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Unexpected Occurrence of Volatile Dimethylsiloxanes in Antarctic Soils, Vegetation, Phytoplankton, and Krill

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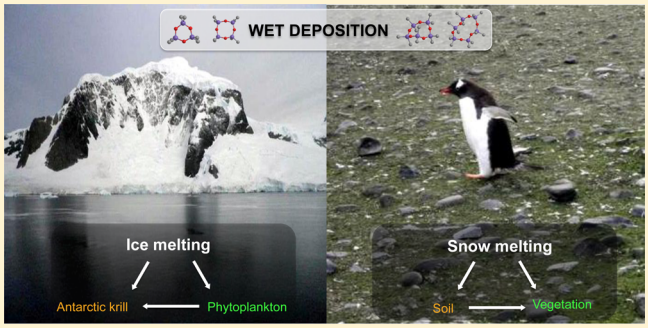
Supporting Information

ABSTRACT: Volatile methyl siloxanes (VMS) are high-production synthetic compounds, ubiquitously found in the environment of source regions. Here, we show for the first time the occurrence of VMS in soils, vegetation, phytoplankton, and krill samples from the Antarctic Peninsula region, which questions previous claims that these compounds are "flyers" and do not significantly reach remote ecosystems. Cyclic VMS are the predominant compounds, with concentrations ranging from the limits of detection to 110 ng/g in soils. Concentrations of cyclic VMS in phytoplankton are negatively correlated with sea surface salinity, indicating a source from ice and snow melting and consistent with snow depositional inputs. After the summer snow melting, VMS accumulate in the Southern Ocean and Antarctic biota. Therefore, once introduced into the marine environment, VMS are eventually trapped by the biological pump and, thus, behave as "single hoppers". Conversely, VMS in soils and vegetation behave as "multiple hoppers" due to their high volatility.



INTRODUCTION

Cyclic and linear volatile methyl siloxanes (cVMS and lVMS, respectively) are synthetic chemicals, the chemical structure of which is characterized by the reiterative alternation between oxygen and silicon atoms with methyl groups. These compounds are used in the manufacture of many industrial and consumer products, such as silicones, in the formulation of many personal care products (PCPs), paints, cleaning products, and coatings, among others.[1,2] Their main emission route into the environment is the direct release into the atmosphere during the manufacturing process and product formulation as well as through the normal use of siloxane-containing consumer products.[3] However, other important sources of emission are landfills disposal, solid waste incineration plants,[4] and wastewater treatment plants.[5−7]

The unusual combination of physical-chemical properties of VMS (cVMS and lVMS) makes difficult the prediction of their environmental fate. High octanol−water partition coefficients (K_{OW}), extremely low solubility in water,[8] and high values of Henry's law constant (H) (Table S1, Supporting Information) are exhibited by VMS. However, due to the combination of their high K_{OW} and H, the octanol−air partition coefficients (K_{OA}) are relatively low. Furthermore, some VMS are resistant to oxidation, reduction, and photodegradation, favoring their persistence in the environment,[9−11] even though little is known about biotic mechanisms of degradation. In the atmosphere, VMS can be degraded, due to reaction with OH radicals.[12] With these physicochemical properties, VMS reservoirs will be associated with the organic carbon pools in terrestrial and aquatic environments, while in the atmosphere they can be ultimately degraded.[13] VMS bioaccumulate in living organisms,[14,15] although the bioaccumulation and biomagnification factors do not follow the same trends as for POPs and are difficult to determine.[15] Due to the high tendency to escape to the atmosphere (low K_{OA} and high H values), cVMS have been identified as flyers,[16,17] favoring their long-range atmospheric transport (LRAT).[9,18−20] Flyers do not reach remote terrestrial and marine ecosystems, because of their low atmospheric depositional fluxes. Nevertheless, VMS and, in particular, cVMS are ubiquitously distributed in the environment close to source regions,[15,21,22] and during the past decade, the occurrence of VMS has been reported in water,[5,23] soils,[24,25] sediments,[26] air,[27−29] and biota.[15,22,30] Several monitoring programmes have been conducted to assess the occurrence of VMS in Canada,[31] Sweden,[32] the United Kingdom,[33,34] and the Nordic countries,[35] confirming the ubiquitous presence of these compounds in the environment, including remote lakes

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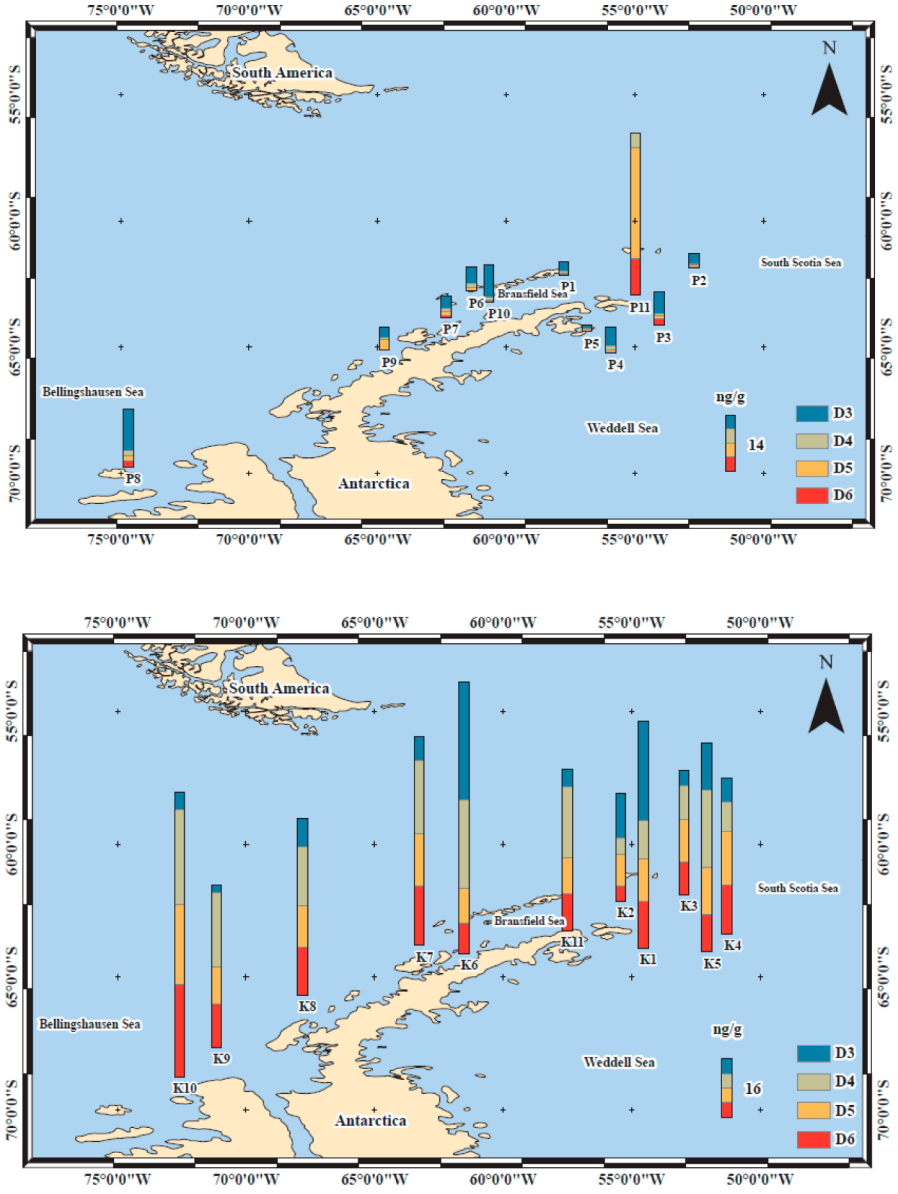

