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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.
- Cl_2 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 (Cl_2) deposition was examined in laboratory chamber experiments at high Cl_2 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 $\approx 3 \times 10^4$ ppm Cl_2 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 Cl_2 into the soil columns and caused lower overall deposition of Cl_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_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_2 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 (Cl_2) 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 Cl_2 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 Cl_2 uptake on aerosol particles [5,6], alfalfa grass [7], and soil [8] indicated that deposition is fast. In addition, measurements of Cl_2 deposition during outdoor releases provided strong evidence that dry deposition is an important factor in the fate of a high-concentration Cl_2 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 Cl_2 release.

Previous laboratory [8] and field measurements [9] demonstrated that soil organic matter affected the Cl_2 deposition rate, so a single deposition velocity would be inadequate to universally predict Cl_2 deposition. An empirical relationship was derived to predict the deposition velocity from the fraction of soil organic matter and the Cl_2 exposure, but this was accomplished for soil blends with constant moisture content. The field measurements showed a positive correlation between the Cl_2 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 Cl_2 deposition and gas-phase transport. Cl_2 reacts reversibly with water to produce HOCl and OCl^-, which oxidize organic molecules, providing an irreversible mechanism for Cl_2 deposition [10]. HCl is also formed, which can react with carbonate minerals, providing another

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Table 1
Soil constituents (w/w) and density.

Constituent	Chemical formula	Compost (%)	Clay (%)	Sand (%)	Density[a] (g/cm^3)
Organic content	N/A	10.2	2.3	0.45	0.9
Quartz	SiO_2	84.3	8.5	94.6	2.65
Clinochlore	$(Mg,Fe)_6(Al,Si)_4O_{10}(OH)_8$		36.9		2.65
Kaolinite	$Al_2Si_2O_5(OH)_4$	2.2			2.65
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	3.4		2.5	2.83
Kyanite	Al_2SiO_5			0.4	3.59
Mn-Cordierite	$Mn_2(Al_4Si_5O_{18})$		7.3		2.66
Epidote	$Ca_2Al_2FeSi_3O_{12}OH$		12.0		3.44
Piemontite	$Ca_2AlMnSi_3O_{12}OH$		3.2		3.49
Albite	$NaAlSi_3O_8$		21.5		2.63
Anorthite	$CaAl_2Si_2O_8$				
Sanidine	$KAlSi_3O_8$		3.7		2.52
Phillipsite	$(Na,K,Ca)(Al,Si)_4O_8$		4.9		2.2
Calculated density[b] (g/cm^3)		2.22	2.59	2.63	

[a] Densities were obtained from [14].
[b] Calculated densities determined from mass-weighted averages of constituent densities.

mechanism for irreversible deposition. Thus, regarding the chemistry of 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 Cl_2 deposition on soil moisture content may not be a simple linear correlation. Here we examine 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 (Cl^-) as a tracer for Cl_2 deposition to measure the depth of penetration of Cl_2 into the soil columns with the same nominal Cl_2 exposure. We expect to see evidence showing that water increases the effective reaction rate of Cl_2 but decreases the transport rate. These competing factors should yield a soil moisture of maximum Cl_2 deposition, below which Cl_2 deposition increases with increasing moisture and above which Cl_2 deposition decreases with increasing moisture.

2. Materials and methods

2.1. Synthetic soil characterization and preparation

Synthetic soil blends 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 Cl_2 exposure. Synthetic soil blends were packed into nominally 5 cm × 10 cm (diameter × 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 (ρ_{bulk}).

Column void fractions (ϕ) were determined from measured bulk soil densities (ρ_{bulk}) and estimated densities for soils with a void fraction of zero (ρ_{solid}). ρ_{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 ρ_{solid} for the soil mixtures. ϕ was then calculated using Eq. (1).

$$\phi = 1 - \frac{\rho_{bulk}}{\rho_{solid}} \quad (1)$$

Table 2 shows soil parameters ϕ, ρ_{bulk}, ρ_{solid}, organic content normalized to the soil column volume, and the maximum water volume fraction (θ_{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 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 Cl_2. Cl_2 and air were introduced through separate ports approximately 10 cm from the base plate. The Cl_2 flow rate was initially set high to quickly reach a Cl_2 concentration ([Cl_2]) of ≈3×10^4 ppm in the chamber and then adjusted to maintain the [Cl_2]. [Cl_2] was measured in real time by a UV absorption cell described previously [8]. [Cl_2] was

Table 2
Soil Parameters.

Soil type	OC[a] (g/cm^3)	ϕ[b]	ρ_{bulk} (g/cm^3)	ρ_{solid} (g/cm^3)	θ_{max}
1:0:0	0.11	0.51 ± 0.04	1.08 ± 0.09	2.22	0.27
4:1:1	0.088	0.48 ± 0.04	1.22 ± 0.10	2.33	0.30
1:1:1	0.061	0.43 ± 0.04	1.41 ± 0.11	2.47	0.35
1:1:4	0.035	0.43 ± 0.04	1.46 ± 0.11	2.55	0.36
1:4:1	0.053	0.36 ± 0.05	1.61 ± 0.13	2.53	0.31
0:1:0	0.041	0.32 ± 0.06	1.71 ± 0.16	2.59	0.34[c]

[a] Organic content.
[b] Void fraction (ϕ) calculated using Eq. (1).
[c] Soil mixture 0:1:0 with the maximum water content (θ_{max}) secreted water when packed.