*"*Unveiling the truth of silicone degradation: the path to full mineralization*"*

Hélène Dihang[1], Marc Eeman[1], Paige Engerer[2], Kathy Plotzke[2], Jaeshin Kim[2], Debra McNett[2], M.-A. Courtemanche[2]

[1] Dow Silicones Belgium SRL, Rue Jules Bordet, Zone Industrielle C, 7180 Seneffe, Belgium

[2] The Dow Chemical Company, Midland, MI, USA

1. Introduction

Made from naturally occurring silica, one of the most abundant mineral present on earth crust, polydimethylsiloxanes (PDMS) are inorganic/organic hybrid polymers that offer distinct benefits to numerous cosmetic formulations [1]. However, due to the unique properties of these hybrid polymers, traditional biodegradation tests (*i.e.* OECD) are not suitable to assess their environmental fate. Some fraction of Volatile Methyl Siloxanes (VMS) and all PDMS released "down-the-drain" may partition to sludge in waste water treatment plants, and be transferred to soil through soil amendment with biosolids. In soil, PDMS and VMS will undergo abiotic hydrolysis to form siloxanediols and then monomeric methylsilanols such as dimethylsilanediol (DMSD) and trimethylsilanol (TMS) as intermediates [2-8]. In water, DMSD and TMS are further degraded to silicic acid and carbon dioxide [9]. As VMS are predominantly distributed to air once released in the environment, VMS atmospheric degradation is mainly driven by hydroxyl radicals [10-13].

In this paper, we highlight a full pathway for the degradation of PDMS that goes down the drain, looking at the overall environmental compartments (soil, water, air) demonstrating the full mineralization of PDMS into silicic acid and carbon dioxide under natural occurring conditions based on several studies conducted in partnership with the Global Silicone Council.

2. Materials and Methods

Previous work had demonstrated that PDMS will degrade into dimethylsilanediol (DMSD) when in contact with soil *[1-8]*. To understand the ultimate fate of PDMS, movement studies have been conducted either in controlled lab conditions or outdoor conditions in the presence or absence of plants using 14C-radiolabeled DMSD (14C-DMSD). 14C-DMSD and regular non-labeled DMSD (DMSD) were synthesized in-house. Details on the characterization of DMSD and the source of two Michigan soils (sandy and loamy soils) were disclosed previously [14-

16]. Briefly, the chemical purity of DMSD was >98% by gas chromatography and the radio-chemical purity of 14C-DMSD was 94.1%.

Residual DMSD in various soil segments or in the sorbent used for air capture of DMSD was speciated and quantitated after extraction with tetrahydrofuran (THF) and analysis using a reversed-phase high-performance liquid chromatography (RP-HPLC) system (Agilent 1100 Series) coupled with a Flow Scintillation Analyszer (FSA) (PerkinElmer 610 TR FSA). The remaining THF extract was analyzed by Liquid Scintillation Counting (LSC) using a PerkinElmer Tri-Carb 3100 TR liquid scintillation analyzer. THF solvent blanks were analyzed and the average counts from the blanks (20 DMP/sample) were subtracted from all radiochemical analysis. The quantitation limit for LSC is about 60 DPM/sample corresponding to 3 ng 14C-DMSD/sample.

Similar quantitation methods were used to measure DMSD and its degradation products during photooxidative degradation under UV or solar irradiation through water [17]. Speciation of intermediate degradation products was further investigated using high performance liquid chromatography/electrospray ionization/quadrupole time-of-flight/mass spectrometer (HPLC/ESI-QTOF/MS).

