

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/280497974>

Decamethylcyclopentasiloxane (D5) environmental sources, fate, transport, and routes of exposure

Article in *Environmental Toxicology and Chemistry* · July 2015

DOI: 10.1002/etc.2941 · Source: PubMed

CITATIONS

21

READS

326

7 authors, including:



Christina Cowan-Ellsberry

CE 2 consulting, LLC

23 PUBLICATIONS 540 CITATIONS

[SEE PROFILE](#)



David Emerson Powell

Dow Chemical Company

42 PUBLICATIONS 869 CITATIONS

[SEE PROFILE](#)



Kent B Woodburn

Dow Corning Corporation

52 PUBLICATIONS 1,161 CITATIONS

[SEE PROFILE](#)



Shihe Xu

Dow Chemical Company

46 PUBLICATIONS 1,547 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



human exposure to consumer products [View project](#)



Analysis of field data of cyclic methylsiloxane (cVMS) concentration in air to determine their empirical persistence and long-range transport in air [View project](#)

Risk Assessment and Regulation of D5 in Canada

DECAMETHYLCYCLOPENTASILOXANE (D5) ENVIRONMENTAL SOURCES, FATE, TRANSPORT, AND ROUTES OF EXPOSURE

DONALD MACKAY,[†] CHRISTINA E. COWAN-ELLSBERRY,^{*‡} DAVID E. POWELL,[§] KENT B. WOODBURN,[§] SHIHE XU,[§]
GARY E. KOZERSKI,[§] and JAESHIN KIM[§]
[†]Trent University, Peterborough, Ontario, Canada
[‡]CE Consulting, Cincinnati, Ohio, USA
[§]Dow Corning, Midland, Michigan, USA

(Submitted 1 August 2014; Returned for Revision 15 November 2014; Accepted 13 February 2015)

Abstract: The environmental sources, fate, transport, and routes of exposure of decamethylcycllopentasiloxane (D5; CAS no. 541-02-6) are reviewed in the present study, with the objective of contributing to effective risk evaluation and assessment of this and related substances. The present review, which is part of a series of studies discussing aspects of an effective risk evaluation and assessment, was prompted in part by the findings of a Board of Review undertaken to comment on a decision by Environment Canada made in 2008 to subject D5 to regulation as a toxic substance. The present review focuses on the early stages of the assessment process and how information on D5's physical–chemical properties, uses, and fate in the environment can be integrated to give a quantitative description of fate and exposure that is consistent with available monitoring data. Emphasis is placed on long-range atmospheric transport and fate in water bodies receiving effluents from wastewater treatment plants (along with associated sediments) and soils receiving biosolids. The resulting exposure estimates form the basis for assessments of the resulting risk presented in other studies in this series. Recommendations are made for developing an improved process by which D5 and related substances can be evaluated effectively for risk to humans and the environment. *Environ Toxicol Chem* 2015;34:2689–2702. © 2015 The Authors. *Environmental Toxicology and Chemistry* Published by Wiley Periodicals, Inc. on behalf of SETAC

Keywords: Fate and transport Risk assessment Atmospheric transport Environmental fate Environmental transport

INTRODUCTION

Cyclic volatile methylsiloxanes (cVMS) are a group of organosilicon substances that are used in personal care products such as shampoos, cosmetics, and deodorants and in industrial applications such as dry-cleaning solvents and industrial cleaning fluids [1–4]. They are produced in high volumes in the United States, Europe, and Asia. Although not manufactured in Canada, cVMS are imported and are present in consumer products in Canada. Of these cVMS materials, decamethylcycllopentasiloxane (D5; CAS no. 541-02-6) is of particular interest because of its high-volume use in consumer products.

As a result of their widespread use in consumer products, cVMS have been detected and monitored in air, water, sediments, and biota and have thus become the subject of considerable scientific and regulatory interest. For example, these substances are the focus of a special issue of *Chemosphere* edited by Alaee et al. [3] and a recent review by Rücker and Kümmerer [4]. The special *Chemosphere* issue included a comprehensive review by Wang et al. [5] of recent advances in toxicity, detection, occurrence, and fate. Regulatory assessments of these substances have been conducted by the United Kingdom Environment Agency [2] and Environment Canada and Health Canada [1]. The Environment Canada screening assessment of D5 initially concluded that it should be added to the Toxic Substances List in Schedule 1 of the Canadian

Environmental Protection Act [6], which has the potential to restrict uses in Canada. This designation was based on the conclusion by Environment Canada that there was potential for harm to the environment. This regulatory step was contested by industry groups, and in response, a 3-person Board of Review was established by the Minister of the Environment to re-evaluate the risk assessment, especially in the light of more recent information on chemical properties, fate, exposure, and toxicity. The Board of Review reviewed the available data and reported to the Minister of the Environment in 2011 its conclusion that “taking into account the intrinsic properties of Siloxane D5 and all of the available scientific information, ... [s] iloxane D5 does not pose a danger to the environment” [7].

In the present study, we assess the environmental sources, fate, transport, and exposures resulting from the use of D5, including information that was generated to support the Board of Review and subsequently. Much of the research on D5 has been conducted by the producing industry and was made available for the comprehensive risk assessments conducted by the United Kingdom [2,3] and the Siloxane D5 Board of Review [7]. Although these data have been reviewed and accepted by regulatory bodies, not all of the reports have been published in the peer-reviewed scientific literature to date (they are, however, available by request from the Silicones Environmental, Health, and Safety Center, a sector group of the American Chemistry Council). We also address questions and concerns raised by other regulatory agencies on D5 properties, fate, and concentrations in the environment that contribute to an improved assessment of the risk of adverse effects. The numerous studies on the siloxanes demonstrate that these substances have unusual physical, chemical, and degradation properties, which require the assessor to go back to first principles when assessing their fate and exposure potential. A related objective of the present study is to

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

* Address correspondence to cellsberry@gmail.com

Published online 24 July 2015 in Wiley Online Library (wileyonlinelibrary.com).

DOI: 10.1002/etc.2941

Table 1. Sequence of assessment steps^a

Step no.	Topics discussed	Source
Step 1	Chemical identity, structure, manufacture, and uses	Present study
Step 2	Physical–chemical and degradation properties	Present study
Step 3	Narrative statement of sources, fate, and transport	Present study
Step 4	Quantitative, but non–site-specific evaluation of fate	Present study
Step 5	Bioaccumulation	[8,9]
Step 6	Toxicity and other adverse effects	[10]
Step 7	Quantitative site-specific or regional evaluation of exposures	Present study
Step 8	Final assessment of risk and recommendations for actions	[10]

^aSteps 1 to 6 are intensive in nature and do not necessarily require information on chemical quantities that may be commercially sensitive. Steps 7 and 8 contain extensive information including chemical quantities and are region-specific.

use D5 to illustrate how to conduct a fate, transport, and exposure assessment for atypical chemicals by following a logical sequence of steps that build on the knowledge gained in previous steps as a guide. The steps in this process are shown in Table 1. The present review specifically addresses steps 1 to 4 and step 7. Gobas et al. [8,9] address bioaccumulation (step 5), Fairbrother et al. [10] address toxicity and risk evaluation (steps 6 and 8), and Xu et al. [11] provide a more comprehensive treatment of physical and chemical properties (step 2).

STEP 1: CHEMICAL IDENTITY, STRUCTURE, MANUFACTURE, AND USES

At ambient temperature, D5 (Figure 1) is an odorless and colorless liquid that is used primarily as a chemical intermediate in the production of polydimethylsiloxane silicone polymers [2,3,12]. To a lesser extent, D5 is used in blending and formulating a variety of personal care products—including

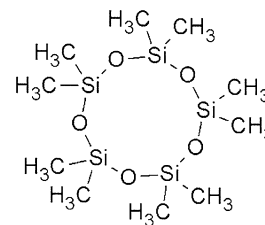


Figure 1. Molecular structure of decamethylcyclopentasiloxane (D5).

shampoos, skin creams, cosmetics, and deodorants—and as a solvent in commercial dry cleaning products and industrial cleaning fluids [13,14]. These uses in silicone polymers and in dry cleaning do not result in the release of significant amounts of D5 to the environment [2,3]. Therefore, the most important use of D5 from the perspective of human and ecosystem exposure is in personal care products (Table 2; B.P. Montemayor, Canadian Cosmetic, Toiletry and Fragrance Association Mississauga, ON, Canada, personal communication). In 2004, personal care product use of D5 in Europe and the United Kingdom was approximately 21 million kg/yr [3]. In 2010, the total volume of D5 used in personal care products in Canada was estimated to be 3.3 million kg/yr [2]. Antiperspirants and hair-care products account for more than 90% of the D5 use in personal care products, of which less than 10% of the total used in personal care products is discharged to sewers (Table 2) [15]. Less than 10% of the D5 in personal care products is used in skin care, cosmetics, and other bath and body products (Table 2), of which less than 1% is discharged to sewers [15]. As a result of its volatility, some 90% of the D5 used in personal care products evaporates and becomes dispersed and degraded in the atmosphere.

STEP 2: PHYSICAL, CHEMICAL, AND DEGRADATION PROPERTIES

Table 3 provides a summary of the recommended physical and chemical properties of D5, including key intermedia

Table 2. Estimated percentage of total D5 volume used in consumer products in various consumer product categories and the percentage of the D5 in these products that is discharged to sewers

Consumer product category	% of total D5 production used in consumer product category ^a	% of D5 in these products discharged to sewers ^b	% of total D5 production discharged to sewers from this product category	Notes on % discharge to sewers data
Antiperspirants	70.2–72.2	1	0.7	
Hair care	19.3–20	40	7.7–8	Used worst-case in-shower product (conditioner)
Skin care ^c	2.7–3.0	1	0.03	
Color and other cosmetics	2.2–4.4	1	0.04	Assumed to be the same as skin care products
Bath and body products	0.12–0.16	40	0.06	Assumed to be the same as worst-case in-shower hair care product (conditioner)
Sunscreen (primary)	0.45–1.4	1	0.01	Assumed to be the same as skin care products
Makeup remover	0.85–0.93	40	0.4	Because D5 may be used in wash-off situation, used worst-case in-shower hair care product (conditioner)
Other cosmetic-like drugs/natural health products ^d	0.88–1.1	1–40	0–0.4	Used range from other product types

^aMinimum and maximum percentage distribution of D5 in finished products within this consumer product category in Canada from 2006, 2009, and 2010 based on Canadian Cosmetic, Toiletry and Fragrance Association survey (B.P. Montemayor, Canadian Cosmetic, Toiletry and Fragrance Association, Mississauga, ON, Canada).

^bMontemayor et al. [15].

^cIncludes skin care products that contain sunscreen ingredients.

^dIncludes skin and hair care products that are registered as drugs and natural health products used in skin and hair care.

D5 = decamethylcyclopentasiloxane.

