

Natural Formation of Vinyl Chloride in the Terrestrial Environment

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Vinyl chloride is a highly reactive and toxic substance which is widely used in industry. It is the parent compound of poly(vinyl chloride) (PVC), one of the most important industrial polymers. Until now, it was thought that vinyl chloride found in the environment is exclusively man-made or results from the degradation of other anthropogenic substances, such as trichloroethylene and tetrachloroethylene. Here, we demonstrate that vinyl chloride also has natural sources. Soil air and ambient air from a rural area in Northern Germany were investigated for volatile chlorinated halocarbons. The concentrations of vinyl chloride in the soil air were significantly enhanced as compared to ambient air, indicating a natural formation of this compound in the soil. A series of laboratory experiments using different soils and model compounds was conducted, which clearly proved that vinyl chloride could be produced during soil processes. We propose that this highly reactive compound can be formed during the oxidative degradation of organic matter in soil, for example, in a reaction between humic substances, chloride ions and an oxidant (ferric ions or hydroxyl radicals). The redox-sensitive aromatic compounds in soil such as catechols and *o*-quinones can be degraded to CO₂, accompanied by the release of vinyl chloride and other volatile chlorinated compounds. This process could have started in the Late Silurian to Early Devonian, 400 million years ago, when the first soils on earth evolved.

Introduction

Many halocarbons found in the environment have both anthropogenic and natural sources. More than 1800 organochlorine compounds are known to be naturally produced in a range of chemical, geological, or biological processes (1, 2), but current knowledge of the known sources, sinks, and global burdens of these organochlorines is incomplete. In some cases, natural sources exceed anthropogenic emissions. Chloromethane (CH₃Cl) is by far the most abundant volatile halocarbon in the atmosphere (3) with mainly natural sources (4). For the terrestrial environment, both biological and abiotic sources of CH₃Cl have been identified (5–9). Chlo-

roform, chlorophenols, and chlorinated dioxins, long believed to be only of anthropogenic origin, also have significant natural terrestrial sources (10–12). Thus, the terrestrial environment plays an important role for the emission of chlorine into the atmosphere and the biogeochemical cycling of chlorine in soil (13).

In contrast to many organochlorine compounds, it is still believed that vinyl chloride (VC) found in the environment is solely man-made. VC is a known carcinogen and regulated chemical (14, 15). Most VC produced is further polymerized to poly(vinyl chloride) (PVC). A part of the industrially produced VC (95%) enters the environment by air or wastewater. VC in water or soil evaporates easily into the troposphere, where it is rapidly oxidized by photochemically produced hydroxyl radicals (lifetime, 2–3 days). Any VC which does not evaporate may leach to the groundwater and may be subject to biodegradation under aerobic and anaerobic conditions (16–18). Another anthropogenic source of VC in the environment comes from the degradation of chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE) (19–22). Here, we present field investigations, controlled laboratory studies, and model experiments which imply that vinyl chloride also has natural sources.

Materials and Methods

Chemicals. Catechol (1,2-hydroquinone), potassium chloride, iron(III) sulfate, hydrogen peroxide (30%), and methanol were purchased from Sigma-Aldrich (Steinheim, Germany). Humic acid was obtained from Fluka (Buchs, Switzerland). Volatile organic compounds calibration standards were from Supelco (Taufkirchen, Germany). The water used in all experiments was freshly prepared doubly distilled, deionized water.

Soil Samples for Laboratory Studies. Soil samples were collected on September/October 1998 at two different sampling sites on the basis of their relatively uninfluenced history: soil no. 1, a grassland soil of western Patagonia/Chile (52°48'36"S/72°55'45"W); and soil no. 2, a peatland soil from the natural reserve Rotwasser Odenwald/Germany (49°36'39"N/8°53'11"E). Using a clean spade, four samples (500–1000 g) were collected from the top soil (O and A horizon) in a square 1 × 1 m. The four samples were combined to a bulk sample in a polyethylene plastic bag and transported to the laboratory. The soil samples were freeze-dried, milled (0.24 mm mesh), and stored in a freezer (–24 °C) until chemical analyses or laboratory experiments were conducted. Soil samples and the humic acid were analyzed for pH, organic carbon (C_{org}), total iron, and halogens.

