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PRELIMINARY ENVIRONMENTAL ASSESSMENT OF ORGANOSILICON SUBSTANCES

R. James Maguire

NWRI Contribution No. 01-037

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Preliminary Environmental Assessment of Organosilicon Substances

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Management Perspective

This short review was written to provide an overview of potential environmental hazards posed by organic silicon substances. It is noted that there are very few data on the environmental occurrence of organic silicon substances in the Canadian environment, so a confident risk assessment cannot be made. The information will be communicated to the Toxics Pollution Prevention Directorate, the Canadian Wildlife Service, and the Meteorological Service of Canada.

Sommaire à l'intention de la direction

On a rédigé ce bref examen afin de présenter un aperçu des dangers environnementaux possibles des composés organosiliciés. On a constaté qu'il existe très peu de données sur leur occurrence dans l'environnement canadien; c'est pourquoi on ne peut évaluer leurs risques avec un niveau suffisant de confiance. On doit communiquer ces informations à la Direction de la prévention de la pollution par les toxiques, au Service canadien de la faune et au Service météorologique du Canada.

Abstract

Organosilicon substances comprise a complex array of synthetic chemicals. Polydimethyl siloxanes (PDMS), volatile methylsiloxanes (VMS) and polyethermethylsiloxanes (PEMS) are high volume organosilicones with a wide variety of dispersive uses, so their presence in the environment is expected. Once these chemicals reach the environment their persistence depends upon the nature of the particular substance, and ecosystem specific characteristics. Although all silicones will eventually degrade to naturally-occurring silica and carbon dioxide and water, there is evidence for persistence of some substances in some media, *e.g.*, in sediments and wet soils the half-lives of disappearance can be of the order of months or longer. Some volatile methylsilicones (VMS), and a prominent volatile degradation product of PDMS, dimethylsilane diol (DMSD), may be subject to atmospheric long-range transport. Preliminary evidence indicates that VMS do not contribute significantly to global warming, nor to the formation of ozone in the urban atmosphere. It should be noted that even though many silicones and degradation products do not persist in certain environments, there may be constant introduction of such chemicals to the environment and thus a constant potential hazard.

The high molecular weight PDMS and PEMS appear to have low acute toxicity in soil and in water. The prominent PDMS degradation product dimethylsilane diol (DMSD) is also not very toxic to aquatic organisms (at least to those tested), with a chronic NOEL to *Daphnia magna* of > 10 mg/L. The low molecular weight VMS compounds, by contrast, are much more toxic to aquatic organisms, with NOECs in the µg/L range, and can bioaccumulate significantly.

There are few data on the environmental occurrence of organosilicones. They have been found in air in the low ng/m^3 range; in water at up to 50 µg/L; in sediments at up to 320 mg/kg; in fish at up to 4.5 mg/kg; in STP influents, effluents and sludges at up to 710 µg/L, 13 µg/L, and 5,200 mg/kg, respectively; in industrial effluents and sludges at up to 1,150 µg/L and 6,300 mg/kg, respectively; and in sludge-amended agricultural soils at up to 10 mg/kg. A comparison of these occurrence data to toxicity values for PDMS, PEMS and VMS indicates that residues reported to date are below reported toxicity thresholds, generally by significant margins.

There are very few data on the environmental occurrence of organosilicon substances in the Canadian environment. It is recommended that such chemicals be included in lists of chemicals sought in on-going research studies in southern and northern Canada in order to build a database that would allow a confident assessment of the hazards posed by such substances. Such studies should concentrate on the low molecular weight VMS and PDMS degradation products, and initial sampling strategies should include STP influents, effluents and sludges, agricultural soil that is amended with sewage sludge, ambient water, sediments, fish and air.

Résumé

Les composés organosiliciés forment un ensemble complexe de composés chimiques synthétiques. Parce que les polydiméthylsiloxanes (PDMS), les méthylsiloxanes volatils (VMS) et les polyétherméthylsiloxanes (PEMS) sont des composés organosiliciés produits en grands volumes dont les utilisations dispersives sont très variables, leur présence dans l'environnement est prévisible. Lorsque ces composés chimiques passent dans l'environnement, leur persistance dépend de la nature des substances particulaires, ainsi que des caractéristiques spécifiques des écosystèmes. Même si les silicones finissent par se dégrader en produits naturels comme la silice, le dioxyde de carbone et l'eau, selon certaines indications, on note la persistance de certaines d'entre elles dans des milieux particuliers, p. ex. dans les sédiments et les sols humides; alors, la demi-vie de leur disparition peut être de l'ordre de plusieurs mois ou plus. Certaines méthylsilicones volatiles (VMS) et un important produit de dégradation volatil du PDMS, le diméthylsilanediol (DMSD), pourraient faire l'objet de transport atmosphérique à grande distance. Les résultats préliminaires indiquent que les VMS ne contribuent de façon significative ni au réchauffement planétaire, ni à la formation d'ozone troposphérique. Il faut noter que, même si de nombreux composés organosiliciés et produits de dégradation ne persistent pas dans certains milieux, un apport constant de ceux-ci dans l'environnement pourrait être à l'origine de risques permanents.

Les PDMS et PEMS à poids moléculaires élevés semblent avoir une faible toxicité aiguë dans le sol et dans l'eau. Le principal produit de dégradation du PDMS, le diméthylsilanediol (DMSD), n'est pas très toxique pour les organismes aquatiques (du moins, pour ceux qu'on a testés), avec une CSEO chronique pour *Daphnia magna* de plus de 10 mg/L. Par contre, à cause de leur faible poids moléculaire, les VMS sont beaucoup plus toxiques pour les organismes aquatiques, avec des CSEO mesurées en g/L, et ils peuvent se bioaccumuler en concentrations significatives.