Figure 1. Location and cVMS concentrations of phytoplankton (above) and krill (below) samples.

withoug direct sources.[36] However, most of the information has been focused on the study of a limited number of cVMS. Even though the LRAT potential of VMS and the results reporting their occurrence in remote atmospheres, their potential to affect surface environments (either terrestrial or marine) has not been properly evaluated. It has been assumed that the atmospheric deposition of these compounds is negligible, due to their high volatility, but there have been scarce field studies for assessing this assumption.

VMS have been related to different toxicological effects,[11,37−39] and they have raised concern by regulatory agencies. Recently, octamethylcyclotetrasiloxane (D4) was included by the U.S. EPA in a list of 23 chemicals to be reviewed in 2013 for their further assessment under the Toxic Substance Control Act.[40] The European Commission classifies D4 as an endocrine disruptor, based on evidence that it interferes with human hormone function[41] and that it may impair human fertility.[42] Environment Canada, after the assessment of D4 and decamethylcyclopentasiloxane (D5), concluded that these two compounds are toxic and persistent and have the potential to be bioaccumulated in the aquatic organisms.[43,44] In contrast, dodecamethylcyclohexasiloxane (D6) has a similar structure to D4 and D5, and its occurrence in the environment has been confirmed in the literature.[5,45] These three cVMS (D4, D5, and D6) are those with larger emissions into the environment.[15,34,46]

As committed in *The Protocol on Environmental Protection to the Antarctic Treaty*, the Antarctic environment and the dependent/associated ecosystems are objects of comprehensive protection. The study of the transport, distribution, and bioaccumulation of persistent organic pollutants (POPs) in the Antarctic environment has been recognized as a research priority.[47] However, there is still a gap of knowledge about the distribution of emerging organic contaminants, such as VMS, in the Antarctic Region. Snow scavenging is a very effective process sequestering atmospheric pollutants and could drive the occurrence of VMS in Antarctic soils and biota.

In this work, we present the occurrence of eight VMS, four cVMS (D3, D4, D5, and D6) and four lVMS (octamethyltrisiloxane (MDM or L3), decamethyltetrasiloxane (MD2M or

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L4), dodecamethylpentasiloxane (MD3M or L5), and tetradecamethylhexasiloxane (MD4M or L6)), in terrestrial Antarctica (soils, lichens, mosses and grass), and we assess for the first time the occurrence of VMS in phytoplankton and krill from the Southern Ocean. In addition, we aim at assessing the fate, accumulation, and sources of VMS in remote cold ecosystems.

EXPERIMENTAL SECTION

Sampling. The soil and vegetation samples were mostly collected at Livingston and Deception Islands (Southern Shetlands, Antarctica) during the period January−February 2009, while the phytoplankton and krill samples were collected in the Southern Ocean during the ATOS II sampling cruise, on board RV Hespérides, covering the Drake Passage, Bransfield Strait, and the South Scotia, Bellingshausen, and Weddell Seas (February 2009). Sample locations and ancillary information are given in Figure 1, Figure S1, and Table S2(a−d). All sampling operations were performed using silicone-free materials, in order to avoid any possible contamination source during these operations. The occurrence and cycling of other POPs during the ATOS II campaign have been reported in companion papers.[34,35,48−50]

Surface soil (top cm) and vegetation samples (lichens, grass, mosses) were collected at 11 and 17 sites, respectively, as described elsewhere.[47] Except for a few samples, located proximate to the Juan Carlos I research station, most sample sites were located in isolated areas in Deception and Livingston Islands (including the Byers Peninsula, an Antarctica Specially Protected Area), but some of the soils correspond to sites with Penguin colonies and soils covered with vegetation.

Samples of krill individuals (*Euphausia superba*) were collected at 11 stations. Krill swarms were detected using a Simrad EK60 (Norway) multifrequency echo sounder. Specimens were collected using an Isaacs-Kidd mid water trawl (IKMT) with nets of 1 cm mesh size. Trawls were taken for 20 min at the depth where the swarms were detected (ranging from 20 to 30 m[51]). After retrieval, krill individuals were collected and wrapped in aluminum foil envelopes in glass flasks. Then, samples were frozen and stored at −20 °C until analysis.