Experimental Procedure. For laboratory experiments on the formation of vinyl chloride from two different soils and a commercially available humic acid, 20-mL glass vials were used as reaction bottles (crimp-capped sealed with a PTFE-lined butyl rubber septum). All experiments were conducted at room temperature (22 °C). A total of 1000 mg milled soil or humic acid was added to 10 mL of doubly distilled deionized water. The vials were sealed and shaken on a rotary board (200 rpm) for 1 min. The helium carrier gas of the gas chromatograph was introduced by piercing the septum with two stainless steel tubes, one as an inlet and one as an outlet. The volatile compounds in the flasks were purged by helium (20 mL/min) for either 15, 30, 45, or 60 min and focused on a preconcentration trap. After the purge cycle was completed, the volatile chlorinated compounds were measured by capillary gas chromatography and mass spectrometric detection as described in the following section below (analytical methods). Three replicates were measured for each sample

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($n = 3$), and the mean is shown in the figures. The coefficient of variation (RSD) was in the range of 12–33%. Blanks were analyzed according to the same procedure but without the addition of soil or humic acid.

The experiments with the model compound catechol were carried out in a 20 mL sealed glass vial containing 10 mL of doubly distilled deionized water and an initial concentration of 2 mM catechol, 10 mM KCl, and either 10 mM $\text{Fe}_2(\text{SO}_4)_3$ or 10 mM H_2O_2 or both 10 mM $\text{Fe}_2(\text{SO}_4)_3$ and 10 mM H_2O_2 . The same experiments were performed using 1000 mg of milled grassland soil from Patagonia instead of catechol. The volatile compounds in the flasks were monitored as described previously. Three replicates were measured for each sample ($n = 3$), and the mean is shown in the figures. The coefficient of variation (RSD) was in the range of 7–56%. Blanks were measured by the use of doubly distilled deionized water, which were, for vinyl chloride, very close to detection limit of the analytical system (around 2 pg).

Ambient and Soil Air Sampling in the Field. Three sampling sites were selected in a rural area of Schleswig-Holstein in Northern Germany (54°25'N/8°50'E) on the basis of their vegetation and the proximity to the North sea: a coastal salt marsh, a peatland, and a deciduous forest (predominantly birch forest). The sampling was carried out in early spring, April 2001. Ambient air was sampled from about 1 m above the soil surface (on a stand) by pumping 1 L of air through an adsorbent tube filled with Carbotrap 300 (Supelco) at a rate of 40 mL/min. After sampling the adsorbent tubes were sealed in stainless steel tubes and kept at -24°C in darkness until analysis. Three to five measurements were done at each sampling site. For collecting air from topsoil a stainless steel cylinder with a volume of 1 L ($r = 5\text{ cm}$, $h = 12.7\text{ cm}$) was used (Figure 1). The cylinder was completely hammered into the soil and carefully removed from the soil with a clean spade. Two stainless steel screw-caps (including a PTFE seal) with a connector (stainless steel tube) were used to close the cylinder immediately from both ends. Nearly no headspace was present between the soil and the caps. The tube of the top screw-cap was connected to an adsorbent tube while the tube of the bottom screw-cap was connected to a nitrogen stream. Then, the cylinder (including the topsoil core) was purged for 1 h at a rate of 30 mL/min (1.8 L), and the volatile compounds of the soil air were trapped by the adsorbent tube. The flow rate was checked at both ends with a flow meter to make sure that the soil core was permanently purged by a constant nitrogen stream. For all samples, no significant discrepancies between the flow rate at the in- and outlet of the cylinder were observed, indicating that there was no overpressure formed in the system. Three to five soil cores were used to measure the soil air from each sample site. After the field measurements, all of the samples were transported to the laboratory and stored in a freezer until further analyses were carried out.

Analytical Methods. The adsorbent tubes were analyzed by mounting them to an automatic thermal desorption unit (in-house preparation) which was connected to a gas chromatograph and a ion trap mass spectrometer. The adsorbed compounds were desorbed with helium gas at 200°C for 15 min, and they were trapped -196°C (liquid nitrogen) in a stainless steel loop filled with glass beads. For injection, the cold trap was heated to 90°C . Gas chromatographic separation was carried out on a DB1 column ($60\text{ m} \times 0.32\text{ mm}$, film thickness $1\ \mu\text{m}$) using the following temperature program: initial oven -65°C , increasing rate 8°C min^{-1} to 175°C , 5 min isothermal. Mass spectrometric detection was performed over a scan range of 48–200 amu. Vinyl chloride and other chlorinated compounds were identified from their retention time and mass spectrum (Figure 2). External calibration standards and multipoint calibration curves were

