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Global Distribution of Linear and Cyclic Volatile Methyl Siloxanes in Air

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S *Supporting Information*

ABSTRACT: The global distribution of linear and cyclic volatile methyl silxoanes (VMS) was investigated at 20 sites worldwide, including 5 locations in the Arctic, using sorbent-impregnated polyurethane foam (SIP) disk passive air samplers. Cyclic VMS are currently being considered for regulation because they are high production volume chemicals that are potentially persistent, bioaccumulative, and toxic. Linear and cyclic VMS (including L3, L4, L5, D3, D4, D5, and D6) were analyzed for in air at all urban, background, and Arctic sites. Concentrations of D3 and D4 are significantly correlated, as are D5 and D6, which suggests different sources for these two pairs of compounds. Elevated concentrations of D3 and D4 on the West coast of North America and at high elevation sites suggest these sites are influenced by trans-Pacific transport, while D5 and D6 have elevated concentrations in urban areas, which is most likely due to personal care product use. Measured concentrations of D5 were compared to modeled concentrations generated using both the Danish Eulerian Hemispheric Model (DEHM) and the Berkeley-Trent Global Contaminant Fate Model (BETR Global). The correlation coefficients (r) between the measured and modeled results were 0.73 and 0.58 for the DEHM and BETR models, respectively. Agreement between measurements and models indicate that the sources, transport pathways, and sinks of D5 in the global atmosphere are fairly well understood.

INTRODUCTION

Cyclic and linear volatile methyl siloxanes (VMS) are widely used in personal care products including lotions, cosmetics and deodorants, and in industrial applications as solvents, lubricants, coatings and sealants[1] (Supporting Information Table SI.1). The properties of cyclic VMS (cVMS) exceed the United Nations Environment Programme (UNEP) screening criteria for persistent, bioaccumulative, and toxic substances;[2−5] however, the potential of siloxanes to adversely affect ecosystems and bioaccumulate in biota is controversial. Risk assessments in Canada have concluded that D4 (octamethylcyclotetrasiloxane) and D5 (decamethylcyclopentasiloxane) have the potential to cause ecological harm and are currently entering the environment at a rate that may have current or future damaging effects on the environment and its biological diversity.[3,4] However an assessment by the UK Environment Agency concluded that D5 poses no risk to the air, water, and terrestrial environments, and only some risks to organisms dwelling in freshwater sediments.[6] Some studies report endocrine disrupting effects for D4 and carcinogenic and immunosuppressant effects for D5[7−11] while other studies have observed no toxicity for D4 in marine and freshwater invertebrates and fish.[12] All risk assessments agree that further investigations of environmental and human exposures are needed to evaluate the risks posed by cVMS to humans and the environment. Currently, there are no restrictions or regulations on the use of cVMS in any jurisdiction, and they are classified as high-production volume chemicals by the Organization for Economic Cooperation and Development (OECD).

In 1993 the annual environmental loading of cVMS for the United States was estimated to be 19.71×10^6 kg (excluding site limited intermediates) with more than 90% released to the atmosphere, and the remaining discharged to wastewater.[1] Once released into the atmosphere, the major sink for cVMS is reaction with hydroxyl radicals to produce silanols, which are further removed by wet deposition.[13] Global average half-lives for this reaction have been determined to be approximately 30 days for D3, 15 days for D4, and 10 days for D5, while linear VMS are estimated to have half-lives around 9 days.[13,14] Modeling studies have predicted that these half-lives are sufficient for cVMS to undergo long-range transport to remote regions, including the Arctic.[15]

Until now, very few measurements have been made to characterize the occurrence and fate of cVMS in the atmosphere,

especially in the Arctic. Measurements in remote areas are especially challenging due to the lack of electricity, difficulty in accessing sites, and high sampling costs. A recently developed passive air sampler called the sorbent-impregnated polyurethane foam (SIP) disk sampler is cost-effective, requires no electricity, and has the capacity to measure highly volatile compounds, such as cVMS in remote regions.[16] Here we report the results of a pilot study within the Global Atmospheric Passive Sampling (GAPS) network that used SIP disk samplers to examine the global distribution of cVMS in the atmosphere and to evaluate emission scenarios and results from the two models that have been used previously to predict background concentrations of D5 in the global atmosphere.