Phytoplankton samples were collected at 11 sampling sites using a trawl net (50 μm mesh) in the photic zone from 10 m below the deep chlorophyll maximum depth (average 54 m depth) to the surface. Copepods and *E. superba* individuals were actively separated when present in the sample with a clean Pasteur pipet and tweezers, respectively. The samples were then filtrated with precombusted (4 h at 450 °C) GF/D filter (47 mm diameter, 2.7 μm mesh size, Whatman GE, UK), wrapped in aluminum foil, sealed in polyethylene bags, and frozen at −20 °C until analysis.

Filter blanks consisted of GFD filters, following the same precombustion, storage, and analyses conditions as samples.

Chemicals. cVMS and lVMS standards hexamethylcyclotrisiloxane (D3, 98%), octamethylcyclotetrasiloxane (D4, 98%), decamethylcyclopentasiloxane (D5, 97%), octamethyltrisiloxane (MDM, 98%), decamethyltetrasiloxane (MD2M, 97%), dodecamethylpentasiloxane (MD3M, 97%), and tetrakis(trimethylsilyloxy)silane ($Si(OTMS)_4$, 97%) were purchased from Sigma-Aldrich (Madrid, Spain). Dodecamethylcyclohexasiloxane (D6) and tetradecamethylhexasiloxane (MD4M) of the highest available purity were purchased from Fluorochem (Hadfield, UK). Table S1, Supporting Information, summarizes the physicochemical properties of the selected analytes. Standards *m*-xylene-d_{10} (98%) and naphthalene-d_8 (99%) were purchased from Sigma-Aldrich (Madrid, Spain). *m*-Xylene-d_{10} and naphthalene-d_8 were used as surrogate, while $Si(OTMS)_4$ was used as an internal standard.

Individual stock standard solutions of each compound and internal standards (1000 mg/L) were prepared in hexane from their respective pure standards in amber glass bottles. Secondary individual standard solutions were prepared by successive dilution of the stock standard solutions in hexane to give a concentration of 100 mg/L. A standard mixture solution of 10 mg/L in hexane containing all compounds was prepared. This solution was stored at −20 °C and monthly prepared. Standard mixtures solutions at concentrations ranging from 1 to 5000 μg/L were prepared in hexane by dilution from the mixed stock standard solution.

Hexane Suprasolv (purity ≥ 98%) was purchased from Merck (Darmstadt, Germany). Liquid nitrogen was obtained from Abello Linde (Barcelona, Spain).

Samples Pretreatment and Extraction. Extraction of the samples was performed by an ultrasound-assisted extraction procedure with hexane,[5] with some minor modifications depending on the type of matrix. Very briefly, three/four krill individuals (1.00−1.73 g) were homogenized using an agate mortar, previously rinsed with hexane. Then, the mixture was transferred to a glass vial of 5.0 mL, and it was spiked with the surrogates (15 μL of *m*-xylene-d_{10} and naphthalene-d_8 10 ng/μL) and let reach the equilibrium for 3 h at 4 °C. The extraction was carried out inside the vial with 3.0 mL of hexane for 25 min. After this process, the vials were centrifuged at 1700*g*.

Filters with phytoplankton (∼1 g of phytoplankton) were lyophilized in 15 mL of polyethylene terephthalate (PET) tubes and spiked with surrogates (30 μL of *m*-xylene-d_{10} and naphthalene-d_8 10 ng/μL). After 3 h at 4 °C, 6.0 mL of hexane was added and the extraction was performed using the ultrasonic bath for 25 min. Finally, the tubes were centrifuged 10 min at 1700*g*.

Soil samples were ground with an agate mortar, and 3 g of soil was weighted and placed in 5 mL glass vials. A 15 μL amount of *m*-xylene-d_{10} and naphthalene-d_8 10 ng/μL were used as surrogates. Extraction was carried out with 3.0 mL of hexane in the ultrasonic bath for 25 min.

Vegetation samples were frozen with liquid N_2 in a Teflon vase and ground with a blender. About 3 g of pulverized sample was placed in a 10 mL vial, and they were spiked with 15 μL of *m*-xylene-d_{10} and naphthalene-d_8 10 ng/μL. Samples were let to equilibrate for 3 h at 4 °C and extracted as in the case of soils.

For all matrices, 1.0 mL of extract was collected and transferred to a vial. A 5 μL amount of $Si(OTMS)_4$, 10 ng/μL, was spiked as internal standard prior to their analysis.

Instrumental Analysis. Analysis of VMS was performed using gas chromatography coupled to tandem mass spectrometry (GC-MS/MS) adapting the method described elsewhere[5] using a Trace GC-Ultra coupled to a triple-quadrupole (QqQ) mass spectrometer TSQ Quantum (Thermo Fischer Scientific). The inlet temperature was maintained at 200 °C, and the injection (injection volume 2.0 μL) was carried out in splitless mode. Chromatographic separation was achieved with a DB-5 MS (5% phenyl, 95% methylpolysiloxane) fused silica capillary column (Agilent Technologies, CA, USA), 30 m × 0.25 mm i.d., and 0.25 μm film thickness using helium as carrier gas. The oven temperature was programmed as follows: 50 °C for 1 min, increased to 100 °C at 6.0 °C/min, then linearly increased to 250 °C at 12 °C/min, then linearly increased at 25 °C/min to 310 °C, and finally held at 310 °C for 1 min.

Transfer line and ion source temperatures were set at 250 and 280 °C, respectively. Electron ionization (EI) was set at 70 eV, and solvent delay was maintained for 3.5 min. Acquisition was performed for 3.5−20 min by selected reaction monitoring (SRM) mode (see Table S3, Supporting Information).

Quality Assurance/Quality Control. In order to ensure the quality of the data a series of precautions was included to minimize and assess the contamination during sample manipulation, extraction, and analysis: As in previous works,[5] glass materials were heated at 400 °C overnight. After the heating process, glass materials were covered with aluminum foil during their storage and washed with hexane prior to their use. In addition, all silicon-based materials were avoided during the sampling and analytical process, and during GC-MS/MS analysis, PTFE-folded silicone-based septa were replaced by aluminum foil. In order to assess the potential contamination during the whole analytical procedure, instrumental, procedural, and field blanks were analyzed together with the samples.

