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ARTICLE *in* ENVIRONMENTAL SCIENCE & TECHNOLOGY · OCTOBER 2010

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Volatile Siloxanes in the European Arctic: Assessment of Sources and Spatial Distribution

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Received May 12, 2010. Revised manuscript received August 23, 2010. Accepted August 31, 2010.

The purpose of this study was to investigate presence and potential accumulation of cyclic volatile methyl siloxanes (cVMS) in the Arctic environment. Octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) were analyzed in sediment, zooplankton, Atlantic cod (*Gadus morhua*), shorthorn sculpin (*Myxocephalus scorpius*), and bearded seal (*Erignathus barbatus*) collected from the Svalbard archipelago within the European Arctic in July 2009. Highest levels were found for D5 in fish collected from Adventfjorden, with average concentrations of 176 and 531 ng/g lipid in Atlantic cod and shorthorn sculpin, respectively. Decreasing concentration of D5 in sediment collected away from waste water outlet in Adventfjorden indicates that the local settlement of Longyearbyen is a point source to the local aquatic environment. Median biota sediment accumulation factors (BSAFs) calculated for D5 in Adventfjorden were 2.1 and 1.5 for Atlantic cod and shorthorn sculpin, respectively. Biota concentrations of D5 were lower or below detection limits in remote and sparsely populated regions (Kongsfjorden and Liefdefjorden) compared to Adventfjorden. The levels of cVMS were found to be low or below detection limits in bearded seal blubber and indicate a low risk for cVMS accumulation within mammals. Accumulation of cVMS in fish appears to be influenced by local exposure from human settlements within the Arctic.

Introduction

Cyclic volatile methyl siloxanes (cVMS) have come under environmental scrutiny in recent years in regard to their potential persistence and bioaccumulative nature. As polymeric ingredients in the synthesis of silicone products, cVMS are categorized as chemicals of high production and use (*1–3*). Although their dominant use is within the personal care product and cosmetic industry, use can also be seen in other facets of industry (i.e., biomedical applications, defoamers, surface treatment agents (cleaners, lubricants, water repellents), plasticizers, construction materials, and mechanical fluids) (*4, 5*). Strict regulation, particularly in regard to human health, is implemented in production of personal care products (including their ingredients) (*6*). However, it is difficult to assess what environmental implications may arise when other organisms are exposed to such chemicals.

Concern over the environmental fate of cVMS is linked to their physical/chemical properties. Volatilization to the atmosphere is the dominant mode of emission of cVMS to the environment due to their high vapor pressure (*7, 8*). cVMS can persist within the atmosphere with half-lives via hydroxyl radical oxidation ranging between 6.9 and 10.6 days (*9*). Such persistence combined with their inherent volatility creates a high potential for long-range transport, potentially impacting Arctic regions. Approximately 90% of cVMS used in personal care products are estimated to be volatilized to the atmosphere, with the remaining being discharged to wastewater (*10*). Volatilization can still occur during the wastewater treatment process; however, adsorption to sewage sludge (sediment to water partitioning coefficient, $K_d = 2.2-5.0$) is an equally important removal mechanism (*11*), which can significantly hinder volatilization (*12, 13*). Trace levels of cVMS have been detected in wastewater effluent (0.01−1.0 μg/L) (*14–16*), indicating that wastewater treatment plants act as sources of cVMS to the aquatic environment. cVMS are highly hydrophobic, with octanol/water partition coefficients (log K_{ow}) ranging between 6.5 and 9.1 (*1, 2, 17*). Aquatic exposure studies of cVMS to fathead minnows (*Pimephales promelas*) have reported bioconcentration factors (BCF) greater than 7000 over a 6-day exposure (BCF = 12 400 over a 28-day exposure) (*18*). Under the Stockholm Convention on Persistent Organic Pollutants (POPs), atmospheric half-life, BCF, and log K_{ow} values for cVMS meet the screening criteria for bioaccumulative substances (atmospheric half-life > 2 days, BCF > 5000, log $K_{ow} > 5$) (*19*). Occurrence of cVMS has been reported in marine and freshwater biota from Scandinavia (*14*), with concentrations ranging from 5 to 100 ng/g wet weight (ww). However, significantly higher levels have been detected in fish from the inner Oslofjord surrounding the capital of Norway, Oslo (52−3000 ng/g ww) (*16*). These concentrations combined with BCF and K_{ow} values indicate a potential for cVMS accumulation within aquatic biota.