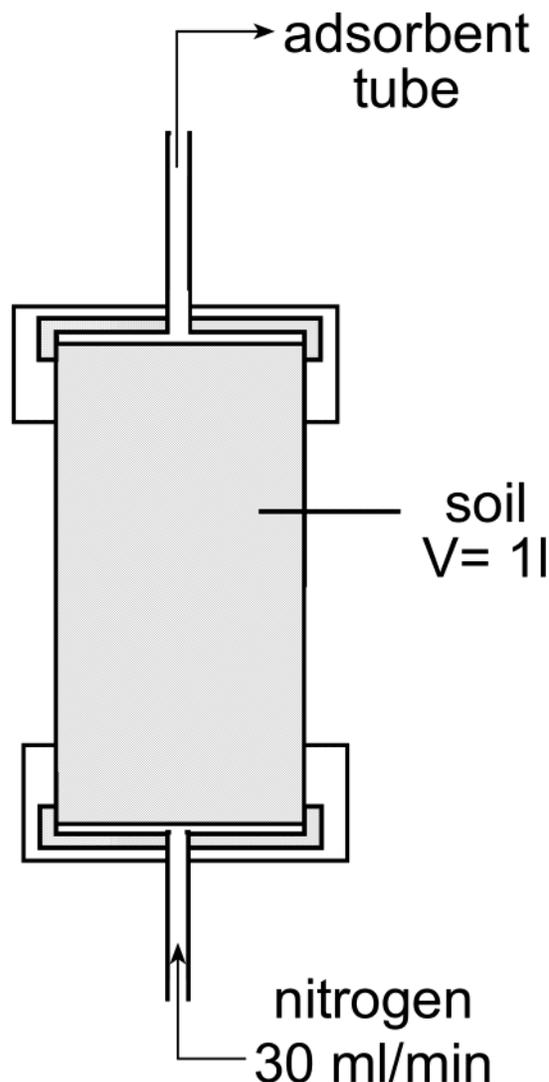


FIGURE 1. Apparatus for sampling soil air from the top soil layer (O and A horizon).

used to quantify the following compounds: chloromethane, vinyl chloride, trichloroethylene, tetrachloroethylene, and 1,1,1-trichloroethane. The detection limits of the compounds were in the range of 2–5 pg. All samples were clearly above the detection limit. Blanks of the adsorbent tubes were measured after thermal conditioning.

Calculation of the Concentration in the Soil Air. The concentrations (ng L^{-1}) of the compounds in the soil air were calculated from the amounts of adsorbed compounds on the adsorbent tubes (ng) and the volume of air in the soil (L). Therefore, it was assumed that all volatile chlorinated compounds in the soil air were purged and trapped by the adsorbent tube. Total air volume in the soil was calculated from the porosity and the measured water content of the soil samples. Porosity of the soil was determined from the measured bulk (BD) density and the particle density (PD). The air volume of the soils was in the range of 180–400 mL/L ($n = 3$).

Results and Discussion

Volatile chlorinated hydrocarbons were measured in ambient air and soil air from the coastal salt marsh, peatland, and deciduous forest. The mean concentration of vinyl chloride in the air of topsoil was in the range of 0.6–7.7 ng L^{-1} (Table 1) with a large variation among the replicates (RSD 10–65%). Compared to ambient air, the vinyl chloride concentration

