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Fate of Cyclic Methylsiloxanes in Soils. 1. The Degradation Pathway

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To determine the degradation pathway for cyclic volatile methylsiloxanes (cVMS) in soil, 40−200 mg kg^{-1} of ^{14}C-labeled octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5), and dodecamethylcyclohexasiloxane (D_6) were incubated in a soil sample at room temperature (∼22 °C) and ∼30% relative humidity. The organosilicon species extracted at different times were analyzed by gas chromatography/mass spectroscopy (GC/MS), gel permeation chromatography (GPC), and reverse-phase high-performance liquid chromatography (RP-HPLC). It was found that the degradation of cVMS was a multistep process, initiated by ring-opening hydrolysis of the cyclics to form linear oligomeric siloxane diols, followed by further hydrolysis of these oligomeric diols to the monomer dimethylsilanediol (DMSD). For D_4, the ring-opening hydrolysis was faster than the subsequent degradation of tetramer and trimer diols $\{H[OSi(CH_3)_2]_nOH$, $n = 3$ and $4\}$, resulting in substantial accumulation of these oligomeric siloxane diols at early stages. In contrast, ring-opening was the rate-limiting step for D_5 and D_6, as indicated by the lack of oligomeric diol accumulation at any stage of the cVMS degradation. Nevertheless, all oligomeric siloxane diols were unstable in air-dried soil and ultimately hydrolyzed to DMSD within a few hours to a week, depending on the humidity. When the soil was re-wetted to water saturation, some of the intermediates continued to hydrolyze to DMSD, and some were converted back to cVMS, which then evaporated from wet soil.

Introduction

Cyclic volatile methylsiloxane compounds (cVMS) such as octamethylcyclotetrasiloxane (D_4), decamethylcyclopentasiloxane (D_5), and dodecamethylcyclohexasiloxane (D_6) are volatile, low-viscosity silicone fluids. The annual US production of cVMS in 1993 was 153 000 t, of which 87% was used as site-limited precursors for synthesizing high molecular weight poly(dimethylsiloxane) (PDMS) polymers (*1*). The rest (∼20 000 t) was used in personal care products as carriers or emollients (*2*). The future may see increased use of these compounds, largely due to an emerging application as environmentally safe solvents to replace ozone-forming volatile organic compounds (VOCs) (*3*) and ozone-depleting chlorofluorocarbons (CFCs) (*4*).

Due to their high production volume, the environmental fate of cVMS is of great importance. Previous studies focused on the atmospheric and aquatic fate of these compounds (*5, 6*). The conclusion is that cVMS react with OH radicals in the air with atmospheric lifetime of 10−15 days (*5, 6*).

In the aquatic compartment, the fate of cVMS compounds is determined by their low water solubility (*7*) and relatively high vapor pressure (*8*). In other words, once cVMS fluids enter the aquatic system, they partition rapidly to the atmosphere due to their high volatilities and large Henry's law constants (*2*). Therefore, the concentrations of cVMS are expected to be low and transient in water and sediments (*2, 9*).

Cyclic methylsiloxanes may enter the soil compartment through direct and indirect routes, including treated sludge, spills, and landfill. For example, of the 20 000 t of cVMS used in personal care products, ∼3% went to wastewater treatment plants (WWTPs). Up to 46% of the cVMS that enters a WWTP will be sorbed by sludge (*10*) and thus enter soil directly by land application of the sludge.

Also, cVMS compounds may enter the soil through an indirect route, which also involves PDMS in sludge. It is well-known that cVMS are often formed as rearrangement products of PDMS polymers through a ring-chain equilibrium (*11, 12*). This ring−chain equilibrium may lead to formation of cVMS in soil amended with PDMS-containing sludge. In laboratory studies, formation of cVMS from PDMS was observed in soil clays at high humidity (e.g., at 100% RH) (*13*) or in dry clays flushed with a stream of air (*14*) but not in soils exposed to constantly dry (*15*) or drying conditions (*16*). Raising the humidity to near 100% and flushing clays with air can both desorb and remove hydrophobic volatile compounds such as cVMS from the clays (*17, 18*). The fact that no significant amount of cVMS was detected in soils in the absence of such a removal mechanism (*15, 16*) pointed to the possibility that cVMS compounds themselves may undergo degradation in soil (*13*).