To assess the potential matrix interferences and the adsorption of cVMS during the extraction procedure, blank matrixes with a close composition to the real samples were used as procedural blanks and analyzed together with the real samples. One procedural blank was

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Table 1. Summary of the Concentrations of CVMS and lVMS in Antarctic Soils, Vegetation, Phytoplankton, and Krill

		D3 (ng/g_{dw})	D4 (ng/g_{dw})	D5 (ng/g_{dw})	D6 (ng/g_{dw})	MDM (pg/g_{dw})	MD2M (pg/g_{dw})	MD3M (pg/g_{dw})	MD4M (pg/g_{dw})	ΣcVMS (ng/g_{dw})	ΣlVMS (pg/g_{dw})
soil (n = 11)	mean[a]	15.6	14.3	33.0	22.3	269	275	401	219	73.7	959
	median	12.2	13.9	19.0	20.3	260	170	449	219	57.1	1030
	min	<MLOD	<MLOD	<MLOD	<MLOQ	6.93	<MLOD	<MLOD	<MLOQ	0.46	153
	max	25.2	23.9	110	42.0	573	602	606	313	175	1890
vegetation	mean[a]	1.62	6.16	18.5	31.8	<MLOD	<MLOD	<MLOD	<MLOD	56.4	<MLOD
(n = 17)	median	0.81	5.38	10.0	27.9	<MLOD	<MLOD	<MLOD	<MLOD	49.2	<MLOD
	min	<MLOD	<MLOD	<MLOD	0.86	<MLOD	<MLOD	<MLOD	<MLOD	0.86	<MLOD
	max	5.74	21.0	55.4	88.0	<MLOD	<MLOD	<MLOD	<MLOD	150	<MLOD
phytoplankton	mean[a]	4.22	0.93	3.24	1.17	29.1	7.41	11.0	9.90	9.15	57.9
(n = 11)	median	3.00	0.70	0.80	0.20	24.0	4.70	<MLOQ	9.90	5.70	60.0
	min	<MLOD	0.30	0.30	0.10	6.10	<MLOD	<MLOQ	<MLOQ	1.40	6.10
	max	10.0	3.50	27.0	8.80	88.0	17.0	15.0	120	39.0	140
krill (n = 11)	mean[a]	36.4	48.9	36.6	35.2	69.6	<MLOD	<MLOD	<MLOD	157	69.6
	median	17.4	41.1	33.9	35.5	<MLOD	<MLOD	<MLOD	<MLOD	135	<MLOD
	min	4.48	12.3	21.3	11.5	<MLOD	<MLOD	<MLOD	<MLOD	78.4	<MLOD
	max	154	117	63.1	72.7	81.6	<MLOD	<MLOD	<MLOD	357	81.6

[a]Average of concentrations higher than MLOQ.

analyzed each for three real samples. Krill and prawns are both crustaceans belonging to the class Malacostraca with similar contents in lipid and proteins. Therefore, for krill samples, a pool of blank prawns was used as procedural blank. For both phytoplankton and vegetation, a pool of blank tea leaves was employed as procedural blank. Finally, for soils analysis, a prepared blank soil matrix was used. Prior to their extraction and analysis, blank matrices were dried for 48 h at 60 °C in order to facilitate the evaporation of residual cVMS.

The contamination levels of procedural blanks were subtracted from real samples. Several examples of extracted ion chromatograms of real samples vs blank signals are presented in Figure S2, Supporting Information. The typical intensities of blank and samples signals are also represented there. The procedural contamination was maintained constant, with an extremely low standard deviation (Figure S3, Supporting Information). The mean values of the signal of the compounds quantified in the samples were at least the mean plus four times the standard deviation of the contamination. The K_{OA} values of VMS are low, and thus, there is a low potential to contaminate the sample from the ambient air, and the blank levels seem to be of instrumental origin.

To assess the potential contamination during sampling, storage, and shipment, field blank samples were carried out and analyzed together with the real samples. Field blanks consisted of GFF and GFD filters that were transported during the whole sampling campaign. The filters were transported in closed containers like those used as for sampling. During sampling, the blanks were exposed to the ambient air conditions. After this time, the field blanks were stored using the same recipients as the samples and transported back to the laboratory frozen under the same condition used for the samples. The concentrations of cVMS in field blanks did not present significant differences from the levels of contamination of procedural blanks. Consequently, no extra contamination was introduced during sampling (see Figure S3, Supporting Information).

Instrumental quality parameters (instrumental limits of detection (ILOD) and quantification (ILOQ), linearity, and accuracy) were determined with hexane standard solutions. For lVMS, ILOD and ILOQ were defined as the amount of analyte that provides a response in the field blank equal to the mean noise plus 3 and 10 times the standard deviation, respectively, and they were experimentally assessed by consecutive dilution of the same standards. In the case of cVMS, which were present in the blanks at concentrations higher than the theoretical limits of detection and quantification, ILOQ were calculated by analyzing the blank background in 10 instrumental blanks using a statistical approach based on Warner et al. from 2012.[52] ILOQ was defined as $t_{0.95,n} \times s_{ins}$, where $t_{0.95}$ represents the one-tailed t value at 95% confidence, n represents the number of individual procedural blanks, and s_{ins} refers to the standard deviation of the background concentration in the hexane blanks.

Instrumental interday and intraday repeatability were calculated as the relative standard deviation obtained when standards solutions were analyzed at three concentration levels (15, 50, and 100 pg/μL).

In order to validate the analytical method, linearity, method intra-assay precision (n = 10), method interday accuracy (n = 10), and method limits of detection (MLOD) and quantification (MLOQ) were determined using spiking experiments in blank matrices.

For lVMS, MLOD and MLOQ were defined as the amount of analyte that provides a response equal to 3 and 10 times the procedural blank noise. For cVMS, MLODs and MLOQs were determined with blank matrix applying t = 0.95 and n = 10.