Models calculating global transport based on partition coefficients (octanol/air (log K_{oa}), air/water partition (log K_{aw})) have predicted cVMS to have low Arctic accumulation potential due to their volatility and inability to undergo deposition, even under Arctic climate conditions (*20*). However, no previous investigations of cVMS within Arctic abiotic or biotic matrices have been carried out to evaluate model predictions. In addition to long-range transport, human communities located within the Arctic may act as sources for cVMS to the Arctic environment and need to be assessed.

The present study investigates the occurrence of cVMS within sediment and various biota from the European Arctic to assess environmental fate, accumulation, and sources of cVMS. To the best of our knowledge, this is the first peer-reviewed study to investigate cVMS accumulation within Arctic matrices.

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10.1021/es101617k
Published on Web 09/13/2010

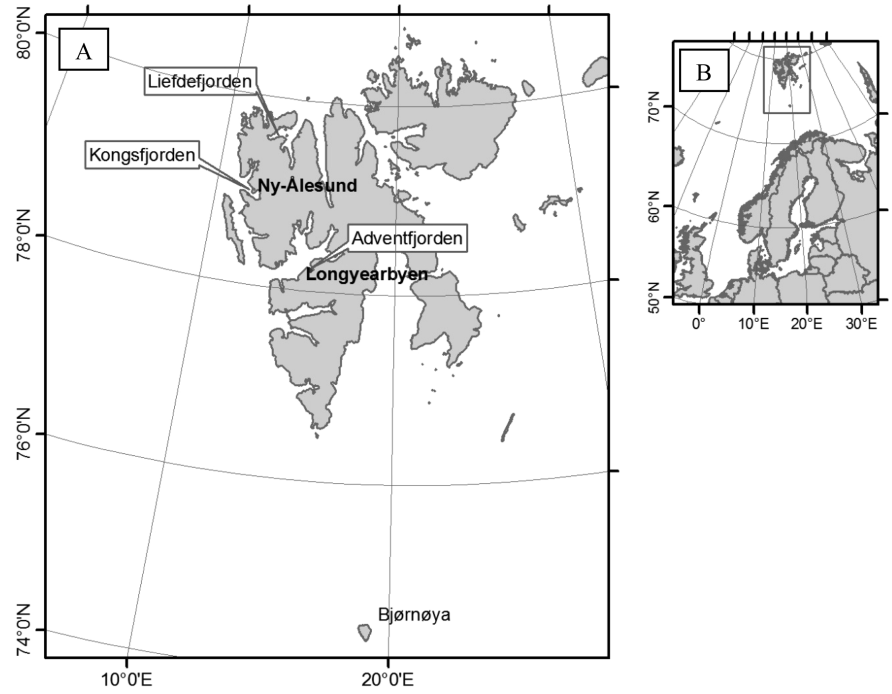

FIGURE 1. Map of Svalbard (A) and location within the European Arctic (B).

Methods and Materials

Sample Collection. Samples were collected during the research expeditions of the RV *Lance* of Adventfjorden, Kongsfjorden, and Liefdefjorden located with the Svalbard archipelago in July 2009 (Figure 1). Samples consisted of marine sediment, mixed zooplankton (predominantly calanoid copepods, krill, and pelagic amphipods), Atlantic cod (*Gadus morhua*), and shorthorn sculpin (*Myxocephalus scorpius*) livers, and bearded seal (*Erignathus barbatus*) blubber.