For the atmospheric indirect photolysis of octamethylcyclotetrasiloxane (D4), measurements were performed on an Agilent G6530 quadrupole time-of-flight (Q-TOF) mass spectrometer combined with the Agilent G1978B Multimode Ion Source operating in atmospheric pressure chemical ionization (APCI) mode [18]. In positive ionization mode (+APCI), the parent D4 and putative reaction products were expected to be detected as protonated ion adducts mainly, although some ammoniated species were also observed. In negative ionization mode (–APCI), ions were expected to be formed by loss of H^+ or possibly addition of anions such as OH^- or O_2^-.
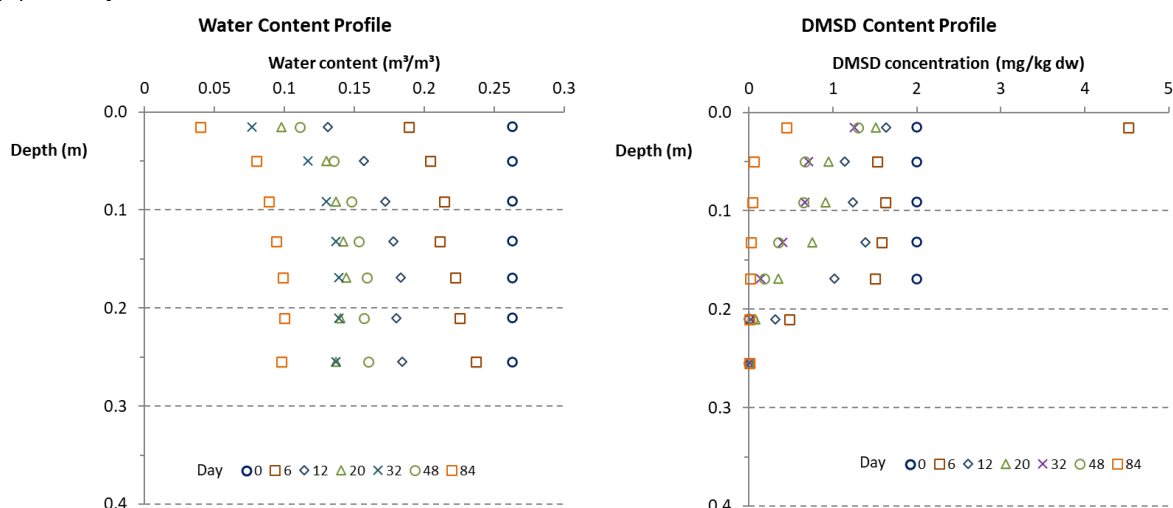
3. Results and Discussion

3.1. Fate of DMSD in bare soil and soil-plant systems

3.1.1. Volatilization of DMSD from bare soil systems

The profiles of moisture contents (left) and solvent extractable DMSD (right) measured on dry weight basis at different times are shown in Figure 1 for both sandy (a) and loamy (b) soils. The trends in both soils were similar, *i.e.*, a decrease of the remaining DMSD as the evaporation time increased in the deeper soil profile, while the DMSD concentration in the topmost layers were higher than their corresponding lower layers [15]. Transportation of DMSD depends on porewater flow in the soil mainly because the predominant fraction of DMSD is distributed in the porewater due to low partition to organic phase (i.e., K_{OC} in a range of 0.19-1.24). During the drying process, the bulk of DMSD moves upward along with porewater. As long as there are enough water molecules at the soil surface to evaporate to the atmosphere, DMSD does not volatilize but accumulates in the topsoil layer [5, 15]. DMSD volatilizes only after water has evaporated completely. The highest measured concentrations of DMSD were observed at day 6 for the sandy soil system and days 6 & 87 for the loamy soil system (Figure 1).

