Polydimethylsiloxanes Do Not Bioaccumulate

Environmental Information - Update

Why are there Concerns about Bioaccumulation?

Bioaccumulation is the process where a substance is taken into a living organism, either from the water or through food, and steadily increases in concentration (bioconcentrates) as it is stored in the tissue [1]. As an example, a substance may enter a fish directly from the water through the gills, or as a result of the fish eating a worm or insect which contains the substance. The substance may thus be transferred up the food chain and increase in concentration (biomagnify) with each step until, for “top-predators” including humans, it may reach a toxic concentration.

The most likely substances to bioaccumulate are those which are poorly soluble in water, but which are highly soluble in the fatty (lipid) tissues of fish and other organisms. These materials have a strong tendency to partition from water to an organic solvent such as octanol, which serves as a model for fish lipids. They are thus described as having a high octanol-water partition coefficient ($K_{ow}$). Due to its very low water solubility [2,3], PDMS (polydimethylsiloxane) has a high octanol-water partition coefficient which increases with increasing molecular weight. For example, the log $K_{ow}$s of PDMS polymers of molecular weight 1050, 1124, and 1198 are (respectively) 11.3, 11.9, and 12.5 [4]. It is thus reasonable to ask whether PDMS can bioaccumulate.

Definition of PDMS

PDMS is a shorthand notation for polydimethylsiloxane. It has the structure $\text{Me}_3\text{SiO}(\text{Me}_2\text{SiO})_n\text{SiMe}_3$, where Me = methyl groups and $n$ varies from ~15 for small polymers with a viscosity of 10 centistokes, to ~1000 for large polymers of 100,000 centistoke viscosity. PDMS is thus a family of large, linear polymers with viscosities $\geq 10$ centistokes, molecular weights $\geq 1000$ [5], and with essentially no water solubility [2,3] or volatility [3]. They represent an estimated 99% of the linear dimethylsiloxane fluids sold by Dow Corning, and they are the focus of this Update. The other ~ 1% are low molecular weight dimethylsiloxanes; these materials are volatile and should partition to the atmosphere, where they will degrade in sunlight [6].

The Importance of Molecular Weight

In order for a substance to bioaccumulate, it must be taken into the tissues of a living organism. This means that the substance must first pass through a biological membrane, such as the membranes which line the intestinal wall or the gills. The size of a molecule is important in determining whether it can physically pass through the membrane.

A major principle in bioaccumulation is that molecules which are above a molecular weight of about 600 are too large to cross biological membranes and thus do not bioaccumulate in living organisms [7,8].
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This principle was confirmed by Annelin and Frye [9], who showed that a dimethylsiloxane of ~ 600 molecular weight was not absorbed by the fish [9]. Opperhuizen et al [10] reached a similar conclusion, and showed that after fish had eaten food amended with PDMS (molecular weight > 1000), they did not absorb the PDMS but excreted it within 3 days. As a third example, Bruggeman [4] reported a molecular weight of ~850 above which dimethylsiloxanes should not be absorbed. The difference in cutoff values for the three studies (molecular weights of 600 vs. 850 vs. 1000) probably reflects different experimental techniques used by the three research groups, but a conservative view indicates that PDMS fluids (molecular weight > 1000) cannot pass through biological membranes, and therefore will not bioaccumulate.

Exposure Routes for PDMS

Many consumer products contain small amounts of PDMS. Normal use of these products allows them to enter municipal wastewater treatment plants, in which the insoluble PDMS partitions almost completely to the sludge [11]. The majority of the sludge is either incinerated, landfilled, or added to land as a fertilizer, and thus the major mode of entry of PDMS into the environment is to the soil, where it degrades to natural components [5, 12]. However, small particles of sludge can escape the treatment plant through the effluent, carrying trace amounts of PDMS to surface waters [13], where the PDMS sludge sinks to the sediments and is in contact with aquatic organisms.

Aquatic Organisms

The fact that PDMS is so insoluble in water means that it readily partitions to the sediments. Kukkonen and Landrum [14] thus studied aquatic worms which live in the sediments and found that PDMS did not bioaccumulate in these worms. Similarly, when midge larvae were raised in sediments containing PDMS, they showed no ability to bioaccumulate PDMS [15]. Other experiments have attempted unsuccessfully to dissolve PDMS in water to test bioaccumulation from the water column. For example, Watanabe et al. reported that fish in laboratory studies could take up PDMS from water [16], but in the actual environment they could find no evidence of silicone uptake in fish above silicone contaminated sediments in Japan [17]. This discrepancy was explained by Annelin and Frye [9] as adsorption of floating PDMS globules (in laboratory experiments) to the outside of the fish. To avoid this problem, they washed the outside of their fish and found no bioaccumulation of a dimethylsiloxane (molecular weight ~ 600) by either rainbow trout or fathead minnows [9]. Similarly, no uptake or bioaccumulation of PDMS from the water was found in bluegill sunfish [18], while exposure of guppies to PDMS-amended fish food resulted in no absorption or bioaccumulation of PDMS [4]. Another study showed that when guppies and goldfish were fed PDMS-amended food, the PDMS passed through the gastrointestinal tracts of the fish and was soon eliminated from the body, resulting in no bioaccumulation [10].

Other investigators have added PDMS (as an aqueous emulsion) to seawater to test the potential for PDMS to be transferred up the food chain [19,20,21]. They showed that PDMS did not bioconcentrate in plankton, the lowest level of the food chain. In addition, organisms which fed on the plankton, including sediment-dwelling worms, crustaceans (which fed on the worms), filter-feeding molluscs, and fish (both bottom-feeding and open-water), often contained PDMS at even lower concentrations than in the plankton, thus showing no food chain transfer (no biomagnification). PDMS was also judged to have a very low, if any, acute toxicity to these various species.
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Terrestrial Organisms

When $^{14}$C-labeled PDMS was added in a sludge to soil microcosms (10 ppm) in which soybeans and wheat were grown to maturity in a greenhouse, the PDMS was not taken up into the plants. Trace amounts (1-2% of the $^{14}$C), however, may have been taken up as the soil degradate, $^{14}$C-dimethylsilanediol, or sorbed as $^{14}$C-PDMS to the outside of the plant shoots during the course of the study [22]. The plants grew well and produced a good crop with no harm from the PDMS [23]. The wheat grain had no $^{14}$C in it, and the amount of (unidentified) $^{14}$C-tracer in the soybeans was so low (0.02%) that, even if it were PDMS or dimethylsilanediol, no biomagnification could result from a human eating the soybean.

When earthworms were grown in organic soil amended with very high levels (100 and 1000 ppm) of PDMS, the earthworms ingested the PDMS during their normal course of ingesting the soil. The PDMS did not accumulate in the earthworms, but was instead eliminated with the soil within about 2 days [24].

Summary

In summary, PDMS fluids of commercial interest (i.e., linear dimethylsiloxanes with viscosities $\geq 10$ centistoke and molecular weights $\geq 1000$) do not bioaccumulate in living organisms because they are too large to be absorbed by biological membranes.

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References

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