

Degradation of Silicone Polymers in Nature

Environmental Information - Update

Health Environment & Regulatory Affairs (HERA)

Many consumer products containing silicone polymer, or polydimethylsiloxane (PDMS), are used in a fashion which allows them to enter municipal wastewater treatment plants. Because PDMS is so insoluble in water, it partitions onto the sludge, causing no adverse effect on the operations of the treatment plant [1]. The sludge is then either destroyed by incineration, entombed in a landfill, or spread out on golf courses, woodlands, and agricultural fields as a fertilizer. This latter disposal technique allows PDMS to enter the soil environment.

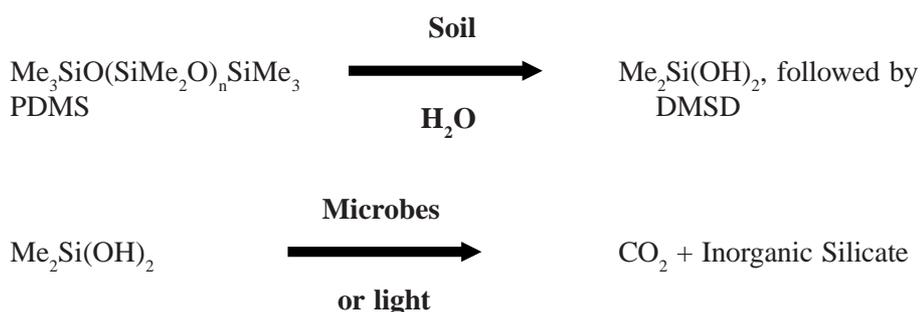
In soil, the PDMS polymer can hydrolyze to small, water soluble siloxanols [2, 3, 4], with the ultimate product being the monomeric dimethylsilanediol (DMSD) [4, 5]. This hydrolysis is probably abiotic, because it can take months to years in wet soil, but only days as the soil dries [3, 6]. The phenomenon has been documented in a wide range of soils throughout the U.S. [7] and in 12 common soil minerals [8], meaning that the catalyst is widespread in nature. Although these experiments were done with pure PDMS, the incorporation of PDMS into sludge does not prevent the hydrolysis. It does, however, make the process more gradual [9], possibly because the PDMS must first diffuse out from the sludge before it can contact the soil surfaces and begin hydrolyzing. If the sludge is first composted, PDMS will remain intact with no effect on the composting process [10], and will then degrade after the compost is mixed in with soil.

The hydrolysis product, DMSD, can microbially degrade to CO₂ [5, 11, 12] and inorganic silicate [13], the latter of which should merge with the silicate already present in the soil [14]. The production of CO₂ from DMSD degradation varied from 0.4-1.6% per week [11]. In addition, DMSD volatilizes from soil at about 1-7% per week [15], with the higher losses occurring from sandy soils. These loss mechanisms suggest that DMSD will not persist in the soil environment. For example, only small amounts of DMSD were found in soils following the hydrolysis of sludge-applied PDMS [9], while an extensive program of field monitoring has found less DMSD than expected in sludge-amended soils showing loss of PDMS [16].

Once in the atmosphere, DMSD is expected to degrade by sunlight-induced reactions, much like other volatile silicones [17, 18, 19]. If it is instead washed out of the air in rainfall, DMSD can be oxidized in water by a similar sunlight-induced reaction [20], or it can be microbially oxidized in soil [5]. Downward movement through the soil profile is not expected because it was not observed in agricultural microcosms during PDMS degradation [9]. Moreover, neither PDMS nor its degradation products harmed soil microorganisms or affected the growth of wheat and soybeans [21].

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The above concepts were tested in field plots sprayed with PDMS emulsions [22]. Extensive losses of PDMS (half-lives of 1-2 months), coupled with dramatic decreases in molecular weight, were observed during a typical Michigan summer season. Only small amounts of DMSD (corresponding to <5% of the original silicone) were found, and deeper sampling revealed that the DMSD had not simply moved downward in the soil profile. This result is thus consistent with laboratory studies showing polymer hydrolysis followed by biodegradation and/or volatilization of the monomer to natural components (CO₂ and inorganic silicate). The overall reaction is:



An apparent contradiction to the degradation of silicones in nature is that these polymers are used for many outdoor applications because of their stability to high temperatures and their resistance to UV and O₃ exposure. This stability during the polymer's intended use is a bulk phenomenon. However, when PDMS is disposed down-the-drain and is eventually applied to the soil as a component of sludge, it becomes dispersed at low concentrations on soil minerals. This allows the **PDMS** to contact the catalysts needed to begin its depolymerization, which eventually results in its complete conversion to natural components. The conclusions in this fact sheet are being further examined in an ongoing program of laboratory and field research.

