td>
<td>0.45</td>
<td>0.9</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO(_2)</td>
<td>84.3</td>
<td>8.5</td>
<td>94.6</td>
<td>2.65</td>
</tr>
<tr>
<td>Clinohlore</td>
<td>(Mg,Fe)(_2)(AlSi(_3))OH(_3)</td>
<td>36.9</td>
<td></td>
<td></td>
<td>2.65</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al(_2)Si(_2)O(_5)(OH)(_3)</td>
<td>2.2</td>
<td></td>
<td></td>
<td>2.65</td>
</tr>
<tr>
<td>Muscovite</td>
<td>K(_2)Al(_2)Si(_2)O(_8)(OH)(_2)</td>
<td>3.4</td>
<td></td>
<td></td>
<td>2.83</td>
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<tr>
<td>Kyanite</td>
<td>Al(_2)SiO(_3)</td>
<td></td>
<td></td>
<td>0.4</td>
<td>3.59</td>
</tr>
<tr>
<td>Mn-Cordierite</td>
<td>Mn(_2)(Al(_2)Si(_2)O(_8))</td>
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<td></td>
<td></td>
<td>2.66</td>
</tr>
<tr>
<td>Epidote</td>
<td>Ca(_2)Al(_2)FeSi(_2)O(_8)OH</td>
<td>12.0</td>
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<td></td>
<td>3.44</td>
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<tr>
<td>Piemontite</td>
<td>Ca(_2)Al(_2)MnSi(_2)O(_8)OH</td>
<td>3.2</td>
<td></td>
<td></td>
<td>3.49</td>
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<tr>
<td>Albite</td>
<td>NaAl(_2)SiO(_3)</td>
<td>21.5</td>
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<td></td>
<td>2.63</td>
</tr>
<tr>
<td>Anorthite</td>
<td>CaAl(_2)SiO(_6)</td>
<td></td>
<td></td>
<td></td>
<td>3.66</td>
</tr>
<tr>
<td>Sandine</td>
<td>K(_2)Al(_2)SiO(_3)</td>
<td>3.7</td>
<td></td>
<td></td>
<td>2.52</td>
</tr>
<tr>
<td>Phillipsite</td>
<td>(Na,K,Ca)(Al(_2)Si(_2))O(_8)</td>
<td>4.9</td>
<td></td>
<td></td>
<td>2.2</td>
</tr>
</tbody>
</table>

\( a \) Densities were obtained from [14].
\( b \) Calculated densities determined from mass-weighted averages of constituent densities.
calculated using the Beer–Lambert law with a Cl₂ absorption cross section, σ₃₃₀, of 2.52 × 10⁻¹⁹ cm²/molecule [15] and a path length of 10 cm. Cl₂ exposure time totaled 170 min, during which [Cl₂] was above 10⁶ ppm for 120 min. Exposures ([Cl₂]p) averaged (3.9 ± 0.9) × 10⁶ ppm × min.

2.3. Sample analysis

Sample analysis was described previously [8]. Briefly, the soil columns were cored and vertically fractionated with a coring assembly consisting of a stainless steel tube with slits cut to accept a 2.5 cm radius spatula and a plunger to stop the corer when flush with the soil surface. The coring assembly had either coarse fractions (slits at 0.85, 1.69, 2.54, 5.08 and 7.62 cm from the soil surface) or fine fractions (slits at 0.48, 0.95, 1.43, 1.91, and 2.38 cm from the soil surface). Samples from each fraction (−1 g) were obtained and prepared for extraction (10 mL deionized water, 18 MΩ/cm) and subsequent analysis by ion chromatography [16] to measure Cl⁻ concentrations. Ion chromatography was performed in duplicate on an anion exchange column (4 × 250 mm IonPac® AS9-HC, Dionex®, Bannockburn, IL) with a mobile phase of 1.0 mL/min 9.0 mM Na₂CO₃ (pump model GP40, Dionex), and Cl⁻ was detected by a change in conductivity (detector model ED50, Dionex). A small flow of 25 mM H₂SO₄ was used to regenerate the suppressor (model ASRS®-ULTRA II 4 mm, Dionex). Standard solutions of NaCl (99%, Sigma–Aldrich) (0.0178–1.7836 mM) were analyzed to generate a calibration curve, and injections of a standard solution were made after every 10 samples.