(a) Sandy soil

Water Content Profile

DMSD Content Profile

(b) Loamy soil

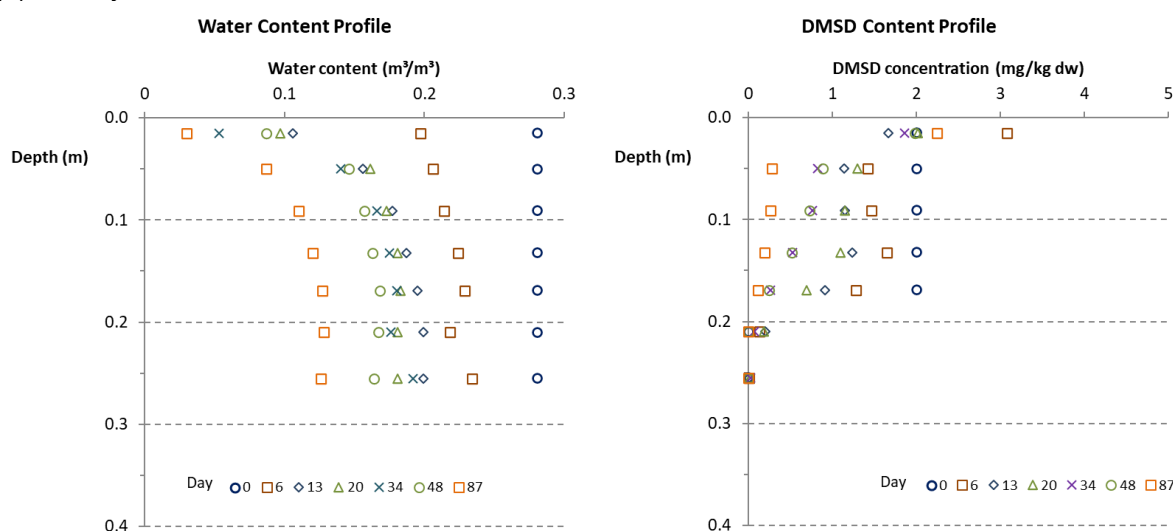**Water Content Profile**

DMSD Content Profile

Figure 1: Soil-depth profiles of moisture contents (left) and DMSD concentrations in different layers of (a) sandy and (b) loamy soils after different volatilization times.

3.1.2. Volatilization of DMSD from plant-soil systems

Similar results were also observed in plant-soil systems with solvent extractable DMSD in soil removed more rapidly and more completely (down to 1% for sandy soil and 2% for loamy soil at the end of the experiment) as shown in Figure 2 [16].

In the study, a corn plant was placed in each soil systems where DMSD was spiked. DMSD in soil was translocated to the roots of the plants, then to the xylem, followed by the leaves, and finally volatilized to air. Calculated overall half-lives of the removal from the plant-soil system were 20 days for a corn plant-sandy soil system and 24 days for a corn plant-loamy soil system. These half-life values are much shorter than 46 and 69 days, respectively, in bare soil systems.
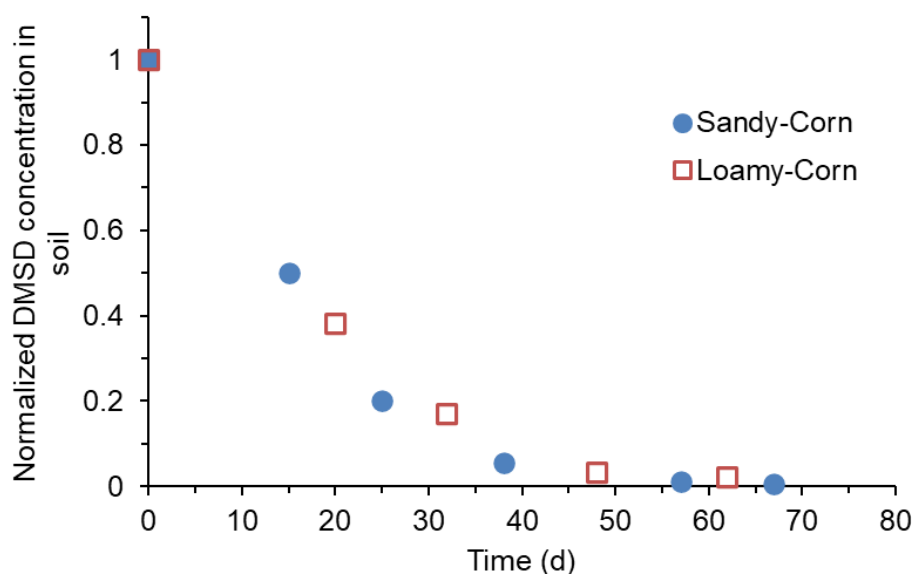
Figure 2. Temporal profiles of DMSD mass remaining in corn plant-soil systems (sandy soil vs. loamy soil).Values are normalized to the initial mass spikes in soils.

3.1.3. The mechanism of DMSD volatilization and sorption in soil

Based on the relationship between DMSD removal as indicated by radioactivity measurements and water evaporation in soil, the DMSD volatilization from a wet soil column could be divided into the following steps:

1) Soil water was evaporated from top layer of soil; Soil water in lower layers underneath the surface moved upward by capillary rise and brought DMSD with it.

2) With the increasing loss of soil water, part of the topmost layer of soil became air-dried; The DMSD in air-dried soil became desolvated and underwent vaporization and sorption. However, sands, clay and organic matter in the topmost layer of soil may not significantly influence the sorption and thus the rate of volatilization due to its low partition coefficient to organic matter.

3) DMSD from the deep layer continued to move up to the topmost layer. At the same time, DMSD concentrations in deeper soil layers decreased as porewater in lower soil layers not spiked with DMSD moved upward.

