

Degradation of Silicone Polymer at Different Soil Moistures

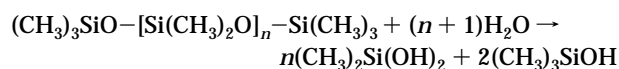
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Silicone polymers [poly(dimethylsiloxane)s, PDMS] are used in down-the-drain consumer products and enter soil through disposal of municipal sludge. We examined PDMS hydrolysis over a range of soil moistures in soils from different geographical regions. [¹⁴C]PDMS 350 cSt was added (50 mg kg⁻¹) to a Michigan Alfisol (Londo sandy clay loam) at six water potentials. Hydrolysis (5-week incubation) was 16, 2.0, 0.14, and 0.09% wk⁻¹ at -76, -18, -5.4, and -1.2 MPa, respectively. Hydrolysis at -0.26 and -0.05 MPa was too slow to distinguish from experimental variability. When dry Londo soil was amended with PDMS and then remoistened to -0.05 MPa, hydrolysis was 0.19% wk⁻¹, meaning that remoistening of soil slows the reaction. Similarly, PDMS hydrolysis in remoistened soils (-0.04 to -0.1 MPa) from Ohio (Alfisol), Georgia (Ultisol), and Puerto Rico (Oxisol) was 0.41, 1.25, and 1.26% wk⁻¹, respectively. Best-fit regression equations ($R^2 > 0.99$) showed a linear dependence of rate constant on water potential from -0.04 to about -100 MPa. Results show that PDMS hydrolysis increased with decreased soil moisture and was faster in Ultisols and Oxisols than in Alfisols at the same soil water potential.

Introduction

Silicone polymers, or poly(dimethylsiloxane)s (PDMS) have the structure (CH₃)₃SiO-[Si(CH₃)₂O]_n-Si(CH₃)₃. They are used in numerous down-the-drain consumer products and thus enter wastewater treatment plants (WWTPs) where they associate with the sludge (1). When the sludge is added to the land as a fertilizer, PDMS enters the soil environment where it hydrolyzes to yield the monomeric dimethylsilanediol (DMSD) (2, 3), which has the structure (CH₃)₂Si(OH)₂:



The finding of DMSD as the dominant soil hydrolysis product of PDMS is consistent with Spivack and Dorn (4), who showed that equilibrium in aqueous solutions strongly favored DMSD over its dimer, trimer, and larger oligomers.

The hydrolysis reaction is probably abiotic, because it is much faster as the soil dries. When Londo sandy clay loam was held at 12% moisture (-0.2 MPa), about 3% DMSD

formed after 6 months, but nearly complete hydrolysis of the polymer occurred in 2 weeks when the soil was allowed to gradually dry (5). Rapid hydrolysis under drying conditions was also observed on seven soils differing in texture, organic matter content, pH, mineralogy, and geographical origin (6). This fact plus recent work showing PDMS hydrolysis on 12 common soil minerals (7) indicate that the reaction should be ubiquitous in the soil environment.

PDMS hydrolysis was also observed under more realistic conditions, such as in greenhouse experiments when PDMS was added to soil as a component of sludge (8). In addition, recent monitoring of sludge-amended fields indicates that PDMS has been degrading in field soils (9). Although the hydrolysis product (DMSD) was detected in some of these soils, the quantities of DMSD were much less than expected from the extent of PDMS loss (9). This is consistent with laboratory studies showing biodegradation of DMSD in soil (2, 10, 11) and volatilization of DMSD from soil (12). Once in the air, the methyl groups of DMSD should be oxidized by OH radicals generated in sunlight, in like fashion to other volatile siloxanes (13, 14).

The widespread use of PDMS and its entry into many soils through the disposal of sewage sludge make it important to understand the fate of this polymer in a variety of soil environments. This paper thus investigates PDMS hydrolysis over a wide range of soil moisture levels. Soils were chosen from three soil orders (Alfisols, Ultisols, Oxisols) along a north-south gradient to provide variety of terms of soil chemistry and mineralogy (15).