Recoveries, method interday, and intraday repeatability were calculated as the relative standard deviation obtained when spiked matrices solutions were analyzed at three concentration levels (16.7, 33.3, and 66.7 ng/g). The method parameters are summarized in Table S4, Supporting Information.

Statistical Analyses. The statistical analysis was performed using SPSS version 22. The normality and log-normality distribution were confirmed by means of the Q–Q normal test. The regression between concentrations or between concentrations and other environmental variables were performed by linear (simple or multiple) least-squares fitting of the data set. The significance of each one of the fitted parameters was confirmed by a t-student test and the significance of the regression line by a F-Snedecor test. Only those regressions with all fitted parameters significantly different than zero are shown.

RESULTS

cVMS were found in almost all samples (soils, vegetation, phytoplankton, and krill), while lVMS were only detected in soil and phytoplankton. Table 1 summarizes the concentrations of each VMS in soils, vegetation, phytoplankton, and krill, which are shown in Figures 1 and 2, and the concentration of each compound for each sample is given in Table S5, Supporting Information.

Occurrence of VMS in Antarctic Soils. Concentrations of cVMS were between 2 and 3 orders of magnitude higher than those of lVMS, consistent with the relative magnitude reported in other studies.[5,35,53] D5 was the predominant compound, ranging from <MLOD to a maximum concentration of 110 ng/g_{dw}, with a mean concentration of 29.9 ng/g_{dw} (Table 1 and

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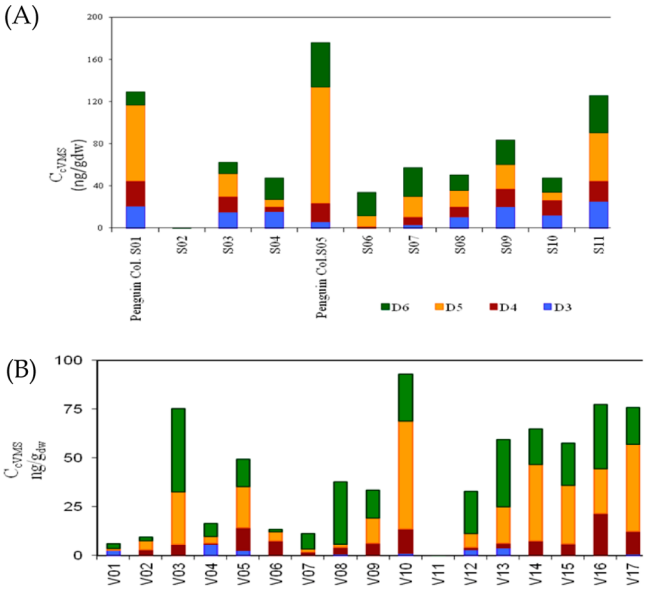

Figure 2. Concentrations of VMS in soils (A) and vegetation (B). Location of sampling sites can be found in Figure S1, Supporting Information. Samples S01 and S05 were located in areas with penguin colonies, whereas samples S08 and S09 were collected within the perimeter of the Juan Carlos I Antarctic station.

Figure 2). lVMS were detected between <MLOD and 0.61 ng/g_{dw}, being MD3M the lVMS with the highest concentration. A significant correlation was found between pairs of compounds with more similar vapor pressures: D3 and D4 (R^2 = 0.58), D4 and D5 (R^2 = 0.49), and D5 and D6 (R^2 = 0.62) (Figure S4, Supporting Information). These results are consistent with a common origin of the different VMS.

In addition, the concentrations of cVMS in soils presented a significant correlation with the concentrations of polychlorinated biphenyls (ΣPCBs) in the same samples as previously reported[47] (Figure S5, Supporting Information, R^2 = 0.77, p < 0.01). Both groups of substances are synthetic hydrophobic compounds with anthropogenic origin, although PCBs are much less volatile than cVMS. However, neither the concentrations of cVMS nor lVMS were significantly correlated with those of other organic pollutants, such as polycyclic aromatic hydrocarbons.

Multiple least-squares linear regressions were tested between cVMS or lVMS concentrations in soils and the measured soil bulk parameters such as the fraction of organic carbon (f_{OC}, g_{OC}/g_{dw}), the soil water content (*SWC*, %), soil redox potential, soil pH, and soil temperature. Soil concentrations of cVMS ($C_{S,cVMS}$) were correlated inversely with SWC (p < 0.05) and directly with f_{OC} (p < 0.05) following eq 1

$$\log S_{S,cVMS} = (0.78 \pm 0.22)\log f_{OC} - (0.10 \pm 0.028)SWC + (5.9 \pm 0.80)$$

$$(R^2 = 0.71,\ p = 0.005) \quad (1)$$

Conversely, lVMS concentrations in soils ($C_{S,lVMS}$) were not significantly correlated with f_{OC} but showed significant inverse correlations with *SWC* (p < 0.05) following eq 2

$$\log C_{S,lVMS} = -(0.046 \pm 0.020)\log SWC + (3.5 \pm 0.30)$$

$$(R^2 = 0.38,\ p = 0.04) \quad (2)$$

Occurrence of cVMS in Antarctic Lichens, Mosses, and Grass. cVMS were also the predominant compounds, in particular, D5 and D6. D6 was present at the highest concentrations in the range between 0.86 and 88.0 ng/g_{dw} (Table 1 and Figure 2). As in soils, the pairs of compounds with similar vapor pressures showed significant correlations among them: D6 and D5 (R^2 = 0.65, p = 0.013), D5 and D4 (R^2 = 0.68, p = 0.008) (Figure S6, Supporting Information). Hair grass samples (*Deschampsia antarctica*) (n = 2) and mosses (n = 7) presented the highest concentrations of cVMS with mean and median concentrations of the sum of cVMS of 55.1 and 44.3 ng/g_{dw}, respectively. Lichen samples (n = 7) presented a mean ΣcVMS concentration of 30.4 ng/g_{dw}. The lowest concentration corresponded to a green algae sample with a concentration of ΣcVMS of 0.86 ng/g_{dw}. Considering these results, the concentration gradient was as follows: hair grass ≈ mosses > lichen > green alga. This gradation was not observed in previous works dealing with legacy POPs in the same region.[47]