Il y a peu de données sur l'occurrence des organosilicones dans l'environnement. Leurs concentrations mesurées dans l'air sont faibles, de l'ordre de quelques ng/m^3. Elles peuvent atteindre 50 g/L dans l'eau, 320 mg/kg dans les sédiments et 4,5 mg/kg chez les poissons. En outre, elles peuvent aller jusqu'à 710, 13 et 5 200 mg/kg, respectivement, dans les influents, les effluents et les boues de stations d'épuration des eaux usées (SEEE), jusqu'à 1 150 et 6 300 mg/kg, respectivement, dans les effluents et les boues des industries, et jusqu'à 10 mg/kg dans les sols agricoles amendés par des boues. Une comparaison des données sur les occurrences avec les valeurs de toxicité des PDMS, des PEMS et des VMS indique que les valeurs des résidus rapportées à ce jour sont inférieures aux seuils de toxicité de la documentation, habituellement par de fortes marges.

Il y a très peu de données sur l'occurrence dans l'environnement des composés organosiliciés dans l'environnement canadien. Il est recommandé de les inscrire sur

les listes des composés chimiques à rechercher lors des études en cours dans le sud et le nord du Canada, en vue de l'établissement d'une base de données permettant d'évaluer les dangers de ces substances avec un niveau de confiance élevé. Ces études devraient porter principalement sur les VMS à faible poids moléculaire et sur les produits de dégradation des PDMS, et les stratégies initiales d'échantillonnage devraient porter sur les influents, les effluents et les boues des SEEE, les sols agricoles amendés à l'aide de boues résiduaires, l'eau ambiante, les sédiments, les poissons et l'air.

Introduction

This short review is based on readily available information from the open literature, and is not exhaustive. It was written to provide an overview of potential environmental hazards posed by organic silicon substances.

Synthetic organosilicon substances are large-volume chemicals used in a variety of industrial, institutional and consumer applications, such as antifoamers for food processing plants or sewage treatment plants, lubricants, dielectric fluids, solvents, mold and paper release agents, penetrating oils, hydraulic fluids, brake fluids, automobile polishes, water repellents, cosmetics, detergents, hair care and skin care products (*e.g.*, Hamelink, 1992; Allen *et al.*, 1997; Spivack *et al.*, 1997). All commercially available organosilicon materials can be classified into one or more of the following structural classes (Allen *et al.*, 1997):

- organosilanes
- organosiloxanes ("silicones")
- polymeric dimethylsiloxanes
- modified polymeric dimethylsiloxanes
- organosiloxane resins
- organosiloxane (silicone) elastomers

Some of these substances are site-limited intermediates, and others are not environmentally mobile. Based on 1993 U.S. data, the major organosilicon chemical producers and importers concluded that the polydimethylsiloxane fluids (PDMS), volatile methylsiloxanes (VMS) and polyethermethylsiloxanes (PEMS) are the only organosilicon materials that have significant environmental loadings (Allen *et al.*, 1997). Consequently, most research on potential environmental hazards of organosilicon materials has focused on these silicones and in particular the PDMS because of their widespread use compared to other silicones. Estimated global production of silicones in 1995 was 630,000 tonnes (Chandra *et al.*, 1997), and the relative market share of these silicones was about 80-90% for PDMS, 5-10% for VMS and 3% for PEMS (Hamelink, 1992; Allen *et al.*, 1997). Chemical structures of PDMS, VMS and PEMS and some degradation products are shown in Figure 1.

PDMS are the most common silicones. They tend to be stable and inert in the presence of heat, chemicals and ultraviolet radiation. In 1993, 62% of all PDMS manufactured or imported in the U.S.A. was used as site-limited intermediates in the manufacture of elastomers, pressure sensitive adhesives and modified PDMS fluids (Allen *et al.*, 1997). The primary non-site-limited intermediate uses of PDMS are in industrial applications such as antifoamers

and in consumer applications such as personal, household and automotive care products. The wide range in molecular weight of PDMS polymers results in a wide variety of uses. In industrial applications, PDMS fluids are used as softeners and wetting agents in textile manufacturing, for example, and as a component of many polishes and other surface treatment formulations. Some PDMS fluids are also sold as end products like transformer dielectric fluids and heat transfer liquids (Allen *et al.*, 1997). PDMS formulations in the literature are often denoted by their viscosity in centipoise, *e.g.*, 100 cs PDMS.

VMS (low viscosity cyclic materials) are primarily (87%) used as site-limited intermediates (Allen *et al.*, 1997). The rest of VMS production is used in personal care applications such as carriers in antiperspirants, deodorants, skin care products, and as conditioners in hair care products. An emerging application for oligomeric methylsiloxanes is their use as solvents to replace ozone-forming volatile organic chemicals and ozone-depleting chlorofluorocarbons

PEMS are also used extensively as site-limited intermediates. Other uses are as urethane foam additives (to control foam cell size), textile and personal care applications, and as adjuvants in agricultural chemical applications.

Environmental Occurrence

Because of the wide variety of dispersive uses of PDMS, VMS and PEMS, their presence in the environment is expected. It should be noted that there are no naturally-occurring organosilicon chemicals. Table 1 shows some data on the environmental occurrence of organic silicon substances and specific products. The environmental occurrence of silicones in the U.S.A. was first reported about twenty years ago by Pellenbarg (1979a,b, 1982), who suggested, on the basis of the high correlation between organic silicon and both total organic carbon and total carbohydrate in sediment, that silicones could be suitable tracers for anthropogenic releases to the environment.

A consortium of U.S. manufacturers and importers of silicones has generated most of what few data exist in the literature on the environmental occurrence of silicones. They have concentrated on PDMS and VMS (D_4 [octamethylcyclotetrasiloxane - see Fig. 1] and D_5 [decamethylcyclopentasiloxane]), and degradation products, and have placed relatively little emphasis on PEMS, apparently because of the much lower amounts of PEMS used compared to PDMS (Chandra *et al.*, 1997).

