Measuring snow scavenging of two airborne cyclic volatile methylsiloxanes under controlled conditions

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ABSTRACT

The objective of this study was to determine snow scavenging of cVMS and its potential effect on the cVMS concentrations in snowmelt water and surrounding soil. Snow scavenging of two cVMS, octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5), was examined in two steps. First, sorption and desorption of D4 and D5 on snowflakes, including snow sorption coefficients (K_{iA}), were measured against a benchmark compound, cyclopentanone, at different temperatures from 0 to -20 °C. Measurements were made using a custom-made snow chamber and ^{14}C-labeled D4 and D5. In addition, the transfer of snow-bound cVMS to snowmelt water and surrounding soil was studied with ^{14}C-D4 and ^{14}C-D5-spiked snowpack placed both in a closed snow chamber and on top of a layer of frozen soil in an open chemical hood. K_{iA} values measured in both sorption and desorption processes were very small ($<10^{-2}$ m). They increased with decreasing temperature and were higher for the D5 compared to D4. The calculated gas scavenging of D4 and D5 was small because of the small K_{iA} values, while particle scavenging of cVMS is predicted to be negligible due to their low octanol/air partition coefficients (K_{OA}). Most importantly, almost all ^{14}C-D4 and ^{14}C-D5 sorbed by a snowpack was lost during the snow melting process through re-volatilization and hydrolysis and became non-detectable in snowmelt water. In short, the experimental measurements demonstrated that snow scavenging could not be a valid deposition mechanism for these volatile hydrophobic compounds.

1. Introduction

Octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) are cyclic volatile methylsiloxanes (cVMS), a group of emerging hydrophobic contaminants emitted mostly to the air through use of personal care (Jovanovic et al., 2008; Montemayor et al., 2013) and household products (Brooke et al., 2009a, b, c). Due to the combination of their high air/water partition coefficients (K_{AW}), relatively low octanol/air partition coefficients (K_{OA}) (Xu and Kropscott, 2014) and low water solubilities (Varaprath et al., 1996), they are predicted to be transported mostly via the atmosphere. Assessments by multimedia chemical fate models (e.g. the GloboPOP) predict that a fraction of released D4 and D5 may travel a long distance to reach the atmosphere over the Polar Regions, but little will be deposited to remote surface media (Xu and Wania, 2013). As summarized recently (Xu et al., 2019), the average concentrations of cVMS measured in the outdoor air at an arctic location, Svalbard Island (Krogseth et al., 2013), are a few percent of those found in urban atmosphere in Europe (Buser et al., 2013) and North America (Yucuis et al., 2013; Ahrens et al., 2014) even though

these compounds have been continuously released for decades. Concentrations of D4, D5 and D6 are generally below the method detection limits except at locations with known influences by local sources (Warner et al., 2010; AMAP, 2017; Evenset et al., 2009), generally consistent with the prediction of low deposition potential of airborne cVMS.

However, the low deposition potential of cVMS was challenged by Sanchís et al. (2015) who claimed that volatile methylsiloxanes (VMS) including D4 and D5 were found in soil and biota in Antarctica. The validity of the study methodology and the credibility of their conclusions were questioned by others (Warner et al., 2015; Mackay et al., 2015). Some questionable results include the reported cVMS concentrations in coarse soil in Antarctica being similar to or greater than those measured in agricultural soil in Canada and Spain with known histories of receiving cVMS-containing biosolids as fertilizers (Mackay et al., 2015), and reported cVMS concentrations in aquatic biota that are in similar ranges of those found in water bodies directly impacted by local wastewater effluents (McGoldrick et al., 2014; Powell et al., 2018). To rationalize the "unexpected findings," Sanchís et al. (2015) suggested

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that cVMS in the Antarctica must come from long-range atmospheric transport and proposed snow scavenging as a mechanism for airborne cVMS to deposit to the Antarctic remote surface media.

Snow scavenging includes vapor sorption by snowflakes (gas scavenging) and the retention by aerosols captured in snow (particle scavenging). For any specific compound, the significance of snow scavenging for chemical fate and transport depends on the compound's physicochemical properties, such as snow sorption coefficient (K_{iA}) and particulate-air partition coefficients (K_P) (Lei and Wania, 2004), as well as other factors such as seasonal temperature changes and amount of snow accumulation (Herbert et al., 2006). However, the effects of snow on deposition of any airborne contaminants will also depend on how much scavenged contaminant may be transferred to snowmelt and to other surrounding surface media in the snow melting process, which, in turn, will be affected by air/water partition coefficients (K_{AW}) and organic carbon/water distribution coefficients (K_{OC}) of the compounds.