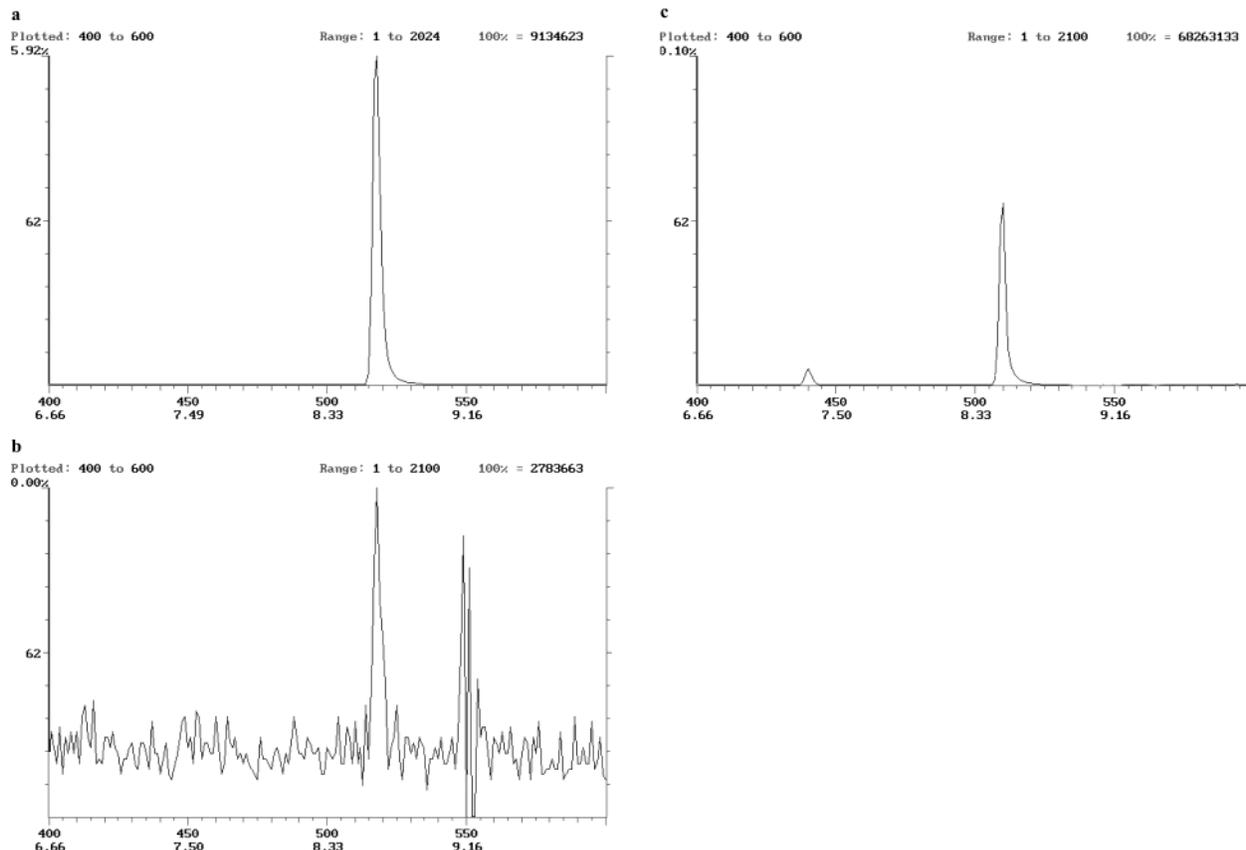


FIGURE 2. GC-MS analysis of vinyl chloride: (a) external standard with 20 ng of VC; (b) adsorbent tube after thermal conditioning used as a blank; (c) soil air from a salt marsh. The chromatograms show the response to the molecular ion m/z 62. The scale of the ordinate is different for each chromatogram; the values at scan 520 for the peak area are 2 000 000, 370, and 120 000, for (a), (b), and (c), respectively.

TABLE 1. Concentration of Volatile Chlorinated Compounds Measured in the Top Soil Layer of Coastal Marsh, Deciduous Forest, and Peatland

	concentrations of compounds (ng L^{-1})			
	vinyl chloride	chloromethane	1,1,1-trichloroethane	trichloroethene
Coastal Marsh				
top soil air ^a	7.68 (5.5; 8.4; 9.14)	53.5 (40.4; 42.3; 77.8)	0.32 (0.18; 0.24; 0.54)	0.15 (0.10; 0.25; 0.10)
ambient air ^b	0.009 ± 0.003	1.24 ± 0.25	0.51 ± 0.11	0.13 ± 0.05
Deciduous Forest				
top soil air ^a	0.58 (0.62; 0.63; 0.48)	4.5 (3.7; 6.8; 3.9; 5.1; 3.0)	0.42 (0.42; 0.38; 0.47)	0.10 (0.12; 0.11; 0.07;)
ambient air ^b	0.009 ± 0.003	1.24 ± 0.25	0.51 ± 0.11	0.13 ± 0.05
Peatland				
top soil air ^a	1.0 (0.35; 1.12 1.2; 1.33)	4.0 (3.4; 4.2; 2.9; 5.4)	0.19 (0.23; 0.2; 0.2; 0.13)	0.17 (0.16; 0.17; 0.18; -)
ambient air ^b	0.009 ± 0.003	1.24 ± 0.25	0.51 ± 0.11	0.13 ± 0.05