Because non-volatile PDMS fluids are essentially insoluble in water and have low surface tension, they are expected to partition heavily to surfaces

such as sludge in STPs, sediments and other interfaces such as the surface microlayer of water and air particulates. Fendinger *et al.* (1997a) (see Table 1) have shown that PDMS partitions readily to sludges in STPs, with very low concentrations in STP effluent. Consequently, it is expected that PDMS will enter the terrestrial environment when the sludge is applied to land, including agricultural soils.

Organic silicon substances have been found in the following media and in the following concentration ranges (see Table 1): air (outdoor) (1-8 ng/m^3); water (n.d.-50 µg/L); surface microlayer (2-44 µg/L); sediment (n.d.-320 mg/kg dry weight); fish muscle (0.2-4.5 mg/kg wet weight); STP influents (n.d.-710 µg/L), effluents (n.d.-13 µg/L) and sludges (30-5,200 mg/kg dry weight); industrial effluents (n.d.-1,150 µg/L), and sludges (40-6,300 mg/kg dry weight); composts from STP sludges (340-410 mg/kg dry weight); and sludge-amended agricultural soils (n.d.-10 mg/kg dry weight).

Environmental Persistence and Fate

The environmental persistence of silicones depends upon the nature of the particular substance and a number of environmental factors. All silicones will eventually degrade to naturally-occurring silica, carbon dioxide and water.

VMS

- in air

Atkinson (1991) determined rate constants for the gas-phase reactions of a number of VMS with OH and NO_3 radicals, and O_3 at 24 °C. The NO_3 radical and O_3 reactions were calculated to be of no importance as tropospheric removal processes for these compounds. Direct photolysis was also not important. Calculated lifetimes of some VMS in the troposphere due to chemical reactions with the OH radical were in the range of 10-30 days. These lifetimes are sufficiently long that these compounds will undergo long-range transport and be regionally and globally distributed. Atkinson (1991) further suggested that wet and/or dry deposition may also be important as tropospheric removal processes for these VMS, but Hobson *et al.* (1997) later estimated that wet and dry deposition of VMS were not significant processes. Sommerlade *et al.* (1993) generally confirmed these observations, and also determined some products of OH radical attack on some VMS. VMS appear not to contribute significantly to global warming, nor to the formation of ozone in the urban atmosphere (Chandra *et al.*, 1997).

- in water

By their very nature, VMS are expected to volatilize readily from water to air (Hamelink, 1992; Mazzoni *et al.*, 1997). For example, the half-life of volatilization of octamethylcyclotetrasiloxane (D_4) from various aquatic systems was estimated to be in the range of 3 hours to 6 days (Hobson *et al.*, 1997). An experiment with a water-sediment system spiked with radiolabeled D_4 showed that only about 5% of the dose remained in the water column after 56 days, and about 7% in the sediment. There appeared to be no degradation to CO_2. Consequently, it appeared that almost 90% of the D_4 had volatilized and that biodegradation was not important (ref. 2 in Hobson *et al.*, 1997)

PDMS

- in soil

It is important to consider the fate of PDMS in soils because PDMS-containing sludges from STPs are frequently applied to agricultural soils. Many studies have indicated that PDMS in soils degrade initially by a chemical mechanism, catalyzed by the clay fraction of soils, especially under dry conditions (*e.g.*, Buch and Ingbrigtson, 1979; Hamelink, 1992; Carpenter *et al.*, 1995; Lehmann *et al.*, 1994a,b, 1995, 1998; Xu *et al.*, 1998; Griessbach and Lehmann, 1999). The primary product is dimethylsilane diol (DMSD), although there are other low molecular weight intermediates. The kinetics of chemical degradation of PDMS depend to a considerable degree on the nature of the soil and clay, and the moisture content of the soil. Half-lives of PDMS are of the order of days to weeks.

DMSD in soil can be microbially degraded to silicate, or incorporated into the soil matrix, or it may volatilize and then be degraded photolytically (Lehmann *et al.*, 1994a,b, 1998; Lehmann and Miller, 1996; Sabourin *et al.*, 1996, 1999). In soil, the kinetics of biodegradation depend to a considerable degree on the nature of the soil and the kinds and concentrations of microorganisms. Overall disappearance half-lives of DMSD from soil can be of the order of months (*e.g.*, Lehmann *et al.*, 1994). In air, DMSD reacts with OH radical, and the calculated tropospheric lifetime for this reaction is 15 days (Tuazon *et al.*, 2000). This is long enough for long-range transport; however, DMSD may also be subject to wet and dry deposition.

- in water

There is limited evidence for the slow hydrolysis of PDMS in water to DMSD (ref. 35 in Chandra *et al.*, 1997). This is to be expected in view of the fact that PDMS is hydrolyzed much faster in dry soil than in moist soil (see above). The half-life of (artificial) sunlight photodegradation of a partially water-soluble oligomeric PDMS in the presence of nitrate (to generate OH radicals)

was 4-9 days (Anderson *et al.*, 1987). However, the corresponding reaction of a high molecular weight PDMS (50 dimethylsiloxane units) was very slow, with only 1.7% conversion to silicate in 5 weeks. In water, PDMS is expected to partition strongly to the sediment phase (*e.g.*, Chandra *et al.*, 1997; Fendinger *et al.*, 1997b). Because the catalytic destruction of PDMS by clays in soils is inversely related to the degree of hydration, PDMS are expected to be more chemically stable in sediments than in soils (Hamelink, 1992). This has been confirmed by experiment (refs. 31-36 in Fendinger *et al.*, 1997b). Carpenter *et al.* (1996) (ref. 37 in Fendinger *et al.*, 1997b) incubated radiolabeled 350 cs PDMS for 1 year in aerobic freshwater sediments, and found only 5-10% of the PDMS had been hydrolyzed to DMSD, and approximately 0.25% of the total ^{14}C had been oxidized to CO_2. Their results suggested that biologically-mediated hydrolysis may have been involved.