■ MATERIALS AND METHODS

SIP Disk Samplers. SIP disk samplers were deployed at 20 sites during period 2 of the 2009 GAPS sampling period (typically April to June) and details on the sampling locations can be found in the Supporting Information (Table SI.3). Each SIP disk was housed inside a precleaned stainless steel chamber. Details on the preparation of SIP disk samplers have been previously reported.[16,17] Briefly, polyurethane foam disks (14 cm diameter × 1.35 cm thick; surface area 365 cm^2, mass 4.40 g, volume 207 cm^3, Tisch Environmental, Cleves, OH) were cleaned using Soxhlet extraction and dipped into a hexane slurry containing finely ground XAD-4 (Supelco, Bellefonte, PA). On average each PUF disk had approximately 435 mg ±68 mg of XAD evenly coated per disk (n = 75).

Analysis. Analysis was performed using an Agilent 6890N gas chromatograph (GC) coupled with an Agilent G2589A selective mass detector (MSD). Splitless injection was used (0.5 μL), along with a DB-5 column, (Agilent 60 m × 0.25 mm i.d. × 0.25 μm film thickness). The temperature program began at 35 °C (hold for 5 min) then increased to 160 at 10 °C/min and 300 at 30 °C/min followed by a 5 min isothermal period. Electronic impact (EI) ionization with selective ion mode (SIM) was used for quantification. Analytical standards for VMSs were purchased from Gelest (Morrisville, PA, USA) and Sigma-Aldrich (Oakville, ON, Canada), and the following isotopically labeled standards were added prior to analysis: octamethylcyclotetrasiloxane (^{13}C D4), decamethylcyclopentasiloxane (^{13}C D5) and dodecamethylcyclohexasiloxane (^{13}C D6) (Moravek Biochemicals, Brea, CA, USA). Fluorene-d_{10} (Cambridge Isotope Laboratories Inc., Andover, MA, USA) was used as internal standard for volume correction.

QA/QC. Method recoveries for the linear and cyclic volatile methyl siloxanes ranged approximately 40−80% for L3, 80−100% for L4 and L5, 20−60% for D3, 70−100% for D4 and D5, and 80−100% for D6. Field blanks were collected at each sampling location, and on average field blanks were ∼4% of the sample concentrations. Further information on MDLs, IDLs, and average field blank concentrations can be found in the Supporting Information (Table SI.2). All siloxane concentrations measured using SIP disks were individually blank corrected for the sampling site location, which assumes the field blank is representative of the LOQ for that site. In two cases (e.g., D3, D4, D5, and D6 at Sable Island, NS Canada and D3 at Sydney Florida) the concentrations measured in the blank were higher than that of the sample. In these cases, these points were excluded from further interpretation.

Sampling Rate Calculation. A previous calibration study was used to assess the uptake rates of VMSs into the SIP disk sampler. Briefly, this study was performed using six low volume air samplers and SIP disk samplers that were deployed and harvested on days 0, 3, 7, 14, 21, 56, and 83. $K_{SIP-AIR}$ values were calculated for each VMS based on their concentration in the low volume sampler and the amounts accumulated on SIP disks at the end of the uptake study when the samplers had reached equilibrium (Table SI.1).