2.4. Mathematical modeling

Deposition of Cl₂ into the soil columns was modeled using Fick’s law of diffusion (Eq. (2)) and a simple rate law for Cl₂ reaction with reactive soil constituents (Eq. (3)), which are primarily organic matter. All variables are defined in Table 3. The quantity (1 + θK/α) in Eq. (2) is the retardation factor [11] (λ) and accounts for the slower transport of a chemical species through a porous material due to dissolution into the aqueous phase. The tortuosity factor (τ), defined in Eq. (4), is an empirical correction to gas-phase diffusion in a porous medium [12,13].

\[
\frac{\partial \bar{R}}{\partial t} = -k\theta KC_S R
\]  

(3)

\[
\tau = \frac{\theta^{2/3}}{\phi^2}
\]  

(4)

It is helpful to use non-dimensionalized variables when solving transport equations, so when the following variables were substituted into Eqs. (2) and (3): C*, R*, T, and z*. In addition, k’ was used, and substituting these variables into Eqs. (2) and (3) yield Eqs. (5) and (6).

\[
\lambda \frac{\partial C^*}{\partial T} = \frac{\partial^2 C^*}{\partial z^2} - k' \theta KC_{S0} R^*
\]  

(5)

\[
\frac{\partial R^*}{\partial T} = -k'\theta KC_{S0} R^*
\]  

(6)

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Fig. 1. Deposition of Cl₂ (measured as [Cl⁻]) as a function of depth using coarse vertical fractions. Soil types, φ, and water mass loadings are indicated. [Cl⁻] is normalized to the soil column volume, and error bars are the standard deviations of replicate measurements. Insets to the top two panels show a close-up of data at 3.8 cm deep to illustrate the higher [Cl⁻] detected in these dry soils.
Eqs. (5) and (6) were solved numerically using COMSOL Multiphysics®, a finite element solver. Boundary conditions were a constant Cl₂ concentration at the soil surface (C₀) and zero Cl₂ flux at the base of the soil column (z = 1). Values or ranges for variables are disclosed in Tables 2 and 3; grid spacing (Δz*) was 0.002. Values for D [17] and K [18] were obtained from the literature. L, C₀, and T were set to values used in the experiments. R₀ was estimated from the experimental results. k’ was estimated as described in Section 2.1, and ranges for α and β were obtained as described in Section 2.1.

3. Results and discussion

3.1. Chamber measurements

Fig. 1 shows the effects of moisture content on three soil types analyzed with the coarse vertical fractions. All soils exhibit Cl⁻ for all moisture contents examined. Cl⁻ present in the dry samples suggests that there is some residual water in the soil columns, which is not surprising since it is unlikely that all the water is removed from the soil mixtures at 90 °C. Significantly more Cl⁻ is observed in all samples when water was added. For the 1:0:0 soil, just 2% (w/w) water loading yielded the same [Cl⁻] as that with 20% (w/w) water. This increased deposition of Cl₂ with added water is consistent with the chemical mechanism of dissolution followed by reaction.

While the 1:0:0 soil exhibits only minor changes in the deposition of Cl₂ for water contents from 2 to 20%, deposition in the other two soil mixtures is strongly dependent on the water loading. Both the 1:1:1 and 0:1:0 soils show increasing Cl₂ uptake to 8% water, but decreasing deposition at higher water loadings. This reduced deposition is evident in decreased [Cl⁻] in the top fraction and those deeper. For example, the 1:1:1 soil with 12% water content shows a slightly reduced [Cl⁻] in the top fraction relative to that with 8% water, but at 1.25 cm deep, there is a significant reduction in the 12% water sample. Further, the insets to the 1:0:0 and 1:1:1 soil mixture

Fig. 2. Deposition of Cl₂ as a function of depth with finer vertical fractions. Soil types, φ, and θ/φ are indicated. Water mass loadings are 0, 4, 8, 12, and 16% for ■, ○, ●, △, and ▲, respectively. [Cl⁻] is normalized to the soil column volume, and error bars are the standard deviations of replicate measurements.
graphs in Fig. 1 show that at 3.8 cm deep the dry sample contains significantly more Cl\(^-\) than those with added water. These observations confirm that moisture does limit Cl\(_2\) transport through soils in conditions similar to those encountered at a hazardous Cl\(_2\) release.