Table 3. Recommended values of D5 physical and chemical properties

Property	Recommended value $\pm$ SD	Reference
Molecular weight (g/mol)	370.77	
Melting point ($^{\circ}$ C)	-38	[82,83]
Boiling point ($^{\circ}$ C)	210	[82,83]
Density (kg/m ³) at 25 $^{\circ}$ C	959	[83,84]
Vapor pressure (Pa) at 25 $^{\circ}$ C	22.7	[84]
Water solubility (μ g/L) at 23 $^{\circ}$ C	17.0 $\pm$ 0.7	[85]
Log K_{AW} at 25 $^{\circ}$ C	3.13 $\pm$ 0.13	[17,18]
Henry's law constant (Pa m ³ /mol) at 25 $^{\circ}$ C	3.344 $\times 10^6$	H = $K_{AW} \times RT$ by definition
Log K_{OW} at 25 $^{\circ}$ C	8.09 $\pm$ 0.22	[11]
Log K_{OC} at 25 $^{\circ}$ C	5.17 $\pm$ 0.17	[16]
Log K_{OA} at 25 $^{\circ}$ C	4.93 $\pm$ 0.09	[11]
Log K_{LW}	6.5-8.3	[23]
Half-life in air (d)	6.90	[32,30]
Half-life in water (d) at pH 7 and 25 $^{\circ}$ C	70.4	[34]
Half-life in soil (d)	12.6	[35]
Half-life in sediment (d)	3100	[37]

D5 = decamethylcyclopentasiloxane; SD = standard deviation; K_{AW} = air-water partition coefficient; K_{OW} = octanol-water partition coefficient; K_{OC} = carbon-water partition coefficient; K_{OA} = octanol-air partition coefficient; K_{LW} = lipid-water coefficient.

partitioning and degradation properties (i.e., half-lives). A more detailed discussion on methods for determining these properties and justification of these recommended properties and their temperature dependence is given in Kozerski et al. [16], Xu and Kropscott [17], and Xu et al. [11]. In the present study, we focus on aspects of these properties that are of particular importance for evaluating fate and transport. In 2008, when the Environment Canada screening assessment was prepared [2], there was considerable uncertainty about many of these properties; however, more accurate data have since been generated and are presented in Table 3. Accurate values for these properties are essential because they are used as input parameters for environmental models used to estimate the fate of, and exposure from, D5 in the various environmental media. Also, accurate values of the organic carbon-water partition coefficient (K_{OC}) and solubility in water (S_w) are needed to predict or to properly interpret and assess the validity of measured or predicted environmental concentrations of D5 and to evaluate the validity of toxicity tests that have been conducted in various environmental media.

Siloxanes, including D5, possess characteristics of both organic compounds and silicates. Their properties arise from the unique chemistry of the Si-O bond and the influences of the organic substituents at the Si atom, -CH₃ in this case. If a chemical has unusual structural features or properties, as is the case with D5, quantitative structure activity relationships (QSARs) must be used with extreme caution, and the user must verify that the chemical is within the domain of QSAR applicability. Ultimately, there is no substitute for accurate and consistent empirical physical, chemical, and degradation properties data, but valid QSAR models can be extremely useful for identifying questionable measurements.

Air-water partition coefficient

As discussed in Xu et al. [11], direct measurement of the air-water partition coefficient (K_{AW}) at concentrations less than the limit of water solubility using a 3-phase equilibrium method [17] is the basis for the recommended value (log K_{AW} = 3.13). This value is higher than that estimated from vapor pressure and

solubility, especially for aqueous concentrations of D5 much less than the water solubility. The high K_{AW} indicates that D5 has a very strong tendency to evaporate, and this behavior has profound implications for the fate of D5 in water. Extreme care must be taken to control loss of D5 by volatilization when designing or evaluating test methods and collecting samples for fate, bioconcentration, and toxicity studies and preparing and maintaining test solutions.

Octanol-water partition coefficient

The recommended octanol-water partition coefficient (K_{OW}) value (K_{OW} = 1.23 $\times 10^8$; log K_{OW} = 8.09) in Table 3 was derived using the 3-phase equilibrium method [17]. This value was selected because its temperature dependence was available and because K_{OA} and K_{AW} were determined simultaneously. This recommended K_{OW} places it in the super-hydrophobic region, and indicates that D5 will strongly absorb to organic matter.

Octanol-air partition coefficient

The octanol-air partition coefficient (K_{OA}) is used primarily to estimate partitioning from air to aerosol particles and to solid surfaces such as vegetation. The recommended K_{OA} value (K_{OA} = 8.51 $\times 10^4$; log K_{OA} = 4.93 $\pm$ 0.09) from the 3-phase equilibrium method [17,18] was selected because its temperature dependence was available and because values for K_{OW} and K_{AW} were simultaneously determined. This log K_{OA} is relatively low compared with substances such as polychlorinated biphenyls (PCBs) of similar hydrophobicity. For example, PCB-194, a hydrophobic substance of comparable K_{OW} , has a recommended log K_{OA} of 11.13 at 25 $^{\circ}$ C [19]. As suggested by Wania [20], compounds with room-temperature log K_{OA} values less than 6.5 have a low tendency to deposit to surface media in remote regions. Similarly, compounds with room-temperature log K_{OA} values less than 6.5 have a low potential for biomagnification in terrestrial food chains [21]. Consequently, partitioning of D5 to aerosols and subsequent deposition to soils and vegetation is likely to be insignificant.

Organic carbon-water partition coefficient

Decamethylcyclopentasiloxane falls outside the domain of applicability for QSARs developed for nonpolar organics and used to estimate K_{OC} from K_{OW} [16]. Based on QSARs for nonpolar organic chemicals, it would be expected that the K_{OC} for D5 would be 10% to 50% of K_{OW} , a value of 35% being widely accepted [22]. However, the measured value of log K_{OC} of 5.17 is much lower (arithmetic factor of 250) than the expected logarithmic value of 7.57 based on nonpolar organic substance QSARs. This highlights the issue that it can be highly misleading to apply single-parameter relationships developed using data on 1 group of chemicals to a new class of chemical whose properties are not fully understood, despite some apparent similarities between the classes. The K_{OC} - K_{OW} relationship for methylsiloxanes, including D5, is discussed in greater detail by Kozerski et al. [16].

Lipid-water partition coefficient

The lipid-water partition coefficient (K_{LW}) is essential for understanding and modeling bioconcentration. Similarly to K_{OC} , K_{LW} is lower than would be expected based on the conventional correlation assumption that K_{LW} equals K_{OW} (Table 3). This assumption is not valid for D5 and possibly for other classes of lipophilic substances, as discussed by Gobas et al. [8,9] and Seston et al. [23]. Again, it is plausible that the

behavior of D5 compared with nonpolar organics having similar K_{OW} values relates to the differing capacities of these chemicals for the various types of molecular interactions controlling their absorption by octanol and lipids [23–25]. An empirical K_{LW} value for D5 is not available, but estimates range from $0.03 \times K_{OW}$ ($\log K_{LW} = 6.5$) for membrane lipids to $1.5 \times K_{OW}$ ($\log K_{LW} = 8.3$) for storage lipids [23]. This is equivalent to a K_{LW} value for D5 of approximately $0.32 \times K_{OW}$ ($\log K_{LW} = 7.6$) for aquatic invertebrates to $1.1 \times K_{OW}$ ($\log K_{LW} = 8.1$) for fish, depending on the type of lipid [26–28].

Solubility limits in water and maximum sorptive capacities in soil and sediment

Because of D5's low solubility in water, it is important when evaluating model results, laboratory test protocols, or monitoring data that the proximity of concentrations to this water solubility and to saturation in organic carbon, as represented by the maximum sorption capacity of organic carbon, be assessed for each medium. When the maximum sorption capacity of water or organic carbon in the medium is approached or exceeded, phase separation in the water, soil, or sediment will likely occur, resulting in the presence of pure phase D5 in the water, soil, or sediment, along with dissolved D5.

The water solubility of D5 at 23 °C is $17.0 \pm 0.7 \mu\text{g/L}$ ($46 \mu\text{mol/m}^3$), which is similar in magnitude to that of n-undecane ($S_W = 77 \mu\text{mol/m}^3$) and to highly chlorinated PCBs such as PCB-180 (with a solubility of $13 \mu\text{mol/m}^3$) or PCB-194 (with a solubility of $5.59 \mu\text{mol/m}^3$) [19]. Although these chemical benchmark comparisons can provide useful perspectives when dealing with a new chemical, they can also be subject to misinterpretation. Fundamentally, the solubility is controlled by ΔG , the free energy of transfer from the pure liquid solute to water, or in the case of K_{OW} , from octanol to water. The value of ΔG depends on contributions from molecular size, polarizability, and hydrogen bonding interactions. Two solutes may coincidentally have the same ΔG but reflect different interaction contributions. For example, D5 is a larger and less polarizable molecule than n-undecane; however, D5 possesses significant hydrogen bond acceptor capacity, whereas n-undecane does not [29,30]. Only when the differences in their inherent properties (e.g., size, hydrogen bond basicity, etc.) result in offsetting contributions from the factors that govern solubility (or any other solution property) will they display equivalent

behavior. Consequently, 2 chemicals with similar solubilities or K_{OW} values may display significant differences in partitioning to other phases such as to organic carbon or lipids, as highlighted above.

The maximum concentration that D5 can achieve in a truly dissolved form in water is $17.0 \mu\text{g/L}$. If the water contains dissolved organic carbon (DOC), then the total concentration will be higher because of the sorption to DOC. At saturation with a DOC concentration of 10 mg/L in river water, and a K_{OC} for D5 of 148 000 L/kg, the sorbed concentration will be $2.52 \mu\text{g/mg DOC}$, corresponding to 25.2 mg/L ; and of the total D5 concentration, 40% will be dissolved and 60% will be in sorbed form. For a range in DOC of 3 mg/L to 10 mg/L, the total D5 concentration (sorbed + dissolved) cannot exceed $24 \mu\text{g/L}$ to $42 \mu\text{g/L}$ (Table 4).

The maximum sorption capacity of sediments and soils (in mg/kg dry wt) may be estimated correspondingly from S_W (in mg/L), the K_{OC} (in L/kg organic carbon), and the mass fraction of organic carbon in the sediment or soil (f_{OC} ; in kg organic carbon/kg dry wt), using the equation

$$\text{Maximum sorption capacity} = S_W \times K_{OC} \times f_{OC} \quad (1)$$

For sediment or soil with 2% organic carbon, this corresponds to a maximum sorption capacity for D5 of approximately $0.017 \times 10^5 \times 0.02$ or $50 \mu\text{g/g dry wt}$. Although this estimated maximum sorption capacity cannot be precisely measured, it is a useful concept because it provides an estimate of the approximate concentration in organic carbon at which phase separation may occur and that neat D5 may be present. The maximum sorption capacity on an organic carbon basis is $S_W \times K_{OC}$, which is $2500 \mu\text{g/g organic carbon}$ (Table 4). When monitoring data for sediment or soil are reported on an organic carbon-normalized basis, they can be compared directly with that maximum sorption capacity.