Site-specific sampling rates (R) were calculated from the use of depuration compounds at PUF disks that were codeployed at each site and averaged ∼6.5 m^3/day (Table SI.3). Details on these calculations have been previously reported.[16] The volume of air sampled for each SIP disk sampler was calculated using the site-specific sampling rate and also the $K_{SIP-AIR}$ value for each VMS using the following expression:

$$V_{air} = K_{SIP-A} \times V_{SIP} \times \left(1 - \exp\left(-\left\{(A_{SIP})/(V_{SIP}) \times (k_A/K_{SIP-A})\right\}t\right)\right) \quad (1)$$

where V_{SIP} is the volume of the SIP disk (cm^3), A_{SIP} is the planar surface area of the SIP disk (cm^2); k_A is the air-side mass transfer coefficient (m/day), t is deployment time (days). Values of k_A (derived from R and the surface area of the SIP disk, A_{SIP}) can be found in Table SI.3.

■ MODELS

The Danish Eulerian Hemispheric Model (DEHM) is a versatile atmospheric chemistry-transport model.[18,19] Included in DEHM are modules to describe the two-way exchange processes of POPs between air and the surface media water, soil, vegetation, and snow as well as a comprehensive chemistry scheme with 67 species including particulate matter and full ozone chemistry and thereby OH radicals. The model grid is defined using a polar stereographic projection centered at the North Pole and it can be applied with a variable spatial setup including nesting options. DEHM was previously used to study the atmospheric fate of α-HCH[20,21] and D5.[15] The model setup for the D5 case study covers the majority of the Northern Hemisphere with a horizontal grid resolution of 150 km × 150 km and 29 vertical layers up to a height of approximately 15 km. The input parameters were meteorological data from the numerical weather prediction model MM5v3 with 3-h temporal resolution and physical−chemical properties for D5 selected from the literature.[15] The applied emission estimates were based on a combination of D5 consumption data (mainly antiperspirant usage) and market shares for 40 countries or regions. Emissions from other countries were estimated assuming similar emissions per capita as for the nearest neighbor country. The total emission for each country was redistributed according to gridded population density data of the world. Details about the emission estimates are described by McLachlan et al.[15]

The Berkeley-Trent Global Contaminant Fate Model (BETR Global) has a global domain with a spatial resolution of 15 ° × 15°.[22,23] The model's environmental parameters represent long-term average environmental conditions with monthly temporal resolution. Contaminant fate and transport including diffusive and advective processes are modeled in 7 bulk compartments; two atmospheric layers, vegetation, soil, freshwater, freshwater sediments, and ocean water. BETR Global was applied to describe the fate of D5 by MacLeod et al.[23] Physico−chemical