Materials and Methods

Silicone. PDMS 350 cSt was randomly ¹⁴C-labeled on the dimethyl units, with a specific activity of 0.52 mCi g⁻¹ (19 Bq μg⁻¹) and ¹⁴C-Si bond purity of 99.9%. This polymer had an actual viscosity of 360 cSt, number-average molecular weight of 8560, and molecular dispersity of approximately 2.0 (data from Dow Corning).

Soils. Soils (Table 1) were collected in 1995 and early 1996, sieved (2 mm), and refrigerated moist until use. Londo soil was chosen for initial experiments because it had been used in previous studies (2, 5, 6).

Soil chemical properties and particle size (Table 1) were determined by A&L Great Lakes Laboratories (Fort Wayne, IN) using standard operating procedures. Soil water potentials (-0.033 to -1.5 MPa) were measured by pressure plate at A&L Great Lakes Laboratories. Potentials drier than -1.5 MPa were determined at the University of Minnesota by measuring relative humidities above soil samples using a CX-2 water activity meter calibrated with saturated salt solutions (16).

Experiment 1: Londo Soil at Six Moistures. Soil (2 kg) was wetted to 25% water content, and 90-g aliquots were weighed into 18 glass jars and then dried to achieve either 18%, 12%, 9%, 6%, 4%, or 2% water content. [¹⁴C]PDMS in 0.5 mL of pentane was added evenly to the soil surface, the pentane was evaporated, and the soils were mixed to yield PDMS concentrations of 50 mg kg⁻¹. Jars were capped, sealed with Parafilm, and incubated in the dark at 22 °C.

Analytical methods were similar to our previous studies (2, 5, 6). On days 0, 1, 3, 6, 10, 13, 17, 22, 27, and 34, a 4-g aliquot of soil was removed from each jar, shaken for 6 h with 20 mL of aqueous 0.01 M CaCl₂, and centrifuged (5 min, 3000 rpm, 22 °C); the supernatant was counted for soluble ¹⁴C. An earlier study had shown that extraction of water-soluble products was nearly complete after 6 h (5). The CaCl₂ solution, which aids in flocculating soil colloids during

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TABLE 1. Properties of Soils

series	origin	great group	texture	pH ^a	organic matter ^b (%)	CEC ^c	sand ^d (%)	silt ^d (%)	clay ^d (%)
Bayamon	Puerto Rico	Hapludoxes	sandy clay loam	6.0	1.1	4.8	57.2	10.0	32.8
Londo	Michigan	Glossaqualfs	sandy clay loam	7.9	2.8	10.8	57.2	20.0	22.8
Miamian	Ohio	Hapludalfs	loam	7.0	5.1	16.5	35.2	40.0	24.8
Wedowee	Georgia	Hapludults	sandy clay loam	5.6	1.3	3.5	63.2	16.0	20.8

^a pH in 1:1 soil:water suspension. ^b Organic matter by chromic acid oxidation. ^c CEC, cation exchange capacity (in cmol kg⁻¹) by NH₄OAc saturation, KCl displacement. ^d Particle size by hydrometer method.

centrifugation (17), is a standard practice for water extraction of organic chemicals (18). Three sequential 20-mL THF extractions (1 h shaking, centrifuging as above) were then each counted for remaining polymer, and a 20-mL 0.1 M HCl extraction (24 h shaking, centrifuging as above) was performed for soil-bound ¹⁴C (2, 5). Soils were then dried and combusted in an R. J. Harvey OX500 combustion unit for residual soil ¹⁴C. All extracts were counted for ¹⁴C on a Packard 2500 scintillation counter using external standards for quench correction.