Degradation half-lives

The degradation half-lives of D5 (Table 3) are important for determining the fate of D5 in the environment and also for comparison with regulatory screening criteria for persistence. In air, airborne D5 is degraded mainly via oxidation by hydroxyl radicals (OH), with a half-life varying temporally and spatially mainly because of the variation of hydroxyl

Table 4. Summary of estimated and measured D5 concentrations in environmental media^a

Media	Maximum solubility	Estimated concentration	Monitoring concentration
Water	17 $\mu\text{g/L}$ at 0 mg/L OC 24 $\mu\text{g/L}$ at 3 mg/L OC 42 $\mu\text{g/L}$ at 10 mg/L OC	95th percentile: 1.94 $\mu\text{g/L}$ 90th percentile: 0.96 $\mu\text{g/L}$ Median: 0.026 $\mu\text{g/L}$	95 percentile: 7.3 $\mu\text{g/L}$ 90 percentile: 2.6 $\mu\text{g/L}$ Median: 0.06 $\mu\text{g/L}$
Sediment	2500 $\mu\text{g/g OC}$ 25 $\mu\text{g/g dry wt}$ at 1% OC 100 $\mu\text{g/g dry wt}$ at 4% OC	95th percentile: 287 $\mu\text{g/g OC}$ 90th percentile: 142 $\mu\text{g/g OC}$ Median: 3.8 $\mu\text{g/g OC}$	95 percentile: 55 $\mu\text{g/g OC}$ 90 percentile: 25 $\mu\text{g/g OC}$ Median: 2 $\mu\text{g/g OC}$
Soil	2500 $\mu\text{g/g OC}$ 13 $\mu\text{g/g dry wt}$ at 0.5% OC 75 $\mu\text{g/g dry wt}$ at 3% OC	0.03 $\mu\text{g/g dry wt}$ at 0.5% OC 1.6 $\mu\text{g/g dry wt}$ at 3% OC	95 percentile: 0.3 $\mu\text{g/g dry wt}$ 90 percentile: 0.2 $\mu\text{g/g dry wt}$ Median: 0.03 $\mu\text{g/g dry wt}$
Air	4.97 $\mu\text{g/m}^3$		Urban: 0.162–0.230 $\mu\text{g/m}^3$ Suburban: 0.052 $\mu\text{g/m}^3$ Rural: 0.018 $\mu\text{g/m}^3$ Arctic: 0.0005–0.004 $\mu\text{g/m}^3$

^aSee text for details on estimation methods and sources of monitoring data. D5 = decamethylcyclotrisiloxane; OC = organic carbon.

radical concentrations in the atmosphere. A half-life ($\tau_{1/2}$) of 6.9 d in air was calculated based on pseudo first-order kinetics when the 12-h average OH radical concentration [OH] was 1.5×10^6 molecules cm^{-3} [31] and a measured bimolecular reaction constant ($k_{\text{D5-OH}}$) was $k_{\text{D5-OH}} = 1.55 \times 10^{-12}$ cm^3 molecule $^{-1}$ s $^{-1}$ [32]

$$\tau_{1/2} \text{ Air} = \ln(2)/(k_{\text{D5-OH}}[\text{OH}]) \quad (2)$$

In water, D5 undergoes hydrolysis catalyzed by both hydronium ions ($k_{\text{H}} = 757$ L/mol/h) and hydroxyl ions ($k_{\text{OH}} = 3314$ L/mol/h) [33,34]. At pH 7 and 25 °C, a half-life of 70.4 d in water was calculated using the pseudo first-order overall reaction rate,

$$\tau_{1/2} \text{ Water} = \ln(2)/(k_{\text{H}}[\text{H}] + k_{\text{OH}}[\text{OH}]) \quad (3)$$

Hydrolysis of D5 also occurs in soil, with its rates depending mainly on soil moisture and types of clay minerals. A half-life in soil of 12.6 d at the standard temperature (25 °C) was calculated based on the measured hydrolysis of D5 in a Michigan (USA) soil at 92% relative humidity ([35]; see supporting information in Xu and Wania [36]). Xu [37] determined half-lives of D5 in Lake Pepin (MN, USA) sediment under both aerobic and anaerobic conditions, yielding estimated half-lives ranging from 800 d to 3100 d. This remarkable difference in D5 half-lives in soils versus sediments is because of the influence of water content on the interaction of D5 with the mineral constituents of soil and sediment. In sediments and water-saturated soil, the D5, because of its high hydrophobicity, is strongly sorbed to organic matter, which reduces the availability of D5 for hydrolysis. At low water contents in soil, some D5 interacts with available soil mineral surfaces, which have been shown to be catalytic sites for hydrolysis of D5, and the measured degradation rate increases. As a result, the degradation rate constant has been observed to change by 3 to 5 orders of magnitude as the soil water content decreases from water saturation toward air-dry.

Based on these data, accepted Canadian thresholds of 2 d in air and 365 d in sediments were exceeded by D5 [2]; however, the soil and water criteria of 182 d were not exceeded. It is important to recognize that environmental factors such as temperature and pH may dramatically influence degradation rates, but the relevant conditions for evaluation against simple threshold criteria are not always specified or rationalized adequately.

In summary, D5 has unusual properties related to its organic-silicate hybrid nature. It is a liquid with a high molar mass but a

relatively high volatility, low solubility in water, relatively long half-lives in air and sediments, extreme hydrophobicity, and a strong tendency to partition to organic matter and to lipids.

STEP 3: NARRATIVE DESCRIPTION OF SOURCES, FATE, AND TRANSPORT

When assessing the environmental fate of a chemical, it is useful to describe how it is used and how these uses contribute to exposures to humans and the environment. An example is the Organisation for Economic Co-operation and Development (OECD) Emission Scenario Documents [38], in which more than 30 use categories are considered, ranging from personal care products to paints and solvents. Models are suggested with which to estimate exposures resulting from such uses. Clearly, there is increasing acceptance that modeled assessments can be more focused and effective if the nature of the chemical uses is taken into account.

As illustrated in Figure 2, the main route of release of D5 to the environment is from use and disposal of personal care products. Based on studies of typical personal care and cosmetic products, these releases are expected to be primarily to the atmosphere, with only a limited amount going down the drain to sewers or septic systems. For leave-on, post-shower applications of antiperspirants, skin care products, and cosmetics, Montemayor et al. [15] have determined that less than 1% was left on the skin after 8 h of application and less than 0.1% was left on the skin 24 h after application. Considering typical washing habits, only a very small fraction (significantly less than 1%) of the D5 used in these post-shower application products is available to wash down the drain (Table 2). Therefore, direct release of over 99% of the D5 to the atmosphere represents the dominant pathway for these types of products to the environment. For products that are used while showering or bathing, such as some hair care and bath and body products (Table 2), the 95th percentile of D5 measured in wash water was approximately 40% based on the experimental data for rinse-off conditioner [15]. More than 60% of the D5 in hair care products was volatilized [15]. This is a reasonable but conservative estimate because the worst-case hair care product (shower conditioners) was used to represent this entire showering and bathing product category. Other hair care products have significantly higher volatilization and less loss down the drain [15].

Integrating the quantity of D5 used in various consumer product categories with the release patterns from these products (Table 2) shows that more than 90% of the D5 used in personal

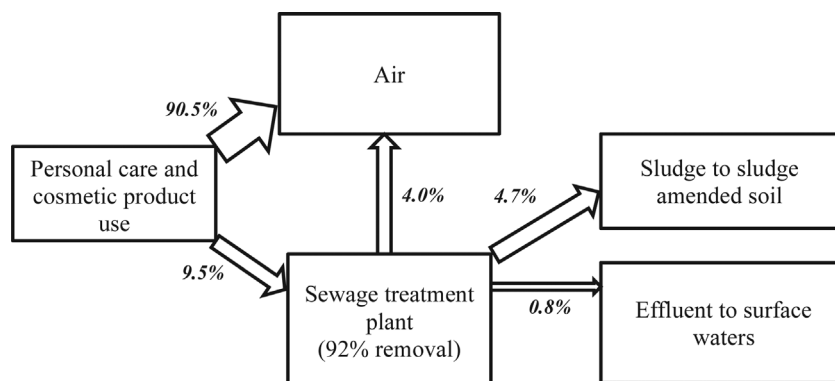


Figure 2. Percentages of decamethylcyclotrisiloxane (D5) emitted to the environment from different pathways.

care and cosmetic products is released to air, and the total quantity of the D5 in consumer products that would be discharged to waste systems is estimated to be approximately 9.5% (Table 2 and Figure 2). Based on a combination of monitoring data [39] of D5 concentrations in various sewage plant influents across Canada, the per capita daily use of D5 in consumer products of 283 mg/capita/d, assuming a Canadian population of 32 million and the average per capita wastewater flow of 495 L/capita/d (Table 1.10 in Canadian Water and Wastewater Association [40]), the average quantity of D5 used in consumer products and released to the sewer is approximately 8%. Based on these data, the 9.5% discharge value is considered to be conservative because it represents the 95th percentile monitored value for the concentration in the influent [39]. It is noteworthy that the above per capita usage is comparable to estimates for Zurich (Switzerland) of 310 mg/capita/d and for Chicago (IL, USA) of 100 mg/capita/d to 400 mg/capita/d [41,42], despite the geographic differences.

Municipal sewer water is treated in wastewater treatment plants (WWTPs) before being discharged to surface waters. In Canada, WWTPs range widely in size and removal efficiencies, from lagoons to secondary treatment facilities. The removal of D5 in primary and secondary (activated sludge) treatment plants and in lagoons can be estimated using models. The activated sludge treatment (ASTREAT) model [43] and the sewage treatment plant (STP) model [44] were used to estimate the fate and removal of D5 during primary and secondary wastewater treatment (Table 5). The resulting removal efficiency for D5 in wastewater influent (loss to sludge and air) were approximately 42% and 97%, respectively, for primary and secondary treatment. Aerated and facultative lagoon models (within the modified STP model [STP-EX]) also have been developed and are discussed by Seth et al. [44]. An evaluation of D5 removal in facultative and aerated lagoons suggests relatively high but variable removal efficiencies, as shown in Table 5. The high removal predictions, especially for secondary treatment plants, are supported by monitoring data from the United Kingdom [45] and elsewhere (see Table 3.18 in Alaee et al. [3]), which found that D5 removal from secondary treatment plants ranged from 91% to 99%. Additional monitoring data [39] across a range of treatment types—including activated sludge, lagoons, and primary treatment—showed that the total D5 removal exceeded 92% and the mean rate of removal was 98%.

Combining the estimate that 9.5% of the total D5 used in personal care products is released to sewers and the estimates of fate in various types of WWTPs, a realistic estimate of the

proportions entering the environment is 94.5% to air (from product use and during sewage treatment), 0.8% to water as treated effluent, and 4.7% to soil in association with addition of sludge or biosolids from WWTPs. These estimates are used in the subsequent quantitative assessments of fate in step 4.

STEP 4: QUANTITATIVE, BUT NON-SITE-SPECIFIC EVALUATION OF FATE

In step 4, evaluative models of fate and transport are used to integrate the information on chemical properties, sources, uses, and likely exposure pathways, to provide a more quantitative description of the chemical's mass balance in the environment. In this case, the equilibrium criterion (EQC) model [46] is applied, but other similar models could be used.