The formation of cVMS from PDMS degradation may also be applicable to other situations. For example, when a PDMS fluid spill contacts the soil, the formation of cVMS is expected because the PDMS concentration in the immediate area is so high (*13, 16*).

Although cVMS may occur in the soil compartment, there is currently no report on their environmental fate in soil. Generally speaking, three major processes may be important in regulating cVMS concentration in soil: sorption, degradation, and volatilization. As part of a project investigating degradation and volatilization of cVMS in soil, the current study concentrated on the degradation process.

Previous work demonstrated that a group of related organosilicon compounds (PDMS) undergoes degradation to ultimately form dimethylsilanediol (DMSD) in soil (*14, 16, 19*). The degradation reaction is mainly a random hydrolytic scission of "Si−O−Si" bonds (*13*). The hydrolysis is catalyzed by all soil clays, with some clay minerals such as kaolinite and montmorillonite in soils of low pH being most effective (*13, 20*). Similar to linear PDMS, cVMS possess Si−O−Si linkages and should be subject to the same soil-catalyzed hydrolysis.

Other possible chemical reactions involving cVMS in soil include demethylation such as that observed in the atmosphere (*5, 6*) and polymerization such as that observed at high cVMS concentration in the presence of catalysts (*21*).

The objective of this work is to elucidate the cVMS degradation process by identifying and monitoring the degradation intermediates and final products in soil. In a follow-up study, the relative importance of degradation and volatilization in regulating cVMS removal from soil will be discussed (*22*).

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Materials and Methods

Soil and Chemicals. The soil used in this study was Wahiawa Series from Kunia area, Oahu, HI. Before use, the moist soil was air-dried on the laboratory benchtop, and the soil clods were gently crushed during the drying process.

The ^{14}C-labeled D_4, D_5, and D_6 were from Wizard Laboratories (Davis, CA). The chemical (by GC/MS) and radiochemical purity (by RP-HPLC) provided by the supplier was >99% for all of these compounds. Before being applied to the soil, a small quantity of each radioactive cVMS was diluted with pentane (Fisher Scientific) to form three spiking solutions. The D_4 spiking solution contained 870 μg mL^{-1} D_4 with a radioactivity of 2.2×10^5 Bq mL^{-1}. The specific activities of the original stocks of the labeled D_5 and D_6 were too high for convenient handling. In preparing D_5 and D_6 spiking solutions, small amounts of the corresponding labeled and unlabeled cVMS were diluted by pentane. The final D_5 spiking solution contained 620 μg mL^{-1} of D_5, with a ^{14}C activity of 1.4×10^5 Bq mL^{-1}. The D_6 spiking solution contained 625 μg mL^{-1} of D_6, with a ^{14}C activity of 1.5×10^5 Bq mL^{-1}.

Soil Spiking. The air-dried Wahiawa soil was weighed into Teflon tubes. The amount of soil in each tube was 1 or 5 g, depending on the targeted concentration (~40−200 ppm cVMS). The soil was then spiked with 0.25 mL of the corresponding spiking solution and flushed for 2 min with air, using a moisture-controlling apparatus (*20*). The soil was incubated in the closed Teflon tubes for 10 min−7 days in the dark at room temperature.

Soil Extractions. *THF Extract*. Cyclic VMS in soil can be transformed via several possible routes, including demethylation, polymerization, and hydrolysis. (Hereafter, hydrolysis is also referred to as degradation). To evaluate the importance of the polymerization process, cVMS-spiked soil (1 g) was extracted with 3 mL of tetrahydrofuran (THF) (Optima from Fisher Scientific) after incubation for 1 h. Extraction time was also 1 h, and the extract was analyzed by GPC, as described later.

THF/H_2O Extraction. THF alone did not extract many hydrolysis products, as shown in a preliminary experiment. The purpose of the following procedure was to increase extraction efficiency for the polar hydrolysis products. After cVMS-spiked soil samples had been incubated in closed Teflon tubes at room temperature for different time periods, 3 mL of THF and 2 mL of saturated solution of $MgSO_4$ (Fisher Scientific) in water were added to each tube.

The saturated solution of $MgSO_4$ in water, which is immiscible with THF, was used as a source of H_2O to desorb siloxanols and silanols from soil. The tubes were vortexed for 2 min, shaken for 30 min, and then centrifuged at 3000 rpm (RCF = 2960*g*) for 5 min. The supernatant in each tube was separated into an upper THF and lower aqueous phase.

