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Influence of Organic Matter Content and Human Activities on the Occurrence of Organic Pollutants in Antarctic Soils, Lichens, Grass, and Mosses

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Supporting Information

ABSTRACT: Banned pesticides such as HCB and *p,p′*-DDE, and other legacy and ongoing pollutants such as PCBs and PAHs, were measured in different vegetation types and soil samples collected at selected areas from Antarctic Peninsula (Deception and Livingstone Islands, Southern Shetlands). Two Antarctic expeditions (in 2005 and 2009) were carried out to assess POPs levels at remote areas, and close to current and abandoned Antarctic research settlements, to assess potential sources of pollutants. Overall, the patterns in lichens, mosses, and grass were dominated by low molecular PCB congeners and PAHs and the presence of HCB and *p,p′*-DDE rather than heavier compounds, suggesting the importance of long-range atmospheric transport of POPs as the main vector for the introduction of these chemicals to Antarctica. Statistically significant correlations (p-level < 0.05) between concentrations in vegetation of PCBs, *p,p′*-DDE, and the more volatile PAHs with lipid content were found with r^2 of 0.22−0.52 for PCBs, 0.42 for *p,p′*-DDE, and 0.44−0.72 for the more volatile PAHs. Thus, lipid content is an important factor controlling POPs in Antarctic lichens, mosses, and grass. A strong significant dependence of HCB (r^2 = 0.83), *p,p′*-DDE (r^2 = 0.60), and PCBs (r^2 = 0.36−0.47) concentrations in soil on its organic carbon content was also observed, indicating the important role of soil organic matter (SOM) in the retention of PCBs and OCPs in Polar Regions, where SOM content is low. Penguin colonies enhance the SOM content in some areas which is reflected in higher concentrations of all POPs, especially of persistent compounds such as *p,p′*-DDE. Higher concentrations of PCBs and PAHs found at the currently active Byers Camp (in an Antarctic Specially Protected Area) were explained by higher SOM content, thus indicating that Antarctic regulations are being successfully fulfilled in this small research area. On the other hand, PAHs in soils proximate to current Juan Carlos I research station show that even small human settlements are an important source of PAHs to the local environment. Therefore, even though the concentrations in Antarctica are low, there is evidence of local hotspots of contamination.

INTRODUCTION

The distribution of persistent organic pollutants (POPs) in Polar Regions has been recognized as a research priority.[1] Global distillation and fractionation, by which semivolatile compounds move from warmer latitudes to the Polar Regions, has been proposed to explain the presence of POPs in remote environments,[2] with lower levels in Antarctica than in the Arctic. Among the classes of POPs which have been recognized as priority pollutants listed by the Stockholm Convention on POPs, polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) such as hexachlorobenzene (HCB) and dichlorodiphenyltrichloroethane (DDTs), and polycyclic aromatic hydrocarbons (PAHs), are mostly contaminants with high persistence, susceptibility for long-range transport (LRT), and potential for biomagnification in food chains. After decades of bans or restrictions on the use of PCBs and OCPs, they are still found worldwide. Apart from LRT of pollutants, potential anthropogenic activities from primary sources (research stations, old equipment, etc.), diffuse secondary sources ("old" PCBs re-emitted from soils and oceans), and migratory biota[3] within the Polar Regions may contribute to the total burden of POPs in these areas. To protect Antarctica, international agreements have been developed. The most notable is the Protocol on Environmental Protection to the Antarctic Treaty.[4] As a result, research stations and practices have been improved and importation of specific POPs has been prohibited. Although research studies in both Poles are increasing, there is much less information for Antarctica due to its isolation from the other continents and the intrinsic sampling difficulties.[5] Soils and Antarctic vegetation (limited to the ice-free cover areas) may play an important role in the

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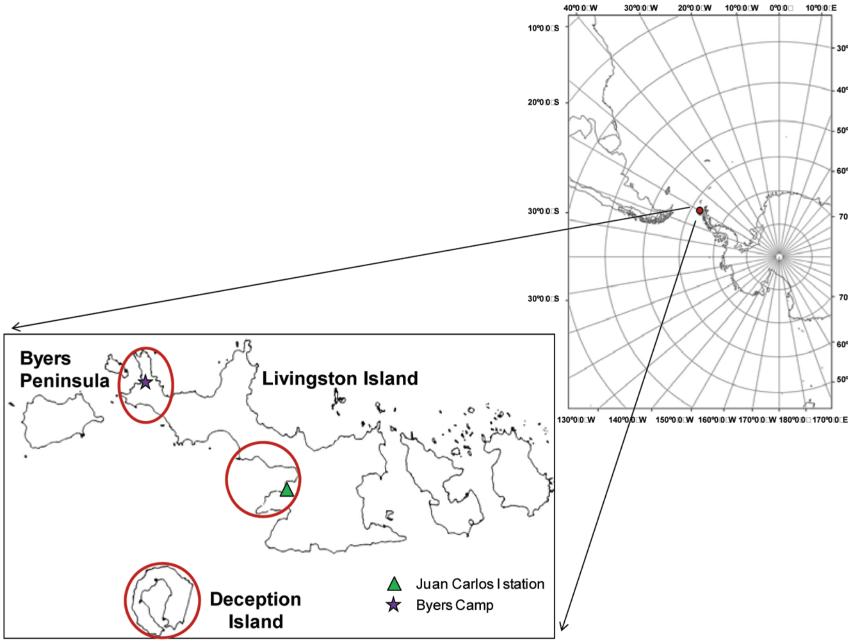