Sediment. Sediment was collected along a linear transect from the wastewater effluent pipe from the communities Longyearbyen (Adventfjorden, approximately 2000 inhabitants) and Ny Ålesund (Kongsfjorden, 40−150 inhabitants) (Figure 1) using a 0.1 m^2 Van Veen grab. Only sediment from grabs where the sediment/water interface was undisturbed was used for analyses. Using an acetone-rinsed stainless steel spoon, the top 2 cm of surface sediment was taken from each grab and transferred to a clean glass jar and frozen immediately at −20 °C. In Adventfjorden, the first sediment grab was collected in front of the wastewater effluent outlet with the proceeding grabs being collected at 50, 100, 200, and 400 m away from the effluent pipe, respectively. In Kongsfjorden, the first sediment grab was collected 90 m away from the wastewater effluent pipe due to poor sediment quality close to the effluent pipe. The proceeding sediment grabs were collected at 155, 220, 300, and 420 m away from wastewater effluent pipe. Sediment characteristics (i.e., dry weight, total organic carbon), station coordinates, and sample depths are listed in Table S1 of the Supporting Information. Sediment collection at both sites incorporated the use of reference sediment provided by Dow Corning Corporation (Midland, MI) to serve as a field blank. Before collection of sediment began, the jar containing the reference sediment was opened and remained opened during sediment collection. Once sediment collection was complete, approximately 5 g of reference sediment was transferred to a clean glass jar with the remaining reference sediment being sealed immediately.

Biota. Mixed zooplankton was collected from Kongfjorden and Liefdefjorden (sampling coordinates are listed in Table S2 of Supporting Information) using a Method Isaac Kid (MIK) net (mesh size 1000 and 500 μm at the end, 3.14 m^2 opening). The MIK net was vertically dropped and raised to collect zooplankton within the water column using a connected canister. For each collection, water was decanted from the canister and collected zooplankton was transferred to a clean glass jar using an acetone-rinsed stainless steel spoon. Homogenized herring gull liver, previously analyzed for siloxanes, was used as a field blank to assess field contamination of siloxanes from background air via partitioning. Before zooplankton collection began, herring gull liver homogenate was transferred to aluminum foil laid out nearby on a box located on deck of the research vessel. After collection was completed, the herring gull liver homogenate was transferred to a clean glass jar and frozen at −20 °C.

Fish were collected opportunistically from all fjords. Multigill nets were used for fish collections in Adventfjorden and Liefdefjorden, whereas a rod and reel was used in Kongsfjorden. All fish collected were immediately wrapped in aluminum foil, placed in plastic bags, and frozen at −20 °C shortly after collection. Homogenized pork fat, provided by Dow Corning Corporation (Midland, MI), was used as a field blank and was handled using the same procedure as for the zooplankton collection. Fish weight, length, and liver weight were measured and are listed in Tables S3 and S4 of the Supporting Information.

Seals were collected opportunistically by shotgun from Kongsfjorden (sampling coordinates listed in Table S2 of Supporting Information). Blubber samples were dissected from the upper back and placed in glass jars. Dissection was carried out directly on the ice surface to minimize possibilities of contamination. Homogenized pork fat was used as a field blank for 2 out of 5 seal blubber collections and handled in a manner similar to that described above to assess field contamination.

Sample Preparation and Extraction. Dissection, homogenization, and extraction of samples were carried out in a fume hood within a clean room facility (U.S. Federal Standard 209e) at the Norwegian Institute of Air Research (NILU), Kjeller, Norway. Samples were allowed to thaw at room temperature before dissection and/or homogenization. Dissection of fish livers was carried out using hexane-rinsed

