

# Climatic and Biogeochemical Controls on the Remobilization and Reservoirs of Persistent Organic Pollutants in Antarctica

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**S** Supporting Information

**ABSTRACT:** After decades of primary emissions, reservoirs of persistent organic pollutants (POPs) have accumulated in soils and snow/ice in polar regions. These reservoirs can be remobilized due to decreasing primary emissions or due to climate change-driven warmer conditions. Results from a sampling campaign carried out at Livingston Island (Antarctica) focusing on field measurements of air–soil exchange of POPs show that there is a close coupling of the polychlorinated biphenyls (PCBs) in the atmosphere and snow/ice and soils with a status close to air–surface equilibrium to a net volatilization from Antarctic reservoirs. This remobilization of PCBs is driven by changes in temperature and soil organic matter (SOM) content, and it provides strong evidence that the current and future remobilization and sinks of POPs are a strong function of the close coupling of climate change and carbon cycling in the Antarctic region and this is not only due to warming.

Whereas an increase of 1 °C in ambient temperature due to climate change would increase current Antarctic atmospheric inventories of PCBs by 21–45%, a concurrent increase of 0.5% SOM would counteract the influence of warming by reducing the POP fugacity in soil. A 1 °C increase in Antarctic temperatures will induce an increase of the soil–vegetation organic carbon and associated POPs pools by 25%, becoming a net sink of POPs, and trapping up to 70 times more POPs than the amount remobilized to the atmosphere. Therefore, changes in soil biogeochemistry driven by perturbations of climate may increase to a larger degree the soil fugacity capacity than the decrease in air and soil fugacity capacity due to higher temperatures. Future research should focus on quantifying these remobilization fluxes and sinks for the Antarctic region.



## INTRODUCTION

Persistent organic pollutants (POPs) have been introduced to the environment through anthropogenic activities during the last century. Concern over their extreme persistence, semi-volatility, potential for long-range atmospheric transport, bioaccumulation potential, and adverse effects on wildlife and humans, has led to international conventions regulating the use of some POPs.<sup>1</sup> Polar regions receive POPs through atmospheric transport and deposition accumulating in soils, ice, and waters.<sup>2–12</sup> Even though once considered a final sink for these chemicals, several studies have shown evidence that historical burdens of POPs are currently being remobilized from retreating glaciers/ice cover in the Arctic and Antarctica.<sup>8–10</sup> This remobilization may be enhanced under climatic change scenarios, increasing their availability for exchange with the atmosphere, and therefore increasing the ecosystem's exposure to POPs that were previously immobilized.<sup>8,11</sup>

The western Antarctic Peninsula is a region clearly perturbed by climate change. Temperatures have increased up to 3 °C since the 1950s,<sup>13–15</sup> and there has been a transition from mean glacial growth (62% advancing in 1954) to retreat (87% in 2004).<sup>16</sup> These environmental changes have the potential to remobilize organic pollutants. Recently, Ma and co-workers<sup>10</sup> used long-term time series of air concentrations and modeling

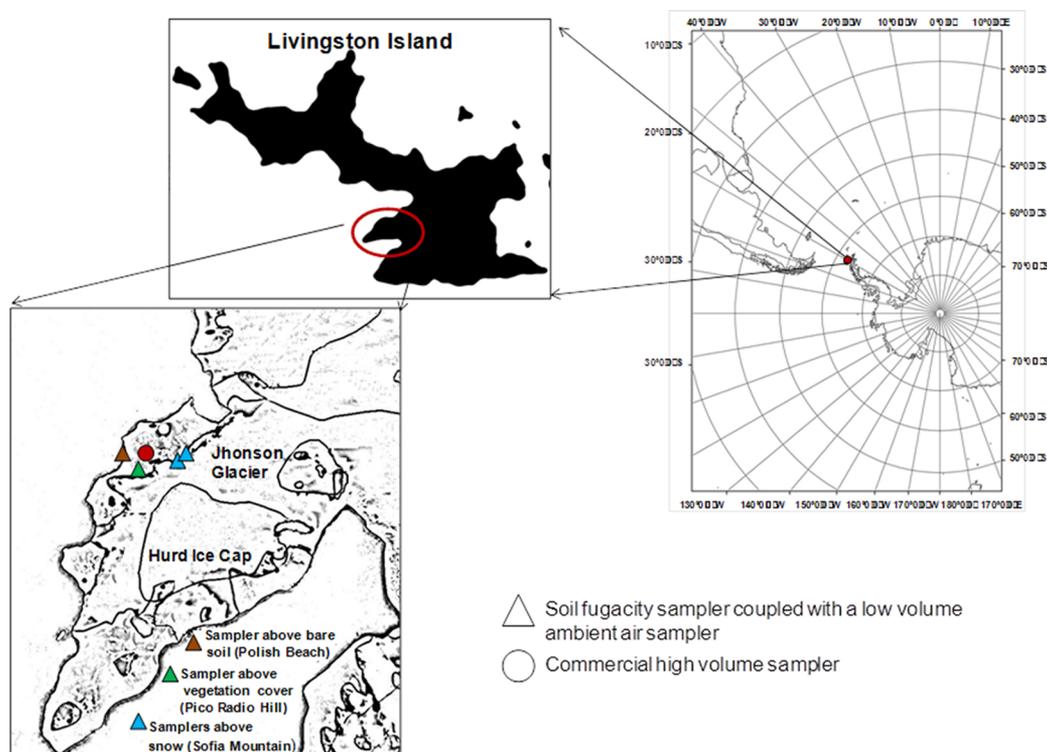
to suggest that Arctic seawater, snow, and presumably soils are becoming important secondary sources remobilizing POPs and modulating the trends of legacy pollutants such as hexachlorobenzene and polychlorinated biphenyls (PCBs) in the Arctic atmosphere.<sup>10</sup> However, there is a poor quantitative understanding of the drivers, other than temperature, of the reservoirs and revolatilization fluxes in polar environments.<sup>8,17</sup> Therefore, the objectives of this work were (i) to assess, for the first time in the field, the factors driving the remobilization of PCBs to the atmosphere from Antarctic soils, vegetation, and snow, and (ii) to investigate and explore the potential perturbations of climatic change on the remobilization and reservoirs of PCBs in Antarctica. Because PCBs encompass compounds with a large range of physical–chemical properties, they were used as surrogates of POPs in a sampling campaign carried out from January to February 2009 at Livingston Island (South Shetlands Islands, Antarctica) to investigate the factors controlling the re-emission of POPs to the atmosphere from soils and snow.