Figure 1. Sampling regions in Livingston and Deception Islands (Southern Shetlands, Antarctica).

cycling of POPs and provide valuable information on the local sources of pollutants and global redistribution of pollution. Primary production (by mosses, lichens, algae, etc.), organic matter (OM) from ancient glacial tills and lakes ("legacy" carbon),[6] or from biota excrements are considered to be important sources of soil organic matter (SOM) in terrestrial Antarctica. Soil is considered as a major repository of POPs[7,8] and vegetation has been reported to play an important role in removing POPs from the atmosphere.[9] Mosses and lichens have been used as natural passive air samplers to evaluate the deposition and/or uptake of airborne pollutants[10−12] as they can accumulate and concentrate toxic substances that may be present at low concentrations in the local environment. Therefore, the main objectives of this study were as follows: (i) to contribute with a large data set of PCBs, HCB, DDTs, and PAHs concentrations in soils, lichens, mosses, and grass in Antarctica during austral 2008/09 summer; (ii) to compare these levels of POPs with those found in soil samples collected in austral 2004/05 summer; (iii) to study in detail potential local sources by assessing the POPs concentrations proximate to the currently used Spanish research station "Juan Carlos I", the Byers research camp in Livingstone Island, and abandoned research stations on Deception Island; and (iv) to study the influence of penguin colonies modifying SOM content and its influence on POPs burden.

■ EXPERIMENTAL SECTION

Study Sites. Collection of soil and vegetation samples was performed at different sites of the South Shetland Islands during the ATOS-2 campaign in austral 2008/09 summer (Jan 10−Feb 14, 2009) and ICEPOS campaign in austral 2004/05 summer (Feb 1−28, 2005). Deception Island at 62° 58′ S, 60° 40′ W, Livingstone Island at 62° 39′ S, 60° 23′ W, and Byers Peninsula (an Antarctic Specially Protected Area) located in the westernmost part of the Livingstone Island, 62° 34′ S, 61° 13′ W were selected as a study area (Figure 1, further details in Annex I Supporting Information (SI)). To the best of our knowledge, no data on POPs concentrations at these selected areas have been found in the literature.

Soil samples (n = 26) from top 1 cm and top 5 cm and vegetation samples (n = 18) were collected at areas far from the research stations in order to study potential regional sources and redistribution of POPs. Many of these areas are not accessible by land and they were reached by sea. Some of these samples were collected at zones with penguin colonies, with vegetation cover, etc. Soil samples proximate to the current main research buildings of Juan Carlos I research station (n = 6), at Byers Camp, which are only open during austral summer, (in Livingstone Island), and abandoned stations (in Deception Island) were also collected to assess its potential contribution as a source of pollutants to the local environment. Soil samples (n = 4) collected in an earlier expedition (in 2005) in the same region will allow an assessment of whether soil POPs levels are increasing/decreasing (Annex I SI for a sampling sites, sampling map, and sampling information).

Different vegetation types were also collected in order to assess vegetation variability (see Annex I SI for sampling sites, sampling map, vegetation types, and sampling details). Lichens, from the specie *Usnea antarctica* (n = 6), mosses from the specie *Sanionia uncinata* (n = 7), and a couple of vascular plants, Antarctic hair grass *Deschampsia antarctica* (n = 2) and Antarctic pearl-wort *Colobanthus quitensis* (n = 1) were also collected. Moreover, two types of algae were studied. The thalloid green algae *Prasiola crispa* (n = 1) is abundant on the upper shores of Antarctica, often near to, and on, penguin colonies, and a red snow algae (n = 1), which usually appears in the spring/summer when the winter snow begins to melt carrying with it dissolved nutrients in the meltwater. In these conditions, the red algae grow within the top layer of the ice or snow. In total, n = 36 soil samples and n = 18 vegetation samples were collected and analyzed for PCBs, OCPs (HCB and DDTs), and PAHs in this study. After sampling, soil and vegetation samples were stored in freezers at −20 °C until analysis.