A 1-mL aliquot of the upper THF phase was transferred into a glass vial, and 0.1 g of anhydrous $MgSO_4$ was slowly added to the vial (to prevent the heat released from salt hydration from dramatically increasing the temperature of the solution) to absorb water from the THF. This process was repeated once more by transferring the THF to a second vial containing 0.1 g of anhydrous $MgSO_4$. This THF extract was then saved in a GC vial for RP-HPLC and GC/MS analyses.

Extract Analyses. *GPC Analysis*. A total of 0.5 mL of the THF extract was injected into a HPLC (HP1050) equipped with a GPC column (PLgel, 3 μm) and a radiomatic detector (Flow Scintillation Analyzer 500TR, Packard). The mobile phase was 100% THF with a flow rate of 0.5 mL min^{-1}.

RP-HPLC Analysis. A total of 0.1 mL of the THF extract from the THF/H_2O extraction was injected into a HPLC (HP1050) equipped with a Polymer C18 column (YMC−Park Polymer C18, 6 μm) and radiomatic detector. The flow rate was 0.5 mL min^{-1}, and each run lasted 65 min. For each one, the mobile phase started as 100% H_2O and linearly changed to 50% H_2O/50% acetonitrile (Fisher Scientific) between 0 and 10 min. Between 10 and 40 min, the mobile phase linearly changed to 100% acetonitrile. From 60 to 65 min, the mobile phase changed linearly from 100% acetonitrile to 100% H_2O. The time to restore equilibrium between separate runs was 13 min, with 100% H_2O flowing at 0.5 mL min^{-1}.

GC/MS Analysis. The hydrolysis products of cVMS contain hydroxyl groups, which can strongly interact with a GC column. The purpose of the derivatization was to convert these hydroxyl groups to −OSiMe$_3$. The dried THF extract (0.3 mL) from the THF/H_2O extraction was transferred into a GC vial and mixed with 0.2 mL of bis(trimethylsilyl)-trifluoroacetamide (BSTFA) (Aldrich). After BSTFA was allowed to react overnight with the extracts, 0.2 mL of methanol (Fisher Scientific) was added to each vial to react for 2 h with the excess BSTFA.

For GC/MS analysis, 1 μL of BSTFA-derivatized THF extract was injected splitless into a GC/MS (HP GC/MSD 5890A/5970B). The initial oven temperature was 50 °C. After 3 min, the oven temperature was increased linearly at a rate of 15 °C/min to a final temperature of 300 °C. The total ion profile was obtained in the range of 140−800 m/z. The mass spectrum of any given peak was compared with that in the MS spectra library for compound identification.

Stability of the Degradation Intermediates in Wet Soil. The above procedures are for investigating the degradation of cVMS in air-dried soil. In field soil, this degradation process may be interrupted by a rain event. To determine the effect of soil re-wetting on the fate of the degradation products, four soil samples (1 g each) were spiked with 0.25 mL of ^{14}C-labeled D_4 solution. The spiked soil samples were air-flushed for 2 min and incubated for 45 min at room temperature and 32% RH. Saturated $MgSO_4$ solution (3 mL) was added into each tube, and the water-saturated soil samples were allowed to stand undisturbed for designated times, ranging from 3 h (day 0) to 7 days. Then 3 mL of THF was added into each tube, and the tubes were shaken for 30 min. After being centrifuged, the upper THF layer of each sample was analyzed immediately by HPLC as before to quantify various degradation products.

Results and Discussion

GPC Traces of the THF Extracts. Cyclic VMS fluids are often used as precursors for synthesizing high molecular weight, linear PDMS. The process involves an initial ring-opening of cVMS in the presence of catalysts to form diols, followed by their subsequent condensation (*21*). Although soil clay minerals are solid acid catalysts and also capable of catalyzing the hydrolysis of Si−O−Si linkages (*13, 20*), the ring-opening polymerization did not occur significantly in soil at a D_4 loading of <200 ppm (Figure 1).

In Figure 1, the GPC traces of the THF extract from soil spiked with D_4 were compared with those for a linear polymer (350 cSt PDMS) and D_4 standards dissolved in THF. Although the GPC profile of the soil sample showed a small variation at molecular weights less than D_4, the majority of the molecules eluted at 22.2 min, matching the retention time of the D_4 standard.