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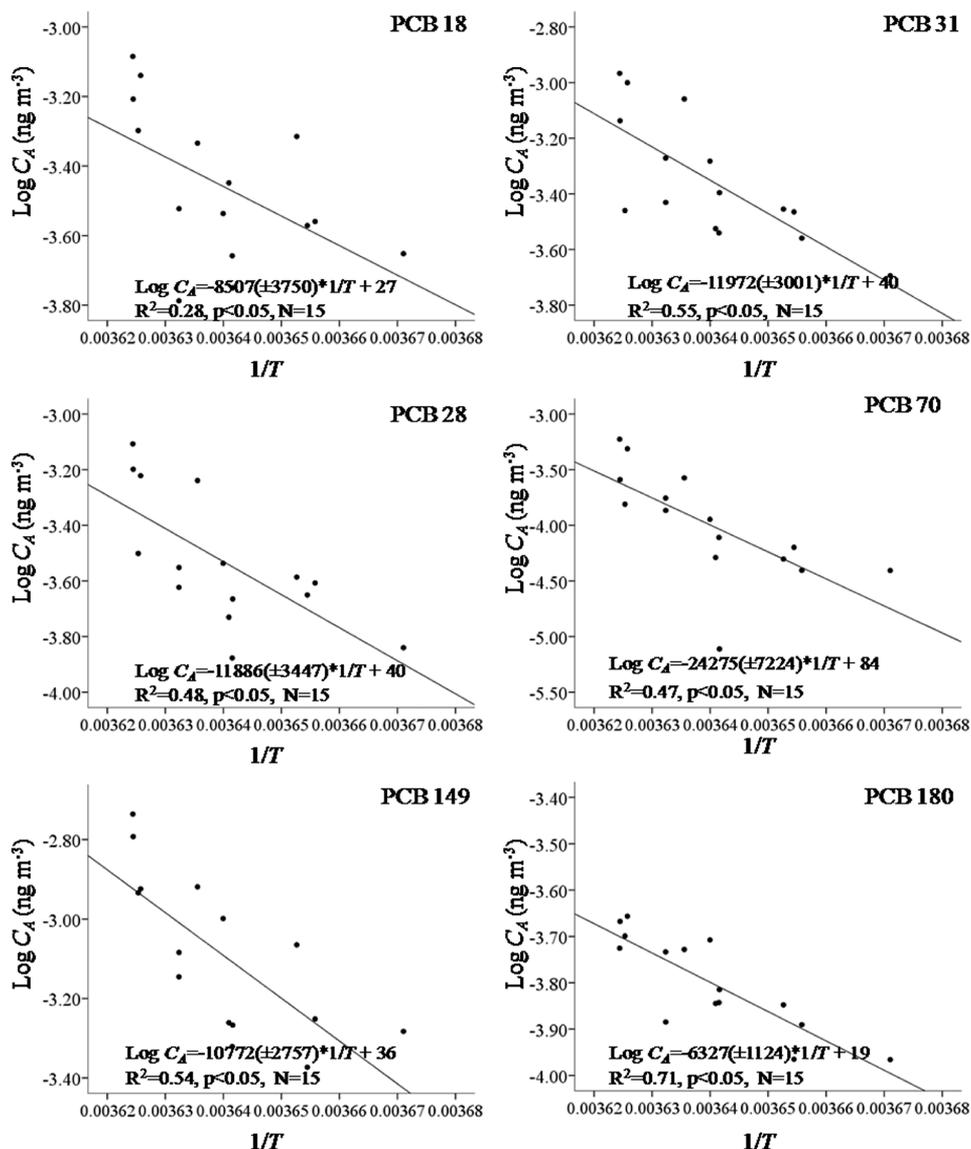
**Figure 1.** Map showing the sampling sites at Livingston Island where the soil fugacity samplers coupled with ambient low- and high-volume air samplers were deployed.