Although snow scavenging has been extensively studied as a deposition mechanism for non-volatile contaminants such as PCBs and PAHs (Grannas et al., 2013), little has been done to study its potential as a deposition mechanism for cVMS except a modeling assessment based on estimated K_{iA} values (Mackay et al., 2015). The objective of this study was to determine the sorption/desorption behaviors of D4 and D5 by snow and their temperature dependence using a novel relative sorption method, and to measure the mass transfer quantities of snow-bound cVMS to snowmelt water and surrounding soil in the snow melting process.

2. Materials and methods

2.1. Materials and equipment

2.1.1. Materials
[14]C-labeled D4 (^{14}C-D4) and D5 (^{14}C-D5) were synthesized in Dow Chemical Company with chemical purities > 95% by GC. The reference compound in snow sorption measurements, cyclopentanone (CP, 99%), ^{13}C-cyclopentanone (97% CP and 99 atom % [13]C), and organic solvents were all obtained from Sigma Aldrich. Snow samples were collected in Michigan, USA multiple times in 2016–2018. None of the snow samples were characterized except for snow density, determined gravimetrically in each experiment.

2.1.2. Snow chamber
A snow chamber (53.9 L) for gas/snow equilibrium was custom-made and is shown in Figure S1. Briefly, the cylindrical chamber wrapped in thermally insulating foam (1 cm thick) was secured to a cart inside a walk-in freezer. The chamber had gas dosing port, gas sampling port and water sampling port. The gas dosing port was connected to a dosing gas bag, while the gas sampling port was connected to a vacuum box outside the freezer. The fittings, including valves, tubing, and sealing O-rings were either glass or Teflon to minimize the wall effects.

2.1.3. Gas bags, sampling syringes and cryogenic cold traps
The Nylon or Aluminum-lined Nylon Tedlar® gas bags used for gas preparation, dosing and waste gas collection, and Hamilton™ gastight syringes (5–100 mL) used for gas and water sampling were all from Sigma Aldrich. When they were used for gas sampling at low temperatures (<0 °C), the plungers were wrapped with Teflon tape to ensure they remained gas tight. Cryogenic cold traps developed by Xu and Kropscott (2012) were used for air sample collection.

2.1.4. LSC, HPLC/RAM and GC/MS analysis
Liquid scintillation counter (LSC) (Packard Tri-Carb 2500 TR LSC) was used to determine the total radioactivity from ^{14}C-D4 and D5. Radiochemical speciation including separation and quantification of both parents and hydrolysis products of the ^{14}C-D4 and D5 was determined using reverse phase High Performance Liquid Chromatography

(HP 1100 system) equipped with a Flow Scintillation Analyzer (PerkinElmer Radiomatic 610 TR) (HPLC/RAM) and a C18 column (Agilent Eclipse XDB-C18, 4.6 × 150 mm, 5 μm) based on a method described by Xu (1999). Analysis of CP in all chloroform extracts from gas and water samples was performed using an Agilent GC/MS (HP 6890 GC/HP 5973 MSD) equipped with a DB-624 capillary column (30.0 m × 320 μm × 1.80 μm) (see Section S3 for details).

2.2. Determination of KiA

K_{iA} of D4 and D5 were determined by a novel relative sorption method using cyclopentanone (CP) as a reference compound. CP was selected because its K_{iA} at −6.8 °C is known (1.55×10^{-3} m from Roth et al., 2004) and because its native concentration in collected snow samples was predicted to be negligible based on its small K_{iA} value and low concentration in outdoor air. The experimental procedure for this novel method together with its theoretical basis is briefly summarized below. Further details are provided in the Supporting Information.

A known amount of (~10 kg) snow was placed in a closed snow chamber in a walk-in freezer overnight to reach temperature equilibrium. A gas mixture was made by evaporating known amounts of ^{14}C-D4 (or ^{14}C-D5) and CP inside a gas dosing bag and was drawn into the headspace of the chamber. The closed snow chamber was kept under the controlled temperature (e.g. −7 °C) in the walk-in freezer for 48 h for gas/solid equilibration. The snowpack inside the chamber was overturned by inverting the snow chamber upside down in the middle of the equilibration time. After two days, three gas samples (100 mL each) were collected through the gas sampling port using gas-tight syringes. The sampled gas was then pushed through a cryogenic cold trap immersed in dry ice/acetone bath following the procedure outlined by Xu and Kropscott (2012) except the condensates in the trap were eluted with 1 mL of ^{13}C-CP (Internal standard for CP analysis)-spiked chloroform, which was demonstrated to quantitatively recover both cVMS and CP in a pre-experiment. After gas sample collection, the chamber was closed and moved to the laboratory at room temperature to melt the snow. The snow melting took approximately two days. The headspace air was again sampled for analysis of cVMS and CP concentrations using the gas sampling port, while the snow melt water was collected via the water sampling port for analysis of cVMS radioactivity and CP concentrations.