The EQC level III fugacity model has been widely used in Canada and elsewhere in the assessment of the fate of chemicals to gain a perspective on how a substance is likely to partition among air, water, soils, and sediments in a hypothetical evaluative environment. This model, which was developed in 1996 and made freely available in 1997, used a linear relationship developed by Karickhoff [47] for nonpolar organics to estimate K_{OC} from K_{OW} and used vapor pressure and water solubility or Henry's law constant to estimate K_{AW} . With increasing regulatory demands for more rigorous measurement of K_{OC} and the requirement of the model for K_{AW} , this older version of the model was determined to be inadequate. In 2012, an improved version of the EQC level III fugacity model was developed that allowed the user to directly enter all partition coefficients [46]. This newer version of the model was used to estimate the fate of D5 in the environment based on various modes of entry, using the physical and chemical properties in Table 3 and the environmental properties in Table 6. Table 7 gives these results for the realistic emission scenario in the form of percentages of the mass of chemical in each compartment at steady state and the compartment and overall residence times. To provide insights into source–receptor relationships, Table 7 also gives the results for each single mode of entry. Although the emission rate of 1000 kg/yr is hypothetical, the distribution of D5 between media can be used to gain insights into the general fate of D5 in the environment and the important fate processes contributing to this pattern of distribution and degradation.

When the realistic release scenario of 94.5% to air, 0.8% to water, and 4.7% to soil from step 3 is used (Table 7), the largest fraction of D5 is predicted to be present in air (63.8% of total mass). Although the emission rate to water and subsequent sorption to sediment are small, approximately 33% of the D5 in the environment is estimated to be found in the sediment because of slow degradation in this medium. Kim et al. [48] compiled extensive sensitivity and uncertainty analyses of D5 fate using the EQC model. This study [48] confirmed the importance of K_{OC} and half-lives in water and sediment as the most influential input parameters that require accurate values.

The EQC analysis suggests 2 priority needs for more detailed quantitative assessment in step 7—namely, an evaluation of long-range atmospheric transport and fate in local receiving waters and in larger water bodies such as lakes and estuaries impacted by effluents from WWTPs, as this is the route to the sediment. This step in the assessment process is invaluable for translating information on chemical properties and likely modes-of-entry into a more quantitative (but non-site specific) statement of the environmental fate of a chemical and for identifying where to focus subsequent monitoring and modeling

Table 5. Fate of D5 in various types of wastewater treatment systems

Pathway	Primary treatment only ^a	Secondary treatment (includes primary treatment) ^a	Lagoon treatment ^b
Effluent	58%	3%	11–30% (facultative) 2–5% (aerated)
Sludge	42%	44%	
Air	<1%	53%	3.7%

^aActivated sludge treatment (ASTREAT) model version 1.0 [43] predictions using $\log K_{OW}$ equal to 8.03, Henry's law constant equal to 3.344×10^6 Pa m³/mol, and assuming no biodegradation.

^bModified sewage treatment plant (STP) model [44]. The majority of loss of D5 is sedimentation on solids under facultative conditions but volatilization under aerated conditions.

D5 = decamethylcyclotetrasiloxane; K_{OW} = octanol–water partition coefficient.

Table 6. Environmental properties of D5 used for the EQC and QWASI models

Property	Recommended value	Reference
Environment temperature (°C)	25	
Soil–water partition coefficient (L/kg)	2958	$Z_{\text{solid in soil}}/Z_{\text{water}}/\text{Density}_{\text{solid in soil}}$ by definition
Sediment–water partition coefficient (L/kg)	5916	$Z_{\text{solid in sediment}}/Z_{\text{water}}/\text{Density}_{\text{solid in sediment}}$ by definition
Suspended particles–water partition coefficient (L/kg)	29 582	$Z_{\text{SS in water}}/Z_{\text{water}}/\text{Density}_{\text{SS in water}}$ by definition
Fish–water partition coefficient (L/kg)	13 300	[86]
Aerosol–air partition coefficient (dimensionless)	1.81×10^5	$6 \times 10^6/\text{VP}$, where VP is vapor pressure
Aerosol–water partition coefficient (dimensionless)	2.44×10^8	$K_{\text{aerosol-air}}/K_{\text{AW}}$ by definition
Vegetation–water partition coefficient (dimensionless)	—	
Realistic emission scenario (air:water:soil)	94.5%:0.8%:4.7%	The present study
Temperature dependence coefficients		
ΔU (octanol/water; kJ/mol)	40	[87]
ΔU (air/water; kJ/mol)	92.7	[87]
ΔU (octanol/air; kJ/mol)	−47.9	[87]
E_a for reaction in air (kJ/mol)	0.648	Estimated based on Jiménez et al. [88]
E_a for reaction in water (kJ/mol), pH 7	81.1	Calculated using Arrhenius parameters for hydronium and hydroxide catalyzed hydrolysis reactions [34]
E_a for reaction in soil (kJ/mol)	81.1	Estimated: the value is same as E_a of hydrolysis in water
E_a for reaction in sediment (kJ/mol)	81.1	Estimated: the value is same as E_a of hydrolysis in water

D5 = decamethylcyclopentasiloxane; EQC = equilibrium criterion (model); QWASI = quantitative water–air–sediment interaction (model); K_{AW} = air–water partition; ΔU = internal energy change; E_a = energy of activation.

work. It suggests that most attention be focused on atmospheric processes, wastewater treatment, and subsequent fate in rivers and lakes, including sediments and in sludge-amended soils.

STEP 7: QUANTITATIVE, SITE-SPECIFIC, OR REGIONAL EVALUATION OF FATE AND EXPOSURE

Atmospheric fate, transport, and exposure

Three aspects of atmospheric fate and transport are considered: long-range atmospheric transport to remote regions such as the Arctic, the possibility of deposition to surface media in remote locations, and the ozone depletion potential in the stratosphere.

The potential for long-range atmospheric transport is conventionally expressed as a characteristic travel distance (CTD), which is the distance at which 63% of the chemical has been lost from the atmosphere and thus only 37% remains. This distance cannot be determined directly from monitoring data, but it can be estimated using mass balance models. The authors of the Environment Canada assessment of D5 [2] obtained similar estimated CTDs of approximately 3400 km using the TAPL3 model [49] and the OECD tool [50], respectively. Xu and Wania [36] compiled a global modeling assessment of D5 using the OECD tool and the Globo-POP model [20,51] that estimates global fate in 10 climatic zones, each containing 9 compartments including 4 atmospheric layers. They also compared D5 with other chemicals designated as persistent organic pollutants (POPs). The CTD of D5 was estimated to be 3430 km and was most sensitive to K_{AW} and atmospheric half-life. The CTD values for D5 are less than the minimum value of approximately 5000 km for designated POPs [52].

The Globo-POP model estimated that the average ground layer atmospheric concentrations of D5 in the Arctic region would be in the range of 0.5 ng/m³ to 14 ng/m³, a range found to be consistent with global monitoring data in rural and remote locations [53–56]. For the N-temperate zone at summer time, Yucuis et al. [55] reported that the average airborne D5 concentration was in the range of 162 to 230 ng m^{−3}, 52 ng m^{−3}, and 18 ng m^{−3} in urban, suburban, and rural atmospheres, respectively. In the summer, the average airborne D5 in the

Arctic atmosphere was only 0.5 ng m^{−3} [53,56]. The Arctic ground layer concentration represents a factor of a few hundred lower than that in the source regions, or a corresponding factor of 40 lower compared with that in rural regions in the N-temperate zone. Although the airborne D5 concentrations can increase in the Arctic regions in the winter to an average near 4 ng m^{−3} [56,57], these atmospheric concentrations still represent a very small fraction (~1%) of the total D5 that enters the atmosphere.

The second aspect of atmospheric assessment is the possibility of deposition of D5 to surface media in remote locations by wet and dry deposition. Xu and Wania [36] assessed this possibility by determining the transfer efficiency and the Arctic contamination potential of D5 using the OECD tool and the Globo-POP model. These estimated transfer efficiency and Arctic contamination potential metrics are 100-fold to 1000-fold less than those of reference POPs addressed in the Stockholm Convention. The implication is that although D5 can travel global-scale distances in the atmosphere, it has little tendency to redeposit from the atmosphere back to land (<0.007% of total emissions) based on its relatively low K_{OA} and its high K_{AW} (Table 3).

Finally, there is the issue of the possible effects of D5 on ozone depletion potential. First, D5 could not directly cause ozone destruction because it does not contain any halogens, which are found in the known ozone-depleting chemicals [58]. Second, the only possible aerosol that could be formed from D5 is silica, a major component of natural mineral aerosols in the atmosphere. Any silica formed is likely inert toward the reactions leading to ozone destruction. Most importantly, D5 has a relatively short lifetime in the troposphere compared with transport times to the stratosphere, and thus the amount of residual D5 available to be transferred to the stratosphere is too small to contribute significantly to the natural aerosol mass in these polar stratosphere clouds. Therefore, D5 does not have direct or indirect ozone destruction potential.

The monitoring data and the model evaluations confirm that D5 can become distributed globally in the atmosphere at levels of nanograms per cubic meter, with higher concentrations close to sources and especially indoors [53,55,56]. Appreciable deposition to surface media such as soils and vegetation is

Table 7. Output of EQC level III modeling of D5

Scenario	Air	Water	Soil	Sediment	All
A realistic scenario of emissions to air, water, and soil					
Emission rate (kg/h)	945	8	47	0	1000
Mass fraction (%)	63.8%	1.84%	1.17%	33.2%	
Fugacity (Pa)	4.86E-06	7.37E-02	1.69E-04	2.31E-01	
Reaction loss (%)	29.2%	8.27E-04	2.96E-03	3.39E-04	29.7%
Advection loss (%)	70.1%	2.02E-03	0	7.28E-04	70.3%
Net intermedia transport (normalized rate to the total emission rate)	W→A S→A	4.09E-03 4.40%		W→Sed S→W	1.07E-03 2.04E-07
Overall persistence (h)			110		
Reaction residence time (h)			370		
Advective residence time (h)			156		
Emission to air scenario					
Emission rate (kg/h)	1000	0	0	0	1000
Mass fraction (%)	99.9%	3.69E-06	4.81E-04	6.66E-05	
Fugacity (Pa)	4.72E-06	9.51E-06	4.45E-06	2.98E-05	
Reaction loss (%)	29.4%	1.07E-07	7.79E-05	4.38E-08	29.5%
Advection loss (%)	70.5%	2.61E-07	0%	9.40E-08	70.5%
Net intermedia transport rate (fraction to the total emission rate)	A→W A→S	5.00E-07 7.79E-05		W→Sed S→W	1.38E-07 5.37E-09
Overall persistence (h)			70.6		
Reaction time (h)			240		
Advective time (h)			100		
Emission to water scenario					
Emission rate (kg/h)	0	1000	0	0	1000
Mass fraction (%)	0.744%	5.21%	3.58E-06	94.0%	
Fugacity (Pa)	2.41E-06	9.21E+00	2.27E-06	2.89E+01	
Reaction loss (%)	15.0%	10.3%	3.98E-05	4.24%	29.6%
Advection loss (%)	36.0%	25.2%	0%	9.10%	70.4%
Net intermedia transport rate (fraction to the total emission rate)	W→A A→S	51.1% 3.98E-05		W→Sed S→W	13.3% 2.75E-09
Overall persistence (h)			4841		
Reaction time (h)			16 338		
Advective time (h)			6879		
Emission to soil scenario					
Emission rate (kg/h)	0	0	1000	0	1000
Mass fraction (%)	71.2%	1.41E-05	28.7%	2.54E-04	
Fugacity (Pa)	4.43E-06	4.79E-05	3.50E-03	1.50E-04	
Reaction loss (%)	27.6%	5.37E-07	6.13%	2.20E-07	33.8%
Advection loss (%)	66.2%	1.31E-06	0%	4.73E-07	66.2%
Net intermedia transport (fractional rate to the total emission rate)	W→A S→A	1.69E-06 93.9%		W→Sed S→W	6.93E-07 4.23E-06
Overall persistence (h)			93.0		
Reaction time (h)			275		
Advective time (h)			140		

EQC = equilibrium criterion (model); D5 = decamethylcyclopentasiloxane; A = air; W = water; S = soil; Sed = sediment.

unlikely [36], as is any impact on ozone depletion in the stratosphere.