## EXPERIMENTAL SECTION

**Study Sites and Sampling Methodology.** The sampling was done at selected sites of Livingston Island,  $62^{\circ} 34'S$ ,  $61^{\circ} 13'W$  (South Shetland Islands) during the ATOS-2 campaign in the 2009 austral summer (8th January to 13th February). The use of fugacity samplers have received increasing attention during the past decade due to its appropriateness to study partitioning processes in laboratory and field controlled conditions.<sup>18–20</sup> In this work, the air equilibrated in situ with each surface (bare soil, soil covered with vegetation and snow) were collected using the sampler proposed by Cabrerizo et al.,<sup>20</sup> which have been previously used to study the exchange of POPs in temperate regions.<sup>21,22</sup> In the fugacity sampler, the air is forced to flow below a stainless-steel chamber with a surface of  $1 \text{ m}^2$  and separated 3 cm from the soil/snow surface, allowing the air to equilibrate with the surface soil/snow in terms of the chemical fugacity. Thus, air is sampled in the middle of the sampler after it has been in contact and equilibrated with the surface soil or snow.<sup>20–22</sup> In total, four soil-fugacity samplers were operating simultaneously and distributed above soil covered with lichens (*Usnea Antarctica*) in Pico Radio Hill (one sampler), bare soil at Polish beach (one sampler), and snow in Sofia Mountain (two samplers) (Figure 1). The four samplers were operated in the same conditions and during the same periods (sampling flow rate of  $8\text{--}10 \text{ l min}^{-1}$  and 5-day sampling periods). As in commercial high volume samplers, the air passes through a glass fiber filter to remove dust particles and polyurethane foam plug (PUFs) in which the compounds from the gas phase are retained. Filters and PUF used in this sampler are quartz fiber filters (GF/F) of 47 mm of diameter and  $10 \times 2 \text{ cm}$  were the PUF dimensions. The main advantage of this sampler is that it allows for accurately determining the POPs surface fugacity by sampling

the air, which has been equilibrated for enough time with the soil or snow, thus POPs soil and snow fugacities were determined. Unlike a commercial high volume sampler, the flow rate is much lower ( $8\text{--}10 \text{ l min}^{-1}$ ), thus allowing for air that passes below the sampler to equilibrate in terms of POPs concentrations with the soil surface.<sup>20</sup> At the ambient temperatures during the Antarctic summer, between  $-1$  to  $4^{\circ}\text{C}$  for the region of study, it is assumed that equilibration between the air and the surface soil is also achieved as it was in temperate conditions<sup>20–22</sup> because the kinetics of mass transfer by diffusion at the soil–air interface does not vary significantly due to a change of temperatures of  $10\text{--}15^{\circ}\text{C}$ . Indeed, the molecular diffusivity of a chemical in air depends on  $T^{1.5}$ , where  $T$  is the air temperature (K), then the diffusivities at 288 and 273 K vary by only 8% in their magnitude ( $(288/272)^{1.5} = 1.08$ ). In parallel, another sampler located at 1.5 m was operating at the same condition and sampling flow rate to determine ambient air fugacities. The sampling strategy in Antarctica was modified in comparison to previous sampling efforts in temperate regions<sup>20–22</sup> by extending the sampling time from 1 day to 5 days. The total air volume sampled over a 5 day period was about  $70 \text{ m}^3$  providing a total of 16 surface fugacity measurements and 16 ambient air fugacity measurements. In the middle of the sampling campaign, the fugacity samplers were moved to a proximate site about few meters away to the initial site.

In addition, a commercial high volume sampler (MCV, Collbató, Spain) was also deployed and sampling performed over a 1 day period for comparative purposes. A total of 15 pairs of atmospheric samples (gas + aerosol phases) were also collected using a high-volume air sampler placed on the surroundings of Pico Radio Hill. The high volume air sampler operated at a calibrated flow rate of approximately  $40 \text{ m}^3 \text{ h}^{-1}$ , so that the air volume ranged from  $700\text{--}900 \text{ m}^3$  per sample,



**Figure 2.** Ambient air concentration of PCBs ( $\text{log } C_A$ ) ( $\text{ng m}^{-3}$ ) versus inverse of temperature ( $1/T$ ) at Pico Radio Hill. The temperature range was from  $0.00362 \text{ K}^{-1}$  to  $0.00368 \text{ K}^{-1}$ , i.e.  $2.9$  to  $-0.6$  °C.

allowing the quantification of a larger number of congeners. In this sampler, the air stream passed first through quartz microfiber filters (QM-A, Whatman International Ltd., Maidstone, England) to collect particulate phase, and then through polyurethane foam adsorbents ( $10 \text{ cm} \times 10 \text{ cm}$ ), which retain the gas phase. For this study, only analysis on PUFs are shown.

Top surface soil ( $n = 4$ ) and vegetation samples ( $n = 2$ ) were taken after surface fugacity sampling by gently collecting the soil surface layer (approximately top  $0.5\text{--}1 \text{ cm}$ ) and lichen communities under the sampler device. Concentrations of PCBs in soil and vegetation samples below the samplers are reported in Tables S1–S2 of the Supporting Information. A wider assessment of PCBs in 36 soils and 18 vegetation samples from the studied region has been reported in a companion work<sup>7</sup> and are also used in this study. After sampling, all samples were stored in freezers and transported from Antarctica at  $-20$  °C until analysis.