PDMS hydrolysis was quantified by summing ¹⁴C in water and HCl extracts, since these represent soluble and soil-bound reaction products, respectively. Previous work with this soil had shown that both of these fractions contained almost exclusively (98+%) [¹⁴C]DMSD (2). The [¹⁴C]DMSD in the HCl fraction was not an artifact of acid hydrolysis of sorbed polymer since this technique was only able to extract 0.46% of freshly applied [¹⁴C]PDMS (6). We recognized that the THF fractions probably also contained partial hydrolysis products in the form of oligomers too large to be water soluble, and thus our definition of hydrolysis as conversion to small silanols is conservative.

Experiment 2: Remoistened Londo Soil. Londo soil (80 g) was weighed into six glass jars, dried in the air to equilibrium dryness (about 1.5%), and then amended with [¹⁴C]PDMS in 0.5 mL of pentane to yield soil PDMS concentrations of 50 mg kg⁻¹. After the pentane evaporated (about 10 min), aliquots (4 g) of soil were removed from jars 1 and 2 for analysis, and the rest of the soil in these two jars was remoistened to about 18% water content. After 3 days, aliquots (4 g) of soil were removed from jars 1–4 for analysis, and the rest of the soil in jars 3 and 4 was remoistened as above. After 10 days, aliquots (4 g) of soil were removed from jars 1–6 for analysis, and the rest of the soil in jars 5 and 6 was remoistened as above. Additional soil aliquots (4 g) were removed from each jar for analysis on days 17, 25, and 35. Analysis was by sequential water (0.01 M CaCl₂), THF, and HCl extraction and soil combustion, as described above. THF extracts from soils extracted shortly before remoistening and on day 35 were chromatographed by GPC (gel permeation chromatography) as before (5).

Experiment 3: Other Soils. Bayamon, Miamian, and Wedowee soils were weighed (80 g) into duplicate glass jars, and the soils were dried at room temperature. [¹⁴C]PDMS in 0.5 mL of pentane was added to yield soil PDMS concentrations of 50 mg kg⁻¹. After the pentane had evaporated, soils were remoistened to achieve water potentials of about -0.04 MPa. Jars were either capped immediately or left open to dry to the desired water content (Table 3). Jars were then capped and incubated in the dark at 22 °C. Samples (4 g) were taken for analysis on a weekly basis after intended moistures were reached. Study duration was 5 weeks. Soluble ¹⁴C, residual polymer, and soil-bound ¹⁴C were analyzed by the procedures discussed above.

Results and Discussion

PDMS on Londo Soil. The relationship between water content and water potential for Londo soil is shown in Figure 1. Results from the two techniques fitted well together, and

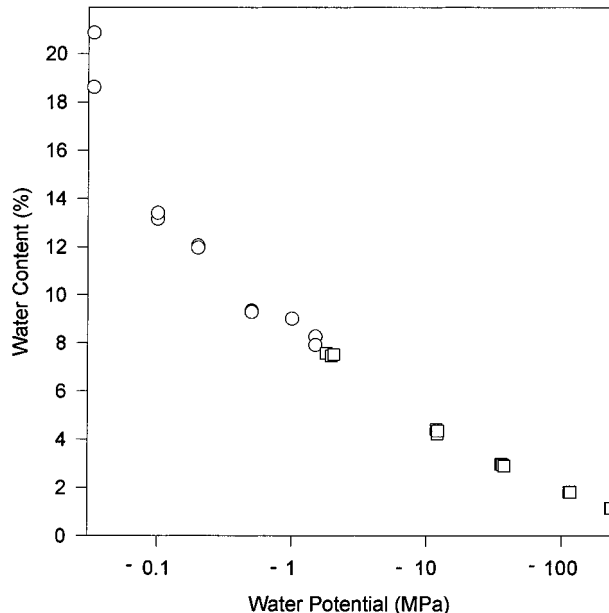


FIGURE 1. Moisture characteristic curve for Londo soil as determined by pressure plate (circles, duplicate measurements) and water activity meter (squares, triplicate measurements).