Fate and exposure in flowing water bodies receiving WWTP effluents

After release into household wastewater and subsequent removal in WWTPs, approximately 0.8% of the total D5 used in consumer products is discharged to surface waters (Figure 2) from WWTP effluents. As indicated in step 3, the fate assessment should examine the fate, transport, and exposure potential in waters that receive WWTP effluents containing D5 to accurately estimate exposure concentrations for quantitative risk assessment.

A simple and transparent approach to estimating local-scale, surface water concentrations at the point of the effluent discharge is to calculate them from the concentration in the

effluent divided by a dilution factor. Although single-default dilution factors are commonly used in screening assessments [59–61], in reality, riverine and estuarine flow rates (and, hence, dilution) vary over several orders of magnitude depending on the flow conditions (e.g., mean or low flow), location, and season [62,63]. Therefore, more accurate and realistic exposure concentrations can be estimated using models that contain parameters describing WWTP infrastructure, population served, and surface water flow and dispersion data at the discharge points to determine individual dilution factors for each effluent.

To estimate the concentration of D5 in flowing waters that receive WWTP effluent, Environment Canada used MegaFlush, a proprietary WWTP effluent dilution model [2]. Because the model is not publicly available, an independent but equivalent assessment was conducted and is outlined in the present study

using the same approach as the MegaFlush model whenever possible. The discharge data for WWTPs across Canada were extracted from the 1996 Municipal (water) Use Database (MUD) reworked to include only those WWTPs in municipalities serving more than 1000 people. The original MUD database contained 1483 WWTP facilities serving a total of 20.7 million people, or approximately 74% of the Canadian population, and approximately 4 million additional people representing approximately 9% of the population who had direct discharges, mostly to marine or estuarine waters. The river flow data (from ~1996) from the Environment Canada HYDAT database was purchased from Greenland Water Resources. This database contains hydrometric data updated to the end of 1996 except for Quebec, which was only current to the end of 1995. These 2 databases were integrated using locational data supplied by MUD and allowed the mean dilution in surface waters at the discharge point of the WWTP to be estimated from the effluent volume of the WWTP and the flow of the receiving stream. When the locations were not exactly known, the most appropriate location and flow data were chosen in consultation with Environment Canada. To simulate low flow conditions, the mean flow was reduced by a factor of 3, as recommended by Environment Canada, and used to estimate the low flow dilution factor. Any WWTP facilities that discharged to lakes or marine or estuarine water bodies were eliminated because it was difficult to estimate the appropriate dilution factor. The final database contains information on 585 WWTP sites across Canada. In the absence of publicly available information on the Environment Canada MegaFlush model and its database, the only option was to use this equivalent database. It is expected to give conservative estimates of effluent and surface water concentrations relative to real world conditions because these WWTP data are distributed across Canada, some of these plants have since undergone upgrading of treatment technology, and this database does not include lakes, estuaries, and marine discharge sites, which have higher dilution factors. The median and 95th percentile values of modeled total D5 surface water concentration (Table 4) are 0.026 $\mu\text{g/L}$ and 1.94 $\mu\text{g/L}$, respectively, which are well below the solubility of D5 in water.

Municipal and industrial influent, effluent, and ambient water concentrations of D5 were available from >80 samples (~40% nondetects), including locations in Nordic countries [64,65], the United Kingdom [66,67], France [67], and Canada [39,65]. These sampling locations include effluent streams from industrial and municipal wastewater, along with ambient water samples. The distribution of D5 water concentration data are shown in Figure 3, where left-censored data are expressed as 50% of the detection limit (generally ~0.02 $\mu\text{g/L}$); data from industrial and municipal WWTP influent samples are not included. The median field-observed D5 water concentration was 0.06 $\mu\text{g/L}$, with a 95th percentile concentration of 7.3 $\mu\text{g/L}$ (Table 4). These values are less than the maximum solubility of 17 $\mu\text{g/L}$ for D5 in water that contains no DOC. The predicted concentrations using the WWTP dilution model are reasonably comparable with the field monitoring data, with observed and modeled 95th percentile D5 concentrations in natural water of 7.3 $\mu\text{g/L}$ and 1.94 $\mu\text{g/L}$, respectively (Table 4).

Fate in larger water bodies receiving WWTP effluent

In addition to discharge to flowing waters, the 0.8% of D5 released in WWTP effluent may be discharged to water bodies such as lakes. To assess the fate and exposure concentration in these water bodies, the quantitative water–air–sediment

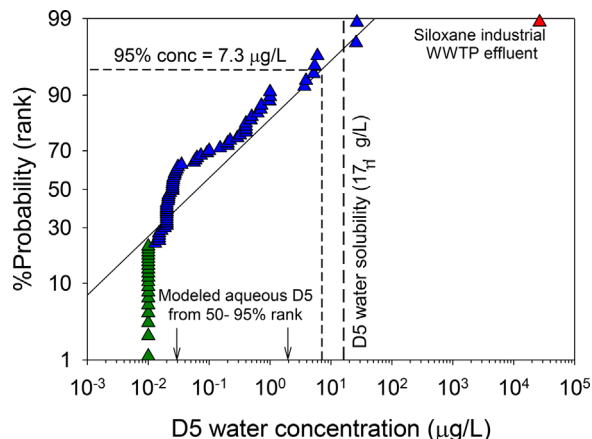


Figure 3. Cumulative probability plot for decamethylcyclotrisiloxane (D5) water concentration data ($\mu\text{g/L}$) measured in field samples, compared with calculated model estimates for D5 in water and its water solubility limit. A linear regression on log-transformed data was used to fit the field water D5 data, with $n = 87$, intercept = 0.95, slope = 0.80, $r^2 = 0.74$. The green symbols at 0.01 $\mu\text{g/L}$ are water samples with left-censored D5 concentrations less than the method detection limit (0.02 $\mu\text{g/L}$), and D5 was assumed to be present at 50% of the method detection limit. The red symbol represents water data from a siloxane industrial wastewater treatment plant (WWTP) effluent stream, and this datum was not used in the linear regression model. Modeled D5 water concentrations are also presented, from median (0.026 $\mu\text{g/L}$) to 95th percentile (1.94 $\mu\text{g/L}$).

interaction (QWASI) model, which was developed in 1983 for lakes and rivers [68,69], was used. This model can be used both for qualitative purposes to understand the fate of a chemical and, when appropriately parameterized, for estimating the concentration in actual water bodies.

Using recommended values for air–water, sediment–water, and suspended sediment–water partitioning and reaction properties of D5 (Table 3) and properties specific to Lake Ontario (USA/Canada; Table 8), QWASI simulations were conducted for Lake Ontario for a D5 emission rate of 1398 kg/yr [70] over the temperature range of 1 °C to 25 °C. This emission rate was calculated from the average per capita usage of D5 for Canada of 103 g/yr/capita, the population of the Lake Ontario watershed of 7 135 800 people, 9.5% discharge of the D5 used per capita to sewers, and 98% removal in WWTP. The water concentration of D5 decreases somewhat linearly from 0.00031 $\mu\text{g/L}$ to 0.00005 $\mu\text{g/L}$ because of an increase in the hydrolysis rate as temperature is increased from 1 °C to 20 °C. These values are orders of magnitude lower than the solubility limit.

In addition, the QWASI model was applied to Lake Pepin (lake-specific properties shown in Table 8) for a D5 emission rate of 823 kg/yr, based on the same realistic emission scenario for 4 200 000 people in its watershed [70]. The modeled water concentration of D5 in Lake Pepin gradually decreases from 0.028 $\mu\text{g/L}$ to 0.016 $\mu\text{g/L}$ because of an increase in hydrolysis rate as the temperature increases from 1 °C to 25 °C. These predicted concentrations are also well below the aqueous solubility of 17 $\mu\text{g/L}$. Whelan [71] recently published simulations for D5 in Lake Pepin and Lake Ontario using a customized version of the QWASI model that gave similar concentration ranges.

The ranges of D5 aqueous concentrations estimated by the QWASI model for Lake Ontario and Lake Pepin are generally consistent with the monitoring data and suggest that the model is capturing the key fate processes that apply to D5 in aquatic receiving environments. Models can thus be useful for providing estimates of prevailing concentrations, but there is

Table 8. Lake-specific properties for Lake Ontario and Lake Pepin used in the QWASI model (QWASI Ver 3.10)^a

	Lake Ontario	Lake Pepin
Lake dimensions		
Water surface area (m ²)	1.91×10^{10}	1.03×10^8
Water volume (m ³)	1.64×10^{12}	5.67×10^8
Sediment active layer depth (m)	0.005	0.005
Concentration of solids		
In water column (mg/L)	0.64	10
In inflow water (mg/L)	24	45
Of aerosols in air (μg/m ³)	30	30
In sediment (m ³ /m ³)	0.15	0.15
Density of solids		
In water (kg/m ³)	2400	2400
In sediment (kg/m ³)	2400	2400
In aerosols (kg/m ³)	1500	1500
Organic carbon fraction of solids		
In water column	0.25	0.12
In sediment	0.04	0.04
In inflow water	0.25	0.12
In resuspended sediment solids	0.035	0.035
Flows		
River water inflow (m ³ /h)	2.00×10^7	2.00×10^6
Water outflow rate (m ³ /h)	2.60×10^7	2.00×10^6
Deposition rate of solids (g/m ² /d)	1.4	33.4
Burial rate of solids (g/m ² /d)	0.6	14.31
Resuspension rate of solids (g/m ² /d)	0.6	14.31
Transfer coefficients		
Aerosol dry deposition velocity (m/h)	7.2	7.2
Scavenging ratio (vol air/vol rain)	2.00×10^5	2.00×10^5
Rain rate (m/yr)	0.92	0.92
Mass transfer coefficient (MTC)		
Volatilization MTC (air side) (m/h)	1	1
Volatilization MTC (water side) (m/h)	0.01	0.01
Sediment–water diffusion MTC (m/h)	0.0004	0.0004

^aDetails on the derivation of these properties are in Mackay et al. [68].
QWASI = quantitative water–air–sediment interaction (model).

no substitute for actual monitoring data. The models can also contribute by identifying the key processes and their relative significance by uncertainty analyses and suggesting how concentrations will respond to changes in emission rate, temperature, and other environmental variables.