DMSD under sterile conditions is chemically stable for at least 1 year (Sabourin *et al.*, 1996). In water lower siloxane diols hydrolyze to DMSD (Spivack and Dorn, 1994). In water DMSD can be oxidatively demethylated by simulated sunlight (intensity 5x greater than sunlight) in the presence of nitrate ion, with a half-life of about 2 days, ultimately producing silicate (Buch *et al.*, 1994). DMSD appeared to volatilize from water in a laboratory experiment only slowly until the sample went dry, at which time most of the DMSD was lost, indicating that volatilization from dilute solution is an unlikely environmental pathway (ref. 76 in Spivack *et al.*, 1997).

PEMS

There is much less information on the environmental persistence and fate of PEMS compared to PDMS. In general PEMS are more soluble in water than PDMS. However, it appears that they are also strongly adsorbed to soils and sludges (Powell and Carpenter, 1997). It is presumed that the degradation pathways for PEMS in such media would be similar to those of PDMS.

Possible methylation of inorganic mercury by silicones in the environment

In the 1980s a considerable amount of research was done on transmethylation reactions between metals and organometals (*e.g.*, Bellama *et al.*, 1988 and references therein). It is not surprising that some low molecular weight siloxanes such as hexamethyldisiloxane could methylate metals such as mercury; indeed, they are used for that purpose in environmental analytical chemistry. Nagase *et al.* (1988) have demonstrated that various organosilicon substances can methylate mercury (at 80 °C and at relatively high concentrations of mercury - 14 mg/L $HgCl_2$) to methylmercury abiotically in laboratory experiments. However, the ability to methylate mercury decreases with increasing molecular weight of PDMS, and at ambient temperatures and

typical environmental concentrations of mercury and PDMS, it appeared that the production of methylmercury would not be significant.

Toxicity

VMS

Table 2 shows that the NOEC for acute and chronic toxicity of octamethylcyclotetrasiloxane (D_4) to a number of aquatic organisms is in the range 4.4-15 µg/L (Hobson *et al.,* 1997). Toxicity in the rainbow trout appeared to be by a narcosis mode of action. For the fathead minnow (*Pimephales promelas*), the BCF at steady state (7-28 days) was calculated to be 12,400 (95% confidence interval = 9,400-16,100). An earlier report had shown that D_4 under flow-through conditions could be bioaccumulated 1,000-5,000x by fish in laboratory experiments (refs. 28, 29 in Hamelink, 1992). No data were found on the toxicity of VMS in soil or by inhalation.

PDMS

- in soil

Because the main route of entry to the environment of PDMS is through the application of STP sludge to agricultural soils, it is important to determine the effects of PDMS and its degradation products on soil invertebrates and crops.

Tolle *et al.* (1995) studied the effects of PDMS-augmented sludge in soil-core microcosms. PDMS at concentrations of 290-3,500 mg/kg had no significant effect on seed germination or seedling survival of spring wheat (*Triticum aestivum*) or soybeans (*Glycine max*) when incorporated into silty clay or sandy loam soil (< 13 mg/kg PDMS) in pots. PDMS at concentrations of 290-3,500 mg/kg in sludge amended to silty clay or sandy loam topsoil (< 10 mg/kg PDMS) in the microcosms also appeared to have no effect on (1) cumulative loss of nitrate-nitrogen in leachate summed over three collection periods, (2) oven-dry biomass of spring wheat or soybean immature shoots, mature shoots, mature grain/seeds or total biomass, (3) *Rhizobium* bacteria, as indicated by number of nodules on soybean roots in sandy loam soil, and (4) numbers of soil microorganisms, including bacteria, actinomycetes and fungi. However, the quantity and timing of sludge amendment may affect (1) loss of nitrate-nitrogen in leachate, and (2) soybean yields.

Lehmann *et al.* (1996) found that only insignificant amounts of radiolabeled PDMS applied to soil were taken up in the shoots of soybeans over a 7-month period

Earthworms (*Eisenis foetidia*) exposed to PDMS in soil at 1,100 mg/kg showed no adverse effects on total number of cocoons, mean cocoon weight, mean number of earthworms per viable cocoon, or mean earthworm weight at 21 days post-hatch compared to controls (ref. 69 in Fendinger *et al.*, 1997b). Survival of the springtail (*Folsomia candida*) in an artificial soil was not affected at PDMS concentrations in the range 250-4,000 mg/kg. However, the number of offspring was statistically reduced at ≥ 500 mg PDMS/kg, with a NOEC of 250 mg/kg (ref. 69 in Fendinger *et al.*, 1997b).

- avian feeding studies

There were no effects on survivability or growth in mallard ducklings (ref. 71 in Fendinger *et al.*, 1997b) and bobwhite quail (ref. 72 in Fendinger *et al.*, 1997b) fed up to 5,000 mg PDMS (100 cs) /kg food for 5 days. There were also no effects on egg-laying, egg quality, hatchability, or chick variability in white leghorn chickens fed up to 5,000 mg/kg PDMS (100 cs) for 4 weeks (ref. 13 in Fendinger *et al.*, 1997b).

- in water

PDMS fluids are not expected to accumulate in aquatic organisms because of their high molecular weight (*e.g.*, Fendinger *et al.*, 1997b).