TABLE 2. Hydrolysis Rates of PDMS at Six Moisture Levels in Londo Soil

soil water contents ^a (%)	soil water potentials (MPa)	hydrolysis rate ^b (% day ⁻¹)	R ² ^c
17.3	-0.05		
11.3	-0.26		
8.4	-1.2	0.0127	0.933
5.5	-5.4	0.0201	0.896
3.5	-18	0.282	0.897
2.0	-76	2.33	0.972

^a % = g of water in 100 g of oven-dried (105 °C) soil. Numbers are means from triplicate jars. ^b Hydrolysis is defined as the production of hydrolysis products = % of ¹⁴C in water + HCl extracts; see text. ^c Coefficient of regression refers to fit of line $y = mx + b$, where y = % hydrolysis products and x = days.

resulting water potentials were deduced from this curve for the water contents in this soil (Table 2).

When PDMS was added to Londo soil at six moisture levels, the hydrolysis rate was slow for the higher water contents but increased rapidly in the drier soils (Table 2 and Figure 2). For the highest water contents (17.3% and 11.3%), a hydrolysis rate could not be determined because the increase in hydrolysis products was not enough during the 5-week incubation to distinguish from experimental variability.

We suspected that the hydrophobic PDMS in the moister soils had not actually contacted the soil surfaces but had existed in a separate phase after the pentane had evaporated. This led to our performing an additional experiment in which PDMS was added to dry (1.5% water content) Londo soil,

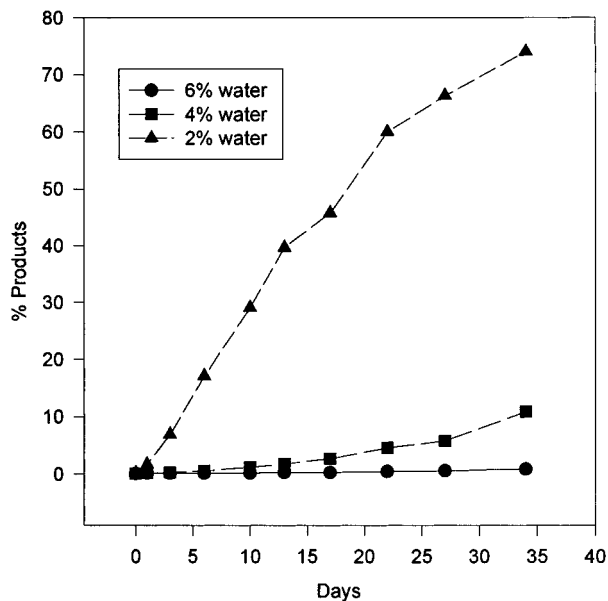


FIGURE 2. Increased hydrolysis of PDMS with decreased water content in Londo soil. PDMS was added to soils after water contents were reached. For triplicate samples, variation from the mean was $\leq 1.5\%$ for 2 and 4% water contents and $\leq 0.1\%$ for 6% water content.

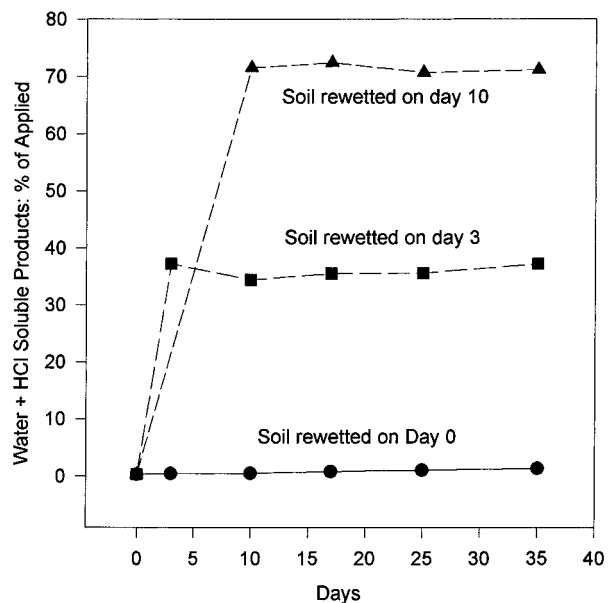


FIGURE 3. Quenching of PDMS hydrolysis after dried Londo soil was rewetted. For duplicate samples, variation from the mean was $\leq 1.5\%$, $\leq 0.5\%$, and $\leq 0.1\%$ for 10, 3, and 0 day rewettings, respectively.