^a The mean value is given ($n = 3-5$) and each single number (in brackets). ^b Ambient air concentration represents the mean value of all samples sites ($n = 9$) \pm standard deviation.

in the topsoil was around 850, 110, and 60 times greater for the coastal salt marsh, peatland, and deciduous forest, respectively. For chloromethane, the concentration of soil air was in the range of 4.0–53.5 ng L^{-1} , and the concentration ratios of soil air/ambient air were around 40, 4, and 3 for the coastal marsh, peatland, and deciduous forest, respectively. The corresponding $\text{CH}_3\text{Cl}/\text{VC}$ ratios were 7, 8, and 4. In contrast to VC and CH_3Cl , the concentration of 1,1,1-trichloroethane (CH_3CCl_3), which is ascribed to anthropogenic sources (23), was in the range of the tropospheric background ($0.51 \pm 0.11 \text{ ng L}^{-1}$); the concentration ratios between soil air and ambient air were close to unity (0.4–0.8). Trichloroethylene and tetrachloroethylene, which are known to be precursors of VC under anaerobic conditions, showed soil air concentrations similar to ambient air. The

discovery of significantly enhanced VC and CH_3Cl concentrations in soil air, in the presence of background tropospheric concentrations of CH_3CCl_3 , TCE, and PCE, indicate a natural formation of VC in soil. As the VC, TCE, and PCE concentrations in ambient air are very low, the significantly enhanced concentrations for vinyl chloride in soil air cannot be explained with a general contamination of the ambient air. However, in environmental analytical studies, the risk of systematic errors can be high and may lead to wrong conclusions. Therefore, careful attention has been paid to the fact that VC, TCE, and PCE are common groundwater and soil pollutants and that TCE and PCE are also atmospheric pollutants. No indication of a contamination source was found in the studied soils, and the contribution of contamination from the sampling equipment and analytical proce-

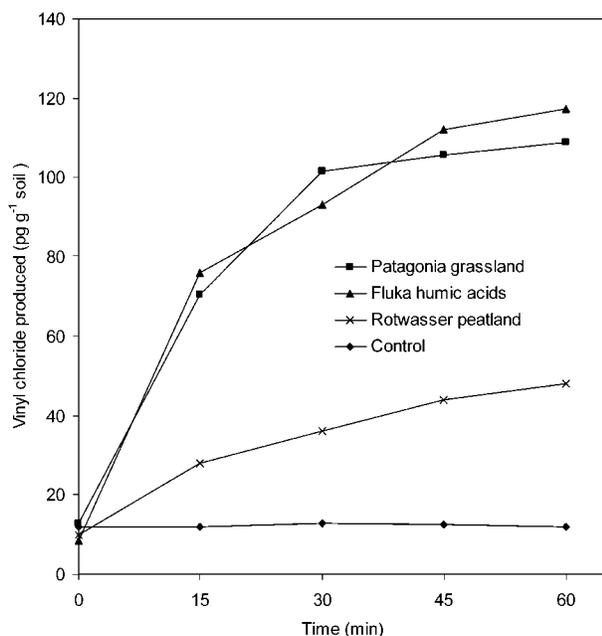
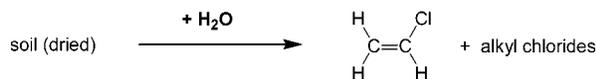


FIGURE 3. Formation of vinyl chloride by two organic-rich soils and humic acid. A total of 1000 mg of grassland, peatland, or humic acid was added to 10 mL of water in a 20-mL glass vial ($n = 3$; RSD 12–33%). The pH in the medium was 4.1, 4.2, and 5.4 for grassland, peatland, and humic acid, respectively.

SCHEME 1



dures were controlled by measuring blanks.

To evaluate the natural production of VC, we performed several series of controlled laboratory experiments in an aqueous medium containing soil material from pristine areas. After suspending the soil samples in distilled water (no additives were used), *in vitro* production of vinyl chloride was observed (Figure 3). Both soil samples showed a significant release of vinyl chloride, at rates of up to 120 $\text{pg g}^{-1} \text{h}^{-1}$. Besides VC, the production of CH_3Cl , $\text{C}_2\text{H}_5\text{Cl}$, and $\text{C}_3\text{H}_7\text{Cl}$ could also be measured (Scheme 1) (data not shown).

