

## Response to Comments on “Unexpected Occurrence of Volatile Dimethylsiloxanes in Antarctic Soils, Vegetation, Phytoplankton and Krill”

We appreciate the close scrutiny of our work<sup>1</sup> by Mackay, Warner and coauthors (hereafter Mackay-2015 and Warner-2015).<sup>2,3</sup> The consideration of blanks when analyzing persistent organic pollutants (POPs) in remote samples is always an important issue. We performed instrumental blanks, field blanks, and procedural blanks, with no significant different levels of volatile dimethylsiloxanes (VMS) among them. The quantification limits are based on these blanks (Table S4).<sup>1</sup> The use of procedural blanks with real matrixes containing organic matter and lipids allowed controlling sample contamination during handling and analysis in the laboratory. Mackay-2015 and Warner-2015 raise concern on potential contamination from air to sample organic matter during sampling. Samples were transported and stored at  $-20\text{ }^{\circ}\text{C}$  and were airtight sealed. The sealing of the soil and vegetation samples was performed in situ at the sampling sites. Krill samples were sealed on the ship deck (outdoors). Only phytoplankton samples were in contact with the ship wet lab air during the filtration process (few minutes), but the levels in these samples are among the lowest we determined. In order that our reported levels had originated from contamination from ambient air during sampling, the concentrations in the atmosphere would need to be very high, with extremely fast uptake kinetics, which are not feasible. The samples processed were duplicate samples from those used in earlier studies.<sup>4,5</sup>

Figure 3 shows the correlation of  $\sum\text{VMS}$  concentrations in phytoplankton against sea surface salinity (SSS),<sup>1</sup> if the sample with the lowest salinity is removed, we obtain  $C_{\sum\text{VMS}} = -7.48\text{ SSS} + 259$  ( $r^2 = 0.51$ ,  $p = 0.047$ ). As noted by Mackay-2015, there was a mistake on the SSS values appearing in Table S2c.<sup>1</sup> The correct salinities for samples P2–P11 appeared as assigned to samples P1–10. We have no SSS measure for sample P1. The correct SSS values can be corroborated by comparing the ancillary data of samples FA1, FA4, FA6, FA7, FA8, FA12, FA13, FA19, FA23, FA24, FA26 (duplicate samples of samples P1–P11) that appear in a companion work.<sup>5</sup>

Mackay-2015 defines the biomagnification factors (BMFs) as the ratio of dry weight concentrations in Krill and phytoplankton. However, the fugacity amplification by biomagnification is better described when concentrations are normalized by lipids or organic matter. We normalized the cVMS concentrations in Krill by the measured lipid content, and the phytoplankton concentrations by organic matter ( $\approx$ dry weight). As stated in the methods section, all samples were collected during the ATOS-II campaign in 2009. There were only four pairs of Krill and phytoplankton samples that could be paired in terms of time and region of sampling, which were those used to derive eq 5 and Figure S7. The values of the octanol–water partition constant ( $K_{\text{OW}}$ ) were temperature corrected using an enthalpy of phase change of  $-30\text{ kJ mol}^{-1}$ .

Warner-2015 raises concern on the high relative abundance of D4 in phytoplankton samples, but the atmospheric pattern of

VMS in the remote atmosphere is dominated by D3 and D4, with field concentrations under-predicted by models.<sup>6</sup> The only available measurement of atmospheric concentrations for the Southern Ocean is of  $0.45$  and  $1.2\text{ ng m}^{-3}$  for D3 and D4, respectively.<sup>6</sup>