after which the soil was remoistened to 18% water content. For some samples, remoistening was done within minutes after pentane evaporation so that the original PDMS would be intact. For other samples, remoistening was done on days 3 and 10 to allow PDMS hydrolysis to partially proceed. We hypothesized that, once PDMS had sorbed onto the dry soil surface, addition of water might have little effect and that PDMS hydrolysis might proceed at the rapid rates observed in dry soil (Figure 2).

In fact, water addition quenched the reaction, as shown by leveling of the curves of product formation (Figure 3), meaning that little additional water-soluble and soil-bound ^{14}C was forming. In addition, GPC analyses of ^{14}C in THF extracts showed that the remaining polymer was not noticeably decreasing in molecular weight (Figure 4). The quench-

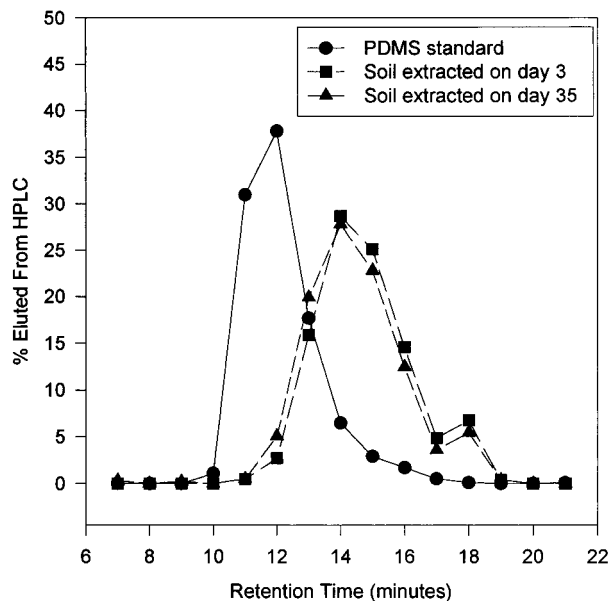


FIGURE 4. Decrease in molecular weight of THF-extractable PDMS from 0 to 3 days when soil was dry, followed by no noticeable decrease after soil was rewetted on day 3. Compare with middle curve of Figure 3.

ing occurred not only for PDMS but also for the oligomeric hydrolysis products that had formed after 3 and 10 days of reaction on dry soil. Probably the increased surface acidity due to soil drying (19), which is thought to be responsible for rapid PDMS hydrolysis (7), was quenched as a result of soil rewetting.

Variability in the data for days 3 and 10 remoistening made it difficult to calculate a hydrolysis rate after remoistening. The data for day 0 remoistening, however, were very consistent, and a hydrolysis rate of $0.19\% \text{ wk}^{-1}$ ($R^2 = 0.99$) at -0.05 MPa was calculated. Although this rate is much slower than in drier soils (Table 2), it is slightly faster than when PDMS was added to soils already moist (Table 2). This suggests that the mode of application of PDMS may affect the hydrolysis rate. But because PDMS normally enters soil as a component of sludge and not in a solvent, both of our techniques are laboratory approximations of actual practice; as discussed later, though, the presence of sludge is not expected to interfere with the rate of PDMS hydrolysis.

PDMS on Other Soils. The highly reproducible data for day 0 remoistening of Londo soil led us to choose this same technique when applying PDMS to other soils; hence, PDMS was added to dry soils, and the soils were rewetted to water potentials of -0.04 MPa and then brought to the desired moisture (Table 3).