The value of K_{iA} for any given cVMS compound was determined using the following equation:

$$K_{iA,cVMS} = K_{iA,CP} \times \{[\text{Rad Snow for cVMS}]/[\text{Rad air for cVMS}]\}/(Q_{CP}/C_{A,CP}) \tag{1}$$

where $K_{iA,cVMS}$ and $K_{iA,CP}$ were snow sorption coefficients for D4 (or D5) and the reference compound CP, respectively; [Rad Snow for cVMS]/ [Rad air for cVMS] was the radioactivity ratio of ^{14}C-D4 (or ^{14}C-D5) in unit volume of snow (i.e., DPM m^{-3}) to that in the same volume of the air in equilibrium, while $Q_{CP}/C_{A,CP}$ were ratio of the measured CP mass in unit volume of snow (ng m^{-3}) to that in the same volume of the air in equilibrium.

2.3. Temperature dependence of K_{iA}

The temperature effects on snow sorption coefficients were determined first at −20 °C, then raised to −13 °C, −7 °C, −2 °C and finally 0 °C sequentially without snow melting. The equilibration time was 48 h at each temperature. The gas phase radioactivity of ^{14}C-D4 (or ^{14}C-D5), and the concentration of CP were measured after each and every equilibration periods. The remaining cVMS and CP on snow solid phase was analyzed after snow melting only after the completion of gas analysis at the final temperature.

The temperature effects on snow sorption coefficients was modeled by the following equation (Herbert et al., 2006):

$$\ln K_{iA} = a + b/T \tag{2}$$

where a and b were temperature-independent constants and T the equilibrium temperature. The constant "b" was determined by plotting the compound's snow/air partition ratio (Q/C_A), the ratio of mass of a compound distributed in unit volume of snow to that in the same volume of air in equilibrium, against T (see Section S1 for the detail):

$$\ln (Q/C_A) = a' + b/T \tag{3}$$

where constant a′ was not the same as "a" in Eq. (2), but constant b was the same as b in Eq. (2). ln K_{iA} at −7 °C determined by Eq. (1) was used to calculate the value of "a" in Eq. (2) after the slope "b" was determined by Eq. (3).

2.4. Transfer of ^{14}C-D4 and ^{14}C-D5 in snowpack to snowmelt water

500 mL of ^{14}C-D4 and ^{14}C-D5 gas was injected into a 50 L air-filled aluminum lined gas bag containing 10 kg of snow and three clean and pre-tared Teflon tubes (30 mL capacity). After equilibration for 5 h, triplicates of snow samples were collected by filling the Teflon sample tubes. The closed Teflon tubes were weighed and the total radioactivity inside each tube was measured after snow melting. A 30 cm layer snow from the bag was then piled on top of a frozen soil layer (10 cm thick) in a glass pan with one side wall removed as shown in Fig. S2. The snow pile/soil in the pan was placed inside a chemical hood (~20 °C) with three sides insulated with aluminum-foil-lined polyurethane foam and dry ice was placed below the frozen soil layer so that the snow melted only from top as might be expected in the field. The snowmelt water was collected in glass pan placed below. The snowmelt water and soil were analyzed for radioactive species after the snow was completely melted.

2.5. Snow scavenging calculations

The details related to the snow scavenging calculations can be found in the supporting information Section S2. Briefly, the unit environment of the snow-covered surfaces was assumed to have a snowpack on top of either an ice/soil mixture or ice beneath the snow cover with negligible cVMS penetration and an air mass with a mixing height of H_A meters. The mass of gas-phase cVMS adsorbed by a given volume of snow above a unit area of leveled ground (e.g., 1 m^2), M_i^G (ng m^{-2}), was calculated by the following equation:

$$M_i^G = SAI \cdot K_{iA} \cdot C_A \tag{4}$$

where SAI was snow area index, or the surface area of snowflakes in a snowpack above a unit area of leveled ground (m^2 m^{-2}). The ratio of gas phase scavenging by snow (W^G) then could be obtained by

$$W^G = (M_i^G/V_i)/C_A \tag{5}$$

where V_i is the volume of snowpack per unit of leveled ground area in m^3 m^{-2}. In addition, W^G was also related to the snow/air partition ratio in the controlled environment,

$$W^G = (Q/C_A)/(V_S/V_A) \tag{6}$$

where V_S/V_A is the snow to headspace volume ratio, e.g. in the snow/air equilibrium chamber.

The scavenging ratio of particulate-bound compound by snow (W^P) could be obtained by

$$W^P = \nu \cdot K_{aeA} \cdot [TSP] \tag{7}$$

where [TSP] was the mass concentration of aerosol (in μg m^{-3}); ν the aerosol scavenging volume ratio; K_{aeA} (m^3 μg^{-1}) was aerosol (ae)/air partition coefficient, and the values for D4 and D5 were calculated from their K_{OA} values (Mackay, 2001):

$$\log K_{aeA} = \log K_{OA} - 11.91 + \log f_{OMae} \tag{8}$$

where f_{OMae} is the fraction of organic matter in aerosol, usually about 0.2.