**Analytical Procedures.** All samples were Soxhlet extracted during 24 h. Details of the fractionation scheme can be found elsewhere.<sup>7,20,21</sup> PCB congeners were analyzed by a gas

chromatograph equipped with a  $\mu$ electron capture detector (GC- $\mu$ -ECD, Agilent Technologies, model 7890N) with a  $60 \text{ m} \times 0.25 \text{ mm}$  i.d. DB-5 capillary column (Agilent HP-5MS) coated with 5% phenyl-95% methylpolysiloxane (film thickness  $0.25 \mu\text{m}$ ). The instrument was operated in splitless mode (close for 1.5 min) and the oven temperature program started at  $90$  °C (held for 2 min) to  $190$  at  $20$  °C/min and then to  $310$  at  $3$  °C/min (holding time 18 min). Injector and detector temperatures were  $280$  and  $320$  °C, respectively. Helium and nitrogen were used as carrier ( $1.5 \text{ mL/min}$ ) and makeup ( $60 \text{ mL/min}$ ) gases respectively and  $2 \mu\text{L}$  of sample were injected. The following PCB congeners were analyzed: tri-PCB 18, 17, 31, 28, 33; tetra-PCB 52, 49, 44, 74, 70; penta-PCB 95, 99/101, 87, 118; hexa-PCB 110, 151, 149, 153, 132/105, 138, 158, 128, 169; hepta-PCB 187, 183, 177, 171/156, 180, 191, 170; octa-PCB 201/199, 195, 194, 205; nona-PCB 206, 208, 209

**Quality Assurance/Quality Control.** To minimize contamination during analysis, PUF samples were initially precleaned with acetone/hexane ( $3:1 \text{ v/v}$ ) before the sampling campaign and handled and extracted after sampling in a

dedicated clean laboratory at Lancaster University that has filtered, charcoal-stripped air, and positive pressure conditions. Both soil and vegetation samples were also extracted at the same clean laboratory. Quality assurance and quality control parameters regarding soil and vegetation samples are reported elsewhere.<sup>7</sup> All analytical procedures were monitored using strict quality assurance and control measures. PUF laboratory blanks and field blanks constituted 30% of the total number of samples processed. PCB congeners 31, 28, 74 were detected in blanks at low concentrations, ranging between 3 and 5% of levels found in samples, indicating minimal contamination during processing. Therefore, samples were not blank corrected. A coelution with PCB 110, 153, and 132 + 105 congeners were detected for samples collected in 10 × 2 cm PUF, so these PCB congeners will not be taken into account in the present work. Method quantification limits for PCBs in ambient air and surface fugacity samples were derived from the lowest standard in the calibration curve, ranged from 0.0053 to 0.043 pg m<sup>-3</sup> for PCBs in air samples. Recoveries were routinely monitored using PCB 65 and PCB 200, and they were in the range between 75 and 120% for air samples. Thus, samples were not corrected for recoveries.

## RESULTS AND DISCUSSION

**Influence of *T* on Atmospheric Concentrations.** Gas phase ΣPCBs concentrations were in the range of 4–29 pg m<sup>-3</sup> (Tables S3–S6 of the Supporting Information) consistent with previous reports.<sup>23,24</sup> Temperature (*T*, K) is usually viewed as a primary control on the deposition/volatilization processes involved in secondary sources of pollutants and atmospheric concentrations of POPs.<sup>20,21,25</sup> Although the range of ambient temperatures during the sampling periods was narrow (−0.6 to 3.4 °C over soil and −0.7 to 1.7 °C over snow), atmospheric PCBs concentrations significantly correlated (*p* < 0.05; *r*<sup>2</sup> = 0.28–0.71) with ambient air temperature (Figure 2 and Figure S1 of the Supporting Information); thus, gas phase concentrations increase for the warmer periods. A temperature dependence of gas phase concentrations is evidence of local sources,<sup>25</sup> and thus, PCBs may originate from proximate Antarctic soils and snow. Conversely, long-range transport of pollutants from distant sources would result in a lack of *T* dependence due to dispersion, deposition, and degradation processes, which smooth the variability in concentrations.<sup>25</sup> This lack of *T* dependence on the short-term does not mean that long-range transport efficiency from source regions to Antarctica could be modified on the long-term due to, for example, climate change. The strong relationship between the atmospheric occurrence of PCBs and *T* cannot only be due to the *T* influence on soil–air partitioning suggesting that other processes are affecting the magnitude of soil–air partitioning and exchange amplifying the apparent influence of *T* on gas phase concentrations (see below).