Fate and exposure to D5 in sediments

As a first approximation, the sediment concentration of any chemical at sewage discharge points (C_s ; μg/g) on an organic carbon normalized basis can be estimated from the aquatic concentration of the chemical at the discharge point (C_w ; μg/L) and the chemical's K_{OC} value (L/kg) with the appropriate unit changes ($C_s = C_w \times K_{OC}/1000$). The organic carbon normalized sediment concentration was estimated for each of the discharge points in the WWTP dilution model. The median sediment concentration is 3.8 μg/g organic carbon, and the 95th percentile concentration is 287 μg/g organic carbon (Table 4), approximately 1 to 2 orders of magnitude less than the maximum sorption capacity on an organic carbon normalized basis of 2500 μg/g organic carbon. For 1% and 4% organic carbon, which is the measured organic carbon content of Lake Ontario sediments [72], the sediment concentration would, based on the 95th percentile sediment organic carbon normalized concentration of 287 μg/g organic carbon, range from 2.9 μg/g dry weight to 11.5 μg/g dry weight.

Sediment concentrations of D5 have been measured in more than 170 samples collected from more than 15 global locations. The measured D5 concentrations in sediment include samples from Norway, Denmark, Sweden, Finland, Iceland [73–76], the United Kingdom [67], the United States [77,78], Canada [6,39],

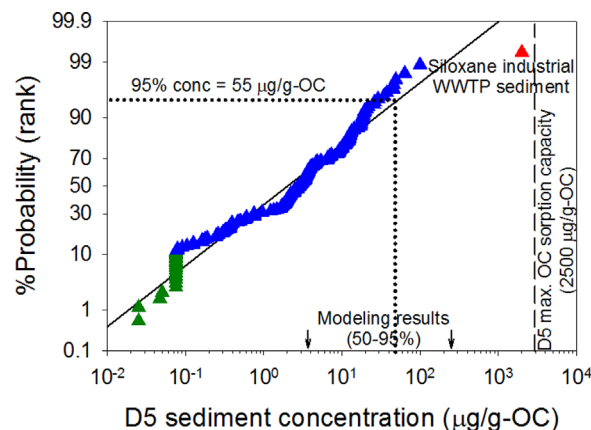


Figure 4. Cumulative probability plot for decamethylcyclopentasiloxane (D5) sediment concentration data measured in field samples, compared with calculated model estimates for D5 in sediment (median to 95th %centile) and the maximum D5 organic carbon (OC) sorption capacity. A linear regression on log-transformed data was used to fit the field sediment D5 data, with $n = 175$, intercept = -0.35 , slope = 1.1 , $r^2 = 0.96$. The red symbol represents sediment data from a siloxane industrial wastewater treatment plant (WWTP) sediment, and this datum was not used in the linear regression model. The green symbols at <0.1 μg/g OC are sediment samples with D5 concentrations less than the method detection limit (≤ 0.15 μg/g OC), and D5 was assumed to be present at 50% of the method detection limit; field-measured D5 sediment data are represented by blue symbols. Modeled D5 sediment concentrations are also presented, from median (3.8 μg/g OC) to 95th %centile (287 μg/g OC).

and Japan (D.E. Powell et al., Dow Corning Corporation, Midland, Michigan, USA, unpublished manuscript). All sediment samples with concentrations that were reported as left-censored values were considered to have residues present at 50% of the method detection limit. If organic carbon levels were not measured for the analyzed sediment samples, a 2% organic carbon content was assumed to normalize the measured D5 concentration on an organic carbon basis. A cumulative probability plot of these D5 field sediment data is presented in Figure 4. The 95th percentile probability concentration of D5 in sediment is 55 μg/g organic carbon, or approximately 45-fold less than the maximum sorption capacity of organic carbon for D5 of approximately 2500 μg/g organic carbon (Table 4).

The D5 sediment concentrations estimated from the WWTP dilution model (Table 4) appear to be higher than, but bracket, the upper end of D5 measured field concentrations (Figure 4). Discrepancies are expected between the monitoring and simple modeling data and are likely attributable to processes within the water bodies that lead to high variability in monitored sediment concentrations and also to sediment loss processes. This approach, assuming equilibrium between the water column and the sediment, does not account for dynamic processes such as deposition, resuspension, and degradation, which can lead to variability in the concentrations.

Fate and exposure in biosolids and biosolids-amended soils

The D5 exposure concentrations were also calculated for agricultural soils to which sludge/biosolids from WWTPs have been added as a nutritional supplement. The ASTREAT model [43] can be used to predict concentrations of D5 in WWTP sludge. Using the 95th percentile range of D5 influent concentrations in Wang et al. [39] of approximately 1 μg/L to 55 μg/L, the ASTREAT model predicted final sludge concentrations of 5.72 μg/g dry weight to 314 μg/g dry weight. Another way to estimate the average D5 in biosolids is to multiply the D5 release per capita per day of 283 mg/capita/d by

the 4.7% distribution to sludge, and the sludge generation rate of 0.12 lb (or 0.054 kg) dry weight/capita/d [80]. This results in an estimated sludge concentration of 246 $\mu\text{g/g}$ dry weight, which is within the range estimated by the ASTREAT model.

The average concentration of D5 in biosolids is highly variable, ranging from approximately 30 mg/kg dry weight in Nordic countries [64] to 297 mg/kg dry weight in Canada (calculated from data in Wang et al. [39], assuming a 70% moisture content of biosolids). The model results for biosolids are thus consistent with and bracket the range found from the monitoring data and further verify that the estimated removal efficiencies are reasonable.

Biosolid application rates in the United States range from 2000 kg to 5000 kg/dry weight/acre, which corresponds to 1.3 g/kg to 3.2 g/kg soil dry weight [79]. Canadian biosolid loading at 5 g/kg soil dry weight, as reported by Wang et al. [39], is considered to be a high-end estimate. This higher Canadian application rate was used to estimate the initial soil concentrations resulting from biosolid applications. Using the range of predicted final sludge concentrations of 5.72 $\mu\text{g/g}$ to 314 $\mu\text{g/g}$ and Canadian biosolid application rate of 5 g/kg soil, the estimated range in initial D5 concentration in soil from biosolid application is 0.03 $\mu\text{g/g}$ to 1.6 $\mu\text{g/g}$ dry weight (Table 4). These concentrations are significantly less than the maximum sorption capacity of D5 in organic matter in agricultural soils. Assuming a maximum sorption capacity in organic matter of 2500 $\mu\text{g/g}$, these capacities for typical North American soils range from 12.6 $\mu\text{g/g}$ for soils of 0.5% organic carbon to 75 $\mu\text{g/g}$ for soils with 3% organic carbon (Table 4).

A probability distribution plot of D5 field monitoring soil data is presented in Figure 5, where the median concentration is 0.03 $\mu\text{g/g}$ dry weight and the 95th percentile concentration is 0.3 $\mu\text{g/g}$ dry weight. The monitoring data, with the exception of a siloxane industrial site in China, do not exhibit concentrations as high as the modeled concentrations. The D5 concentrations in soil from the incorporation of biosolids into soils will be highest immediately after application because of

subsequent volatilization and degradation loss. The measured D5 soil data in Figure 5 were collected at unspecified times after application when loss processes would have reduced the concentration of D5 [39,64]. This is further substantiated by comparing measured soil concentrations of D5 in biosolids-amended soils from southern Ontario and Quebec (Canada) ranging from 0.006 $\mu\text{g/g}$ to 0.221 $\mu\text{g/g}$ dry weight and averaging 0.061 $\mu\text{g/g}$ dry weight [39], which are much less than the predicted initial concentration. Similarly, D5 concentrations in biosolids-amended soils with an unknown number of biosolids applications in Spain were reported to range from 0.031 $\mu\text{g/g}$ to 0.038 $\mu\text{g/g}$ dry weight [80]. These results are consistent with the fate modeling results in step 4, which show that the D5 concentrations in soil will be highest immediately after application and will decrease rapidly because of volatilization. In all cases, the monitoring and modeling concentrations are well below the solubility limit of D5 in soil of 12.6 $\mu\text{g/g}$ dry weight at 0.5% organic carbon and 75 $\mu\text{g/g}$ dry weight at 3% organic carbon.

Exposure concentrations

The resulting analysis of the maximum solubility of D5 in the various environmental compartments of air, water, sediment, and soil, as well as the results of modeling predictions and monitoring data, can be used to provide a range of probable exposure concentrations in the environment. This summary is presented in Table 4. These exposure concentrations are used in the risk assessment [10].

DISCUSSION AND CONCLUSIONS

This example of an assessment of D5 illustrates the need to follow a consistent process for conducting fate and exposure assessment using accurate and consistent physical-chemical property data over the relevant range of environmental temperatures, ideally obtained in a collaborative effort between industry and regulators. Although generating measured data can be expensive, QSARs should be applied only when there is certainty that the chemical is within the relevant domain of applicability. These property data are also essential when laboratory tests are designed for toxicity and bioconcentration and to ensure that subsaturated conditions exist.

Simple mass balance models can play an important role in elucidating the general environmental fate and transport characteristics of the chemical and for undertaking more detailed evaluations of fate in the atmosphere, water bodies, soils, and sediments, as are indicated by the model predictions and monitoring data. Monitoring data and model estimates should be regarded as mutually supportive; indeed, it can be argued that both are essential. Prior to the Board of Review report [7], there was a lack of monitoring data in Canada to support the model assertions. It is unfortunate that even though D5 has been used for decades, monitoring data were not available. A further issue is that the unusual properties and uses of D5 hindered researchers from gaining insights from the fate, transport, and exposure of similar benchmark chemicals. When models are applied, it is essential that the model and its input and output data be freely available to allow other parties to reproduce the results. This need for the adoption of good modeling practice in this context was fully articulated by Buser et al. [81] in a study largely prompted by the Board of Review report [7]. It is hoped that the present series of studies on D5 will result in an increased awareness of the need for rigorous evaluation of the potential environmental impacts of chemicals of commerce.

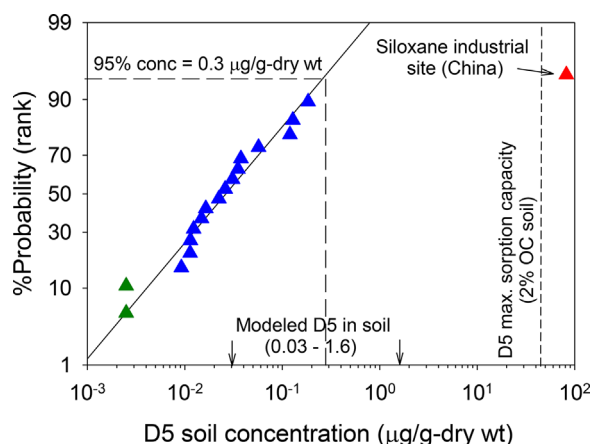


Figure 5. Cumulative probability plot for decamethylcyclotrisiloxane (D5) soil concentration data ($\mu\text{g/g}$ dry wt) measured in field samples, compared with calculated model estimates for D5 in soil. A linear regression on log-transformed data was used to fit the field soil D5 data, with $n = 18$, intercept = 2.38, slope = 1.50, $r^2 = 0.96$. The red symbol represents data soil sample from a siloxane industrial production facility, and this datum was not used in the linear regression model. The green symbols at 0.0025 $\mu\text{g/g}$ dry weight are soil samples with D5 concentrations less than the method detection limit (0.005 $\mu\text{g/g}$ dry wt) for which D5 was assumed to be present at 50% of the method detection limit in these samples. Modeled D5 soil concentrations are also presented, and the D5 maximum sorption capacity at 2% organic carbon (OC) is also shown.