A small number of molecules slightly larger than D_4 were also observed at high humidity (e.g., 100% RH). They were D_5 and D_6 as determined by GC/MS (data not shown). Nevertheless, all species eluted around the peak of the D_4 standard, suggesting that no significant polymerization occurred at such a low concentration of cVMS (<200 ppm) in the soil.

Degradation Intermediates and the Final Product for D_4. Once in contact with soil, D_4 hydrolyzed to form degradation products that were nonextractable by hexane

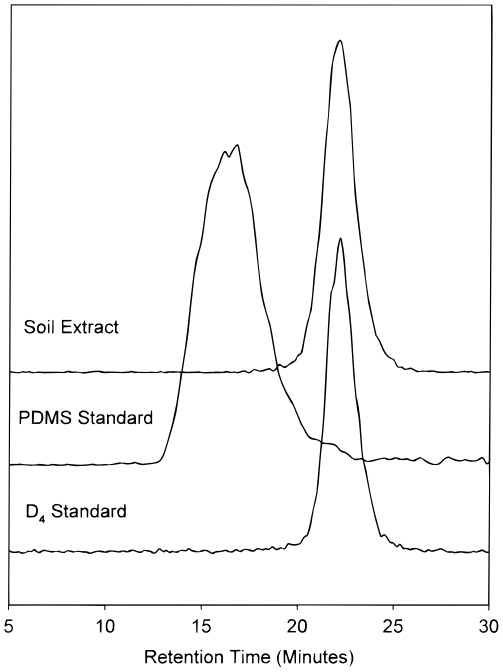

FIGURE 1. GPC profiles of 350 cSt. PDMS and D_4 standards in THF, and the THF extract of a soil spiked and incubated with D_4.

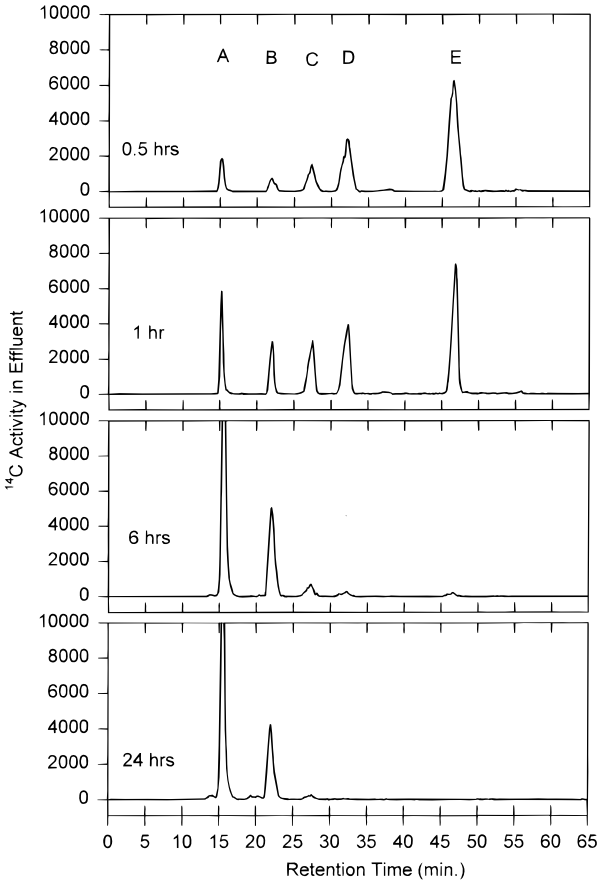

FIGURE 2. RP-HPLC chromatograms of the THF extract from the THF/H_2O extraction of Wahiawa soil spiked with D_4 as a function of incubation time. A = monomer diol; B = dimer diol; C = trimer diol; D = tetramer diol; E = D_4.

but were extractable by more polar solvents such as THF in the presence of water. For example, after D_4 was exposed to Wahiawa soil for only 0.5 h, five different peaks could be