Total snow scavenging ratio (W^T) was defined as the mass ratio of a contaminant in a volume of snow to that in an equal volume of the surrounding air, thus:

$$W^T = W^G + W^P = SAI \cdot K_{iA}/V_i + \nu \cdot K_{aeA} \cdot [TSP] \tag{9}$$

3. Results and discussion

3.1. Snow/air concentration ratios Q/C_A and their temperature dependence

3.1.1. Q/C_A and the measured W^G

Partitioning of ^{14}C-D4 and -D5 between air and snow phases in the closed snow chamber is shown in Table S6 and Table S9. In the temperature range of 0 to −20 °C, the Q/C_A ratios, i.e. the dimensionless snow-to-air concentration ratios, varied from 2.7 ± 0.00 to 14.9 ± 0.03 (mean ± standard error) for D4, and from 14.4 ± 0.9 to 41.4 ± 4.2 for D5. The snow-to-headspace volume ratios calculated using the total mass of snow and measured snow density were 1.03 for the D4 experiment and 0.782 for the D5 experiment. Based on Eq. (6), the W^G values in the snow chamber calculated directly from these Q/C_A ratios varied from 2.6 ± 0.00 to 14.5 ± 0.03 for D4, and from 18.4 ± 1.2 to 52.9 ± 5.4 for D5 in the temperature range of 0 to −20 °C.

3.1.2. K_{iA} values and their temperature dependence

The Q/C_A ratios of D4, D5 (Tables S6 and S9) and CP (Tables S7 and S10) were used to determine the K_{iA} values and their temperature dependence in three steps. First, the natural logarithms of the Q/C_A ratios for D4 and D5, and the natural logarithms of the normalized Q/C_A ratios for CP, were plotted against the reciprocal of the equilibrium temperatures (Figs. 1 and 2) based on Eq. (3). In the entire temperature range (0 to −20 °C), ln (Q/C_A) for D4 and D5 was linearly related to the reciprocal of the test temperatures. Based on the regression equations, the average ln (Q/C_A) values of D4 and D5 were calculated for a given temperature.

The "normalized ln (Q/C_A)" ratios were plotted for CP in Fig. 2, not the measured "ln (Q/C_A)" values like those for D4 and D5 in Fig. 1. This is because there were two sets of ln (Q/C_A) values for CP: one obtained from the D4/CP experiment and another in D5/CP experiment with two different snow samples. Although the slopes of the ln (Q/C_A)-vs-1/T plots should be independent of the snow samples as demonstrated in Eq. (3), the intercepts depend on the snow properties such as density and specific surface area of the snow. To off-set the effects of individual snow samples, the normalized ln (Q/C_A) values for CP were calculated by subtracting the values of ln (Q/C_A) with those measured at −7 °C (2.02 and 1.70 for D4 and D5 experiments, respectively). As shown in Fig. 2, normalized ln (Q/C_A) ratios of CP were also linearly related to 1/T except near the freezing point temperature. Ice surface is at quasi-liquid state near the freezing temperature (Mitra et al., 1990) and the uncharacterized increase in normalized ln (Q/C_A) ratios for CP at this temperature may be explained by its low air/water partitioning coefficient.