Acknowledgment—Support for the present study was provided by the Silicones Environmental, Health, and Safety Center of the American Chemistry Council.

Data Availability—Data may be requested through the Silicones Environmental, Health, and Safety Center of the American Chemistry Council by submitting a request via email to Tracy Guerrero (tracy_guerrero@americanchemistry.com).

REFERENCES

- Environment Canada and Health Canada, 2008. Screening assessment for the challenge: Decamethylpentacyclosiloxane (D5). [cited 2015 February]. Available from: <http://ec.gc.ca/ese-ees/default.asp?lang=En&n=13CC261E-1>
- Brooke DN, Crookes MJ, Gray D, Robertson S. 2009. Environmental risk assessment: Decamethylpentacyclosiloxane. UK Environmental Agency, Bristol, UK. [cited 2013 December 11]. Available from: <http://publications.environment-agency.gov.uk/pdf/SCHO0309BPQX-e-e.pdf>
- Alaee M, Wang, D-G, Gouin T. 2013. Cyclic volatile methyl siloxanes in the environment. *Chemosphere* 93:709–710.
- Rücker C, Kümmerer K. 2015. Environmental chemistry of organosiloxanes. *Chem Rev* 115:466–524.
- Wang DG, Norwood W, Alaee M, Byer JD, Brimble S. 2013. Review of recent advances in research on the toxicity, detection, occurrence and fate of cyclic volatile methyl siloxanes in the environment. *Chemosphere* 93:711–725.
- Government of Canada. 1999. Canadian Environmental Protection Act, 1999. Canada Gazette Part III, Vol 22. [cited 2013 December 11]. Available from: <http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=CC0DE5E2-1&toc=hide>
- Siloxane D5 Board of Review. 2011. Report of the Board of Review for decamethylpentacyclosiloxane (D5). Government of Canada, Ottawa, ON, Canada. [cited 2013 December 11]. Available from: <http://www.ec.gc.ca/lcpe-cepa/default.asp?lang=En&n=515887B7-1&offset=1&toc=show#archived>
- Gobas FAPC, Powell DE, Woodburn KB, Springer T, Huggett DB. 2015. Bioaccumulation of decamethylpentacyclosiloxane (D5): A review. *Environ Toxicol Chem* 34:2703–2714 (this issue).
- Gobas FAPC, Xu S, Kozerski G, Powell DE, Mackay D, Fairbrother A. 2015. Fugacity and activity based analysis of the bioaccumulation and environmental risks of D5. *Environ Toxicol Chem* 34:2723–2731 (this issue).
- Fairbrother A, Burton A, Klaine S, Powell D, Staples CA, Mihiach E, Woodburn K. 2014. Characterization of ecological risks from environmental releases of decamethylpentacyclosiloxane (D5). *Environ Toxicol Chem* 34:2715–2722 (this issue).
- Xu S, Kozerski G, Mackay D. 2014. Critical review and interpretation of environmental data for volatile methylsiloxanes: Partition properties. *Environ Sci Technol* 48:11748–11759.
- Allen RB, Kochs P, Chandra G. 1997. Industrial organosilicon materials, their environmental entry and predicted fate. In Chandra G, ed, *Organosilicon Materials*, Vol 3, Part H—The Handbook of Environmental Chemistry. Springer-Verlag, New York, NY, USA, pp 1–25.
- Horii Y, Kannan K. 2008. Survey of organosilicone compounds, including cyclic and linear siloxanes, in personal-care and household products. *Arch Environ Contam Toxicol* 55:701–710.
- Wang R, Moody RP, Koniecki D, Zhu JP. 2009. Low molecular weight cyclic volatile methylsiloxanes in cosmetic product sold in Canada: Implication for dermal exposure. *Environ Int* 35:900–904.
- Montemayor, BP, Price BB, van Egmond RA. 2013. Accounting for intended use application in characterizing the contributions of cyclopentasiloxane (D5) to aquatic loadings following personal care product use: Antiperspirants, skin care products and hair care products. *Chemosphere* 93:735–740.
- Kozerski GE, Xu S, Miller, J Durham J. 2014. Determination of soil organic carbon-water sorption coefficients of volatile methyl siloxanes. *Environ Toxicol Chem* 33:1937–1945.
- Xu S, Kropscott B. 2012. Method for simultaneous determination of partition coefficients for cyclic volatile methylsiloxanes and dimethylsilanediol. *Anal Chem* 84:1948–1955.
- Xu S, Kropscott B. 2014 Evaluation of the three-phase equilibrium method for measuring temperature dependence of internally consistent partition coefficients (K_{OW} , K_{OA} and K_{AW}) for volatile methylsiloxanes and trimethylsilanol. *Environ Toxicol Chem* 33:2702–2710.
- Li N, Wania F, Lei YD, Daly GL. 2003. A comprehensive and critical compilation, evaluation, and selection of physical-chemical property data for selected polychlorinated biphenyls. *J Phys Chem* 32:1545–1590.
- Wania F. 2006. Potential of degradable organic chemicals for absolute and relative enrichment in the Arctic. *Environ Sci Technol* 40:569–577.
- Kelly, BC, Gobas F. 2003. An arctic terrestrial food-chain bioaccumulation model for persistent organic pollutants. *Environ Sci Technol* 37:2966–2974.
- Seth R, Mackay D, Muncke J. 1999. Estimating the organic carbon partition coefficient and its variability for hydrophobic chemicals. *Environ Sci Technol* 33:2390–2394.
- Seston RM, Powell DE, Woodburn KB, Kozerski GE, Bradley PW, Zwiernik MJ. 2014. Importance of lipid analysis and its implications for metrics of bioaccumulation. *Integr Environ Assess Manag* 10:142–144.
- Endo S, Escher BI, Goss K-U. 2011. Capacities of membrane lipids to accumulate neutral organic chemicals. *Environ Sci Technol* 45:5912–5921.
- Geisler A, Endo S, Goss K-U. 2012. Partitioning of organic chemicals to storage lipids: Elucidations of the dependence on fatty acid composition and temperature. *Environ Sci Technol* 46:9519–9524.
- Bremle G, Ewald G. 1995. Bioconcentration of polychlorinated biphenyls (PCBs) in chironomid larvae, oligochaete worms and fish from contaminated lake sediment. *Mar Freshwater Res* 46:267–273.
- Ewald G, Bremle G, Karlsson A. 1998. Differences between Bligh and Dyer and soxhlet extractions of PCBs and lipids from fat and lean fish muscle: Implications for data evaluation. *Mar Pollut Bull* 36:222–230.
- van der Heijden SA, Jonker MTO. 2011. Intra- and interspecies variation in bioconcentration potential of polychlorinated biphenyls: Are all lipids equal? *Environ Sci Technol* 45:10408–10414.
- Ahmed H, Poole CF, Kozerski GE. 2007. Determination of descriptors for organosilicon compounds by gas chromatography and non-aqueous liquid-liquid partitioning. *J Chromatogr A* 1169:179–192.
- Abraham MH, Chadha HS, Whiting GS, Mitchell RC. 1994. Hydrogen bonding. 32. An analysis of water-octanol and water-alkane partitioning and the $\Delta\log P$ parameter of Seiler. *J Pharm Sci* 83:1085–1100.
- Mount GH, Eisele FL. 1992. An intercomparison of tropospheric OH measurements at Fritz Peak Observatory, Colorado. *Science* 256:1187–1190.
- 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. *Environ Sci Technol* 25:863–866.
- Durham JA, Kozerski GE. 2006. Hydrolysis of decamethylpentacyclosiloxane (D5). Final report to the Silicones Environmental, Health, and Safety Center (SEHSC). Dow Corning, Midland, MI, USA.
- Kozerski G. 2008. SEHSC response to Dr. Bidleman's review on hydrolysis studies of D4 and D5. Dow Corning, Midland, MI, USA.
- Xu S. 2007. Estimation of degradation rates of cVMS in soils. Final report submitted to the Silicones Environmental, Health, and Safety Council (SEHSC). Dow Corning study 10787–102. Dow Corning, Midland, MI, USA.
- Xu S, Wania F. 2013. Chemical fate, latitudinal distribution and long-range transport of cyclic volatile methylsiloxanes in the global environment: A modeling assessment. *Chemosphere* 93:835–843.
- Xu S. 2010. Aerobic and anaerobic transformation of decamethylpentacyclosiloxane (14C-D5) in aquatic sediment systems. CES Report January 27, 2010. Centre Européen des Silicones, Oudergem, Belgium.
- Organisation for Economic Co-operation and Development. 2000. Emission scenario documents. Paris, France. [cited 2013 December 11]. Available from: www.oecd.org/env/ehs/risk-assessment/emissionscenariodocuments.htm
- Wang DG, Steer H, Tait T, Williams Z, Pacepavicius G, Young T, Ng T, Smyth SA, Kinsman L, Alaee M. 2013. Concentrations of cyclic volatile methylsiloxanes in biosolid amended soil, influent, effluent, receiving water, and sediment of wastewater treatment plants in Canada. *Chemosphere* 93:766–733.
- Canadian Water and Wastewater Association. 2001. National survey of wastewater treatment plants. Final report to Environment Canada, National Pollutant Release Inventory (NPRI). [cited 2013 December 11]. Available from: http://www.cwwa.ca/pdf_files/freepub_wastewaterreport.PDF
- Buser AM, Bogdal C, MacLeod M, Scheringer M. 2014. Emissions of decamethylcyclopentasiloxane from Chicago. *Chemosphere* 107:473–475.
- Buser AM, Kierkegaard A, Bogdal C, MacLeod M, Scheringer M, Hungerbühler K. 2013. Concentrations in ambient air and emissions of cyclic volatile methylsiloxanes in Zurich, Switzerland. *Environ Sci Technol* 47:7045–7051.