Mackay-2015 estimates the snow scavenging ratios ( $W_s$ ) from the sorption coefficients for snow–air partitioning ( $K_{\text{SA}}$ ,  $\text{m}^3\text{ m}^{-2}$ ), and the Snow Area Index (SAI  $\text{m}^2\text{ m}^{-2}$ ). Naphthalene has a similar vapor pressure than cVMS and a  $K_{\text{SA}}$  of  $1.05 \times 10^{-3}\text{ m}^3\text{ m}^{-2}$ .<sup>7</sup> Applying Mackay-2015’s estimation method a value of  $W_s$  of  $1.05$  is obtained for Naphthalene, 5 orders of magnitude lower than field measurements ( $4.6 \times 10^5$ ).<sup>8</sup> If instead of SAI we use a reported snow surface area of  $0.37\text{ m}^2\text{ g}^{-1}$ ,<sup>9</sup> and assume a snow density of  $0.3\text{ kg L}^{-1}$ , we obtain  $W_s$  values of  $89$ ,  $62\,000$ , and  $120$  for L3, D6, and naphthalene, respectively. This  $W_s$  for Naphthalene is still 3 orders of magnitude lower than the field measures, suggesting that  $W_s$  for VMS could be significantly higher than these estimates.

Mackay-2015 assumes that the organic carbon–water partition coefficients ( $K_{\text{OC}}$ ) derived from temperate soils and river sediments<sup>10</sup> have applicability to Antarctic soils. Soils at Livingston Island are poorly developed, consisting of fragmented rocks, pyroclastic and volcanic ashes, lichen and animal residues, agglomerates, and penguin feces.<sup>11</sup> The highest soil VMS concentrations were measured at penguin colonies,<sup>1</sup> consistent with the known role of birds, and penguins in particular, amplifying POP concentrations in polar coastal environments.<sup>4,12,13</sup> The VMS fugacity (expressed as concentrations) from soil penguin feces, estimated from the lipid–water partition constant and the dimensionless Henry’s Law constant ( $H'$ ),<sup>10,14</sup> result in concentrations in the range  $40$ – $170\text{ }\mu\text{g m}^{-3}$ , 3 orders of magnitude lower than Mackay-2015’s estimates. This discrepancy is due to the low organic carbon–air partition constant used by Mackay-2015, 3 orders of magnitude lower than the octanol–air partition constant, and their apparent assumption of  $298\text{ K}$ .

VMS fugacity amplification is common in high latitude and polar regions. For example, D5 concentrations in Arctic sculpin have been reported to be as high as  $2150\text{ ng gL}^{-1}$ ,<sup>15</sup> which imply a fugacity of  $88\text{ }\mu\text{g m}^{-3}$ , nearly  $10^5$  times higher than in Arctic air.<sup>16</sup> We agree with Warner-2015 that wastewater is a source of VMS to the Arctic fjords, but despite the VMS dilution from wastewater to marine waters, this fugacity is more than 10 times higher than the atmospheric D5 concentrations in a wastewater treatment plant.<sup>17</sup> The concentration of D5 in zooplankton from Lake Mjosa (Norway) is of  $320$ – $1660\text{ ng gL}^{-1}$ ,<sup>18</sup> with an associated fugacity of  $30$ – $150\text{ }\mu\text{g m}^{-3}$ . From work done with other POPs, it is known that there is an equilibrium partitioning between the dissolved phase and zooplankton lipids.<sup>19</sup> Even though VMS in Lake Mjosa waters

Published: May 22, 2015

strive to reach equilibrium with the atmosphere, their fugacity is  $10^4$ – $10^5$  times higher than gas phase concentrations in Scandinavia.<sup>20</sup> For comparative purposes, D5 in Antarctic phytoplankton, assuming a lipid content of 10%, has a median fugacity of  $0.2 \mu\text{g m}^{-3}$ , 100–700 times lower than that of D5 in Lake Mjosa's zooplankton.

We have been the first to identify snow deposition as a mechanism driving the fugacity amplification of VMS in surface ecosystems. In the Antarctic Peninsula, there are snow deposition events all year round, with up to several meters of seasonal snowpack accumulation during the fall, winter and spring. The potential fugacity amplification by snow; the ratio of the fugacity in melted snow ( $f_{MS}$ ) and fugacity in ambient air ( $f_A$ ), is given by,

$$\frac{f_{MS}}{f_A} \approx W_S H' \quad (1)$$

VMS have  $H'$  values between 10 and 200 at 273 K,<sup>10</sup> assuming a  $W_S$  of  $10^5$ , we obtain a fugacity amplification of  $10^6$ – $10^7$  for cVMS. Snow deposition has been identified as an important input of polychlorinated biphenyls (PCBs) and other POPs to the polar environment, and leading to fugacity amplification,<sup>21,22</sup> but fugacity amplification due to snow deposition for PCBs is  $10^4$  to  $10^5$  times smaller, due to lower  $H'$  values, than that of VMS. Future work should focus on the field determination of VMS concentrations in snow, depositional fluxes, and their  $W_S$  values.