Gettings and Lane (ref. 31 in Fendinger *et al.*, 1997b) studied the effects of a hydroxy-end-blocked PDMS (55 cs) on algae and bacteria in a model ecosystem. The PDMS in the ecosystem was predominantly associated with the sediment, with water concentrations up to 260 µg/L. No adverse effects were noted on the development of aerobic and anaerobic bacteria, algae or protozoa after 24 weeks. Buch *et al.* (1984) showed that diatoms (*Navicula pelliculosa*) could use photolytic degradation products (presumably silicates) from dimethylsilane diol as the only source of silicon-containing nutrient, but they could not use dimethylsilane diol itself for growth.

Toxicity testing with *Daphnia magna* has been confounded by the physical effects of pure PDMS fluids, resulting in a wide range of reported toxicity values. In experiments employing a surfactant, there was no evidence of toxicity, either by physical entrapment or mortality, at PDMS concentrations up to 200 mg/L (ref. 56 in Fendinger *et al.*, 1997b). Another study showed no adverse effects on *Daphnia* exposed for 21 days to sediment containing PDMS at 570 mg/kg. The 96-hr LC_{50} for *Mytilus edulis* was reported to be 1,980 mg/L for a 20% emulsion and > 1,020 mg/L for 50 cs. PDMS (ref. 57 in Fendinger *et al.*, 1997b). The LC_{50} for cockles (*Prothaca spaminea*) was > 1,000 mg/L PDMS (ref. 13 in Fendinger *et al.*, 1997b).

The acute toxicity of PDMS to fish is low, with LC_{50} values generally > 1,000 mg/L (Fendinger *et al.*, 1997b), except for a 96-hr LC_{50} value of 350 mg/L for 50 cs PDMS in the plaice (ref. 60 in Fendinger *et al.*, 1997b). In chronic studies, the NOEC was 91 mg/L for a 50 cs PDMS fluid in a 33-day embryo-larval study with sheepshead minnow (*Cyprinodon variegatus*) (ref. 61 in Fendinger *et al.*, 1997b). In a subchronic study in rainbow trout (*Oncorhynchus mykiss*) receiving food containing 350 cs PDMS, it was estimated that the fish ingested enough PDMS to correspond to 10,000 mg/kg body weight, yet no mortality or growth effects were observed, and histopathological examination of skin, muscle, liver, bile, adrenal gland, stomach and gut revealed no abnormalities (ref. 62 in Fendinger *et al.*, 1997b).

Since PDMS in aquatic environments is expected to partition strongly to sediments, it is important to determine its toxicity to benthic organisms. There were no effects on the survival or growth of midges (*Chironomus tentans*) exposed for 14 days to 350 cs PDMS in sediments at concentrations of 350-560 mg/kg, and there was no significant accumulation in midge tissue (ref. 63 in Fendinger *et al.*, 1997b). No mortality was observed in the marine amphipod *Ampelisca abdita* exposed for 10 days to 350 cs PDMS in sediments at concentrations in the range 140-2,300 mg/kg, (ref. 64 in Fendinger *et al.*, 1997b). No effects on survival or growth over 28 days were observed for the freshwater amphipod *Hyallela azteca* exposed to similar PDMS concentrations (ref. 64 in Fendinger *et al.*, 1997b). A 28-day study with polychaete worms (*Nereis diversicolor*) exposed to sediment-associated PDMS at 1,000 mg/kg showed no adverse effects on survivability or weight gain (ref. 65 in Fendinger *et al.*, 1997b). PDMS had no significant effects on crab respiration or mussel feeding at nominal PDMS concentrations in sediment of up to 100 mg/kg (ref. 67 in Fendinger *et al.*, 1997b).

Dimethylsilane diol (DMSD) degradation product of PDMS

DMSD is not particularly toxic to aquatic organisms; for example, the acute LC_{50} for DMSD to grass shrimp was > 1,000 mg/L (ref. 76 in Fendinger *et al.*, 1997b), and the chronic NOEL to *Daphnia magna* was > 10 mg/L (ref. 77 in Fendinger *et al.*, 1997b).

PEMS

- in soil

PEMS 1 (mw 31,400 Da) sprayed on test plots at a rate of 83 gallons/acre (800 mL/m^2) showed no significant effects on soil invertebrate populations (ref. 59 in Powell and Carpenter, 1997). However, delayed and

damaged flowering was observed for several plant species three weeks after exposure, with a general decrease in plant coverage noted after one month. After one year, there was no grossly observable damage. In a simulated spill at approximately 100 times this dose there was widespread plant mortality within 7 days (refs. 58, 59 in Powell and Carpenter, 1997).

- in water

The toxicity of PEMS varies considerably with size or molecular weight. For PEMS fluids of molecular weight ≥ 3,000, for example, the 96-hr LC_{50} values for rainbow trout (*Oncorhynchus mykiss*) are > 100 mg/L. For PEMS 4 adjuvant of mw 672 Da, the 48-hr LC_{50} for *Daphnia magna* is 41 mg/L and the 96-hr LC50 value for rainbow trout (*Oncorhynchus mykiss*) is 4 mg/L (both nominal concentrations) (see Powell and Carpenter, 1997).

Regulatory Activities in Some Other Countries

In the U.S.A., as of 1997 the U.S. EPA had initiated only one TSCA Section 4 action to require testing of a silicone. In 1984 the 15th report of the U.S. TSCA Interagency Testing Committee identified certain data needs to address the potential of octamethylcyclotetrasiloxane (D_4) to adversely impact aquatic ecosystems. A Section 4 Consent Order was negotiated and executed with five D_4 manufacturers in 1989 to address these data needs. The testing involved aquatic toxicity testing and environmental fate testing, and was completed in 1994. The potential exposure to D_4 was about 46 times below the aquatic concern concentration, or about 460 times below the lowest NOEC found. Based on these results, EPA determined that no further regulatory action was warranted concerning D_4 toxicity testing (Hatcher and Slater, 1997). There are 6 silicones (including groups of silicones) currently on the TSCA ITC Priority Testing List (U.S. TSCA-ITC, 2001) (see Table 3). In all cases, the concern is for human health, uncertainties about human exposure, or paucity of health effects test data. In 1996 the Dow Corning Corporation entered into a Memorandum of Understanding with the U.S. EPA in connection with the ITC siloxane review. Dow Corning agreed to conduct a comprehensive health and safety testing of 6 siloxanes, and committed to product stewardship measures (Hatcher and Slater, 1997).