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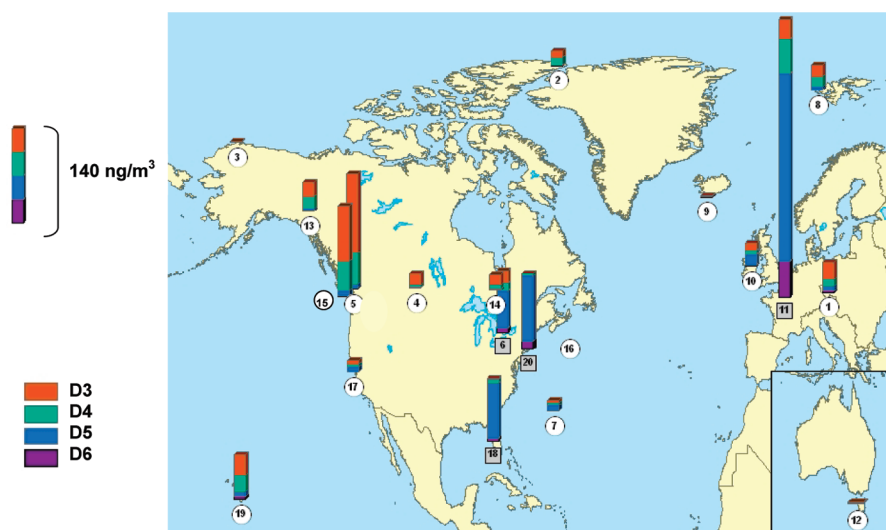
Figure 1. Global concentrations of cyclic volatile methyl siloxanes (ng/m^3). Urban site numbers are enclosed in gray boxes, whereas background site numbers are enclosed in white circles. Due to high cVMS blank concentrations at site 16, no concentrations were reported.
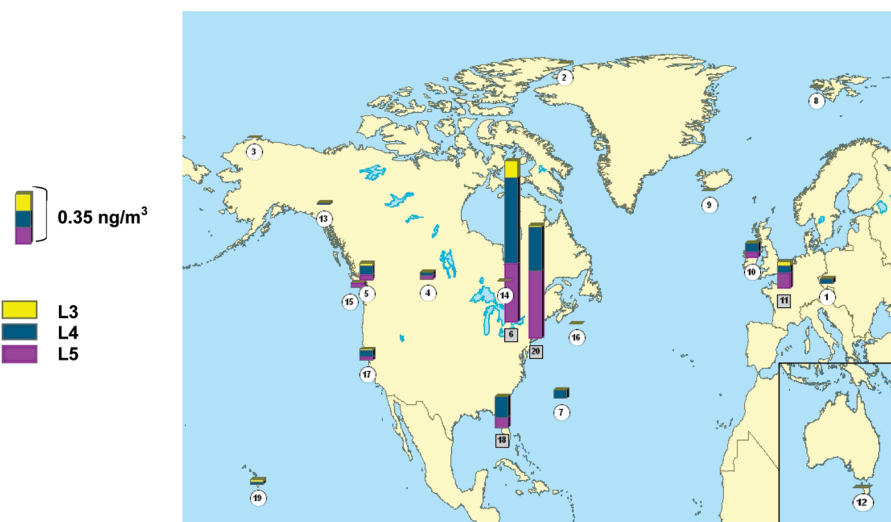

Figure 2. Global concentrations of linear volatile methyl siloxanes (ng/m^3). Urban site numbers are enclosed in gray boxes, whereas background site numbers are enclosed in white circles.

properties for D5 used in the model calculation were taken from Gouin[24] and are nearly identical to those used in the DEHM model. Emissions of D5 were based on the estimate of total emissions from consumer products in the UK risk assessment and were allocated geographically according to the proportion of total night-time light emissions (human-made light that highlights highly populated/industrialized areas) from different parts of the world.[25,26]

■ RESULTS AND DISCUSSION

The global distribution of linear and cyclic volatile methyl siloxanes (VMS), including L3, L4, L5, D3, D4, D5, and D6 at 20 sites worldwide, including locations in the Arctic, remote background sites, and urban areas can be found in Figures 1 and 2. Further details on site concentrations can be found in the Supporting Information (Table SI.4).