Therefore, in response of Mackay-2015 and Warner-2015, we have shown that the occurrence of VMS in the Antarctic Peninsula region is consistent with the common snow depositional events, snow cover, and expected VMS cycling in this region.

Josep Sanchís<sup>†</sup>

Ana Cabrerizo<sup>†,§</sup>

Cristóbal Galbán-Malagón<sup>†,||</sup>

Damià Barceló<sup>†,‡</sup>

Marinella Farré<sup>\*,†</sup>

Jordi Dachs<sup>†</sup>

<sup>†</sup>Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034, Barcelona, Catalonia, Spain

<sup>‡</sup>Catalan Institute for Water Research (ICRA), H2O Building, Scientific and Technological Park of the University of Girona, Emili Grahit 101, 17003 Girona, Catalonia, Spain

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: mfuqam@cid.csic.es.

### Present Addresses

<sup>§</sup>Institute for Environment and Sustainability, European Commission, Via Enrico Fermi 2749, 21027 Ispra, Italy.

<sup>||</sup>Centre for Sustainability Research, Faculty of Ecology and Natural Resources, Universidad Andrés Bello, Chile.

### Notes

The authors declare no competing financial interest.

## REFERENCES

(1) Sanchís, J.; Cabrerizo, A.; Galbán-Malagón, C.; Barceló, D.; Farré, M.; Dachs, J. Unexpected occurrence of volatile dimethylsiloxanes in Antarctic soils, vegetation, phytoplankton, and krill. *Environ. Sci. Technol.* **2015**, *49*, 4415–4424.

(2) Mackay, D.; Gobas, F.; Solomon, K.; Macleod, M.; McLachlan, M.; Powell, D. E.; Xu, S. Comment on "Unexpected occurrence of volatile dimethylsiloxanes in Antarctic soils, vegetation, phytoplankton, and krill. *Environ. Sci. Technol.* **2015**, DOI: 10.1021/acs.est5b01612.

(3) Warner, N. A.; Krogseth, I. S.; Whelan, M. J. Comment on "Unexpected occurrence of volatile dimethylsiloxanes in Antarctic soils, vegetation, phytoplankton, and krill. *Environ. Sci. Technol.* **2015**, DOI: 10.1021/acs.est5b01936.

(4) Cabrerizo, A.; Dachs, J.; Barceló, D.; Jones, K. C. Influence of organic matter content and human activities on the occurrence of organic pollutants in Antarctic soils, lichens, grass, and mosses. *Environ. Sci. Technol.* **2012**, *46*, 1396–1405.

(5) Galbán-Malagón, C. J.; Del Vento, S.; Berrojalbiz, N.; Ojeda, M.-J.; Dachs, J. Polychlorinated biphenyls, hexachlorocyclohexanes and hexachlorobenzene in seawater and phytoplankton from the Southern Ocean (Weddell, South Scotia, and Bellingshausen Seas). *Environ. Sci. Technol.* **2013**, *47*, 5578–5587.

(6) Genualdi, S.; Harner, T.; Cheng, Y.; MacLeod, M.; Hansen, K. M.; van Egmond, R.; Shoeib, M.; Lee, S. C. Global distribution of linear and cyclic volatile methyl siloxanes in air. *Environ. Sci. Technol.* **2011**, *45*, 3349–3354.

(7) Roth, C. M.; Goss, K.-U.; Schwarzenbach, R. P. Sorption of diverse organic vapors to snow. *Environ. Sci. Technol.* **2004**, *38*, 4078–4084.

(8) Zhang, L.; Cheng, I.; Muir, D.; Charland, J.-P. Scavenging ratios of polycyclic aromatic compounds in rain and snow in the Athabasca oil sands region. *Atmos. Chem. Phys.* **2015**, *15*, 1421–1434.