Legacy POPs concentrations in Antarctic vegetation ($C_{V,cVMS}$), such as those of PCBs, are correlated with the lipid content (f_L, g_L/g_{dw}).[47] However, $C_{V,cVMS}$ and the f_L were not correlated when all the vegetation samples were considered. Nevertheless, if the moss samples were removed from the statistical analysis, the following correlation was obtained

$$\log C_{V,cVMS} = (3.7 \pm 0.94) + (1.8 \pm 0.67)\cdot\log f_L$$

$$(R^2 = 0.54,\ p < 0.05) \quad (3)$$

Occurrence of cVMS and lVMS in Phytoplankton. Concentrations of cVMS in phytoplankton were in the low ng/g range (Table 1 and Figure 1), between the MLOD and 27 ng/g_{dw}. D3 was the VMS showing the highest concentrations (median concentration of 3.0 ng/g_{dw}), although the highest cVMS concentration was observed for D5 in an outlier sample (27 ng/g_{dw}). The concentrations of lVMS were much lower, ranging between the MLOD and 0.13 ng/g_{dw}, but they were detected in all phytoplankton samples. A significant inverse correlation was found between the total concentration of VMS in phytoplankton and sea surface salinity (SSS) (Figure 3).

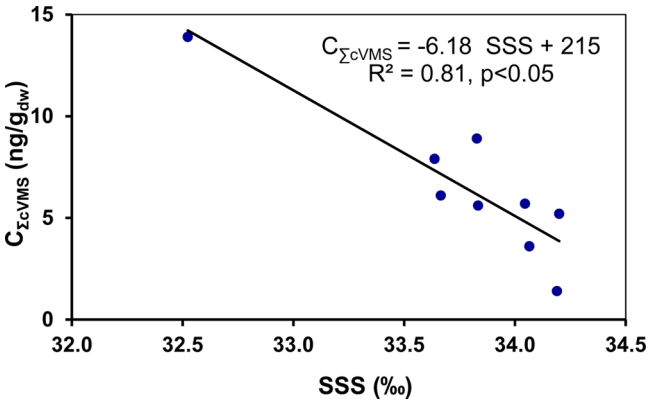

Figure 3. Correlation between concentration of cVMS in phytoplankton and sea surface salinity (SSS).

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Salinity is a surrogate of the inputs of melting waters from seasonal ice and snow melting; thus, VMS concentrations in phytoplankton were higher in those waters which received higher inputs of freshwater from ice/snow melting. In addition, D5 and D6 concentrations in phytoplankton were correlated among them ($R^2 > 0.96$, data not shown), suggesting a similar transport and accumulation/degradation pattern.

Occurrence of cVMS in Antarctic Krill. In krill, cVMS were the predominant compounds and detected in all samples. cVMS were in the range from 4.5 to 154 ng/g_{dw} (Table 1 and Figure 1). Overall, D4 was the compound detected at the highest concentrations (median of concentrations 41.1 ng/g_{dw} and mean value 48.9 ng/g_{dw}), followed by D5, D6, and, finally, D3 (median value 17.4 ng/g_{dw}). A good correlation was found between D5 and D6 ($R^2 = 0.87$, data not shown). MDM was the only lVMS detected in krill and only for four of the samples (Tables 1 and S5-d, Supporting Information).

DISCUSSION

Snow Scavening as a Potential Input of VMS to Antarctica. The measurements of VMS reported here comprise the first data set available for the Antarctic region. Previous works have postulated and modeled the LRAT of VMS (mainly cVMS) in remote areas in the Northern Hemisphere,[54,55] and recently, Krogseth and co-workers[20] have shown that atmospheric concentrations of cVMS in the Arctic region are higher during the winter, presumably due to larger reaction with OH radicals during transport for the summer. Due to the high volatility of VMS, with high H and low K_{OA} values, these chemicals have been classified as "flyers",[17,40] chemicals that once emitted to the atmosphere will hardly be deposited to terrestrial and marine ecosystems.[9] The ubiquitous occurrence of cVMS in Antarctic and Southern Ocean environmental matrices questions the validity of considering VMS as flyers, at least in cold environments. The relatively high concentrations found in Antarctica can only be understood and compared with those reported in other regions once the major transport and partitioning mechanisms of VMS in remote and cold environments are assessed (see discussion below).

The correlation of cVMS concentrations in phytoplankton with SSS (Figure 3), with higher cVMS concentrations at low salinity, suggests that ice/snow melting is a source of cVMS to seawater. Assuming that there is equilibrium between the phytoplankton ($C_{Phyto,cVMS}$) and dissolved phases ($C_{W,cVMS}$), the ratio of concentrations is given by the bioconcentration factor (BCF)

$$BCF = \frac{C_{Phyto,c}VMS}{C_{W,cVMS}} = \frac{f_{Phyto,OC}K_{OW}}{\delta_{Oct}} \quad (4)$$

where $f_{Phyto,OC}$ is the fraction of organic matter in phytoplankton and δ_{Oct} is the density of octanol.

Assuming that the phase exchange energy between organic matter (or octanol) and water is 30 kJ/mol as reported for D4,[56] as it affects the value of K_{OW}, we can estimate the concentration of cVMS in seawater ($C_{W,cVMS}$). The predicted $C_{W,cVMS}$ are obviously also correlated with salinity (not shown); thus, we can roughly predict the cVMS concentration in snow/ice (salinity $\approx$ 0), which would be 14 000 pg/L for cVMS. There is a considerable uncertainty in this estimation (1 order of magnitude or more) due to the fact that the phytoplankton–water partitioning has not been measured yet, and thus, it is not possible to calibrate eq 4. During the austral summer, snow and seasonal ice pack starts thawing, mainly underwater, and VMS may be directly liberated to the seawater. Once VMS enter the water column, they will partition immediately into phytoplankton and other organic matter pools. Then, near the ice-melting areas, with lower salinities, VMS present higher concentrations in phytoplankton. The predicted concentration of 14 000 pg/L for cVMS in ice/snow sets a lower end limit for the real concentrations in snow, since part of cVMS could also be volatilized to the atmosphere or degraded by hydrolysis after being liberated during melting. In addition, there are a number of different ice/snow sources of freshwater to the southern Ocean. While snow deposited during the winter could carry significant amounts of VMS, compacted ice from old glaciers and ice formed from freezing of seawater may have very low VMS content.