In the European Union most high volume organosilicon substances such as VMS, PDMS and PEMS have no classification with respect to danger to the environment (Wischer and Stevens, 1997). In conjunction with the EU, the OECD is carrying out risk assessments on methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, methyldichlorosilane and octamethylcyclotetrasiloxane (D_4) (Wischer and Stevens, 1997). A number of silicones were on Annex II (Grey List) of marine conventions such as the Oslo

Convention, meaning that they are candidates for environmental risk assessment. Hexamethyldisiloxane was listed as a hazardous substance identified for priority action at OSPAR 2000 (UNEP, 2001). The rationale was that "hexamethyldisiloxane is produced in high volume in the European Union for use as a raw material in personal care and other industries and as an intermediate in the production of other silicones. Hexamethlydisiloxane is toxic to aquatic organisms, bioaccumulative and not easily biodegraded, although abiotic degradation is likely".

The Water Resources Act of Germany classifies PDMS, PEMS, silanols and some other organosilicon substances as "slightly hazardous to water" (Wischer and Stevens, 1997).

Preliminary Assessment

Organosilicon substances comprise a complex array of synthetic chemicals. PDMS, VMS and PEMS are high volume organosilicones with a wide variety of dispersive uses, so their presence in the environment is expected. Once these chemicals reach the environment their persistence depends upon the nature of the particular substance, and ecosystem specific characteristics. Although all silicones will eventually degrade to naturally-occurring silica and carbon dioxide and water, there is evidence for persistence of some substances in some media, *e.g.*, in sediments and wet soils the half-lives of disappearance can be of the order of months or longer. Some volatile methylsilicones (VMS), and a prominent volatile degradation product of PDMS, dimethylsilane diol (DMSD), may be subject to atmospheric long-range transport. Preliminary evidence indicates that VMS do not contribute significantly to global warming, nor to the formation of ozone in the urban atmosphere. It should be noted that even though many silicones and degradation products do not persist in certain environments, there may be constant introduction of such chemicals to the environment and thus a constant potential hazard.

The high molecular weight PDMS and PEMS appear to have low acute toxicity in soil and in water. The prominent PDMS degradation product dimethylsilane diol (DMSD) is also not very toxic to aquatic organisms (at least to those tested), with a chronic NOEL to *Daphnia magna* of > 10 mg/L. The low molecular weight VMS compounds, by contrast, are much more toxic to aquatic organisms, with NOECs in the µg/L range, and can bioaccumulate significantly.

There are few data on the environmental occurrence of organosilicones. They have been found in air in the low ng/m^3 range; in water at up to 50 µg/L; in sediments at up to 320 mg/kg; in fish at up to 4.5 mg/kg; in STP

influents, effluents and sludges at up to 710 µg/L, 13 µg/L, and 5,200 mg/kg, respectively; in industrial effluents and sludges at up to 1,150 µg/L and 6,300 mg/kg, respectively; and in sludge-amended agricultural soils at up to 10 mg/kg. A comparison of these occurrence data to toxicity values for PDMS, PEMS and VMS indicates that residues reported to date are below reported toxicity thresholds, generally by significant margins.

Recommendation

There are very few data on the environmental occurrence of organosilicon substances in the Canadian environment. It is recommended that such chemicals be included in lists of chemicals sought in on-going research studies in southern and northern Canada in order to build a database that would allow a confident assessment of the hazards posed by such substances. Such studies should concentrate on the low molecular weight VMS and PDMS degradation products, and initial sampling strategies should include STP influents, effluents and sludges, agricultural soil that is amended with sewage sludge, ambient water, sediments, fish and air.

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Table 1. Environmental occurrence of silicones and degradation products.*				
Substance	**Medium**	**Location**	**Concentration**	**Reference**
organic silicon	fresh water	Nagara River watershed, Japan	2-54 µg/L	Watanabe *et al.* (1984a)
	estuarine water	New South Wales, Australia	n.d.-0.7 µg/L	Batley and Hayes (1991)
	estuarine surface microlayer	Chesapeake Bay and Delaware Bay	23-44 µg/L	Pellenbarg (1989b)
	estuarine surface microlayer	New South Wales, Australia	1.7 µg/L	Batley and Hayes (1991)
	sediment (fresh water)	Nagara River watershed, Japan	0.3-5.8 mg/kg d.w.	Watanabe *et al.* (1984a)
	sediment (fresh water/estuarine)	Potomac River and Delaware Bay	n.d.-3 mg/kg d.w.	Pellenbarg (1989b)
	sediment (estuarine)	New South Wales, Australia	n.d.-0.5 mg/kg d.w.	Batley and Hayes (1991)
	sediment (estuarine)	Chesapeake Bay	n.d.-36 mg/kg d.w.	Pellenbarg (1982)

	sediment cores (estuarine)	Puget Sound	qualitative: n.d. before 1940	Pellenbarg and Tevault (1986)
	sediment (estuarine/marine)	New York Bight	n.d.-48 mg/kg d.w.	Pellenbarg (1979a)
	fish muscle	Nagara River watershed, Japan	0.2-4.5 mg/kg w.w.	Watanabe *et al.* (1984a)
	industrial effluents	Nagara River watershed, Japan	n.d.-1,150 µg/L	Watanabe *et al.* (1984a)
	domestic wastewater	Nagara River watershed, Japan	2-5 µg/L	Watanabe *et al.* (1984a)
	STP effluents	Nagara River watershed, Japan	2-3 µg/L	Watanabe *et al.* (1984a)
	industrial sludges	Nagara River watershed, Japan	40-6,300 mg/kg d.w.	Watanabe *et al.* (1984a)
	STP sludges	Nagara River watershed, Japan	34-144 mg/kg d.w.	Watanabe *et al.* (1984a)
	STP sludge	New South Wales, Australia	138 mg/kg d.w.	Batley and Hayes (1991)