TABLE 1. Measured Length, Lipid Content (%), Method Detection Limits (MDL), and cVMS Concentrations (ng/g lipid) for Biota

location	sample	length (cm)	lipid (%)	concentration (ng/g lipid) D4	D5	D6
Adventfjorden						
	Atlantic cod 1[a]	-	26.7	<MDL	149	11
	Atlantic cod 2[a]	-	30.7	<MDL	358	9.1
	Atlantic cod 3[a]	-	29.0	<MDL	45.5	13.8
	Atlantic cod 4[a]	-	45.3	<MDL	132	5.3
	Atlantic cod 5[a]	-	31.8	<MDL	197	11.3
	Sculpin 1	16	16.5	<MDL	243	10.3
	Sculpin 2	15.4	21.1	<MDL	110	12.3
	Sculpin 3	15.4	12.7	<MDL	54.3	<MDL
	Sculpin 4	15.2	16.0	<MDL	2150	30.6
	Sculpin 5	16.4	12.7	<MDL	96.9	<MDL
			MDL(ng/gww)[b]	**10.8**	**6.5**	**2.1**
Kongsfjorden						
	Atlantic cod 6	50	26.0	<MDL	12.7	23.5
	Atlantic cod 7	54	22.6	<MDL	16.8	18.2
	Atlantic cod 8	61	29.6	<MDL	29.1	52.8
	Atlantic cod 9	51	30.0	<MDL	18.7	10.7
	Atlantic cod 10	48	26.7	<MDL	14.2	22.8
			MDL(ng/gww)[b]	**2.2**	**1.5**	**0.7**
Liefdefjorden						
	Sculpin 6	18	19.4	<MDL	11.3	8.8
	Sculpin 7	22	8.7	<MDL	<MDL	<MDL
	Sculpin 8	22	6.3	<MDL	<MDL	<MDL
	Sculpin 9	24	9.2	<MDL	<MDL	9.6
	Sculpin 10	24	6.5	<MDL	<MDL	<MDL
			MDL(ng/gww)[b]	**2.2**	**1.5**	**0.7**

[a] Individual livers were pooled (2−3 individuals) to obtain sufficient mass for extraction purposes. [b] MDL determined using $n = 5$ replicate analysis of spiked cod matrix and is reported on a ng/g wet weight (ww) basis.

stainless steel scalpel blades and tweezers. Fish livers from Adventfjorden were pooled because individual liver material was insufficient for extraction purposes (Table 1). All tissues removed by dissection were placed in glass jars for homogenization. Zooplankton samples were homogenized directly in the glass jars used for collection. All samples were homogenized using a stainless steel Ultra Turrax homogenizer. The steel homogenizer was rinsed between each sample with water (18.2 MΩ·cm at 25 °C, Milli-Q), acetone (pesticide grade), and hexane (pesticide grade). Aliquots of approximately 0.3−0.5 g of each sample were weighed into 2.0-mL Eppendorf Protein LoBind centrifuge tubes. Mass-labeled octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6) (>60% purity, Dow Corning Corporation, Midland, MI) were added as internal standards. Extraction of cVMS was carried out using a slightly modified method previously developed (*21*). Briefly, 1 mL of hexane was added to a centrifuge tube containing the sample matrix and was shaken for 30 min using a vortex mixer. After mixing, samples were centrifuged at 10000 rpm for 10 min and the supernatant (400 μL) was transferred to a GC vial with the addition of tris(trimethylsilyloxy)silane (M3Q) (98% purity, Aldrich, Germany) as a recovery standard. GC vials were crimp capped and stored at −18 °C until ready to be analyzed. Good extraction recoveries (%) were obtained for mass-labeled internal standards within sample extracts (83 ± 7 (^{13}C-D4), 84 ± 7 (^{13}C-D5), and 91 ± 11 (^{13}C-D6)). Homogenized pork fat used for field blanks was extracted using a procedure slightly modified from the one described above due to matrix-associated challenges. Briefly, 50 mg of pork fat was weighed out to reduce lipid content in the final extract. After extraction in hexane (1 mL) for 30 min, extracts were left overnight at −18 °C to freeze out lipids from the extraction solvent. Frozen lipid material and hexane supernatant were separated by centrifugation at 10 000 rpm for 2 min, followed by transfer of the supernatant to GC vial and addition of M3Q recovery standard.

Lipid content was determined by extracting 0.5−2.0 g of sample material with three separate 50-mL portions of 3:1 cyclohexane/acetone solvent mixture. After solvent was removed, lipid content was determined gravimetrically. Total organic carbon (TOC) for sediment samples was determined by coulometric titration (*22*) using a UIC model 5011 CO_2 coulometer.