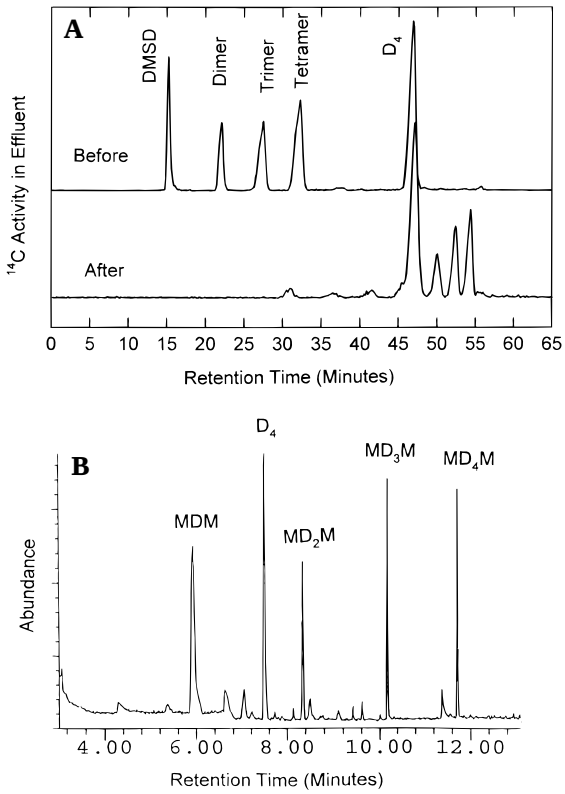

FIGURE 3. (A) RP-HPLC chromatograms of the THF extract from the THF/H_2O extraction of Wahiawa soil spiked and incubated with ^{14}C-labeled D_4 before and after addition of a silylating agent (BSTFA). (B) Total ion GC/MS chromatogram of the THF extract after derivatized with BSTFA.

found in the RP-HPLC profile of its THF extract (peaks A−E in Figure 2). Using ^{14}C-labeled organosilicon standards, the peaks A and E were identified as DMSD and D_4, respectively.

Due to the lack of available ^{14}C-labeled standards for other peaks, GC/MS was employed for identification. In preparation for GC/MS analysis, the THF extract was mixed with a neutral silylating agent (BSTFA) to derivatize the silanols. After an overnight reaction, the BSTFA-treated extract was reanalyzed using RP-HPLC. The HPLC profile (Figure 3A) revealed that all of the peaks except for that of D_4 shifted to longer retention times after derivatization. Notice that after derivatization, only four peaks can be distinguished (Figure 3A). This is because the peak for the derivative of DMSD (at 47.2 min) overlaps with the D_4 peak at 46.8 min. Nevertheless, the shifting of all these peaks verified that the compounds corresponding to peaks A−D (Figure 2) had been completely derivatized to less polar ones.

A GC/MS profile of the same BSTFA-treated extract (Figure 3B) showed five peaks, including D_4, MDM, MD_2M, MD_3M, and MD_4M {General Electric Siloxane Notation, M = $(CH_3)_3$-SiO-, and D_n = $(CH_3)_2SiO_n$}. MDM is the derivative of DMSD, and the latter three peaks (i.e., MD_2M, MD_3M, and MD_4M) are the derivatives of dimer, trimer, and tetramer diols, respectively. On the basis of the hydrophobicity of these derivatives and the gradient change of the mobile phase in the HPLC analysis, peaks B−D in Figure 2 were assigned to the dimer, trimer, and tetramer diols, respectively.

The tetramer diol is the intermediate produced directly from D_4 ring-opening hydrolysis. The high concentration of this intermediate relative to DMSD at early stages of D_4 degradation strongly supports ring-opening hydrolysis as the initial D_4 degradation step:

$$D_4 + H_2O \leftrightarrow L_4 \qquad (1)$$

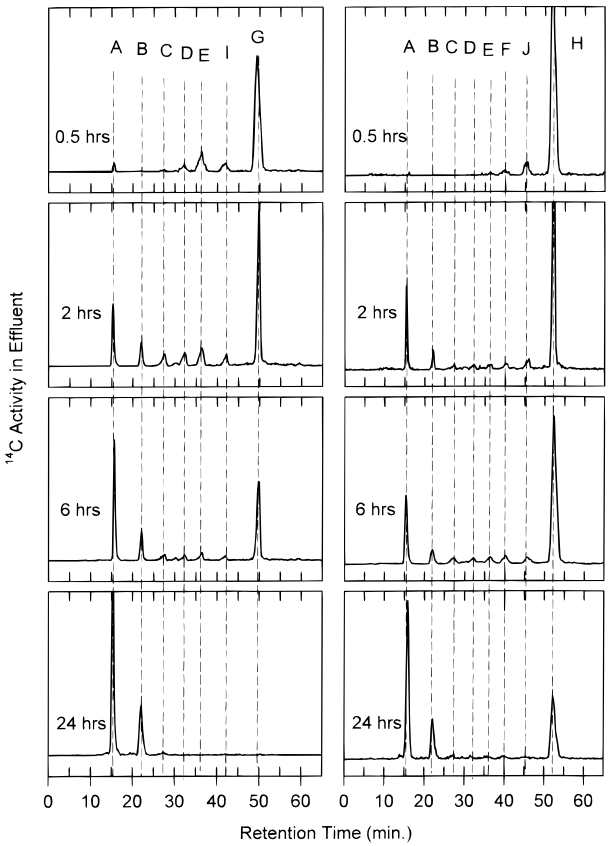

FIGURE 4. RP-HPLC chromatograms of the THF extract from the THF/H_2O extraction of Wahiawa soil spiked and incubated with ^{14}C-labeled D_5 (left) and D_6 (right) as a function of incubation time. A = monomer diol; B = dimer diol; C = trimer diol; D = tetramer diol; E = pentamer diol; F = hexamer diol; G = D_5; H = D_6. I and J were unknown.

where L_4 is the tetramer diol. This and the sequential disappearance of the oligomeric diols (first the tetramer diol and then the trimer diol) as the degradation progressed (Figure 2) are strong support for the degradation scheme as follows, where L_3 and L_2 are trimer and dimer diols, respectively:

$$L_4 + H_2O \leftrightarrow L_3 + DMSD \quad (2)$$

$$L_4 + H_2O \leftrightarrow 2L_2 \quad (3)$$

$$L_3 + H_2O \leftrightarrow L_2 + DMSD \quad (4)$$

$$L_2 + H_2O \leftrightarrow 2DMSD \quad (5)$$

The accompanying increase of DMSD concentration as the concentration of other diols decreased is consistent with previous work (*23*) demonstrating that equilibrium of these diols at low concentration (e.g., monomer diol concentration <2000 ppm) in an aqueous environment favors their hydrolysis toward the monomer, DMSD.

Degradation Intermediates and the Final Product for D_5 and D_6. For D_5-spiked soil, the RP-HPLC profile of a soil extract has seven major peaks (Figure 4, left). In addition to the four diol peaks observed in the D_4 profile (the monomer, dimer, trimer, and tetramer diols), it also had D_5 and two unknown peaks: one at a retention time of ~36 min (peak E) and another at 42 min (peak I). These peaks were especially distinctive for the THF extract obtained after a 2-h incubation (Figure 4, left).

Similar to the situation with D_4-spiked soil, treating the THF extract with BSTFA complete shifted the peaks toward

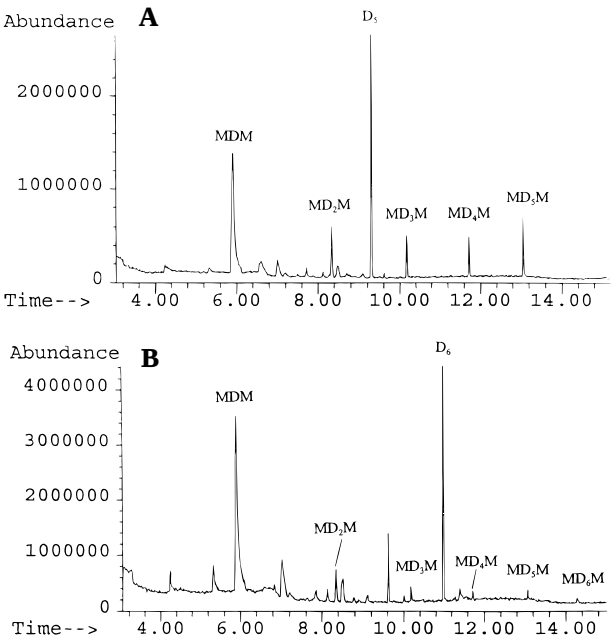

FIGURE 5. Total ion GC/MS chromatogram of the BSTFA-derivatized THF extracts of soil incubated for 2 h with D_5 (A), and 6 h for D_6 (B).

longer retention time on the C-18 column (data not shown). The GC/MS profile of the BSTFA-treated THF extracts (Figure 5A) showed the presence of MD_5M and D_5 in addition to the derivatives of the monomer, dimer, trimer, and tetramer diols as previously identified for D_4 (e.g., in Figure 3). The formation of MD_5M suggested that the ring-opening reaction also occurred to D_5 in soil.