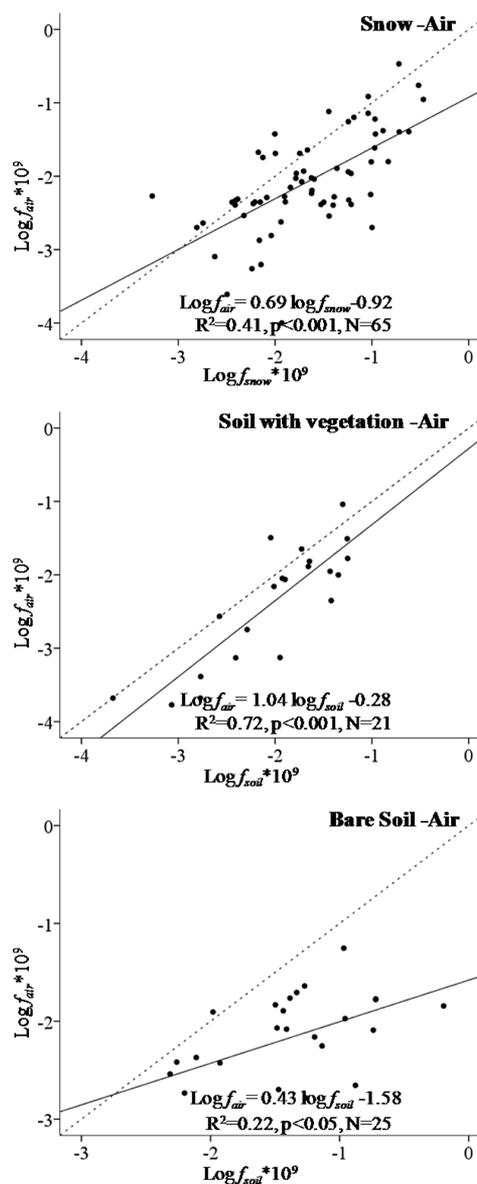
### Remobilization and Reservoirs of PCBs in Antarctica.

If local soils and snow are influencing the atmospheric concentrations, then the atmospheric concentrations (or fugacities) may follow the variability of the POPs fugacities, or escaping tendencies, from the underlying soil and snow. The ambient air fugacity (*f*<sub>a</sub>, Pa) and the snow or soil fugacity (*f*<sub>s</sub>, Pa) are calculated by the following:<sup>26</sup>

$$f_a = 10^{-9} C_A RT / MW \quad (1)$$

$$f_s = 10^{-9} C_{SA} RT / MW \quad (2)$$

where *C*<sub>A</sub> is the measured ambient air concentration at 1.5 m height (ng m<sup>-3</sup>), *R* is the gas constant (8.314 Pa m<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>), *MW* is the chemical molecular weight (g mol<sup>-1</sup>), and *C*<sub>SA</sub> (ng m<sup>-3</sup>) is the gas phase concentration that has been equilibrated with the soil or snow surface (Tables S7–S10 of the Supporting Information) as measured using the soil fugacity sampler.<sup>20</sup> Figure 3 shows that *f*<sub>s</sub> was usually higher than *f*<sub>a</sub> for



**Figure 3.** Fugacity in soil and snow versus fugacity in air for PCBs for the three sampling sites considered, that were covered by snow, soil + lichens, and bare soil.

PCBs, but close air–soil and air–snow couplings were observed and confirmed by the significant correlations between *f*<sub>s</sub> and *f*<sub>a</sub>. Indeed, the mixture of PCBs found in the atmosphere is significantly correlated with the mixture of PCBs which escape from soil and snow (*R*<sup>2</sup> from 0.22 to 0.72, *p*-level < 0.05). *f*<sub>s</sub> and *f*<sub>a</sub> are of similar magnitude (equilibrium), or *f*<sub>s</sub> is higher than *f*<sub>a</sub> (net volatilization), consistent with a strong coupling between the PCBs in the air and soil/snow compartments, and the strong influence that soils and snow have supporting the atmospheric occurrence of PCBs. This tight atmosphere–surface

coupling will be a strong function of the PCB surface–air partitioning coefficients ( $K_{SA}$ ) given by,

$$K_{SA} = 10^6 \frac{C_S}{C_{SA}} = \frac{10^{-3} C_S RT}{f_s MW} = \frac{Z_S}{Z_A} \quad (3)$$

where  $Z_S$  and  $Z_A$  are the fugacity capacity of the soil and air phases (mols  $m^{-3} Pa^{-1}$ ), respectively.  $Z$  values correlate concentrations and fugacities (for example  $C_S = Z_S f_s$ ) and indicate the affinity of the chemical for the matrix.  $Z_S$  and  $Z_A$  are given by<sup>26</sup>

$$Z_A = \frac{1}{RT} \quad (4)$$

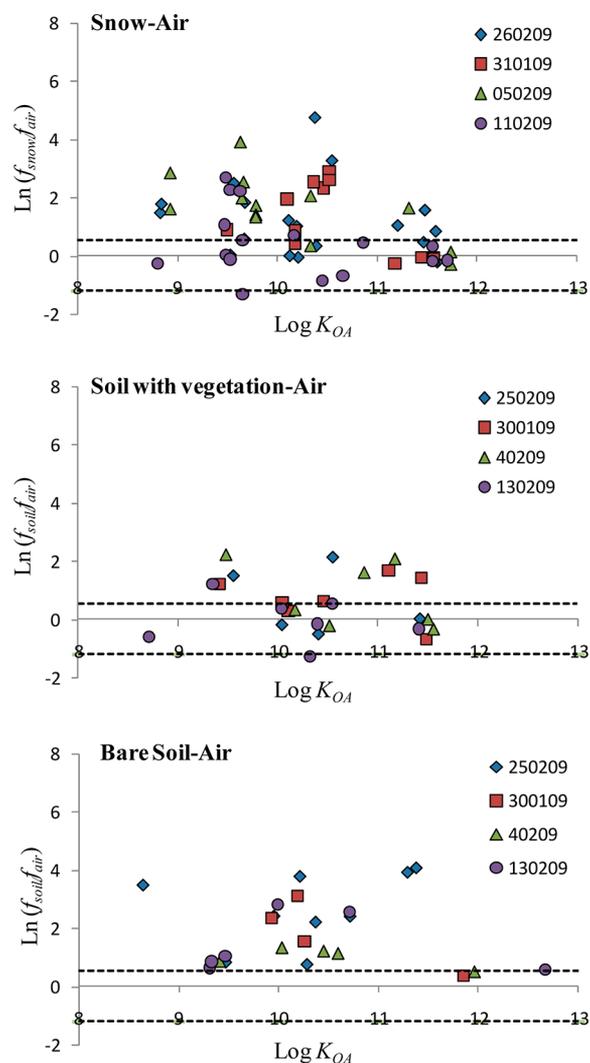
$$Z_S = f_{OC} K_{OA} \theta \frac{1}{RT} \quad (5)$$