4) In irrigated soils with crops, DMSD was shown to be removed along with water moving from soil to plant and finally to air in an evapotranspiration process with no need for soil drying as a pre-condition. One major characteristic of DMSD loss by transpiration is the lack of the non-extractable DMSD (or sorbed DMSD) formation in the surface soil layer.
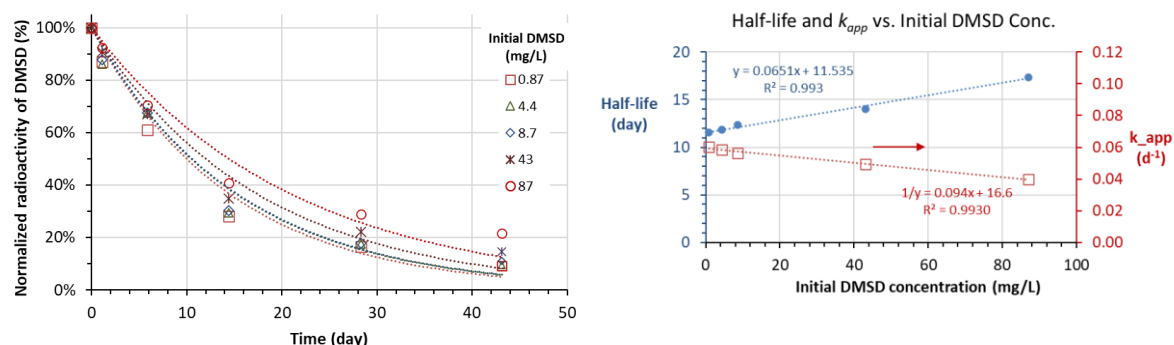
3.2. Fate of DMSD in water via indirect photolysis

3.2.1. Kinetics of DMSD degradation in the presence of nitrate ions in water

Test solutions containing 14C-DMSD in the presence of nitrate ions were placed under simulated solar light with an intensity of ~1000 W/m^2 [17]. Aliquots were removed at various intervals and analyzed by RP-HPLC-FSA for radioactivity to speciate and quantify DMSD

concentrations in the samples. Radioactivity (as 14C-DMSD) normalized to the initial values of 14C DMSD (% radioactivity remaining) are plotted in the left side of Figure 3. With an assumption of pseudo-first order kinetics of the DMSD degradation, rate constants and half-lives were determined as shown in the right side of Figure 3. The indirect photolysis of DMSD in these experiments was sensitive to the initial DMSD concentration only to a small degree, indicating that the production of hydroxyl radicals might not be limited by the increased concentration of DMSD from 0.87 to 87 mg/L (Figure 3a). As nitrate ion concentration was increased from 0 to 30 mg-N/L, oxidation of DMSD was faster as more hydroxyl radicals were produced due the promoting action of the nitrate ion under solar light illumination. Based on the kinetic analysis, degradation half-life of DMSD decreased from 85 to 13 days as nitrate ion concentration increased in the range tested.

(a) Effect of initial DMSD concentration

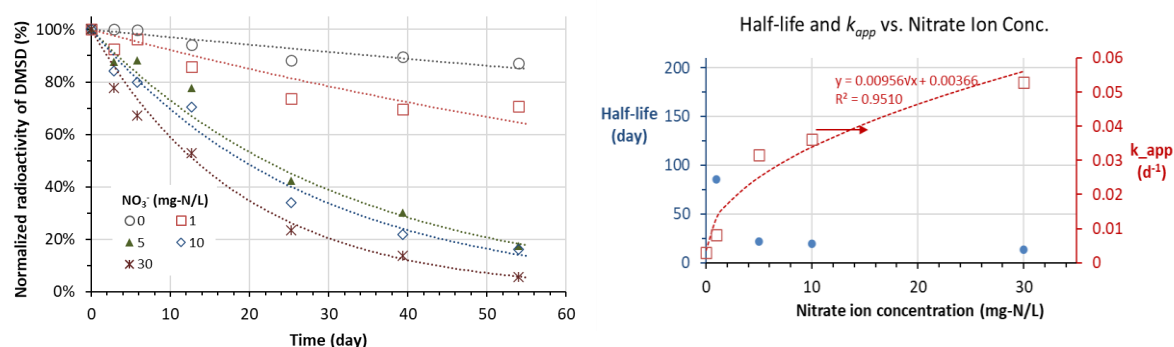(b) Effect of nitrate ion concentration

Figure 3. Left: Percent radioactivity remaining (of initial 14C-DMSD) in the reactor under solar light illumination by (a) varying initial DMSD concentration from 0.87 to 87 mg/L at a fixed nitrate ion concentration of 8.7 mg-N/L and (b) varying nitrate ion concentration from 0 to 30 mg-N/L at an initial DMSD concentration of 1 mg/L. Right: half-lives (blue) and pseudo-first-order rate constants (red) for each system.