Instrumental Conditions. The chromatographic analysis was performed on an Agilent 5890N gas chromatograph equipped with a J&W DB-WAX ETR column (30 m × 0.25 mm i.d. × 0.25 μm film) and Agilent 7683B autosampler. The isomer identification was performed by high-resolution mass spectrometry on a Waters Autospec-V Ultima in positive electron ionization mode (EI+, 35 eV). Two masses were monitored for each analyte, corresponding to the $[M - CH_3]+$ fragment. A volume of 1 μL was injected using a split/splitless injector in splitless mode. Injection temperature of 200 °C was used with helium as a carrier gas at 1 mL/min at constant flow. The GC temperature program incorporated an initial temperature of 40 °C with a hold time of 3 min, increased by 25 °C/min to 190 °C, followed by a second temperature ramp of 40 °C/min to 240 °C and held for 4 min. Nonlabeled standards of D4 (Fluka, Switzerland) D5 (Fluka, Switzerland), and D6 (Gelest Inc., Morrisville, PA) were used for quantification. All sample quantification was performed with MassLynx 4.1 software using internal standard calibration.

Quality Control Procedures. All glassware used for sample collection was cleaned, solvent rinsed, and burned at 450 °C before use. Powder-free nitrile gloves were used for all handling of samples. All personnel involved in sample collection and analysis refrained from using personal care products (deodorants, hair/skin products, soaps) to avoid contamination. Extraction solvent was taken from new bottles

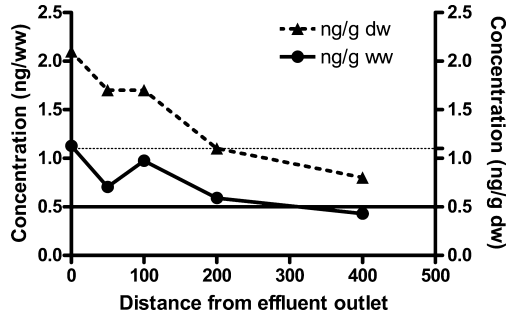

FIGURE 2. Sediment concentration profile for D5 in Adventfjorden reported in ng/g wet weight (ww) and dry weight (dw).

opened within the clean room facility to minimize contamination. Fresh hexane was set aside in small beakers during all dissection and homogenization and was used for the preparation of procedural blanks to assess contamination from the extraction process as well as the clean room air. Additional injections of hexane solvent, with and without internal standards added, were performed repeatedly throughout each analytical run. These hexane injections were included into the calibration curve to correct response values arising from the extraction solvent, carrier gas, or injection system. Due to initial levels of cVMS in all field blank material, analysis of field blanks before and after field exposure was conducted to assess contamination from the field.

To confirm the detection of cVMS within samples found above field blank values, a method detection limit (MDL) was calculated. Reference sediment obtained from Dow Corning Corporation and homogenized liver from Atlantic cod collected in Kongsfjorden were spiked with cVMS solution at 3 ng/g ww (sediment) and 15 ng/g ww (cod liver), respectively. Five aliquots of spiked sediment and cod liver were extracted and analyzed at the beginning of sample analysis for sediment and biota, respectively. Three additional extractions of spiked sediment and/or cod liver were carried out for each additional day of sediment and biota sample extraction. The MDL was calculated based on the analyte response within the spiked sediment and cod liver for the respective matrices investigated:

$$\mathrm{MDL} = t_{n-1} \times \mathrm{SD}_{n,\mathrm{matrix\ QC}} \quad (1)$$

where t represents the statistical t value (one-tailed at 99% confidence), n represents the number of spiked cod liver replicates, and $\mathrm{SD}_{n,\mathrm{matrix\ QC}}$ represents the standard deviation obtained in replicate analysis of spiked reference sediment or cod liver. Samples with cVMS concentration found above the MDL but below the field blank contamination were reported as below detection limits. Comparison of MDL, field blank, and procedural blank values can be found in Tables S5−S7 of the Supporting Information.