Thus,  $K_{SA}$  values depend on the chemical hydrophobicity, as given by octanol-air partition coefficients ( $K_{OA}$ ), soil organic matter (SOM) content ( $f_{OC}$ ), and  $T$ .<sup>21,22</sup>  $\theta$  accounts for the different POP affinity to octanol and SOM.  $K_{SA}$  measured at Livingston Island confirmed these trends with significant correlations between  $K_{SA}$  and the fraction of organic carbon in soil ( $f_{OC}$ ) and between  $K_{SA}$  and  $T$  (Figures S2 and S3 of the Supporting Information).

The revolatilization of POPs from the surface reservoirs can be confirmed by comparing  $f_a$  and  $f_s$ . When  $f_s$  is higher than  $f_a$ , there is a net volatilization of the chemical. In contrast, if  $f_a$  is higher than  $f_s$  there is a net deposition of the chemical. However, because there is an uncertainty in the measurements, equilibrium would be represented by  $\ln f_s/f_a$  in the range of +0.53 and  $-1.20$ .<sup>20–22</sup> PCBs in snow and soil were close to equilibrium with the overlying atmosphere (Figures 3 and 4) but with a tendency for volatilization of the PCB congeners of low-medium chlorination that have lower  $K_{OA}$  values (between 9 and 11). Other studies have suggested that melting ice/snow can potentially release PCBs accumulated over winter or from previous decades.<sup>29,27</sup> However, none of these studies directly measured the ice/snow to air volatilization of POPs.

Differences in the magnitude of re-emission, or the ratio  $f_s/f_a$ , of PCBs were observed between bare soil and soil covered with vegetation. The latter has a significantly higher SOM content. SOM is a key variable driving the capacity of soils to act as reservoirs in temperate areas.<sup>21,22,28,29</sup> The results from the least-squares linear regressions of  $\log f_s/f_a$  versus SOM (measured as  $f_{OC}$ ) for individual PCB congeners show significant inverse correlations ( $R^2$  from 0.80 to 0.87,  $p$ -level  $<0.05$ , Figure S4 of the Supporting Information), thus suggesting that lower volatilization fluxes (or  $f_s/f_a$  ratios) would occur at higher SOM content. The magnitude of re-emission of PCBs from soils is therefore affected not only by temperature but also by SOM. Any biogeochemical process driving SOM will also exert an influence on the revolatilization of PCBs. Regardless of the low SOM content of Antarctic soils, these have a storage capacity to hold POPs larger than the overlying atmosphere with the inventory of POPs in soils being between 6 and 74 times that of the atmosphere (Annex III for uncertainty on these estimations).