	supernatant from STP sludge	New South Wales, Australia	180 µg Si/L	Batley and Hayes (1991)
PDMS	4 month old compost of STP sludge	New York State	408 mg/kg d.w.	Spivack and Dorn (1994)
	fresh compost of STP sludge	New York State	338 mg/kg d.w.	Spivack and Dorn (1994)
	STP influent	U.S.A. and Canada	87-714 µg/L	Fendinger *et al.* (1997a)
	STP effluent	U.S.A. and Canada	n.d.-13 µg/L	Fendinger *et al.* (1997a)
	river downstream from STP effluent	U.S.A. and Canada	n.d. (generally) - 7 µg/L	Fendinger *et al.* (1997a)
	sediment downstream from STP effluent	U.S.A. and Canada	n.d.-7 mg/kg d.w.	Fendinger *et al.* (1997a)
	sludge-amended agricultural soils	U.S.A. and Canada	n.d.-10 mg/kg d.w.	Fendinger *et al.* (1997a)
	STP sludge	U.S.A. and Canada	280-5,200 mg/kg d.w.	Fendinger *et al.* (1997a)
	sediments in areas of heavy STP discharge	U.S.A. and Canada	n.d.-320 mg/kg d.w.	Powell *et al.* (1999)

	sediments (fresh water)	Germany	n.d.-83 mg/kg d.w.	ref. 24 in Fendinger *et al.*, (1997b)
	sediments (fresh water)	U.S.A.	n.d.-23 mg/kg d.w.	ref. 40 in Fendinger *et al.*, (1997b)
	air (particulate matter)	Barrow, Alaska and Narwhal Island	8 ng/m^3	Weschler (1981)
	air (particulate matter)	several cities in U.S.A.	1-2 ng/m^3	Weschler (1988)
D_4	sediment	several locations in U.S.A.	only found at 1 of 21 locations	ref. [70] in Chandra *et al.* (1997)
	STP influents	5 locations in U.S.A.	0.6-7.1µg/L	ref. [71] in Chandra *et al.* (1997)
	STP effluents	5 locations in U.S.A.	0.06-0.41 µg/L	ref. [71] in Chandra *et al.* (1997)
D_5	STP effluents	5 locations in U.S.A.	0.005-0.54 µg/L	ref. [72] in Chandra *et al.* (1997)
D_4 and D_5	air outside buildings	U.S.A.	0.5 µg/m^3	ref. [66] in Chandra *et al.* (1997)

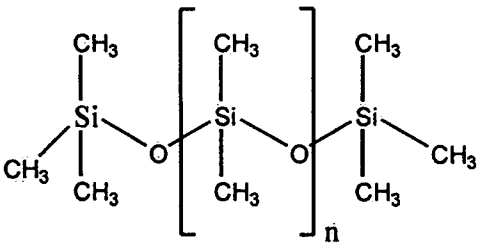
DMSD	4 month old compost of STP sludge	New York State	46 mg/kg d.w.	Spivack and Dorn (1994)
	fresh compost of STP sludge	New York State	22 mg/kg d.w.	Spivack and Dorn (1994)
	sludge-amended agricultural soils	U.S.A. and Canada	n.d.-15 mg/kg d.w.	Fendinger *et al.* (1997a)

* PDMS = polydimethylsiloxane; D_4 = octamethylcyclotetrasiloxane; D_5 = decamethylcyclopentasiloxane; DMSD = dimethylsilane diol; d.w. = dry weight; w.w. = wet weight.

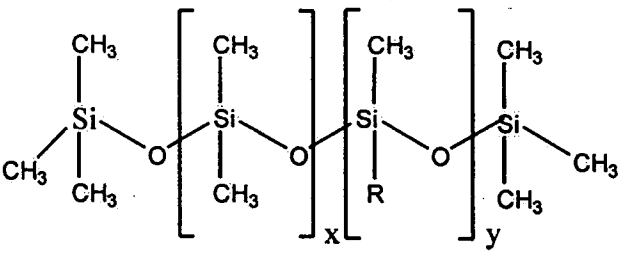
Table 2. Summary of D_4 (octamethylcyclotetrasiloxane) aquatic toxicity data.*			
Species	**Test type (time)**	**NOEC (μg/L)**	**L(E)C_{50} or LOEC (μg/L)**
rainbow trout	acute (14 d)	4.4	LC_{50} = 10
sheepshead minnow	acute (14 d)	6.3	LC_{50} > 6.3
Daphnia magna	acute (48 hr)	15	EC_{50} > 15
mysid shrimp	acute (96 hr)	9.1	LC_{50} > 9.1
rainbow trout	chronic (90 d)	4.4	-
Daphnia magna	chronic (21 d)	7.9	LOEC = 15
*Hobson *et al.* (1997)			

Table 3. Silicone substances on U.S. TSCA-ITC Priority Testing List in May 2001.*		
Chemical	**CAS Registry No.**	**Rationale**
silicic acid, tetraethyl ester	000078104	Potential for human exposure and suspicions of genotoxicity or carcinogenicity based on *in vitro* mammalian data. Current health and exposure data are needed for review.
hexamethyldisiloxane	000107460	Substantial production, uncertainties about human exposure, paucity of health effects test data. FDA request.
dodecamethylcyclohexasiloxane	000540976	Substantial production, uncertainties about human exposure, paucity of health effects test data. FDA request.
decamethylcyclopentasiloxane (D_5)	000541026	Substantial production, uncertainties about human exposure, paucity of health effects test data. FDA request.
octamethylcyclotetrasiloxane (D_4)	000556672	Substantial production, uncertainties about human exposure, paucity of