3.2.2. The mechanism of DMSD degradation in water

The above results are consistent with nitrate ions promoting the formation of hydroxyl radicals which can in turn oxidize DMSD and as such, the measured OH oxidation rate of DMSD was found to be similar to those of ethanol or 2-propanol [18]. Radioactivity loss over time suggests volatilization or further decomposition of the carbon-based intermediates, while the monotonic increase in silicic acid over time confirmed that some DMSD underwent complete oxidation.

To simultaneously quantitate the formation of the ultimate degradation product silicic acid (using a spectrophotometer) and total radioactivity loss (via RP-HPLC-FSA), nitrate containing

samples with either non-labeled DMSD or 14C-DMSD were exposed to UV light (500 W). While DMSD concentration decreased over time, intermediates were detected such as methylhydroxymethylsilanediol, methylmethoxysilanediol, methylformatesilanediol, and methylsilanetriol. This suggests that rearrangement of C and O atoms would be an essential pathway during the oxidation of DMSD (Figure 4). In addition, silicic acid concentration increased up to 10%-30% when DMSD was oxidized by 50% during the exposure period.
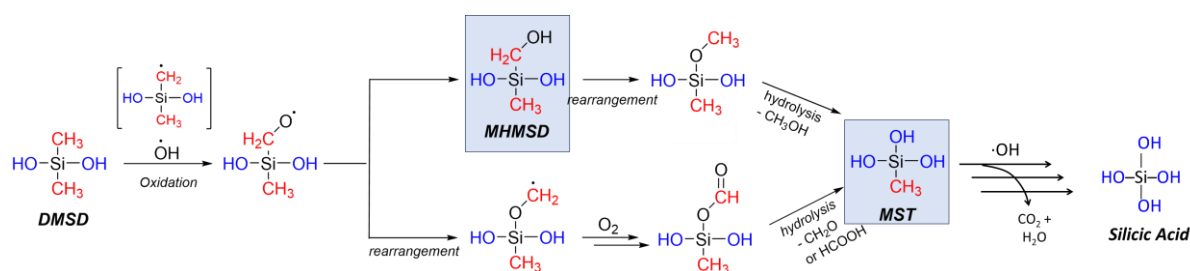

Figure 4. Proposed pathways for the decomposition of DMSD with identified intermediates and final products observed.

3.3. Siloxanes and their degradation products in air

Degradation products were identified during atmospheric oxidation of octamethylcyclotetrasiloxane (D4) by hydroxyl radicals (•OH) in an oxidation flow reactor (OFR) by direct on-line sampling into the atmospheric pressure chemical ionization source of a time-of-flight mass spectrometer (APCI TOF-MS) [18]. Atmospheric •OH are one of the main oxidants to react with airborne compounds. This offers an important contribution to demonstrating a degradation pathway for volatile Si-based substances including DMSD that volatilizes to the air.

For each set of experimental conditions, both ionization methods (positive and negative) were employed and the APCI TOF-MS spectra were analyzed. There was evidence for first-, second and possibly third-generation products, as well as condensation products with different linkages as illustrated in Figure 5.