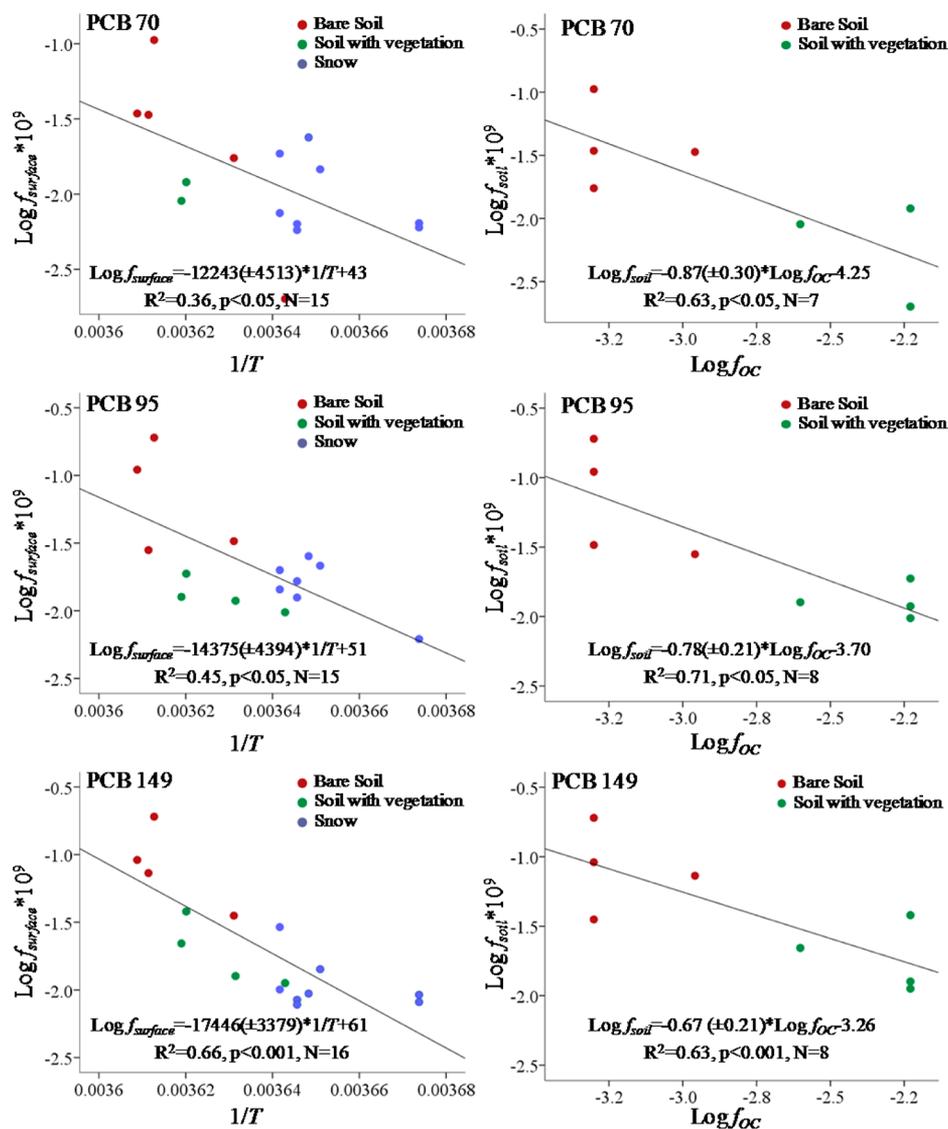
In this study, SOM was in the range from below detection limit (0.1%) in bare soil to 0.59% in soil covered with vegetation. Soils covered by vegetation (lichens, mosses) had higher SOM content<sup>7</sup> that resulted in lower values of  $f_s/f_a$  (Figure S4 of the Supporting Information). The magnitude of



**Figure 4.** Surface to air fugacity ratios ( $f_{snow}/f_{air}$  and  $f_{soil}/f_{air}$ ) versus  $\log K_{OA}$  for individual PCBs in the three sites considered that were covered by permanent snow, soil + lichens, and bare soil. Dashed lines indicate the equilibrium interval. Initial sampling dates are also indicated in the figure (day/month/year) as 250209 or 260209 (blue diamonds), 300209 or 310209 (red squares), 040209 or 050209 (green triangles), and 110209 or 130209 (purple circles) depending on the sampling site.

$f_s/f_a$  is affected by those variables affecting  $f_s$  and  $f_a$ .  $f_a$  is a function of temperature and ambient air concentrations (eq 1 and Figure 1). Similarly,  $f_s$  also shows an inverse significant dependence with temperature ( $R^2$  between 0.36 and 0.66,  $p$ -level  $<0.05$ , left panels of Figure 5). In addition, at higher SOM content  $f_s$  is also significantly reduced ( $R^2$  from 0.63 to 0.71,  $p$ -level  $<0.05$ ) due to the higher retention capacity of soils for POPs (right panels in Figure 5), indicating that even low amounts of SOM retard the re-emission of legacy pollutants to the atmosphere.

The concentrations of PCBs in soil ( $C_S$ ) from different locations at Livingston Island are proportional to SOM content<sup>7</sup> (Figure S5 of the Supporting Information), consistent with other studies in temperate regions.<sup>21,22,28</sup> SOM explains from 36 to 47% of the variability of PCB concentrations in soils, thus there are other soil physical and biogeochemical variables that may affect the soil concentrations and reservoirs of POPs. Thus, soils with higher SOM are relatively more important as



**Figure 5.** PCB fugacity in soil and snow ( $f_{\text{soil}}$  and  $f_{\text{snow}}$ ) versus inverse of temperature ( $1/T$ ) (left panels), and fugacity in soil ( $f_{\text{soil}}$ ) versus soil organic carbon content ( $\log f_{\text{OC}}$ ) (right panels). The temperature range was from 0.00361 K<sup>-1</sup> to 0.00367 K<sup>-1</sup>, i.e. 4.1 to -0.8 °C.

reservoirs of POPs, and a change in SOM will result in a modified reservoir potential.<sup>29</sup> Current and future re-emission from the soil will occur preferentially when  $f_s$  is higher due to lower SOM and higher  $T$ , which both reduce the capacity of the soil to retain hydrophobic organic pollutants.

Interestingly, the dependence of  $C_A$ ,  $f_s$ , and  $K_{SA}$  on  $T$  is very strong in all cases (Figures 2 and 5, and Figures S1 and S3 of the Supporting Information). Taking into account that the range of temperature variation is narrow, it is unlikely that this dependence on  $T$  is due only to its direct influence on soil–air partitioning. Macdonald and co-workers<sup>30</sup> have suggested that amplification of concentrations and fugacities can be explained in most cases by solvent switching and solvent depletion processes, and this framework can be used for a preliminary exploration of the factors driving the strong  $T$  dependence observed in this study. Solvent depletion processes induce an increase of the fugacity of the chemical. Degradation of SOM by soil respiration is a solvent depletion process affecting the quantity of SOM, thus of  $Z_s$ . Day and co-workers<sup>31</sup> have performed experiments of soil respiration at different temperatures in the Antarctic Peninsula. An increase of the ambient