The Mann−Whitney nonparametric t test was used to analyze statistical differences in concentration distributions in fish species collected between fjords using GraphPad Prism v. 4 for Windows.

Results and Discussion

Sediment. Sediment analysis from Adventfjorden found D5 to be the only detectable cVMS (Figure 2) with D4 (MDL = 0.9 ng/g ww) and D6 (MDL = 0.6 ng/g ww) found below detection limits. The highest concentration of D5 was found directly in front of the wastewater effluent outlet in Adventfjorden with concentration decreasing at distances further away from the outlet. Concentration of D5 within field blank reference sediment was below the calculated MDL (0.5 ng/g ww), thus observed concentrations were not due to contamination during collection. Our results are in agreement with previous findings within Scandinavia and other Nordic countries, where higher sediment concentrations of cVMS were found near urban areas in Denmark, Sweden, Finland, and Norway compared to remote locations, with D5 dominating the cVMS profile (*14, 16*). Similar spatial patterns have been reported in river water collected from the River Nene in the UK, where D5 concentration decreased with increasing distance from a wastewater treatment plant (*15*). No treatment or filtration to the wastewater effluent occurs in Longyearbyen. Under such circumstances, cVMS have greater potential to be released from wastewater effluent via binding to suspended or dissolved organic matter in the water phase. This indicates that wastewater from the settlement of Longyearbyen in Adventfjorden is a source of D5 to the local aquatic environment.

cVMS concentrations were below detection limits in sediment from Kongsfjorden, which supports previous findings from 2008 (*23*). Levels below the MDL could be attributed to the lower TOC content with Kongsfjorden sediment (0.38−0.95%) compared to Advenfjorden (1.38−2.08%) (Table S1 of Supporting Information) which will influence adsorption of D5 to sediments (*2*). However, our results are most likely attributed to the lower population, hence lower exposure, at Ny-Ålseund in Kongsfjorden (40−150 inhabitants) compared to the settlement of Longyearbyen in Adventfjorden (approximately 2000 inhabitants).

Biota. *Zooplankton and Fish.* cVMS concentrations within zooplankton samples were found below detection limits (MDL = 8.7 ng/g ww (D4), 4.7 ng/g ww (D5), 4.8 ng/g ww (D6)). Fish livers analyzed from Adventfjorden and Kongsfjorden showed detectable levels of both D5 and D6 (Table 1). The highest concentrations of cVMS were found in fish from Adventfjorden, with D5 being the dominant cVMS detected. Concentrations were found as high as 538 and 2150 ng/g lipid weight (lw) in Atlantic cod and shorthorn sculpin, respectively. Field blank contamination for D5 (0.4 ng/g ww) and D6 (1.7 ng/g ww) in Adventfjorden was below the calculated MDLs (6.5 ng/g ww (D5) and 2.1 ng/g ww (D6)). No detection of D4 can be attributed to the high MDL calculated during this study. However, concentrations below the MDL in fish may also be due to greater hydrolysis rates of D4 in water (half-life < 45 days, temperature 5−25 °C, pH 6−9) compared to other cVMS investigated (*1, 2*). Usage of D4 has also been largely replaced by D5 in personal care product formulations (*1, 14*) due to reproductive and aquatic toxicity risks (*24–26*). Lower concentrations of D6 compared to D5 in Adventfjorden are in agreement with cVMS accumulation profiles in biota from Scandinavia and other Nordic countries (*14, 16*). This also correlates well to our findings in sediment collected from Adventfjorden as D5 was the only cVMS detected. Concentrations of D5 within Adventfjorden fish were between 1 and 2 orders of magnitude higher than fish collected from Kongsfjorden ($p < 0.01$). Higher D5 concentrations observed in fish from Adventfjorden are likely due to the larger population inhabiting Longyearbyen; the largest human settlement on Svalbard. Atlantic cod collected in Adventfjorden were probably juvenile (based on the measured fish lengths, 14−22 cm). Juvenile cod are considered to be relatively stationary (*27–29*), indicating that D5 concentrations in cod from Adventfjorden are likely due to exposure/uptake from this area. Similar concentrations found within shorthorn sculpin, also a highly stationary species, support this hypothesis, further implicating the settlement of Longyearbyen as a point source for D5.