Once ·OH or chlorine atom radicals are produced, the initial reaction is abstraction of H-atom from a methyl group on the siloxane to form an alkyl radical, which reacts with O_2 to form a peroxy radical. Depending on atmospheric conditions (e.g., high/low Nox and hydroperoxyl) different subsequent reaction pathways are proposed [19, 20]. The predominant first-generation reaction products of cVMS such as D4 and D5 seem to be the cyclosiloxanol and the formate ester, although other minor products were reported [19]. Subsequent generation products such as the siloxanediol or siloxanol/formate ester were detected.
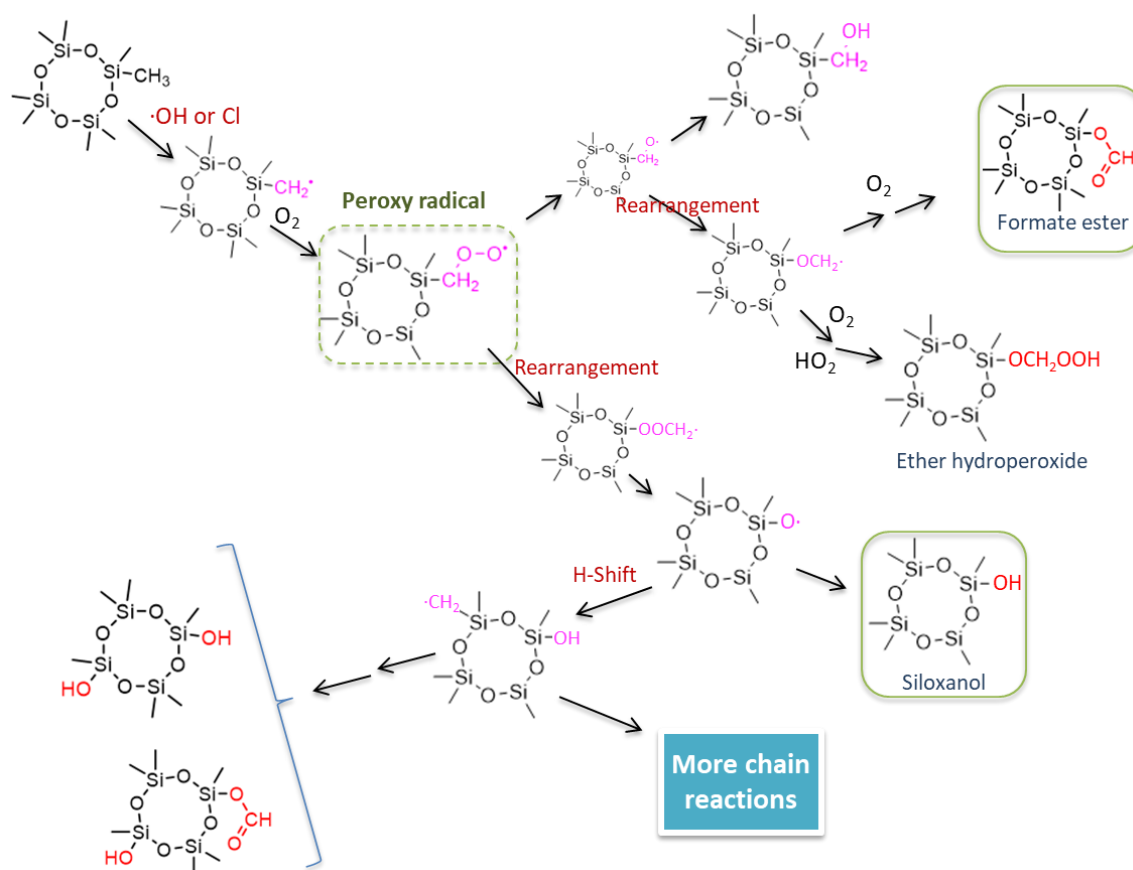
Figure 5. Proposed degradation pathways during oxidation of D4 and siloxanols by ·OH and/or chlorine atom, *in situ* formed from the reaction of ozone (or Cl_2) and water molecules in air under solar light.

4. Conclusion

In dry soil, PDMS rapidly degrades all the way to the monomeric DMSD via an abiotic degradation mechanism as demonstrated [1-8]. New findings demonstrate that the resulting DMSD is shown to migrate upwards with water in soil and volatilize directly or with the aid of plants through phytovolatilization. Siloxanols are also shown to degrade through the action of OH radicals in the atmosphere. DMSD reaching the surface water, with the action of sunlight on naturally occurring nitrates, generates ·OH radicals that fully oxidize DMSD to CO_2 and silicic acid. This work highlights the importance of considering the full spectrum of environmentally relevant degradation pathways (abiotic, photooxidative, biotic) in assessing the fate of silicone polymers in the environment. Consequently, the shortcomings of generally accepted compartment specific isolated tests to establish persistence of inorganic/organic hybrid polymers are accentuated.

References

1. Griessbach, E.F.C., Lehmann, R.G., **1999**. Degradation of polydimethylsiloxane fluids in the environment - A review. Chemosphere, 38, 1461–1468.