temperature by 1 K induces an increase of respiration of 0.2 mg CO<sub>2</sub> g<sup>-1</sup> h<sup>-1</sup>, which is about 0.001 g<sub>SOM</sub> g<sup>-1</sup> per day. Therefore,  $f_{\text{OC}}$  could decrease by 0.1% in only 1 day due to a 1 K increase in  $T$ , a variation that is similar in magnitude to the SOM content of some Antarctic soils. Therefore, the variation of SOM due to soil respiration can modify  $Z_s$  and  $f_s$ . The extent of this solvent depletion process is also  $T$  dependent. Microbial respiration of dissolved organic carbon from melting snow has also the potential for inducing an increase of the chemical fugacity. However, during snow melting, there are other solvent depletion processes that may be important. The  $Z$  value of snow or ice is much higher than that of water,<sup>30,32</sup> therefore, during snow melting there is an increase of fugacity of the chemical due to a decrease of the  $Z$  value. In this study, it is not possible to quantify to which degree the observed influence of  $T$  on  $f_s$  and  $K_{SA}$  is due to surface–air partitioning, respiration of organic matter, and/or snow melting. However, it is noteworthy the fact that there are potential biogeochemical (soil respiration) and physical (snow melting) processes that may be expressed as an indirect effect of  $T$  on the remobilization of POPs.

This study demonstrates, for the first time, that Antarctic atmosphere and reservoirs (soil and snow) are currently closely coupled, presumably air and soils/snow affecting each other inventories, but with a tendency for net volatilization of PCBs to the atmosphere. These secondary sources are influencing the atmospheric occurrence of POPs in the polar atmosphere, driven by changes in not only temperature but also biogeochemical processes. Presumably, this secondary source plays a predominant role in comparison to long-range atmospherically transported POPs, especially for periods with higher temperatures and regions with lower stocks of SOM. From this study, it is not possible to determine to what extent this remobilization is part of a seasonal cycle with volatilization during summer and deposition during winter, or whether it is the result of global change. Besides this limitation, the elucidation of the drivers of remobilization and reservoirs of POPs opens the door for evaluating POP cycling under a scenario of global change.

**Climate Change and Remobilization of POPs.** Higher temperatures have been reported so far for the Antarctic Peninsula<sup>13,14</sup> and changing stocks of SOM have also been suggested for this and other polar environments, which are due to a number of factors such as changes in the soil metabolism, changes in vegetation cover, increase of impact from human settlements, and so forth.<sup>7,33,34</sup> There is increasing evidence that the extent of terrestrial biota habitats is changing in the Antarctic Peninsula,<sup>34,35</sup> for example with the population increase of vascular plants (*Deschampsia antarctica* and *Colobanthus quitensis*), increased annual growth rates of lichens, or by the introduction of invasive species.<sup>35–38</sup> These changes in vegetation cover can exert a significant influence over C and N cycling<sup>31,35</sup> and thus potentially on POPs cycling through changing SOM pools.

Global change with different temperatures and organic matter stocks will affect the volatilization and reservoirs of POPs due to the close coupling of climatic and biogeochemical controls. An increase of 1 °C in the ambient air temperature would increase current atmospheric levels and inventories of PCBs by 21–45% (derived from Figure 2) due to the influence of *T* on soil–air partitioning. A SOM increase of 0.5%, a scenario likely to occur in the Antarctic Peninsula because of expanding autochthonous vegetation types,<sup>31,35–37,39</sup> could counterbalance this volatilization of POPs by decreasing the fugacities in soil. Day and co-workers<sup>31</sup> showed that an increase of 1 °C in the diel temperature induced an increase of approximately 25% of the soil–vegetation organic carbon stocks in experiments performed in western Antarctic Peninsula, similar in percentage to the increase of the atmospheric inventory. However, because the storage capacity of soils is high, the amount of PCBs stored in soils would be up to 74 times higher than in the atmosphere. An alternative comparison of possible changing POPs burdens under a warming scenario, is that the increase in the atmospheric mass loading of PCBs due to 1 °C temperature rise, is on the same order as that obtained in soils by increasing SOM in the range of 0.02–0.07% (estimated from Figure S5 of the Supporting Information), a very small percentage that can be modified over a short period. At the current rate of warming in the Antarctic Peninsula, an increase of 1 °C in temperature can occur within a period of two decades.<sup>14</sup> Therefore, the western Antarctica has the potential to become a net sink of POPs.

This study shows the importance of studying biogeochemical cycling and climate change to understand, and eventually

predict, the current and future remobilization of POPs. The effects due to the direct manifestations of climate change (increase of temperature) may be counterbalanced by the indirect effects of climate change (habitat modification, changes in biogeochemistry). In terms of fugacity capacity, greater SOM increases  $Z_S$ , and higher temperatures decreases  $Z_S$  (and to a minor extent  $Z_A$ ), but variation of  $Z_S$  dominates, so varying *T* and SOM effects can counteract each other. Future research should focus on the quantitative understanding of these complex interactions that control the reservoirs, remobilization and sinks of POPs, as well as on the quantification of the mass fluxes involved at local and regional scale.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The data reported in this article are tabulated in the annexes I, II, and III. 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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