For the THF extracts of the D_6-spiked soil, eight peaks were found in the RP-HPLC profiles. Except for the strong peaks of the monomer diol (peak A) and D_6 (peak H), the concentrations of the degradation intermediates for D_6 (Figure 4, right) were very low, regardless of incubation time. However, the distinctive peaks at an incubation time of 6 h suggested that DMSD, dimer, trimer, tetramer, and pentamer diols all existed in the extract. This conclusion was also supported by the GC/MS profile of the BSTFA-derivatized extract (Figure 5B). In addition, the GC/MS profile indicated the existence of a hexamer diol, a ring-opening product of D_6 (Figure 5B).

Cyclic methylsiloxane compounds such as D_4 and D_5 undergo demethylation in the air to form cyclosiloxanols such as cyclotetrasiloxanol (D_3TOH, where $T = CH_3SiO_{3/2}$) and cyclopentasiloxanol (D_4TOH), due to reactions with OH radicals (*6*). Using BSTFA-derivatized D_3TOH and D_4TOH standards, the GC/MS retention times were found at 9.3 and 10.7 min for these derivatives (data not shown). No such peaks can be found in GS/MS chromatograms in Figures 3 and 5, suggesting no significant amount of D_3TOH or D_4-TOH in the THF extract, although these compounds are soluble in THF.

It should be pointed out that the formation of the degradation products for D_5 and D_6 is slower than for D_4, judged by the reduction of the peak area corresponding to the cVMS. For example, after 0.5 h incubation, more than 72% of ^{14}C is found as D_5 and 90% as D_6 (Figure 4), compared to only ~50% as D_4 (Figure 2). The decrease of cVMS degradation rates as the molecular weight increases has been verified by rate measurement (*22*).

Other differences between HPLC profiles for D_4, D_5, and D_6 were related to the accumulation of the siloxane diols at different incubation times. At early stages of degradation, the concentrations of the larger oligomeric diols relative to

TABLE 1. Organosilicon Speciation (%) in THF Extracts after the D_4-Spike Soil Was First Incubated for 45 min and Then Exposed to Saturated $MgSO_4$ Solution for Different Times before the THF Extraction

organosilicon species	time exposed to $MgSO_4$ solution before THF extraction (days)				aged THF extract from day 1/8[a]
	1/8	1	3	7	
monomer diol	11.5	13.9	17.1	21.1	12.2
dimer diol	5.2	4.1	1.8	1.4	6
trimer diol	11.9	6.1	2.4	1.2	11.1
tetramer diol	26.1	17.2	5.2	1.1	25.7
D_3	nd[b]	2.3	4.8	6.2	nd
D_4	45.4	55.1	66.6	66.8	44.9
total ^{14}C extracted (%)[c]	51.4	64.6	68.6	80	51.4

[a] An aliquot of the THF extract from day 1/8 was stored at 22 °C for 3 days before derivatization. [b] nd, not detectable. [c] The total ^{14}C recovery after combustion of the soil residue ranged from 94.5% to 101.2%.

the corresponding parental cVMS were much higher for D_4. In fact, the tetramer diol accounted for more than 22% of total ^{14}C activity after D_4 was incubated with soil for 0.5−2 h (Figure 2). On the other hand, pentamer diol never exceeded 9% of the total ^{14}C activity during D_5 degradation (Figure 4), and a single intermediate (excluding the dimer diol) accounted for less than 4% of the total ^{14}C activity during D_6 degradation. The substantial accumulation of the tetramer and trimer diols in the early stage of D_4 degradation suggested that the ring-opening hydrolysis for D_4 was faster than the hydrolysis of these oligomeric diols. The lack of significant accumulation in the cases of D_5 and D_6 indicated the ring-opening rate decreased with increasing molecular weight, and the ring-opening hydrolysis became the rate-limiting step in D_5 and D_6 degradation.