Unfortunately, VMS were not measured in the atmosphere during the 2009 campaign. The concentrations of cVMS in the Antarctic atmosphere may be low. For other POPs, such as PCBs and other organochlorine compounds, we know that their measured concentrations in the atmosphere of the Antarctic Peninsula region are comparable but in the lower limit to those reported for the Arctic.[49,57−59] The atmospheric degradation rates due to reaction with OH radicals of PCBs with 2−4 chlorines are similar to those of VMS,[60,61] and thus, both chemical classes will be subject to similar degradation losses during atmospheric transport. Because PCBs are less volatile than VMS (higher H and lower K_{OA} values for VMS), PCBs can be easily deposited mainly through air−water and air−soil exchange,[50,53] processes of presumably lower importance for VMS. Therefore, the potential for long-range atmospheric transport of VMS may be comparable to that of other hydrophobic POPs. Because the degradation rates of VMS increase with the number of Si molecules, D3 will have a higher potential for atmospheric transport than D5 or D6. cVMS concentrations in the Arctic atmosphere are in the low ng/m^3 range,[11] with higher concentrations during the winter. Unfortunately, there are not measures of the snow scavenging ratios for cVMS, but these have been shown to range from 10^4 to 10^7 for other POPs.[62,63] Assuming a concentration of a VMS of 1 ng m^{-3} in the Antarctic atmosphere, this would result in concentrations ranging from 10 to 10 000 ng L^{-1} in snow.

Presumably, VMS are mainly transported to the Antarctic region during the winter when the atmospheric OH^- concentrations are lower. It is thus possible to envisage a scenario where VMS are deposited to the Antarctic and Southern Ocean mainly during winter and VMS are released from snow melting during the austral summer entering seawater and soils. The atmospheric deposition by snow events may be the predominant source of VMS to Antarctic soils and seawaters. Other processes, such as diffusive air−soil and air−water exchanges, are unlikely to result in concentrations at the range of the measurements reported in this work due to the high H and low K_{OA} values for VMS.[56]

Significance of VMS Accumulation in Phytoplankton and Krill. In the ocean, once VMS enter seawater, these will immediately partition to phytoplankton due to their high hydrophobicity, explaining the correlations of their concentrations with salinity. Conversely, cVMS concentrations in krill were not correlated with the salinity of the water mass where they were captured. However, Antarctic krill is a much more complex organism than phytoplankton, with a much longer life cycle, and krill swarms follow migrations. Thus, the high

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mobility through different regions explains the lack of correlation of cVMS burdens in krill with seawater salinity. Krill feeds directly on phytoplankton, and the occurrence of cVMS in krill can be explained by a transfer of VMS through the Southern Ocean food web. The biomagnification and the potential metabolic transformation of VMS are processes that should be considered. Biomagnification factors for D3, D4, D5, and D6 (BMF_{cVMS}) are given as the ratio between the concentrations in krill to the concentration in phytoplankton. There is a significant increase in BMF for the more hydrophobic compounds (lower solubility in water) according to the following expression

$$\log BMF_{cVMS} = 0.51 \log K_{OW} - 1.12$$
$$(R^2 = 0.61, p < 0.01) \quad (5)$$

This trend (see Figure S7, Supporting Information) shows the high biomagnification potential of these chemicals in the Southern Ocean, which may be related to the low temperatures in the studied region (around 273 K) and a presumably low metabolic potential for krill to degrade VMS. Krill is a central node of the Antarctic food web, and thus, VMS have the potential to be transferred to other organisms. Once VMS are bioconcentrated in phytoplankton, they can be transferred to upper levels of the food web (krill), redisolved to seawater once the phytoplankton lipids are remineralized, or transferred to deep waters and sediments. The biological pump mediated by phytoplankton is the key sequestration pathway of hydrophobic organic compounds in the ocean.[20,57] The high VMS levels in phystoplankton suggest that the Southern Ocean is a significant sink for VMS, at least regionally. The biological pump (sinking of organic matter bound chemicals) removes the highly hydrophobic compounds, such as VMS and PCBs, from the surface mixing water column in a few weeks (see Text S1, Supporting Information); thus, concentrations of VMS will be significantly lower in the water column and phytoplankton a few weeks/months after they have entered the surface waters from snow/ice melting, since atmospheric inputs by air−water diffusive exchange alone cannot support the high levels measured here in phytoplankton. In addition, hydrolysis could also be a significant sink for the dissolved VMS, even though due to their high hydrophobicity this is a small fraction of the marine inventory of VMS.

VMS in Antarctic Soils and Vegetation. Snow scavenging driven deposition of VMS can also explain the occurrence of VMS observed in Antarctic soils and vegetation. Indeed, VMS will be released after snow melting entering the soils, lichens, mosses, and grass matrixes. Generally, the higher the organic carbon and lipid content of these matrices, the higher the concentration of cVMS observed (eqs 1−3). The soil organic matter content of Antartic soils is generally low, and its higher values occur when the soil is covered by vegetation and also in the areas where there are penguin colonies.[47] The highest cVMS concentrations in soils were observed in samples S01 and S05, which are located within the perimeter of penguin colonies. Penguins feed on krill, and the large BMF described for krill could explain a high input of cVMS in soils due to penguin faeces. The levels of cVMS for the remaining soil samples are lower, and this occurrence of VMS may be driven by inputs derived from snow melting. Snow melting has been identified as a "fugacity amplification" process.[64] Snow has a large surface area, with a high capacity to retain POPs (high fugacity capacity) that is lost during melting. Indeed, the measured cVMS concentrations in Antarctic soils are higher than those predicted from the few ng/m^3 of cVMS presumably found in the Antarctic atmosphere, which can only be consistent with snow scavenging being the dominant input vector.