(9) Hoff, J. T.; Gregor, D.; Mackay, D.; Wania, F.; Jia, C. Q. Measurement of the specific surface area of snow with the nitrogen adsorption technique. *Environ. Sci. Technol.* **1998**, *32*, 58–62.

(10) Xu, S.; Kozerski, G.; Mackay, D. Critical review and interpretation of environmental data for volatile methylsiloxanes: Partition properties. *Environ. Sci. Technol.* **2014**, *48*, 11748–11759.

(11) Navas, A.; López-Martínez, J.; Casas, J.; Machín, J.; Durán, J. J.; Serrano, E.; Cuchi, J. A.; Mink, S. Soil characteristics on varying lithological substrates in the South Shetland Islands, maritime Antarctica. *Geoderma* **2008**, *144*, 123–139.

(12) Blais, J. M.; Kimpe, L. E.; McMahon, D.; Keatley, B. E.; Mallory, M. L.; Douglas, M. S. V.; Smol, J. P. Arctic seabirds transport marine-derived contaminants. *Science* **2005**, *309*, 445.

(13) Roosens, L.; Van den Brink, N.; Riddle, M.; Blust, R.; Neels, H.; Covaci, A. Penguin colonies as secondary sources of contamination with persistent organic pollutants. *J. Environ. Monit.* **2007**, *9*, 822–825.

(14) Endo, S.; Goss, K. U. Predicting partition coefficients of polyfluorinated and organosilicon compounds using polyparameter linear free energy relationships (PP-LFERs). *Environ. Sci. Technol.* **2014**, *48*, 2776–2784.

(15) Warner, N. A.; Evensen, A.; Christensen, G.; Gabrielsen, G. W.; Borga, K.; Leknes, H. Volatile siloxanes in the European Arctic: Assessment of sources and spatial distribution. *Environ. Sci. Technol.* **2010**, *44* (19), 7705–7710.

(16) Krogseth, I. S.; Kierkegaard, A.; McLachlan, M. S.; Breivik, K.; Hansen, K. M.; Schlabach, M. Occurrence and seasonality of cyclic volatile methylsiloxanes in Arctic air. *Environ. Sci. Technol.* **2013**, *47*, 502–509.

(17) Cheng, Y.; Shoeib, M.; Ahrens, L.; Harner, T.; Ma, J. Wastewater treatment plants and landfills emit volatile methyl siloxanes (VMSs) to the atmosphere: Investigations using a new passive air sampler. *Environ. Pollut.* **2011**, *159*, 2380–2386.

(18) Borgå, K.; Fjeld, E.; Kierkegaard, A.; McLachlan, M. S. Consistency in trophic magnification factors of cyclic methyl siloxanes in pelagic freshwater food webs leading to brown trout. *Environ. Sci. Technol.* **2013**, *47*, 14394–14402.

(19) Sobek, A.; Reigstad, M.; Gustafsson, O. Partitioning of polychlorinated biphenyls between arctic seawater and size-fractionated zooplankton. *Environ. Toxicol. Chem.* **2006**, *25*, 1720–1728.

(20) McLachlan, M. S.; Kierkegaard, A.; Hansen, K. M.; van Egmond, R.; Christensen, J. H.; Skjøth, C. A. Concentrations and fate of

decamethylcyclopentasiloxane (D5) in the atmosphere. *Environ. Sci. Technol.* **2010**, *44*, 5365–5370.

(21) Grannas, A. M.; Bogdal, C.; Hageman, K. J.; Halsall, C.; Harner, T.; Hung, H.; Kallenborn, R.; Klan, P.; Klanova, J.; Macdonald, R. W.; Meyer, T.; Wania, F. The role of the global cryosphere in the fate of organic contaminants. *Atmos. Chem. Phys.* **2013**, *13*, 3271–3305.

(22) Macdonald, R.; Mackay, D.; Hickie, B. Contaminant amplification in the environment. *Environ. Sci. Technol.* **2002**, *36*, 456A–462A.