CH_3CCl_3 , TCE, and PCE were within the range of the blank values, indicating that there was no *in vitro* production of these compounds. The average $\text{CH}_3\text{Cl}/\text{VC}$ ratio was around 7 for grassland soil and around 12 for peatland. Furthermore, the formation of vinyl chloride was also observed with the commercially available humic acid. The production rate of VC from humic acids was similar to those of the grassland soil.

VC could be formed by a variety of biotic and abiotic soil processes. In this study, we focused our investigations on abiotic processes. Our previous work (5) has shown that methyl halides are produced naturally in soil during the degradation of organic matter. In the presence of Fe(III) and halide ions, monomeric constituents of humic substances (HS) such as 2-methoxyphenol (guaiacol) can undergo oxidation to quinones with concomitant formation of the corresponding monohalomethane. A second reaction that may occur in soil during the oxidation of organic material is the formation of a highly reactive chlorinated compound such as VC. In this case, we considered the redox-sensitive functional aromatic groups of HS such as catechols and *o*-quinones (Figure 4) as precursors for VC. Next to being aromatic groups of HS, catechols also play a key role in the biological degradation of aromatic structures. Laboratory experiments with phenolic substances have shown that

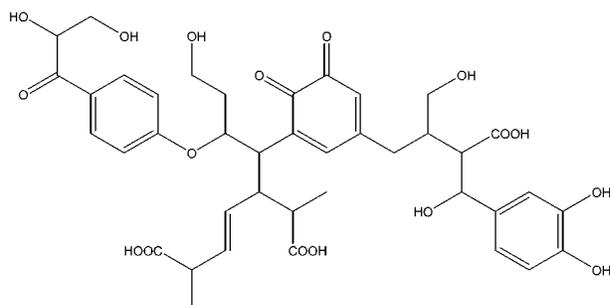


FIGURE 4. Proposed building block of humic acid.

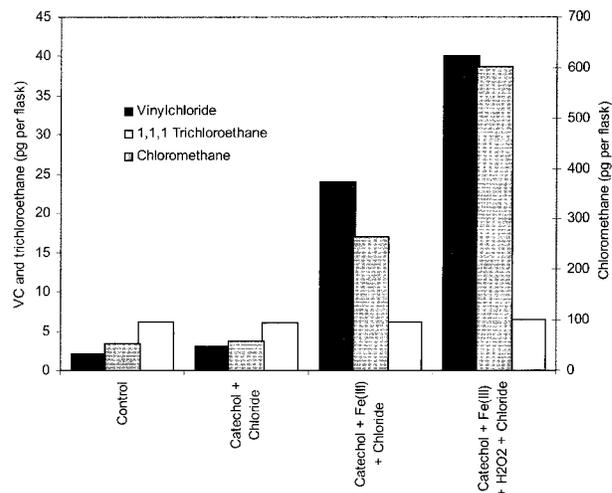


FIGURE 5. Production of VC and CH_3Cl by the reaction of catechol, chloride, and Fe(III). Initial concentrations were 2 mM catechol, 10 mM KCl, and 10 mM $\text{Fe}_2(\text{SO}_4)_3$ or 2 mM catechol, 10 mM KCl, 10 mM $\text{Fe}_2(\text{SO}_4)_3$, and H_2O_2 ($n = 3$; RSD 7–56%). The pH in the medium was in the range of 2.5–3.0.

catechol can be oxidized by Fe(III) to produce CO_2 (24). Neither sunlight nor microbial mediation are required for this process. For this reason, catechol was selected for model experiments. The reaction of catechol and Fe(III) in the presence of chloride demonstrates that CO_2 production is accompanied by additional volatile breakdown products such as VC and monochlorinated alkanes (CH_3Cl , $\text{C}_2\text{H}_5\text{Cl}$, $\text{C}_3\text{H}_7\text{Cl}$).

Fe(III)-induced formation of VC from the model compound catechol is illustrated in Figure 5. The $\text{CH}_3\text{Cl}/\text{VC}$ ratio was ~ 8 . There was no production of VC and CH_3Cl when Fe(III) was absent. Moreover, no VC production was observed by using H_2O_2 , another naturally occurring oxidant. When both Fe(III) and H_2O_2 were used to oxidize catechol, the VC production increased significantly. This is probably caused by the Fenton reaction, where H_2O_2 reacts with Fe(II) to generate hydroxyl radicals ($\cdot\text{OH}$); Fe(II) is provided by the reaction of catechol with Fe(III). The $\cdot\text{OH}$ radical is a powerful oxidant and could be responsible for the increased concentration of VC generated. In addition to the volatile compounds, a variety of semivolatiles and aliphatic oxidation products could be produced, but these compounds were not examined in this study. However, our reaction scheme describes a novel chemical pathway from catechol to VC and also a new source of monochlorinated alkanes (Scheme 2).