Concentrations of linear VMS were up to 3 orders of magnitude lower than those of the cyclic VMS in outdoor air. Higher average concentrations (0.63 ng/m^3 ± 0.49) of the sum of linear VMS were observed at the urban sites compared to the background sites (0.03 ± 0.04) (Figure 2, Table SI.4), with concentrations below the detection limit at all Arctic sites except Little Fox Lake, YK, Canada which had a total linear VMS concentration of 0.013 ng/m^3 (Table SI.4). Low concentrations of linear VMS at background and Arctic sites suggest that linear VMS are not undergoing long-range transport to the Arctic and the high concentrations in populated regions are likely from personal care product use and other indoor sources. Higher concentrations of linear VMS have been associated with indoor dust samples increasing with the number of occupants and electronics in a household.[27] Previous investigations estimate the exposure rate from personal care product use to be 256 mg/day for cyclic VMS and 50 mg/day for linear VMS.[28]
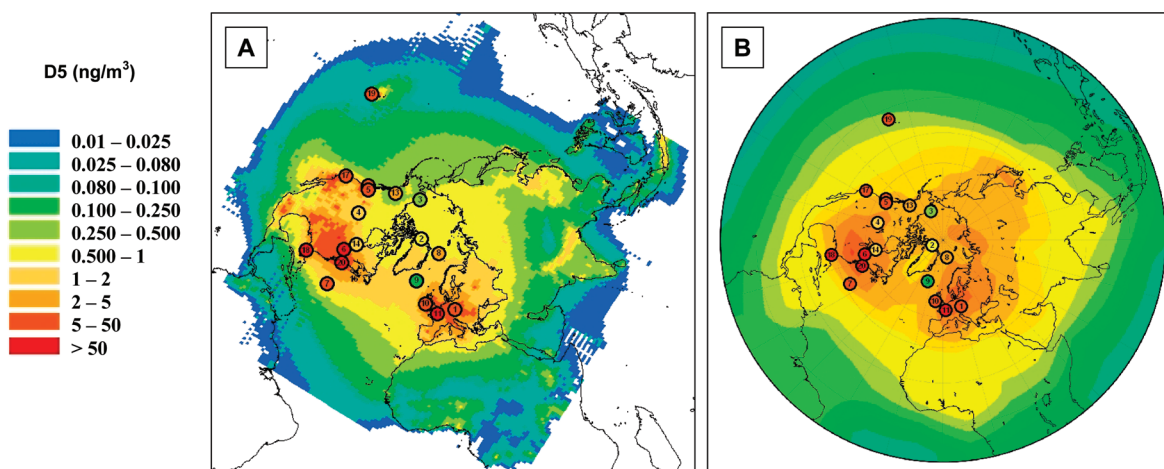
Figure 3. Overlay of measured and modeled results for decamethylcyclopentasiloxane (D5) using the (A) DEHM and (B) BETR models. The circles with numbers correspond to concentrations at GAPS sampling locations.
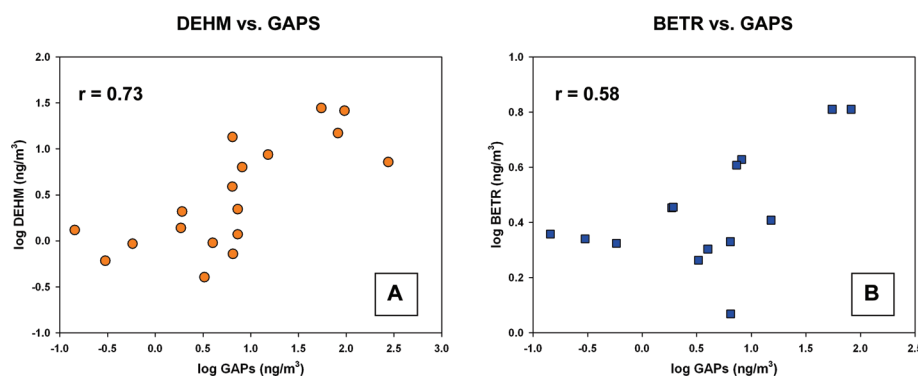

Figure 4. Linear regressions of ln(D5 concentrations) measured at GAPS sites compared with ln(D5 concentrations) determined by the (A) DEHM model and(B) BETR model.

Cyclic VMS (cVMS) concentrations varied among urban, background, and high-elevation sites. The urban sites (sites 6, 11, and 18) and site 20, which is a site highly influenced by industrial activity, are dominated by D5 and D6, and range in concentration from below the detection limit (BDL) to 280 ng/m^3. The background and Arctic sites are dominated by D3 and D4 and range in concentration from BDL to 44.3 ng/m^3. Few studies have measured cVMS in air, however a recent study found concentrations of D5 ranging from 0.3 to 9 ng/m^3 in January to June 2009 at a background site in Sweden.[15] This is in good agreement with the range of 0.1 to 8 ng/m^3 that was measured at background GAPS sites.