Hydrolysis of the Degradation Intermediates in an Aqueous Environment. Cyclic VMS hydrolyzed rapidly in air-dried soil to form the degradation intermediates. Given sufficient time, these intermediates ultimately hydrolyzed to DMSD (Figures 2 and 4). To determine what would happen if the degradation process were disturbed by a rain event before all the intermediates hydrolyzed to DMSD, 3 mL of aqueous solution were added into each soil sample after D_4 was incubated with the soil for 45 min. The HPLC analysis of the THF extracts sampled at different times after addition of the aqueous solution (Figure 6) suggested that the degradation intermediates will not be persistent in wet soil (Figure 6 and Table 1).

Two important points are demonstrated in Figure 6. First, the fraction of ^{14}C extractable by THF in the presence of H_2O increased as the incubation time of soil in the aqueous solution became longer (Table 1). For example, the ^{14}C extracted by THF was only slightly over 50% after 3 h exposure to $MgSO_4$ solution but increased to 80% after 7 days exposure (Table 1).

In addition, the distribution of degradation products also slowly changed with time. The day 0 profile showed D_4 and all the degradation intermediates, a typical species distribution after a short incubation time. The speciation did not change with time when the day 0 THF extract was stored for 3 days (Table 1). However, the amount of larger oligomeric diols decreased with the time that the D_4-spiked soil samples were exposed to water before the final THF extraction (Table 1). In fact, after 7 days in aqueous solution, the dimer, trimer, and tetramer diols almost completely disappeared (Figure 6), while peak areas for DMSD and D_4 increased and a new peak for D_3 appeared.

The increase of total ^{14}C in the THF extract, with the concomitant reduction in concentrations of the dimer, trimer, and tetramer diols suggested that the intermediates can be transformed through two parallel pathways in an aqueous solution. First, they continue to hydrolyze to the monomer diol, similar to the situation in an acidic solution (*23*). Second,

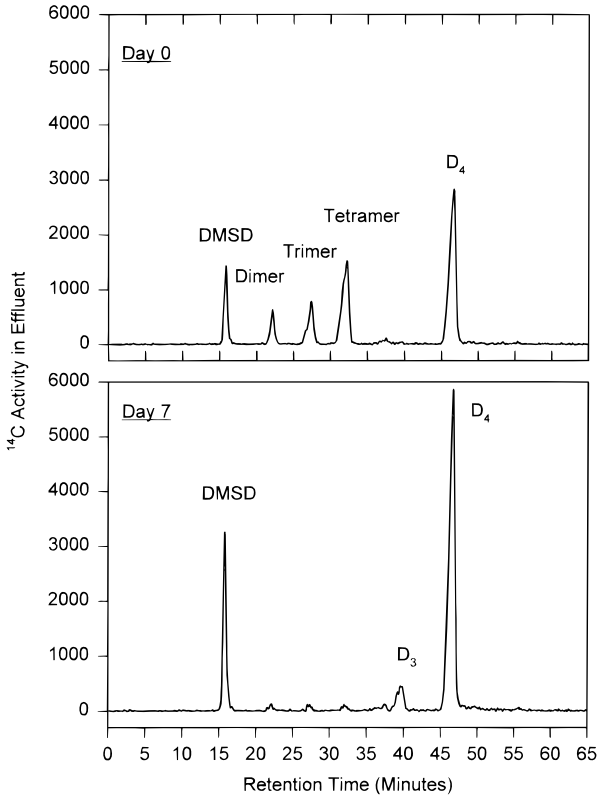

FIGURE 6. RP-HPLC chromatograms of the THF extracts for an air-dried soil spiked with D_4, incubated for 45 min, and then re-wetted with saturated $MgSO_4$ solution for 3 h (day 0) and 7 days before the THF extraction.

larger oligomeric diols such as the trimer and tetramer diols can condense to form cVMS, a backward reaction of the ring-opening hydrolysis (e.g., eq 1). This backward reaction may be promoted by water because once the cyclics (such as D_4 and D_3) are formed, they should be desorbed from clay surfaces in the presence of water (*22*). The increase in total THF-extractable ^{14}C with longer soil/water incubation time implied that some bound diols (i.e., nonextractable by THF/H_2O mixture originally) may have been desorbed slowly in the soil re-wetting process (Table 1).

Nevertheless, the above data all demonstrate that oligomeric diols are unstable in soil. The ultimate degradation product for cVMS is DMSD. Previous studies reveal that DMSD can dissipate from soil via two pathways: volatilization (*24*), and biodegradation (19, *25*, *26*). The combination of these natural processes and multistep hydrolysis (eqs 1−5) provide a complete degradation pathway for cVMS in soil environments.

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