All soils showed increased PDMS degradation at lower (more negative) water potentials (Table 3). Degradation curves were best described by the equation $y = (a_1 + k_1x)$ for the initial linear phase and by the equation $y = (a_2 + k_2x^{0.5})$ for the second, nonlinear phase after most of the PDMS had already been degraded. In these equations y is the amount of hydrolysis products formed (% of total ^{14}C in water + HCl extracts) and x is the incubation time (days). When rate constants for the initial, linear portion of the degradation curve were plotted against soil water potential, straight line relationships resulted (Figure 5 and Table 4).

At all water potentials, degradation was faster in Bayamon and Wedowee soils than in Miamian. Rates in Londo soil (Table 2) were performed by a different technique (addition of PDMS to soil already dried to the desired moisture), so the data are not strictly comparable. However, PDMS hydrolysis at a water potential of -0.05 MPa in Londo soil (Figure 3)

TABLE 3. Hydrolysis Rates of PDMS in Three Soils at Four Soil Water Potentials

soil	water content ^a (%)	water potential (MPa)	PDMS concn (μg g ⁻¹)	hydrolysis rate ^b (% day ⁻¹)	R ² ^c
Bayamon	15.2	-0.113	50.9	0.179	0.992
	10.0	-2.08	50.4	0.417	0.999
	4.8	-13.0	50.4	3.02	0.992
	1.4	-90.8	50.9	21.3	* ^d
Miamiian	28.5	-0.035	56.7	0.0581	0.989
	9.9	-1.99	56.2	0.0686	0.995
	5.3	-14.0	56.2	0.459	0.984
	2.7	-82.7	56.7	5.71	0.995
Wedowee	14.6	-0.038	54.1	0.179	0.995
	6.8	-1.63	53.6	0.395	0.999
	2.4	-14.9	53.6	3.15	>0.999
	0.9	-115	54.1	22.0	* ^d

^a % = g of water in 100 g of oven-dried (105 °C) soil. Numbers are means from triplicate jars. ^b Hydrolysis is defined as the production of hydrolysis products = % of ¹⁴C in water + HCl extracts; see text. ^c Coefficient of regression refers to fit of line $y = mx + b$, where $y =$ % hydrolysis products and $x =$ days. ^d Asterisk (*) indicates that hydrolysis was so fast that the rate had to be estimated using only two time points.

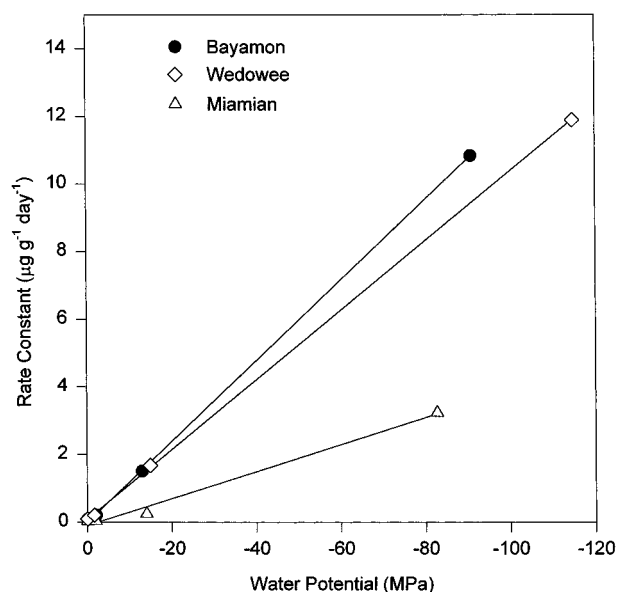


FIGURE 5. Increased hydrolysis of PDMS with lower (more negative) water potential for three soils. Regression coefficients are in Table 4.

TABLE 4. Coefficients for Equations $y = mx + b$ of Figure 5^a

soil	<i>m</i>	<i>b</i>	R ²
Bayamon	-0.1193	0.006412	>0.999
Miamiian	-0.03987	-0.09181	0.992
Wedowee	-0.1029	0.09496	>0.999

^a Where $y =$ PDMS hydrolysis rate constant (μg g⁻¹ day⁻¹), $x =$ soil water potential (MPa), and R² = coefficient of regression for the line.

was performed by the same technique as in later experiments with the three soils. When hydrolysis curves for the wettest soil treatments are compared (Figure 6), the four soils are seen to group into two categories, with the two Alfisols (Londo and Miamiian) being distinguished from the Ultisol (Wedowee) and Oxisol (Bayamon).