In the second step, the K_{iA} values at −6.8 °C were calculated using these average ln (Q/C_A) values; −6.8 °C was chosen because the value of K_{iA} for CP is known only for this temperature (Roth et al., 2004). Based on the regression equations presented in Figs. 1 and 2, the average ln (Q/C_A) values should be 1.74 and 3.14 for D4 and D5 at temperature −6.8 °C. The average value of ln (Q/C_A) for CP at −6.8 °C was 2.20 for the D4 experiment, and 1.88 for D5 experiment. Based on Eq. 1 and $K_{iA,CP}$ of 1.55×10^{-3} m at −6.8 °C by Roth et al. (2004), the calculated log K_{iA} values were −3.03 and −2.27 for D4 and D5 based on these Q/CA
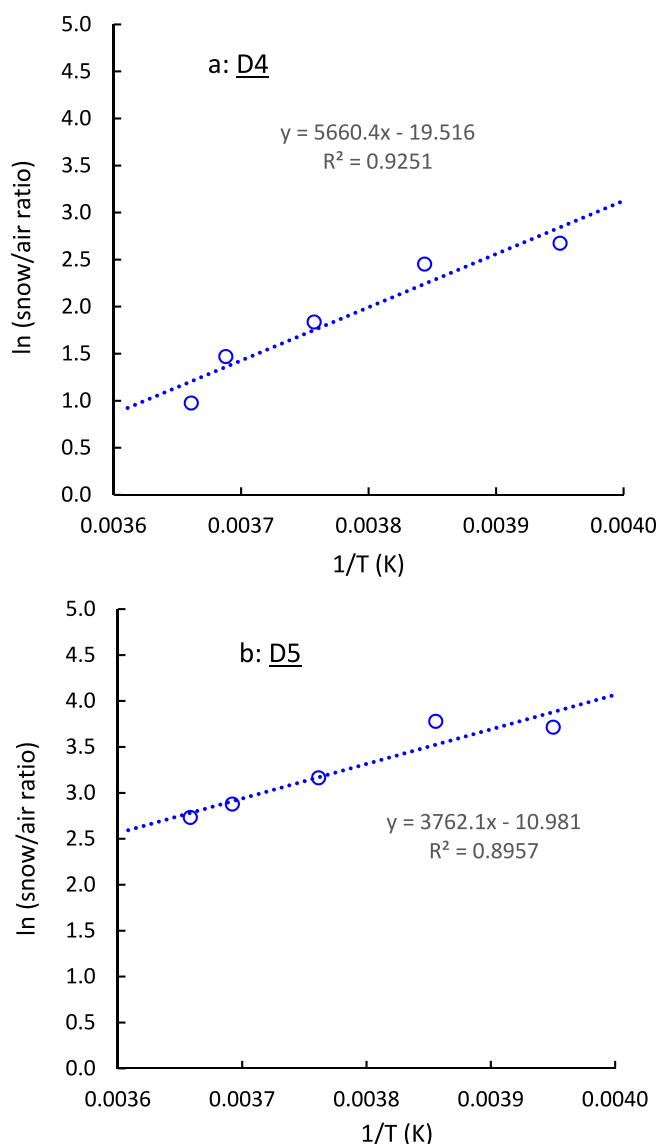
Fig. 1. Relationship between the natural logarithms of measured snow to air concentration ratios (ln (Q/C_A)) of D4 (a) and D5 (b) and their reciprocal of temperature (1/T).

values.

In the third step, the values of "a" in Eq. (2) were determined based on values of ln K_{iA} at −6.8 °C (266.35 K) and the slopes ("b") in Figs. 1 and 2:

$$a = \ln K_{iA} - b/(266.35) \quad (10)$$

The calculated values of "a" are −28.2, −19.4 and −30.2 for D4, D5 and CP, respectively. Using these values of "a" and the slopes shown in the regression equations in Figs. 1 and 2, the K_{iA} values can be obtained for any temperatures in the tested temperature range:

$$\ln K_{iA, D4} = -28.2 + 5660/T \ (-20-0 \ ^\circ C) \quad (11)$$

$$\ln K_{iA, D5} = -19.4 + 3762/T \ (-20-0 \ ^\circ C) \quad (12)$$

$$\ln K_{iA, CP} = -30.2 + 6318/T \ (-20 \sim -2 \ ^\circ C) \quad (13)$$

3.1.3. Reconfirmation of K_{iA} values with gas-bag experiment

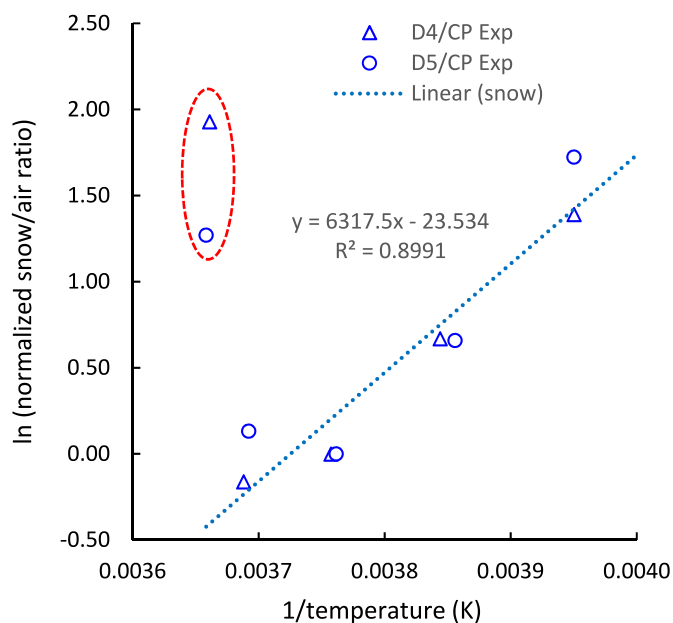K_{iA} is sorption/desorption equilibrium constant in a porous medium