In Fig. 1, very little Cl\(^-\) was detected at depths larger than \(\approx 2\) cm, so to provide a more detailed picture of Cl\(_2\) deposition in soil, samples were vertically fractionated with finer resolution and additional mixtures were examined. Fig. 2 shows the results for the indicated soil mixtures to a depth of 2.2 cm. Soil type 4:1:1, similar to 1:0:0, shows no reduction in [Cl\(^-\)] at the highest water content investigated (16%, \(\theta/\phi = 0.48\)); however, at the highest water content, Cl\(_2\) does show lower deposition at the deeper fractions relative to those samples with less water.

While soil 4:1:1 exhibits similar Cl\(_2\) deposition for moisture contents higher than the dry case, the other soil mixtures in Fig. 2 show significant effects of water on Cl\(_2\) deposition. Soils 1:1:1, 1:1:4, and 1:4:1 show a maximum deposition in the top fraction at 8% (w/w) water. At 16% water, these soil mixtures exhibit very little penetration. From Fig. 1, Cl\(_2\) deposits to a maximum depth of 0.85 cm for soil 1:1:1, and results from the more finely resolved fractions in Fig. 2 indicate that very little Cl\(_2\) deposits deeper than 0.48 cm. Clearly, the higher water content affects Cl\(_2\) transport. The legends in Fig. 2 show \(\theta/\phi\), which is a measure of the fractional pore space filled with water and, therefore, unavailable for gas-phase transport. Soils 1:1:1 and 1:1:4 show very little deposition in fractions deeper than 0.48 for \(\theta/\phi = 0.62\) and 0.64, whereas soil 1:4:1 shows significant deposition in deeper fractions for \(\theta/\phi = 0.61\). However, at \(\theta/\phi = 0.85\), Cl\(_2\) deposition in the deeper fractions of soil 1:4:1 is zero.

It is clear that the void space in the soil column plays an important role in the overall deposition of Cl\(_2\), and the amount of water affects \(\alpha\) by filling the void space. However, the water may not only fill pore space, it could also affect the packing of the soil columns since samples were prepared with the prescribed amount of water already mixed in. To test whether better packing affects the observed depth penetration of Cl\(_2\), six identical soil samples were prepared and three of them were dried in an oven at 60°C for two days. All six samples were exposed to Cl\(_2\) at the same time, so the only difference was the presence or absence of water. This experiment was repeated for soil 1:1:1 with 8% and 16% water loadings, and the results are shown in Fig. 3.

For the wet soils in Fig. 3, the depth profile of [Cl\(^-\)] was similar to that observed in Fig. 2. Soil with 16% water loading showed very little Cl\(^-\) in the second fraction down, and soil with 8% water showed a nearly linear dependence of [Cl\(^-\)] on depth. The dried soil columns exhibited only a small [Cl\(^-\)] in the top fraction, consistent with the dry samples in Fig. 2. In addition, [Cl\(^-\)] shows essentially no dependence on depth for the dried samples in Fig. 3. If water significantly affected the packing of the soil columns, the dried samples would show a similar depth profile of [Cl\(^-\)] as the wet ones. Instead, Cl\(_2\) transport is unhindered to a depth of 2.2 cm. Thus, the deeper relative penetration of Cl\(_2\) in the dry samples of Figs. 1 and 2 is not due to an artifact of the column packing procedure. Further, the flat depth profile of the 18% water soil that was dried in Fig. 3 demonstrates that its packing does not hinder Cl\(_2\) transport, so the sharp drop-off of [Cl\(^-\)] at a depth of 0.7 cm for the highest water loading of soils 1:1:1, 1:1:4, and 1:4:1 in Fig. 2 is due primarily to water filling available void space.

3.2. Numerical modeling

There are several variables that affect Cl\(_2\) deposition, \(C_0\), \(t\), \(R_0\), \(\phi\), and \(\theta\). In these experiments, \(C_0\) and \(t\) were kept constant but the latter three parameters were varied. To corroborate the conclusion that water is decreasing the rate of transport of Cl\(_2\) through the soil column, Eqs. (5) and (6) were solved numerically using COMSOL. These equations use the non-dimensional variables \(T\) and \(z^*, C^*\), and \(R^*\), defined in Table 3. To generate model results that reasonably represent the conditions of these experiments, \(R_0\) and \(k^*\) must be known. Extrapolating the linear depth dependence of [Cl\(^-\)] for soil 1:0:0 (which contained the highest amount of organic matter) in Fig. 1 to \(z = 0\) yields approximately 0.28 mmol/cm\(^3\), so an upper limit of 0.4 mmol/cm\(^3\) ([400 mol/m\(^3\)]) was used for \(R_0\). Soils 0:1:0 and 1:1:4 (both with low amounts of organic matter) exhibited maximum [Cl\(^-\)] at about 0.1 mmol/cm\(^3\), so a lower limit of 0.05 mmol/cm\(^3\) ([50 mol/m\(^3\)]) was used for \(R_0\). These lower and upper limits of \(R_0\) adequately cover the experimental parameter space. The effective rate constant (\(k^*\)) was only known, thus \(k^*\) was adjusted to find agreement with the experimental results.