2. Lehmann, R.G., Varaprath, S., Frye, C.L., **1994**. Degradation of silicone polymers in soil. Environ. Toxicol. Chem., 13, 1061–1064.

3. Lehmann, R.G., Varaprath, S, Annelin R.B., and Arndt J.L. **1995**. Degradation of silicone polymer in a variety of soils Environ. Toxicol. Chem., 14,   1299–1305.

4. Lehmann, R.G., Frye, C.L., Tolle, D.A., Zwick, T.C., **1996**. Fate of sludge-applied silicones in agricultural soil microcosms. Water, Air, Soil Pollut., 87, 231–243.

5. Lehmann, R.G., Miller, J.R., Kozerski, G.E., **2000**. Degradation of silicone polymer in a field soil under natural conditions. Chemosphere, 41, 743–749.

6. Xu, S. Lehmann, R. G. Miller, J. R., Chandra G. **1998.** Degradation of polydimethylsiloxanes (silicones) as influenced by clay minerals. Environ. Sci. Technol., 32, 1199–1206.

7. Xu S., **1999**, Fate of Cyclic Methylsiloxanes in Soils.. 1. The Degradation Pathway. Environ. Sci. Technol., 33, 603-608.

8. Xu, S., **1998**. Hydrolysis of Poly(dimethylsiloxanes) on Clay Minerals As Influenced by Exchangeable Cations and Moisture. Environ. Sci. Technol.,32, 3162–3168.

9. Buch, R.R., Lane, T.H., Annelin, R.B., Frye, C.L., **1984**. Photolytic oxidative demethylation of aqueous dimethylsiloxanols. Environ. Toxicol. Chem., 3, 215–222.

10. Atkinson, R., **1991**. Kinetics of the gas-phase reactions of a series of organosilicon compounds with hydroxyl and nitrate(NO3) radicals and ozone at 297 ± 2 K. Environ. Sci. Technol., 25, 863–866.

11. Kim, J., Xu, S., **2017**. Quantitative structure-reactivity relationships of hydroxyl radical rate constants for linear and cyclic volatile methylsiloxanes. Environ. Toxicol. Chem., 36, 3240–3245.

12. Bernard, F., Papanastasiou, D.K., Papadimitriou, V.C., Burkholder, J.B., **2018**. Temperature Dependent Rate Coefficients for the Gas-Phase Reaction of the OH Radical with Linear (L2, L3) and Cyclic (D3, D4) Permethylsiloxanes. J. Phys. Chem. A ,122, 4252−4264.

13. Alton, M., Browne, E.C., **2020**. Atmospheric chemistry of volatile methyl siloxanes: Kinetics and products of oxidation by OH radicals and Cl atoms. Environ. Sci. Technol., 54, 5992−5999.

14. Xu, S., Courtemanche, M.-A., Miller, J. Volatilization of dimethylsilanediol (DMSD) under environmentally relevant conditions: Sampling method and impact of water and soil materials. Chemosphere, **2024**, 354, 141681.

15. Xu, S., Courtemanche, M.-A., Miller, J. Fate of Dimethylsilanediol (DMSD) in outdoor bare surface soil and its relation to soil water loss. Chemosphere, **2024**, 352, 141478.

16. Xu, S., Courtemanche, M.-A., Miller, **2024,** J. Fate of Dimethylsilanediol (DMSD) in soil-plant systems. Chemosphere, 352, 141454.

17. Kim, J., McNett, D. A., McClymont, E. L., Courtemanche, M.-A. , **2024**, Fate of dimethylsilanediol (DMSD) via indirect photolysis in water. Chemosphere362, 142670.

18. Buxton, G.V., Greenstock, C.L., Helman, W.P., Ross, A.B., **1988**. Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot$OH/$\cdot$O$^-$ in Aqueous Solution. J. Phys. Chem. Ref. Data 17, 513–886.

19. Rekken, B.D., Kozerski, G.E., Kim, J., **2024**. Identification of Degradation Products from Atmospheric Indirect Photolysis of Octamethylcyclotetrasiloxane (D4) http://dx.doi.org/10.2139/ssrn.4760247.

20. Van Hoomissen, D., Chattopadhyay, A., Burkholder, J.B., **2025**. Rate Coefficients for the Cl Atom Gas-Phase Reaction With Permethylsiloxanes (PMS): L2, L3, L4, L5, D3, D4, D5, and D6. Int. J. Chem. Kinet., 57 , 213 —231