Fig. 2. Relationship between the natural logarithms of measured snow to air concentration ratios of CP and their reciprocal of temperature (1/T) measured in the D4/CP gas mixture and D5/CP gas mixtures. The linear regression was conducted for temperatures from −2 to −20 °C, while the two data points at 0 °C (inside of the red oval) were not included (see discussion). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

where the sorption/desorption of a chemical may have hysteresis. The temperature dependence shown in Figs. 1 and 2 was constructed with data obtained from the sorption at −20 °C and desorption from 0 to −13 °C on the assumption that sorption/desorption hysteresis was insignificant for these compounds in snow. To verify this assumption, multiple runs of D4/CP relative sorption were conducted at −7 °C using 1 L gas bags with a sampling port for gas sample collection after equilibration, and three Teflon tubes inside for snow sampling without opening the bag. Due to small sample sizes, the analytical variations were larger than in the snow chamber experiments and the measured log K_{iA} values varied between −2.68 and −3.49 for D4 at −7 °C for five runs in triplicate (Table 1). However, the average value of log K_{iA} was −3.05 ± 0.06, which is almost identical to the value (−3.01) calculated from the temperature dependence relationship based on mixed sorption and desorption data shown in Tables S6 and S9. This confirmed that sorption/desorption hysteresis was not important for our test system.

Another purpose of this experiment was to check if D4/CP concentration ratios may affect the measured K_{iA} values via sorption competition, by varying the D4/CP concentration ratios in the dosing gas. This resulted in a variation of D4/CP concentration ratios (Table 1) by more than three orders of magnitude both in air (log ratios from 3.87 to 7.04) and in snow (log ratios from 3.77 to 6.79); yet there was no observable relationship between the measured log K_{iA} values and the D4/CP concentration ratios, suggesting no effects from the relative concentrations of D4 and CP.

3.1.4. Comparison with literature values of K_{iA} and gas-phase scavenging ratios

There are no measured K_{iA} or W^G values available in literature for cVMS. However, the K_{iA} values at −6.8 °C could be estimated using a poly-parameter linear free energy relation (pp-LEFR) derived by Roth et al. (2004). Using the measured values of three Abraham solute descriptors (Ahmed et al., 2007), the estimated log K_{iA} values were −2.3 for D4 and -1.3 for D5. The measured log K_{iA} values in this study are smaller than these estimated values by 0.7 – 1 log units.

Table 1
Summary of sorption of D4 and CP by snow at −7 °C at different D4/CP concentration ratios in gas bags.

Exp run	Conc in headspace air			Conc in snow			log K_{iA} for D4
	D4 (DPM m^{-3})	CP (μg m^{-3})	log (D4/CP conc ratio)	D4 (DPM m^{-3})	CP (μg m^{-3})	log (D4/CP conc ratio)	
EXP10-1	9.11 E+09	4.20 E+03	6.34	5.62 E+10	1.86 E+04	6.48	−2.68
	2.20 E+09	2.20 E+02	7.00				−3.34
	5.75 E+09	8.27 E+02	6.84				−3.18
EXP10-4	3.31 E+09	2.15 E+03	6.19	2.59 E+10	2.99 E+04	5.94	−3.07
	4.06 E+09	4.63 E+03	5.94				−2.83
	3.71 E+09	2.78 E+03	6.13				−3.01
EXP10-10	6.07 E+10	7.55 E+03	6.90	6.07 E+10	2.39 E+04	6.41	−3.32
	5.56 E+10	5.02 E+03	7.04	5.56 E+10	2.36 E+04	6.37	−3.49
	5.14 E+10	7.51 E+03	6.84	5.14 E+10	2.34 E+04	6.34	−3.31
EXP11-2	6.77 E+07	7.46 E+03	3.96	8.10 E+08	1.05 E+05	3.89	−2.89
	1.12 E+08	8.47 E+03	4.12	7.14 E+08	1.22 E+05	3.77	−3.17
	6.20 E+07	8.33 E+03	3.87	8.32 E+08	1.13 E+05	3.87	−2.82
EXP11-5	1.34 E+10	2.60 E+03	6.71	5.99 E+10	1.33 E+04	6.65	−2.88
	1.07 E+10	1.65 E+04	6.81	1.18 E+11	1.90 E+04	6.79	−2.84
	1.21 E+10	1.88 E+03	6.81	1.13 E+11	2.20 E+04	6.71	−2.92
Average							−3.05
St Error							0.06

Gas scavenging ratios (W^G) in Table 2 (V_i assumed to be 1 m^3) refer to the mass ratio of a substance in any unit volume of snow relative to that in the same volume of the surrounding air. Because of the small measured K_{iA} values, the W^G values are estimated < 20 for D4 at temperatures $\geq$ −20 °C and SAI $\leq$ 6000 m^2 m^{-2}. The gas scavenging ratios for D5 are between 3.5 and 62 under these same conditions. The W^G values based on the measured Q/C_A ratios (Section 3.1.1) without using sorption relative to CP (2.6 – 14.5 for D4 and 18.4 to 52.9 for D5 at 0 to −20 °C) are slightly smaller than the W^G values at SAI of 6000 m^2 m^{-2}, but larger than those values for SAI of 1000 m^2 m^{-2} in Table 2.