The two primary sources of cVMS to the urban environment are their release from industrial processes related to the production of silicone polymers and the use and disposal of personal care products.[3−5] D5 is the most frequently used cVMS in personal care products, followed by D6 and D4.[28,29] Concentrations of D5 and D6 measured in the global atmosphere are strongly correlated (Pearson $r = 0.89$, two-sided p-value = 2.25×10^{-7}), and D5 was the dominant siloxane found at urban sites followed by D6 and D4. This indicates that cVMS measured in urban air in North America and Europe likely reflects their use in personal care products. Indoor dust samples taken in China also had a pattern similar to those of the personal care products[27] and urban air.

Concentrations of D3 and D4 are also highly correlated (Pearson $r = 0.85$, two-sided p-value = 3.16×10^{-6}) However, concentrations of D3 and D4 are not significantly different at urban and background sites (two-sided p-value = 0.53, and 0.70, respectively). The highest concentrations of D3 and D4 were measured on the west coast of North America (Figure 1) and also at high altitude sites (sites 5, 13, 19). Trans-Pacific transport events are more prevalent during the spring and are more conclusively identified at sites located in the free troposphere,[30] which suggests D3 and D4 measured at these sites may have originated from sources in Asia. Air measurements made at urban, industrial, and background sites in 3 cities in China (Guangzhou, Macau, and Nanhai) found concentrations of D3 and D4 up to 20 μg/m^3, and D5 was only found in trace concentrations in a few samples and was mostly not detected.[31] Dominance of D3 and D4 was also observed at an industrial site, a landfill, and a wastewater treatment plant in Guangzhou. This indicates that the sources of siloxanes vary between Asia and North America/Europe, with industrial emissions related to silicone production being more important in Asia. In the future, further studies that include all the GAPS sampling locations will better resolve the spatial distribution and source patterns of siloxanes.

Concentrations of D5 measured in the atmosphere were compared to results from two chemical fate and transport

models, the Danish Eulerian Hemispheric Model (DEHM)[21] and the Berkeley-Trent Global Contaminant Fate Model (BETR Global)[23] (Table SI.4). These models use spatially resolved emission estimates and physicochemical properties of D5 as inputs to calculate concentrations in the atmosphere.

Results from the two models that correspond to the GAPS sampling period (April to June 2009) are compared to measured values in Figure 3. Results from both models are highly correlated with measured values; the correlation coefficients (r) are 0.73 and 0.58 for DEHM and BETR, respectively. The good agreement between measurements and the model results confirm that the main source of D5 to the environment is through the use of personal care products in urban areas, and that the major atmospheric sink is degradation by hydroxyl radicals, and demonstrates that the atmospheric transport pathways of D5 in the environment are fairly well understood. These models can thus be applied to assess the impact of a variety of possible emission and regulatory scenarios on D5 concentrations in the atmosphere.

The measurements reported here represent the first survey of concentrations of cVMS in the global atmosphere. The cVMS are currently under consideration for regulation in Canada and Europe because of concerns about persistence, toxicity, and potential for bioaccumulation in aquatic food chains.[3−6,25] Levels in air at the five monitoring sites in the Arctic are in the nanogram per cubic meter range, i.e., 1−2 orders of magnitude higher than atmospheric concentrations of polychlorinated biphenyls (PCBs) and hexachlorocyclohexanes (HCHs),[32] which are regulated internationally under the Stockholm Convention. However, unlike PCBs and HCHs, the high volatility of cVMS makes it unlikely that they will be deposited from the atmosphere to the surface in remote regions, and their environmental lifetimes suggest that emission regulations would be successful in decreasing their levels in the atmosphere on a time-scale of weeks to months.[24] Determining whether the relatively high exposure of the Arctic atmosphere to cVMS translates into risks to the ecosystem and/or human health will require further assessing the impacts associated with exposure by inhalation.[33−35] In addition, the possible impacts of the silanols formed by degradation of cVMS by hydroxyl radicals, which are expected to be rapidly scavenged from the atmosphere, should be examined.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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■ ACKNOWLEDGMENT

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