The data in Figure 6 suggest some influence of soil order on PDMS hydrolysis, since rates were faster at all moisture

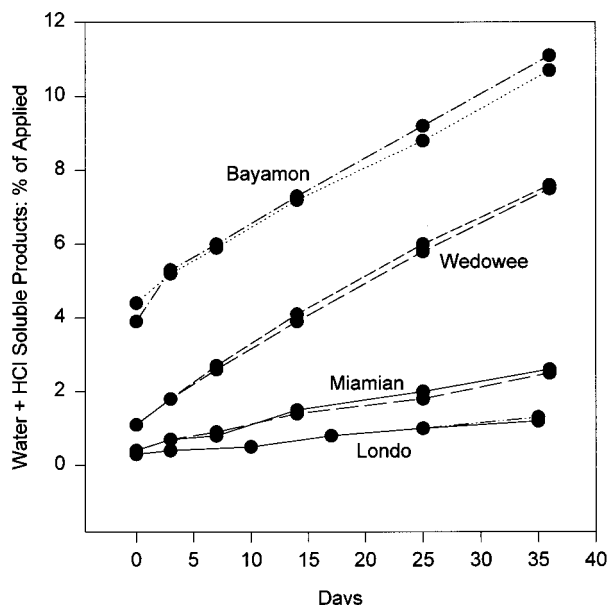


FIGURE 6. Hydrolysis of PDMS in the wettest soil treatments. Water potentials were -0.1 MPa (Bayamon), -0.04 MPa (Wedowee), -0.04 MPa (Miamiian), and -0.05 MPa (Londo).

levels in the Wedowee (Ultisol) and Bayamon (Oxisol) soils. These soil orders contain more kaolinite and aluminum/iron oxides than Alfisols (15). Similarly, in a previous study in which soils were allowed to dry in several days, PDMS began to hydrolyze in a Hawaiian Oxisol while the soil was still moist (6) and to a lesser extent in a moist Ultisol (6). In contrast, Alfisols and Mollisols from the northern United States finished drying before PDMS began to hydrolyze (6). Taken together, these data suggest that PDMS is more susceptible to hydrolysis in Ultisols and Oxisols.

This hypothesis is supported by concurrent studies with pure clay minerals. Xu et al. (7) examined PDMS hydrolysis in 12 common soil minerals. Rates, when normalized to mineral surface areas, were highest in the Al-rich minerals gibbsite and kaolinite, both of which are more common in Ultisols and Oxisols (15).

Implications for the Field. In field situations, PDMS reaches the soil as a component of an organic sludge instead of in a solvent as in this study. Previous work showed, however, that extensive amounts of ¹⁴C-labeled PDMS had hydrolyzed 7 months after it was added to two soils as a component of sludge (8). More recent laboratory experiments are showing that PDMS in a sludge-amended field soil (Miamiian series) hydrolyzes as rapidly as PDMS added in a solvent to sludge-free soil (S. J. Traina, personal communication). The presence of sludge in the soil apparently did not inhibit PDMS hydrolysis. These results suggest that the rates obtained in the present study are valid for sludge-amended soils.

This study shows that PDMS hydrolysis rates are primarily controlled by soil moisture and to a lesser extent by soil type. PDMS hydrolysis for all soils is thus expected to be most rapid at the surface, where the soil is most likely to dry, and during periods of hot, dry weather. Hydrolysis should also be somewhat more rapid in Ultisols and Oxisols, which are more prevalent in subtropical and tropical regions (15). A further understanding of the mechanism of this hydrolysis reaction can be found in Xu et al. (7).

Acknowledgments

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