It bears repeating that the W^G values depended not only on the characteristics of the contaminants (i.e. K_{iA}), but also the characteristics of snowpack (i.e., SAI) and environmental temperatures. Although some fresh snow may have high SAI values closer to 6000 m^2 m^{-2} due to their low density and loose structures, the measured SAI values for snowpack

in the fields of Alaska were closer to 500–1500 m^2 m^{-2} with an average about 1000 m^2 m^{-2} (Taillandier et al., 2006) and 3300–3500 m^2 m^{-2} in East Antarctica (Gallet et al., 2010).

3.2. Concentrations of water-insoluble aerosols in snow and cVMS scavenging via atmospheric aerosols captured by snow

In this study, gas-phase ^{14}C-D4 and D5 were introduced to the snow chamber after aerosol particles already formed. All the recovered ^{14}C-D4 and D5 from snowpack discussed in the previous sections were, therefore, assumed to be sorbed on the surface of the snow crystals, not associated with aerosol particulates occluded in snowflakes. However, the particulates recovered in snowmelt (Tables S5 and S8) of two snow samples corresponded to 16.2 ± 2.2 and 14.4 ± 0.9 g m^{-3}. If we assume that the average aerosol concentration (TSP) is 100 μg m^{-3} (Mackay, 2001) in the source region where the snow was collected, the calculated particulate scavenging ratios (ν in Eq. (7)) were 1.44 – 1.62 × 10^5, higher than the typical value (1.0 × 10^5) used in the snow scavenging modeling assessments (Mackay, 2001). The snow scavenging of particulate bound D4 and D5 (W^P in Table 2) was calculated using the higher measured value of ν, i.e. 1.62 × 10^5, and the measured K_{OA} values from Xu and Kropscott (2014) (Eq. (8)). In the entire temperature range, W^P values of D4 are < 0.1 and those of D5 < 1. The contributions from W^P to the total W^T values were negligible for both compounds.

3.3. Snow to water transfer efficiency

Gas phase and particulate scavenging of cVMS by snow are related to the retention of airborne contaminants by snowpack before snow melting. It is well-known that snow-bound contaminants may not be all transferable to snowmelt due to the loss mechanisms during the snow melting process (Herbert et al., 2006). For cVMS, the removal processes should include re-volatilization to air, and the hydrolysis of cVMS in water (Kozerski and Durham, 2006).

3.3.1. Snow melting in close system

Both re-volatilization and hydrolysis mechanisms have been demonstrated in the data from the snow chamber experiments. For example, in the snow chamber with almost equal volumes of snow and headspace at 0 °C just before snow melting, 37% of D4 was found to be sorbed on snow. After snow was completely melted, 92.9% of the D4 was found in the headspace, 0.07% of D4 was recovered as dissolved and 0.02% as bound in the particulates in snowmelt water (Table 3). Silanols as hydrolytic degradation products of D4 in water accounted for 7% total radioactivity loaded into the chamber. In other words, more than 99.8% of D4 that had been sorbed in snow was removed during the snow melting process by the combination of re-volatilization and hydrolysis.

Similarly, 86.3% of snow bound D5 was removed during snow melting in the chamber by the two removal mechanisms including 80.7% by re-volatilization and 5.6% by hydrolysis based on the data shown in Table 3. Of the remainder of D5 in snow meltwater, only 0.28% existed as dissolved D5 (Table 3). The fraction sorbed on particulates

Table 2
The estimated snow scavenging ratios using the measured log K_{iA} and log K_{OA} values, and measured particulate scavenging ratios and TSP for the Arctic regions (5 μg m^{-3}).

cVMS	Temp (°C)	log K_{iA}	W^G at diff. SAI		W^P estimation			W^T at SAI 6000
			1000	6000	log K_{OA}	log K_{aeA}	W^P	
D4	−20	−2.54	2.9	17.5	5.64	−6.96	0.09	17.5
	−6.8	−3.02	1.0	5.8	5.20	−7.41	0.03	5.8
	0	−3.25	0.6	3.4	4.98	−7.62	0.02	3.4
D5	−20	−1.98	10.4	62.3	6.42	−6.19	0.52	62.8
	−6.8	−2.31	4.9	29.7	5.93	−6.68	0.17	29.8
	0	−2.46	3.5	20.8	5.70	−6.91	0.10	20.9

Table 3
Distribution of radiochemical species in the snowmelt/air system in the closed snow chamber after the ^{14}C-D4 and D5 exposed snow samples were completely melted.

Experiment	Speciation		Percentage
D4/CP experiment	Air		92.9%
	Water	Particle bound D4	0.02%
		Dissolved D4	0.07%
		Dissolved silanols	7.0%
D5/CP experiment	Air		82.8%
	Water	Particle bound D5	12.03%
		Dissolved D5	0.28%
		Dissolved silanols	4.94%

increased to about 12%, much higher than that of D4, consistent with the effect from the higher K_{OC} value of D5.