43. Lee KC, Rittmann BE, Shi J, McAvoy DC. 1998. Advanced steady-state model for the fate of hydrophobic and volatile compounds in activated sludge wastewater treatment. *Water Environ Res* 70:1118–1131.
44. Seth R, Webster E, Mackay D. 2008. Continued development of a mass balance model of chemical fate in a sewage treatment plan. *Water Res* 42:595–604.
45. Sparham C, Van Egmond R, O'Connor S, Hastie C, Whelan M, Kanda R, Franklin O. 2008. Determination of decamethylpentacyclosiloxane in river water and final effluent by headspace gas chromatography/mass spectrometry. *J Chromatogr A* 1212:124–129.
46. Hughes L, Mackay D, Powell DE, Kim J. 2012. An updated state of the science EQC model for evaluating chemical fate in the environment: Application to D5 (decamethylpentacyclosiloxane). *Chemosphere* 87:118–124.
47. Karickhoff SW. 1981. Semi-empirical estimation of sorption of hydrophobic pollutants on natural sediments and soils. *Chemosphere* 10:833–846.
48. Kim J, Powell DE, Hughes L, Mackay D. 2013. Uncertainty analysis using a fugacity-based multimedia mass-balance model: Application of the updated EQC model to decamethylpentacyclosiloxane (D5). *Chemosphere* 93:819–829.
49. Beyer A, Mackay D, Matthies M, Wania F, Webster E. 2000. Assessing long-range transport potential of persistent organic pollutants. *Environ Sci Technol* 34:699–703.
50. Wegmann F, Cavin L, MacLeod M, Scheringer M, Hungerbühler K. 2009. The OECD software tool for screening chemicals for persistence and long-range transport potential. *Environ Model Softw* 24:228–237.
51. Wania F. 2003. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in polar regions. *Environ Sci Technol* 37:1344–1351.
52. Scheringer M, MacLeod M, Wegmann F. 2006. *The OECD POV and L RTP Screening Tool*, Version 2.0. [cited 2015 February]. Available from: www.sust-chem.ethz.ch/docs/Tool2_0_Manual.pdf
53. McLachlan MS, Kierkegaard A, Hansen KM, van Egmond R, Christensen JH, Skjoth CA. 2010. Concentrations and fate of decamethylpentacyclosiloxane (D5) in the atmosphere. *Environ Sci Technol* 44:5365–5370.
54. Genualdi S, Harner T, Cheng Y, MacLeod M, Hansen KJ, van Egmond R, Shoeib M, Lee S. 2011. Global distribution of linear and cyclic volatile methyl siloxanes in air. *Environ Sci Technol* 45:3349–3354.
55. Yucuis RA, Stanier CO, Hornbuckle KC. 2013. Cyclic siloxanes in air, including identification of high levels in Chicago and distinct diurnal variation. *Chemosphere* 92:905–910.
56. Krogseth IS, Kierkegaard A, McLachlan MS, Breivik K, Hansen KM, Schlabach M. 2013. Occurrence and seasonality of cyclic volatile methyl siloxanes in Arctic air. *Environ Sci Technol* 47:502–509.
57. MacLeod M, Kierkegaard A, Genualdi S, Harner T, Scheringer M. 2012. Junge relationships in measurement data for cyclic siloxanes in air. *Chemosphere* 93:830–834.
58. Finlayson-Pitts BJ, Pitts JN Jr. 2000. *Chemistry of Upper and Lower Atmosphere*. Academic, London, UK.
59. US Food and Drug Administration Center for Drug Evaluation and Research. 1998. Guidance for industry-environmental assessment of human drugs and biologics applications (revision 1). Rockville, MD. [cited 2013 December 11]. Available from: <http://www.fda.gov/downloads/Drugs/GuidanceComplianceRegulatoryInformation/Guidances/ucm070561.pdf>
60. European Agency for the Evaluation of Medicinal Products. 2006. Guideline on the environmental risk assessment of medicinal products for human use. EMEA/CHMP/SWP/4447/00. Committee for Medicinal Products for Human Use, EMEA. [cited 2013 December 11]. Available from: <http://www.emea.eu.int/pdfs/human/swp/444700en.pdf>
61. European Commission. 2003. Technical guidance document on risk assessment in support of Commission Directive 93/67/EEC on risk assessment for new notified substances, Commission Regulation (EC) 967 No. 1488/94 on risk assessment for existing substances. Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market. [cited 2013 December 11]. Available from: http://ihcp.jrc.ec.europa.eu/our_activities/public-health/risk_assessment_of_Biocides/doc/tgd
62. Rapaport RA. 1988. Prediction of consumer product chemical concentrations as a function of publicly owned treatment works, treatment type and riverine dilution. *Environ Toxicol Chem* 7:107–115.
63. Reiss R, Mackay N, Habig C, Griffin J. 2002. An ecological risk assessment for triclosan in lotic systems following discharge from wastewater treatment plants in the United States. *Environ Toxicol Chem* 21:2483–2492.
64. Kaj L, Andersson J, Schlabach M, Cousins AP, Remberger M, Brorström-Lundén E, Cato I. 2005. Results from the national Swedish screening program. Subreport 4: Siloxanes. Swedish Environmental Institute, IVL, Stockholm. [cited 2013 December 11]. Available from: http://www.imm.ki.se/Datavard/PDF/B1643_siloxaner.pdf
65. Schlabach M, Andersen MS, Green N, Schøyen M, Kaj L. 2007. Siloxanes in the environment of the Inner Oslofjord. Report 986/2007. Oslo: Norwegian Pollution Control Authority, Oslo, Norway. [cited 2013 December 11]. Available from: <http://www.nilu.no/Default.aspx?tabid=62&ctl=PublicationDetails&mid=764&publicationid=18508>
66. Sparham C, van Egmond R, Hastie C, O'Connor S, Gore D, Chowdhury N. 2011. Determination of decamethylpentacyclosiloxane in river and estuarine sediments in the UK. *J Chromatogr A* 1218:817–823.
67. Boehmer T, Gerhards R. 2003. Decamethylpentacyclosiloxane (D5)—A compilation of environmental data. Degussa. Sponsor: CES. Goldschmidt, Essen, Germany.
68. Mackay D, Joy M, Paterson S. 1983. A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in lakes. *Chemosphere* 12:981–997.
69. Mackay D, Paterson S, Joy M. 1983. A quantitative water, air, sediment interaction (QWASI) fugacity model for describing the fate of chemicals in rivers. *Chemosphere* 12:1193–1208.
70. Kim J. 2012. Non-regulated study: Fate, distribution and transport of decamethylpentacyclosiloxane (CAS No. 541-02-6) in Lake Ontario and Lake Pepin as predicted by the quantitative water air sediment interaction (QWASI) model. Dow Corning HES Study 11923–101. Dow Corning, Midland MI, USA.
71. Whelan MJ. 2013. Evaluating the fate and behaviour of cyclic volatile methyl siloxanes in two contrasting North American lakes using a multi-media model. *Chemosphere* 91:1566–1576.
72. Kemp ALW. 1971. Organic carbon and nitrogen in the surface sediments of Lake Ontario, Erie and Huron. *J Sediment Petrol* 41:537–548.
73. Evenset A, Christensen GN, Skotvold T, Fjeld E, Schlabach M, Wartena E, Gregor D. 2004. A comparison of organic contaminants in two high arctic lake ecosystems, Bjørnøya (Bear Island), Norway. *Sci Total Environ* 318:125–141.
74. Lennart K, Schlabach M, Andersson J, Cousins AP, Schmidbauer N, Brorström-Lundén E. 2005. Siloxanes in the Nordic environment. TemaNord report 2005:593. Nordic Council of Ministers, Copenhagen, Denmark. [cited 2013 December 11]. Available from: <http://nordic-screening.org/index.php?module=Pagesetter&type=file&func=get&tid=5&fid=reportfile&pid=4>
75. Bakke T, Boitsov S, Brevik EM, Gabrielsen GW, Green N, Helgason LB, Klungsøyr J, Leknes H, Miljeteig C, Måge A, Rolfsnes BE, Savinova T, Schlabach M, Skaare BB, Valdernes S. 2008. Mapping selected organic contaminants in the Barents Sea 2007. SPFO report 1021/2008, TA-2400/2008. Norwegian Pollution Control Authority. [cited 2013 December 11]. Available from: <http://brage.bibsys.no/xmlui/bitstream/handle/11250/173197/MappingBarentsSea2007.pdf?sequence=1>
76. Powell DE, Durham J, Huff DW, Bohmer T, Gerhards R, Koerner M. 2010. Bioaccumulation and trophic transfer of cyclic volatile methylsiloxane (cVMS) materials in the aquatic marine food webs of the inner and outer Oslofjord, Norway. HES Study 11060-108. Document Control Office, Office of Pollution Prevention and Toxics, US Environmental Protection Agency, Washington, DC. [cited 2014 December 12]. Available from: http://www.epa.gov/oppt/tsca8e/pubs/8ehq/2010/feb10/8ehq_0210_17834a.pdf
77. Powell DE, Kozerski GE. 2007. Cyclic methylsiloxane (cVMS) materials in surface sediments and cores for Lake Ontario. Final report, Dow Corning HES study 10724–108. Document Control Number 88100000163. Document Control Office, Office of Pollution Prevention and Toxics, US Environmental Protection Agency, Washington, DC. [cited 2014 December 12]. Available from: http://www.epa.gov/oppt/tsca8e/pubs/8ehq/2010/feb10/8ehq_0210_17834a.pdf
78. Powell DE, Woodburn KB, Drotar KD, Durham J, Huff DW. 2009. Trophic dilution of cyclic volatile methylsiloxane (cVMS) materials in a temperate freshwater lake. Final report, Dow Corning HES study 10771-108. Document Control Number 88100000163. Document Control Office, Office of Pollution Prevention and Toxics, US Environmental Protection Agency, Washington, D.C. [cited 2014 December 12]. Available from: http://www.epa.gov/oppt/tsca8e/pubs/8ehq/2010/feb10/8ehq_0210_17834a.pdf

79. Lu Q, He ZL, Stoffella PJ. 2012. Land application of biosolids in the USA: A review. *Appl Environ Soil Sci* 2012:1–11.
80. Sánchez-Brunete C, Miguel E, Albero B, Tadeo JL. 2010. Determination of cyclic and linear siloxanes in soil samples by ultrasonic-assisted extraction and gas chromatography–mass spectrometry. *J Chromatogr A* 1217:7024–7030.
81. Buser AM, MacLeod M, Scheringer M, Mackay D, Bonnell M, Russell MH, DePinto JV, Hungerbühler K. 2012. Good modeling practice guidelines for applying multimedia models in chemical assessments. *Integr Environ Assess Manag* 8:703–708.
82. SRC Inc. 2011. *PhysProp Database*. Syracuse Research, Syracuse, NY, USA. [cited 2011 January] Available from: <http://www.syrres.com/what-we-do/databaseforms.aspx?id=386> (with input CAS number 541-02-6).
83. Hayes WM, ed. 2014. *Handbook of Chemistry and Physics*. CRC, Boca Raton, FL, USA.
84. Epona Associates. 2005. *IUCLID Dataset for Decamethylcyclopentasiloxane*. Willington, CT, USA.
85. Varaparth S, Frye CL, Hamelink J. 1996. Aqueous solubility of permethylsiloxanes (silicones). *Environ Toxicol Chem* 15:1262–1265.
86. Drott KR. 2005. ¹⁴C-Decamethylcyclopentasiloxane (14C-D5): Bioconcentration in the fathead minnow (*Pimephales promelas*) under flow-through test conditions. Final report to the Silicones Environmental, Health, and Safety Council (SEHSC). Dow Corning, Midland, MI, USA.
87. Xu S. 2009. Temperature dependence of air/water, 1-octanol/air, 1-octanol/water partitioning coefficients of octamethylcyclotetrasiloxane (D4), and decamethylcyclopentasiloxane (D5). Centre Européen des Silicones, Oudergem, Belgium.
88. Jiménez E, Ballesteros B, Martínez E, Albaladejo J. 2005. Tropospheric reaction of OH with selected linear ketones: Kinetic studies between 228 and 405 K. *Environ Sci Technol* 39:814–820.