REFERENCES:

1. Watts, R.J., S. Kong, C. S. Haling, L. Gearhart, C. L. Frye, and B. W. Vigon. 1995. Fate and effects of polydimethylsiloxanes on pilot and bench-top activated sludge reactors and anaerobic/aerobic digestors. *Water Research* 29: 2405-2411.
2. Buch, R. R. and D. N. Ingebrigtsen. 1979. Rearrangement of polydimethylsiloxane fluids on soil. *Environmental Science and Technology* 13: 676-679.
3. Lehmann, R. G., S. Varaprath and C. L. Frye. 1994. Degradation of silicone polymers in soil. *Environmental Toxicology and Chemistry* 13: 1061-1064.
4. Carpenter, J. C., J. A. Cella and S. B. Dorn. 1995. Study of the degradation of polydimethylsiloxanes on soil. *Environmental Science and Technology* 29: 864-868.
5. Lehmann, R. G., S. Varaprath and C. L. Frye. 1994. Fate of silicone degradation products (silanols) in soil. *Environmental Toxicology and Chemistry* 13: 1753-1759.
6. Lehmann, R. G., J. R. Miller, S. Xu, U. B. Singh, and C. F. Reece. 1998. Degradation of silicone polymer at different soil moistures. *Environmental Science and Technology* 32: 1260-1264.
7. Lehmann, R. G., S. Varaprath, R. B. Annelin and J. Arndt. 1995. Degradation of silicone polymer on a variety of soils. *Environmental Toxicology and Chemistry* 14: 1299-1305.
8. Xu, S., R. G. Lehmann, J. R. Miller, and G. Chandra. 1998. Degradation of silicone polymer as influenced by clay minerals. *Environmental Science and Technology* 32: 1199-1206.
9. Lehmann, R. G., C. L. Frye, D. A. Tolle and T. C. Zwick. 1996. Fate of sludge-applied silicones in agricultural soil microcosms. *Water, Air, and Soil Pollution* 87: 231-243.
10. Smith, D. M., R. G. Lehmann, R. Narayan, G. E. Kozerski, and J. R. Miller. 1998. Fate and effects of silicone polymer during the composting process. *Compost Science and Utilization* 6: 6-12.
11. Lehmann, R. G., J. R. Miller, and H. P. Collins. 1998. Microbial degradation of dimethylsilanediol in soil. *Water, Air, and Soil Pollution*: in press.
12. Sabourin, C. L., J. C. Carpenter, T. K. Leib, and J. L. Spivack. 1996. Biodegradation of dimethylsilanediol in soils. *Applied and Environmental Microbiology* 62: 4352-4360.
13. Sabourin, C. L. 1996. Unpublished results.
14. Lindsay, W. L. 1979. *Chemical Equilibria in Soils*. John Wiley and Sons, New York, NY.
15. Lehmann, R. G. and J. R. Miller. 1996. Volatilization and sorption of dimethylsilanediol in soil. *Environmental Toxicology and Chemistry* 15: 1455-1460.
16. Fendinger, N. J., D. C. McAvoy, and W. S. Eckhoff. 1996. Environmental occurrences of polydimethylsiloxanes (PDMS). *Environmental Science and Technology* 31: 1555-1563.
17. Atkinson, R. 1991. Kinetics of the gas-phase reactions of a series of organosilicon compounds with OH and NO₃ radicals and O₃ at 297 ± 2 K. *Environmental Science and Technology* 25: 863-866.
18. Sommerlade, R., H. Parlar, D. Wrobel, and P. Kochs. 1993. Product analysis and kinetics of the gas-phase reactions of selected organosilicon compounds with OH radicals using a smog chamber-mass spectrometer system. *Environmental Science and Technology* 27: 2435-2440.

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19. Martgraf, S.J., and J. R. Wells. 1997.
The hydroxyl radical reaction rate constants and atmospheric reaction products of three siloxanes. *International journal of Chemical Kinetics* 29: 445-451.
20. Buch, R. R., T. H. Lane, R. B. Annelin, and C. L. Frye. 1984. Photolytic oxidative demethylation of aqueous dimethylsiloxanols. *Environmental Toxicology and Chemistry* 3: 215-222.
21. Tolle, D. A., C. L. Frye, R. G. Lehmann, and T. C. Zwick. 1995. Ecological effects of PDMS-augmented sludge amended to agricultural microcosms. *The Science of the Total Environment* 162: 193-207.
22. Lehmann, R. G. In preparation.