It needs to be pointed out that the aforementioned transfer of snow-bound D4 and D5 was obtained in a closed chamber which greatly limited the re-volatilization loss of cVMS from water. In the natural environment, the amount remaining in snowmelt water would be significantly less.

3.3.2. Snow melting in open system

Snow-to-water and snow-to-soil transfer were determined in simulated snow melting at ~20 °C in a chemical hood. Snow was first exposed with gas-phase ^{14}C-D4 or ^{14}C-D5 in closed aluminum-lined PE gas bags. After 4–5 h of equilibration with frequent mixing, the snow was sampled and the total radioactivity and chemical speciation in snow were determined. The aluminum-lined bag, used to minimize the exposure of the laboratory personnel to ^{14}C-D4 or ^{14}C-D5 that might bleed out of the gas bag, seemed to have increased the hydrolysis rate of the ^{14}C-D4 or ^{14}C-D5 as indicated by the measured high percentage of silanols in the snow before melting (Table S12).

Nevertheless, a layer of snow (~30 cm thick) was then placed on top of frozen Michigan soil (10 cm thick) for snow melting inside a chemical hood. Immediately after the snow was completely melted, no dissolved ^{14}C-D4 or ^{14}C-D5 could be detected in the snowmelt water (detection limits ~ 60 DPM, < 0.0005% of the total radioactivity in snow) (Table S12), although 66.8% D4 and 31.1% D5 were found to be converted to hydrolytic degradation products during melting process (Table S13). Four peaks were found in the HPLC/RAM chromatograms with the retention times corresponding to four hydrolysis products, dimethylsilanediol and its dimer, trimer and tetramer diols, respectively (Fig. S11). The transfer of total radioactivity to soil is 8.7% for D4 and 3.9% for D5 (Table S13). However, the exact identities of the compounds in soil could not be determined due to low radioactivity in soil. The higher transfer for D4 than that of D5 in soil may suggest significant contribution of silanols on the radioactivity. Nevertheless, the non-detection of D4 and D5 in the snowmelt for such high loadings in the original snow samples suggest that snow scavenging contribution to D4 and D5 concentrations in surface media would be negligible.

3.4. Overall discussion

Snow scavenging for compounds dominated by sorption on snow such as cVMS, higher scavenging ratios may be expected for fresh snow at lower temperatures, but re-volatilization is expected to happen as the snow becomes densified (with SAI decreased) in the aged snowpack, or as the air temperature increases in association in snow melting process (Herbert et al., 2006; Taillandier et al., 2006). Based on the W^T values for D4 and D5 at 0 °C, the concentration of D4 and D5 in snow will be < 1 (D4 at SAI of 1000 m^2 m^{-2}) to 21 times (D5 at SAI of 6000 m^2 m^{-2}) of their concentrations in the air. For any given polar location with average 1-m snow accumulation and an average concentration of 1 ng m^{-3} for D4 and 4 ng m^{-3} for D5 in air in winter (Bohlin-Nizzetto and Aas, 2016), the calculated concentrations of D4 and D5 in snowmelt would be in the range of 3–80 pg L^{-1} when all cVMS retained by snow were 100% transferred to snowmelt water. However, the actual exposure of cVMS in surrounding soil and water impacted by snow should be much smaller than these values because the measured snow-to-snowmelt transfer for cVMS was small (up to 12%) due to re-volatilization and hydrolysis. Therefore, the actual D4 and D5 concentrations in snowmelt in the Polar regions as a result of snow scavenging may be expected below 80 × 12% or 10 pg L^{-1}. These estimated concentrations in snowmelt, without any dilution, should be lower than the analytical detection limits by about 3 orders of magnitude.

4. Conclusion

Snow scavenging is an insignificant deposition mechanism for cVMS like D4 and D5 in Polar Regions. The snow scavenging of gas-phase D4 and D5 was minimal for the tested temperature range (from −2 °C to −20 °C), especially near the freezing point, because of their small K_{iA} values, while snow scavenging of particle-bound D4 and D5 was estimated to be negligible due to their small K_{OA} values. Most of the D4 and D5 present in a snowpack at low temperature was found to be lost during the snow melting process even in the closed system and became non-detectable in snowmelt water in the open system mostly due to the combination of re-volatilization (driven by high K_{AW} values) and hydrolysis.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Although the work was funded by the Silicones Europe (CES), a sector group of the European Chemical Industry Council, and both authors are employed by a silicone manufacturer, neither of the authors has a financial interest in the production or sale of the chemicals. Employment is not dependent upon the preparation of the paper nor the conclusions reached in the analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.131291o.

Author contribution

S. Xu was the principle investigator responsible for the development of the concept, original study design, data interpretation and manuscript writing. A. Vogel was the key member of the study team and responsible for design of some experimental procedures and implementing the study plan for data acquisition.

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