Under field conditions, biota sediment accumulation factors (BSAFs) incorporate all environmental sources and processes that influence bioaccumulation and are an appropriate metric for assessing bioaccumulation potential within fish (*30*). BSAFs (kg organic carbon/kg lipid) for D5 in Adventfjorden ranged from 0.6 to 4.9 in Atlantic cod and

TABLE 2. Adventfjorden Biota−Sediment Accumulation Factors for D5

	cod (ng/g lw)	sculpin (ng/g lw)	BSAF cod[a]	BSAF sculpin[a]
mean	176	531	2.4	7.3
min	45.5	54.3	0.6	0.7
max	358	2150	4.9	30
median	149	110	2.1	1.5

[a] BSAF = fish concentration (ng/g lipid)/sediment concentration (ng/g total organic carbon (TOC)). BSAF calculated using average sediment concentration of D5 (72.5 ng/g TOC) in all samples above MDL (0.5 ng/g ww; excluding sample collected at the effluent).

0.7 to 30 in sculpin, with median values of 2.1 and 1.5, respectively (Table 2). BSAFs greater than one indicate how much the chemical has magnified in the organism with respect to the sediment (*31*). Variation in BSAFs between fish can be due to biological differences among different age classes (diet, lipid content, metabolism) within a given fish species (*32*). However, physical/chemical properties and their response to environmental factors (i.e., black carbon affinity) can affect the bioavailability of a chemical and also contribute to BSAF variation (*32*). Only sediment samples in which cVMS were found above the MDL were used in BSAF calculations. Sediment collected in front of the effluent outlet was excluded from BSAF calculations as these grounds were not considered representative habitats for the cod and sculpin, and thus not representative of exposure levels to fish in this area.

Detectable levels of D5 and D6 were also found in fish collected from Kongsfjorden. Concentration of D5 within field blank material (2.0 ng/g ww) was found above the calculated MDL (1.5 ng/g ww). However, fish liver was not exposed to the outdoor conditions as the field blank was, but only in a clean room environment (i.e., dissection). Therefore, procedural blanks and the calculated MDL were considered more appropriate to assess detection limits. D5 concentration within fish liver were also 1 order of magnitude above field blank, procedural blank, and MDL values (Table S6 of Supporting Information), confirming D5 exposure to these fish. D6 concentration in fish from Kongsfjorden was higher compared to fish from Adventfjorden ($p < 0.05$) (Table 1.). The ratio of D5/D6 in Adventfjorden ranged from 3.3 to 39, whereas in Kongsfjoren, ratios were all less than one with the exception of one fish. These results were unexpected as D5 dominated the siloxane profile in Adventfjorden and has been reported to dominate in biota collected from other areas of Scandinavia (*14, 16*). One possible explanation is that the local community of Ny Ålesund has a different emission profile compared Adventfjorden. Rubber-containing products (i.e., sealants, cookware) have been shown to dominate in D6 compared to D5 (*5*) and emission from such sources could contribute to a different cVMS profile. However, this is difficult to confirm since both D5 and D6 concentrations in Kongsfjorden sediment were below the MDL. cVMS profile may also reflect variable emissions from Ny Ålesund with its small population fluctuating throughout the year. Further research is needed to confirm emission patterns of D5 and D6 in Kongsfjorden.