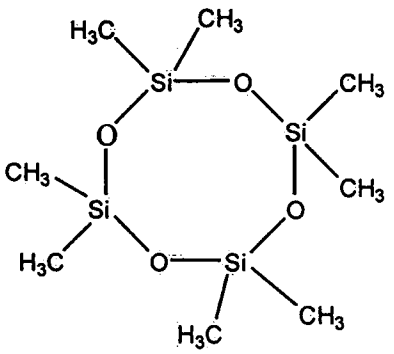
		health effects test data. FDA request.
dimethyl silicones and siloxane	063148269	Substantial production, uncertainties about human exposure, paucity of health effects test data. FDA request.
*Ref: http://.tsca-itc.syrres.com/prilist/do_search.cgi; CAS = Chemical Abstracts Service		



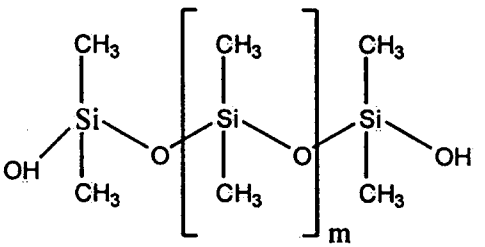
PDMS, n = 10 - 10,000
linear end-capped



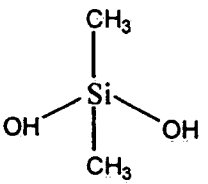
PEMS, R = polyoxyalkylene



a VMS, "D4"

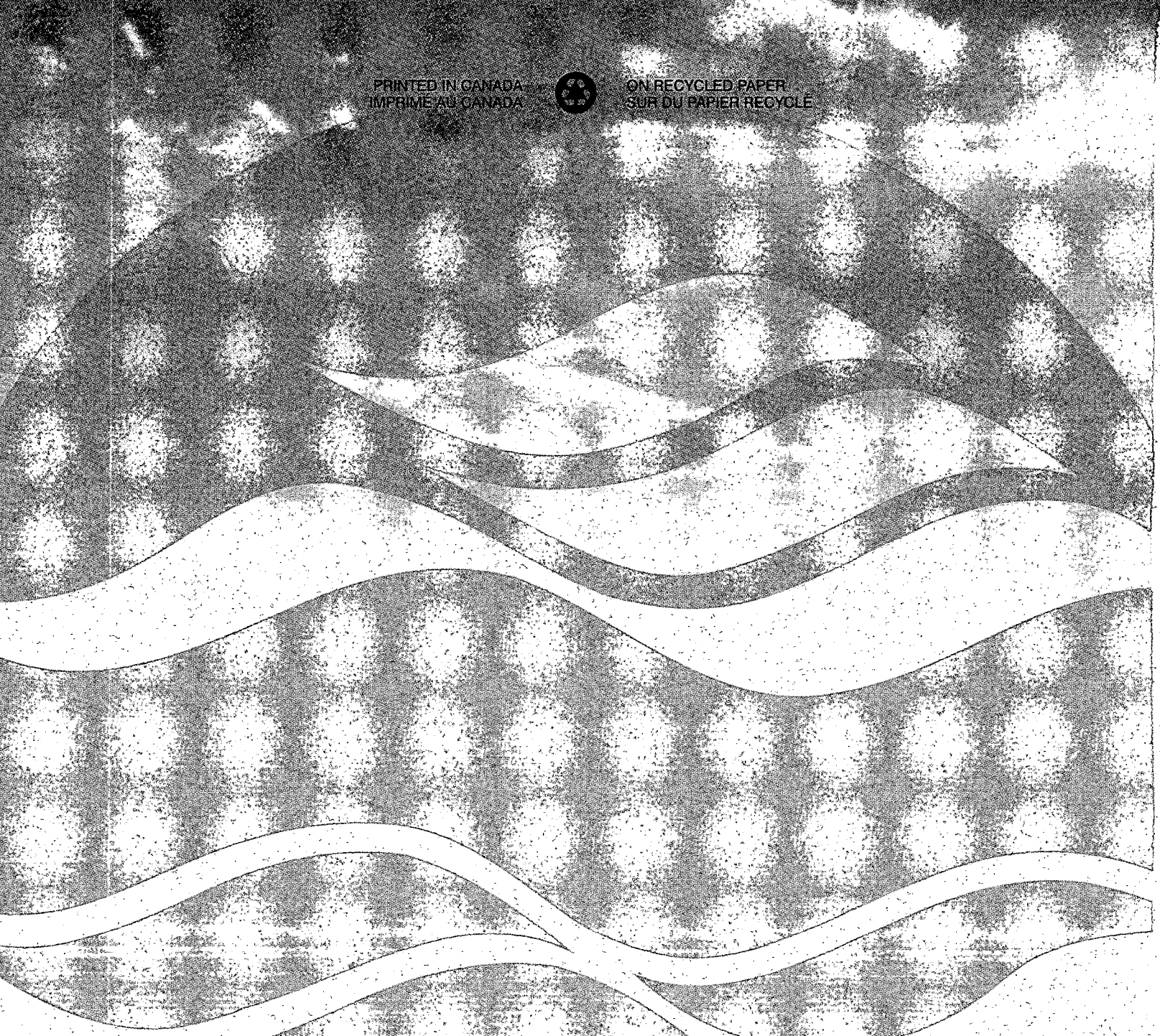


oligodimethylsiloxane-alpha,omega-diol
m < 10



dimethylsilane diol (DMSD)

Figure 1. Structures of common silicones and degradation products.



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