In additional experiments, the influence of Fe(III) on VC formation was confirmed with natural soils. The enhanced Fe(III)-mediated production of VC is shown in Figure 6. After adding Fe(III) in water containing soil and chloride, the concentration of VC was twice that of the untreated sample.

SCHEME 2

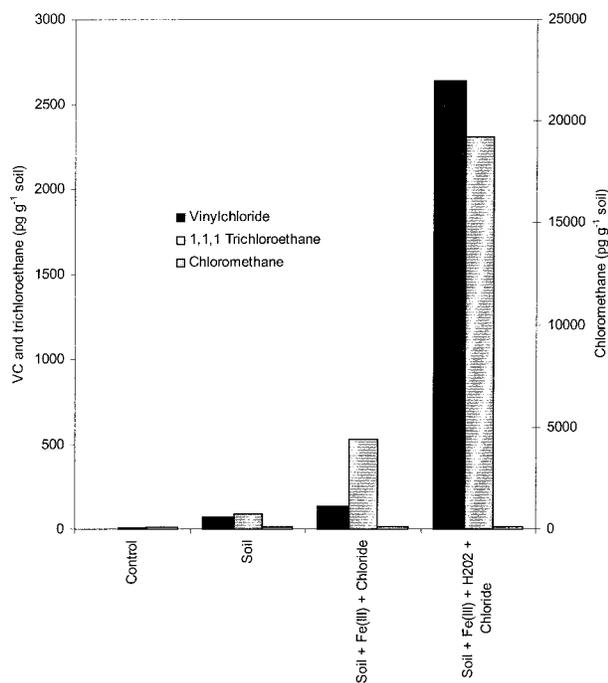
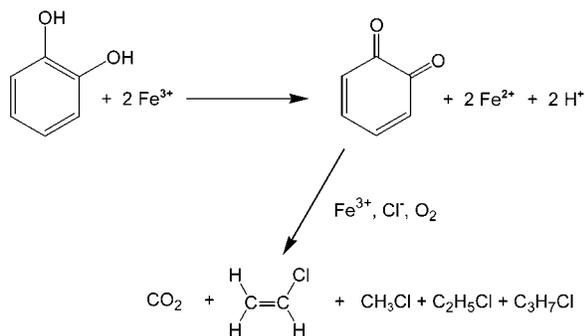


FIGURE 6. Influence of Fe(III) and H₂O₂ on the formation of VC and CH₃Cl in soil. A total of 1000 mg of grassland soil from Patagonia was suspended in 10 mL of water containing 100 μmol of KCl. Before the flask was sealed, 100 μmol of the oxidant was added to the medium ($n = 3$; RSD 4–48%). The pH in the medium was in the range of 2.5–3.2.

The production of VC was accompanied by CH₃Cl, C₂H₅Cl, and C₃H₇Cl, but there was no increase in CH₃CCl₃, TCE, and PCE concentrations. When the same amounts of Fe(III) and H₂O₂ were added to the soil, the VC concentration was 40 times higher as compared with the untreated soil sample. Higher concentrations were found for CH₃Cl and the average CH₃Cl/VC was approximately 7.

The presumption that vinyl chloride is solely man-made must now be considered as incorrect. There is no doubt that industrial and anthropogenic activity has contributed significantly to the burden of VC in the environment, but our results show that vinyl chloride in the environment also has natural sources. One possible soil source comes from the reaction of organic matter, Fe(III), and chloride. As humic substances, catechols, Fe(III), and chloride ions are widespread in nature (25–27), the magnitude of this soil source of VC and other volatile chlorinated substances is potentially enormous and could make a contribution to the budget of vinyl chloride in the environment. Nevertheless, the magnitude of VC production in soil is difficult to estimate and will depend on many factors, including the ambient environmental conditions. The natural formation of VC could be

relevant to many soil processes such as the formation of chlorinated high molecular substances (chlorinated humus), metabolic processes, or as an energy source for microorganisms. However, to understand the formation and significance of naturally produced VC in soil, more detailed investigations are necessary.

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