Although the local settlement of Ny Ålesund is considered the most probable source of cVMS, concentrations observed within cod may also be a result of exposure to sources from southern populated regions. After spawning along the Norwegian coast during winter/spring, Atlantic cod migrate northward to the Barents Sea and Svalbard regions during spring/summer following the warmer water of the West Spitzbergen Current. Climate change has created a situation where Arctic regions are becoming more influenced by inputs of Atlantic water, allowing for greater northward shifts in cod migration (*33, 34*). Atlantic cod can now been found in Kongsfjorden, which was not the case in previous years. Cod collected from Kongsfjorden were larger (50−60 cm) than those collected in Adventfjorden (14−22 cm) and are capable of traveling greater distances through migration (*35*). Therefore, cod collected in Kongsfjorden may have migrated into this area during the spring and summer months from more southern locations, which could influence cVMS concentrations observed.

In Liefdefjorden, most sculpins collected had cVMS concentrations below the calculated MDL. From five sculpins collected, detectable levels were found only in two sculpin for D6, and one sculpin for D5 (Table 1.). This may be attributed to the higher lipid content within these sculpins (i.e., high lipid affinity of cVMS ($\log K_{ow} > 5$)); however, results below the MDL are most likely attributed to lower exposure levels in this region. Sculpins are considered quite stationary and overwinter within the fjords on Svalbard (*36*), therefore observed concentrations are most likely due to uptake from this area. However, no human settlements exist in Liefdefjorden, with cruise ship tourism traffic during the summer being the only human influence impacting this fjord. Cruise ships entering this area may be a possible source of cVMS to this area (i.e., ballast water release); however, our results indicate low cVMS exposure to fish and impact from ship traffic to be minimal.

Seals. Blubber dissected from bearded seals collected in Kongsfjorden showed D5 to be above our calculated MDL (1.5 ng/g ww) for three seal blubber samples (1.9 ± 0.2 ng/g lw) but below average field blank levels taken on two separate seal blubber collections (10.3 ± 12.3 ng/g ww). Since seal blubber was exposed to the open environment as the field blank, levels observed were considered below detection limits. Detectable levels of D6 were found within two seal blubber samples at 0.8 and 1.1 ng/g lw with field blank levels below the MDL (0.7 ng/g ww). Fish concentrations of D6 from the same region were a factor of 10 or more higher compared to concentrations detected within seals; indicating greater elimination capacity of cVMS in seals compared to fish. Previous studies in rodents have shown the majority of D4 and D5 systemically absorbed by inhalation is eliminated through exhalation (*37, 38*), although metabolic excretion was found to be of equal importance following oral administration of D4 (*37*). In rodents exposed to a single dose of ^{14}C-D5 via inhalation, 30% of radioactivity measured within fat tissue was attributed to metabolite formation (*38*). However, it is unclear whether metabolite presence within fat tissue was due to formation or uptake. Within the same study, D5 metabolites accounted for more than 50% of the radioactivity measured in liver and lung tissues after a 168-h inhalation exposure, indicating metabolism of D5 (*38*). This indicates that low concentrations (and nondetects) of cVMS observed in seal blubber are likely due to high elimination rates through respiration and metabolism and risk to cVMS bioaccumulation is low.

Acknowledgments

We thank Michel De Poortere and the Centre Européen des Silicones (CES) for funding support of this research. Funding for this project was also provided from the Norwegian Research Council via the International Polar Year (IPY) program; Contaminants in the Polar Regions (COPOL 176073/S30). We also thank Roy Campbell and Jeremy Durham from the Dow Corning Corporation for providing mass-labelled standards for experimental work, sediment characterization, and assistance with field sampling; Pernilla Carlson and Peter Leopold (University Centre in Svalbard (UNIS)); Martine Krerner (Evonik Goldschmidt gmbH), Christian Lydersen,

and Kit Kovacs (Norwegian Polar Institute) for assistance with field sampling.

Supporting Information Available

Tables providing information regarding sediment collection location, depth, and characteristics (dry weight, total organic carbon) (S1), sampling locations of zooplankton and seals (S2), information regarding sampling collection and biological characteristics of fish from Adventfjorden, Kongsfjorden, and Liefdefjorden (S3, S4), and method detection limit (MDL), field blank, and procedural blank values for all samples analyzed (S5−S7). This information is available free of charge via the Internet at http://pubs.acs.org.

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ES101617K