Fig. 4 shows the results of the numerical solution to these partial differential equations, in which the effects of \(k^*, R_0\), \(\phi\), and \(\theta\) are shown. Note that the y axis is the amount of product formed normalized to the product formed at \(T = \infty\), and the x axis is the normalized depth. While the focus of this work is on the effects of water on Cl\(_2\) deposition, it is important to examine the effects of other variables in Eqs. (5) and (6) to garner a comprehensive understanding of the factors that affect deposition in soil.
matrices. In panel A, faster $k'$ increases the amount of product near the soil surface ($z^* < 0.05$), but decreases the amount of product at larger depths. The effective aqueous-phase rate constant ($k'$) was unknown, but a value of $100 \text{m}^3/\text{mol}$ approximates the depth dependence of the product concentration observed in the data of Fig. 2 with similar $\theta/\phi$. Thus, $k' = 100 \text{m}^3/\text{mol}$ was used for the numerical results in the other panels of Fig. 4. Panel B shows that higher $R_0$ does not affect the relative amount of product at the surface ($z = 0$), but it does reduce the relative penetration of Cl$_2$. Panel C shows the effect of void space ($\phi$), and a larger amount of void space yields more product and deeper penetration. Note that in Panel C that $\theta/\phi$ is kept constant for the three values of $\phi$.

Finally, Fig. 4D shows the effects of water on the deposition of Cl$_2$. Increasing the water fraction decreases Cl$_2$ depth of penetration and increases the product concentration at the surface ($z = 0$). As a more direct comparison with the experimental results, the inset to Fig. 4D shows the numerical modeling results integrated over the depth fractions used in the experimental analysis. The same trend is observed in the numerical results as those in Figs. 1 and 2. High water content attenuates the transport of Cl$_2$ into deeper soil fractions, and the top fraction exhibits significantly less product at high water contents. These results corroborate the conclusion from the experimental results.

As further comparison between numerical modeling and experimental results, Fig. 5 shows results from the top 0.48-cm fraction for each. Experimental results (Fig. 5B) show peaks in the product yield at $\theta/\phi = 0.3–0.4$, and the modeling results (Fig. 5A) shows peaks in the product yield at progressively higher $\theta/\phi$ for higher $R_0$. The $\theta/\phi$ range for the modeling results (0.4–0.55) is near those of the experiments. However, the experimental results show no apparent trend of the $\theta/\phi$ value for the product peak with the organic concentration (note organic content in Table 2). This may indicate that other processes or factors are not adequately accounted for in Eqs. (5) and (6). Nevertheless, the similar trends observed in the modeling and experimental results support the conclusion that water restricts transport of Cl$_2$ into the soil column.

As mentioned in Section 1, water’s restriction of vapor transport through a porous soil matrix is established in the literature. However, much of the environmental literature is concerned with longer time scales and lower concentrations than that relevant to the transport and evolution of hazardous chemical plumes. The experiments and numerical solutions here show that in the case of Cl$_2$, the same mechanism is operable for deposition of Cl$_2$ into a soil matrix for conditions that are relevant for hazard prediction and analysis (high [Cl$_2$] for a couple of hours). However, water in these experiments was stationary (i.e., there was no advective transport of water). For conditions of water flow (e.g., rainwater
seeping through the soil), the added transport term would change the results.

4. Conclusions

\( \text{Cl}_2 \) deposition was measured on synthetic soil blends with the aim of elucidating the role of soil moisture content on the rate of \( \text{Cl}_2 \) removal. Experimental results demonstrated that water increased the rate of reaction but it decreased the vapor transport through the soil column. The maximum \( \text{Cl}_2 \) deposited corresponded to conditions for which the water volume fraction was approximately half of the total void space in the soil matrix. Numerical solutions to transport and reaction equations that describe the problem confirmed the conclusions. On a final note, we remind the reader that these results represent conditions for which condensed phase water is stationary. For conditions where water is moving, the results will be different.

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