After snow melting and following the cVMS sorption to soil organic matter, there will be a volatilization net flux to the atmosphere, due to the high soil to air fugacity gradient. Laboratory experiments have shown that volatilization from soil may be a fast process for cVMS.[50] However, the same experiments have also shown that when soils are saturated with water (high water content), the volatilization is slower. It has been suggested that if a cVMS needs to be transferred to the soil water phase before it is volatilized, since its solubility in water is very low, this transfer may become the limiting step in the kinetics of volatilisation. The relative humidity of air in the Southern Shetlands region is high, and soils have high water content due to snow melting, abundant fog periods, and precipitation events. This scenario is consistent with the negative correlations between VMS concentrations in soils and soil water content (eqs 1 and 2). The larger the water content, the lower the VMS concentration in soil. If the water content is higher, more cVMS can be dissolved in the water phase, thus facilitating a faster volatilization flux of cVMS. In addition, higher water content may facilitate losses by hydrolysis.

Laboratory experiments have shown that less than 40% of D5 is lost in 6 days for a soil saturated with water. It is difficult to extrapolate this rate to the Antarctic environment, but the same mass transfer velocity would require 27 days to reduce the concentration to 10% of the initial value (originated from snow melting). At low temperatures, the diffusivity will be smaller. The diffusivity also depends on the molecular size, and VMS are molecules with similar molecular weight to other POPs, such as PCBs, for which a net volatilization during the austral summer has been described at Livingston Island.[48]

Research stations have been reported to be sources of polycyclic aromatic hydrocarbons and other currently used POPs, to proximate Antarctic environments.[47] Samples S08 and S09 were taken within the perimeter of the Spanish Scientific Station at Livingston Island. Although these concentrations fall in the upper range of the background levels, they are not significantly higher. Therefore, it is unlikely that small human settlements (less than 20 people) represent significant sources to the proximate soils, presumably because these cVMS from these sources may be directly linked to the atmosphere.

The accumulation of cVMS in lichens and grass, with cVMS concentrations correlated with lipids, are also consistent with inputs from snow melting and a release to the atmosphere after this fugacity amplification event, which will be retarded at high lipid content. Mosses present a high content of cVMS, but their concentration was not correlated with the lipid content, most probably due to the higher water content in mosses in comparison with the other types of vegetation included in this study, such as lichens.

Polar Ecosystems as Unique Environments in Terms of Occurrence, Fate, and Transport of VMS. The concentrations of VMS in soils, phytoplankton, and krill reported here are lower than those described in impacted environments but similar to those described in soils and fish from some regions in North America and Europe.[22,25,53,54]These relatively high concentrations of VMS in Antarctica and the Southern Ocean can only be explained if important inputs by snow deposition are considered, which will

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require further research. The environmental fate of VMS in terrestrial and aquatic environments suggests that their occurrence may be very variable temporally, since once introduced in the environment losses by volatilization and the biological pump may reduce their environmental levels (see Text S1, Supporting Information). This could explain the similar concentrations of VMS in phytoplankton and krill when compared in fish from Scandinavian and Canadian Lakes.[22,36] There are, however, other field evidence of diffuse sources of VMS, not originating from direct inputs from local sources. Warner et al. (2014)[65] reports high concentrations of D5 but also D4 and D6 in cod from waters close to Tromso, a region away from relevant local sources. In addition, this region potentially also receives inputs from melting snow (even though not considered by the authors). These authors also report an allometric relationship, with higher concentrations for smaller specimens. The extrapolation of this allometric relationship to other species is uncertain but suggests higher concentrations in small organisms such as krill. Warner et al. (2010)[54] also reported VMS in Arctic fjords, with concentrations of VMS increasing close to the coast, also consistent with inputs of VMS due to snow melting. Of course, this source of VMS will also be of higher magnitude in those locations with higher anthropogenic impact (as suggested in the original publication). Recently, McGoldrick and co-workers[36] described the concentrations of cVMS in remote and impacted Canadian Lakes. The VMS concentrations found in this study in remote lakes suggests that there are unquantified (nonlocal) diffuse sources, which is consistent with snow deposition as a source of VMS to aquatic environments.

cVMS were found as the predominant compounds; however, the results here showed that D3 was the predominant compound in phytoplankton but not in soils, vegetation, and krill. More probably, this result reflects the profile in the Antarctic atmosphere or responds to a higher snow scavenging ratio for D3. The degradation rates of D3 with OH radicals are lower than for D4, D5, and D6;[60] thus, it has a higher potential for LRAT, even though its contribution to total cVMS is lower in source regions. If cVMS enter the ocean due to snow melting, directly from snow, phytoplankton may reflect this higher relative predominance of D3. In krill, the predominance of D3 is lower than in phytoplankton, because there is a selective predominance of the most hydrophobic cVMS (eq 5). In soils and vegetation, the relative contribution of D3 is lower than in phytoplankton, because it will volatilize significantly faster than the other cVMS, due to its higher solubility in the soil water phase and smaller size (higher diffusivity).

lVMS were also detected in some of the samples of phytoplankton but at much lower concentrations, and lVMS were not detected in krill, due to either the low levels or potential metabolic processes. lVMS were also detected in soils, also with concentrations much lower than cVMS. Their concentrations in soil are also inversely correlated with the soil water content, pointing to higher losses at high water content.

The results obtained here highlight the importance of monitoring these compounds and demonstrate that they can be deposited from the atmosphere, entering into the aquatic food chain and terrestrial ecosystems, underpinning the risk of these compounds for the polar environments. In addition, due to the importance of the snow scavenging process, especially in a cold subpolar region such, as the Antarctic Peninsula, we have shown that VMS should not be considered as "flyers". Instead, since they can undergo atmospheric deposition by snow scavenging, they should be considered as single hoppers (for the marine environment) or "multiple hoppers" for the Antarctic terrestrial environment.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Supporting Information contains supplementary figures and tables about samples location, analytical results and lineal least-squares regressions. Further discussion about the role of the biologic pump in the removal of VMS is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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