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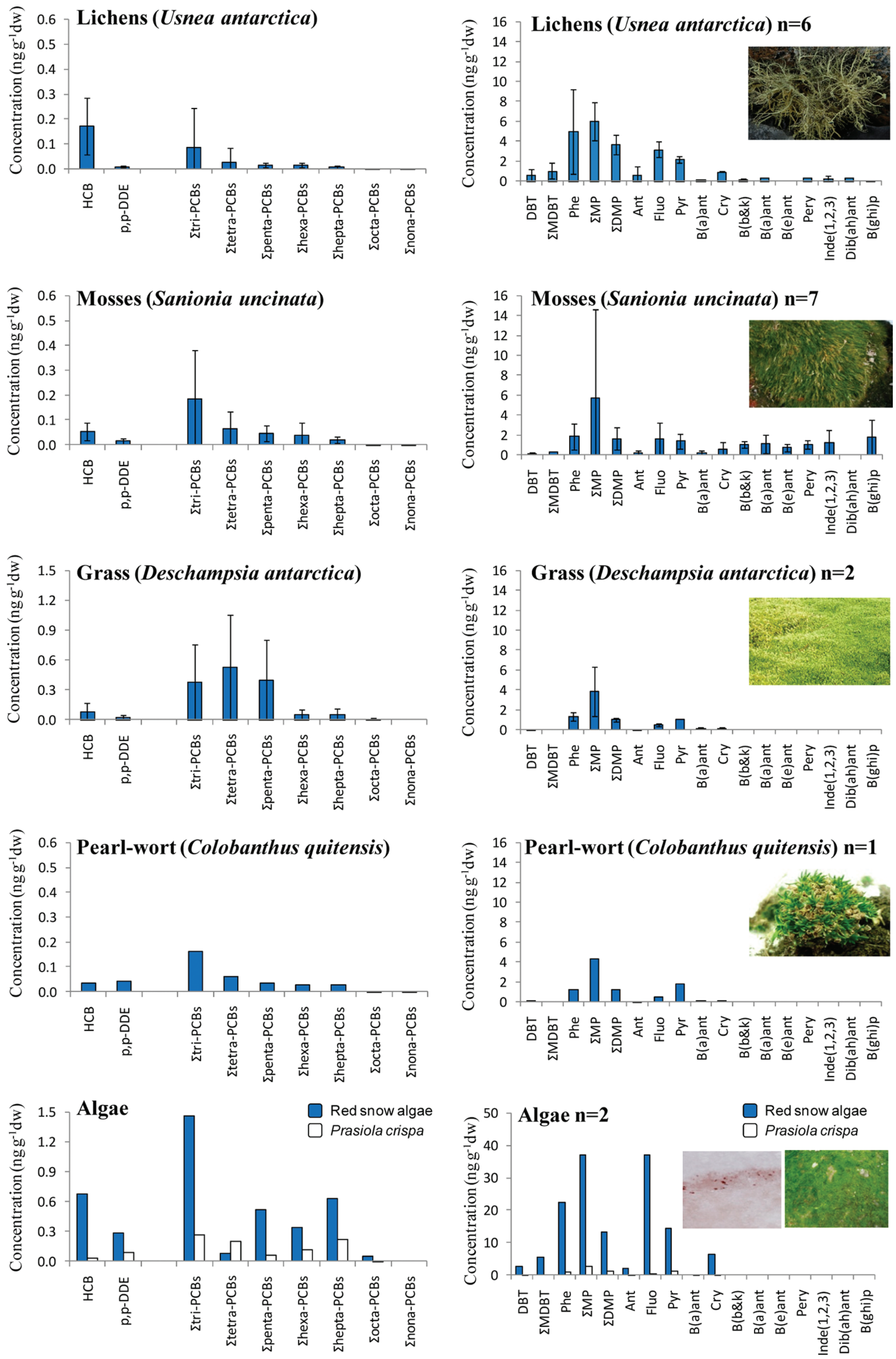

Figure 2. OCPs, PCBs, and PAHs concentrations (ng g^{-1} dw) in Antarctic vegetation. Right panels show individual PAHs concentrations (mean ± SD) and left panels show concentrations of PCB homologues groups and OCPs (mean ± SD).

Analytical Methods. Prior to the extraction, soil samples were homogenized and dried by mixing with anhydrous sodium sulfate, and vegetation samples were dry frozen with liquid nitrogen. Only the sample of red algae was lyophilized during 6 h as it was collected in a quartz fiber filter. Briefly, all samples were Soxhlet extracted for 24 h in dichloromethane/methanol (2:1). Extracts were cleaned and fractionated using alumina and silica chromatography to separate the PCBs and OCPs fraction from the PAHs fraction. Details of soil analysis and cleanup procedures are given elsewhere.[13−15] Determination of PCBs, OCPs, and PAHs in vegetation samples used methods reported elsewhere.[16,17] More specific details are given in Annex II SI. The following PCB congeners and OCPs were analyzed by gas chromatography coupled with electron detector capture (GC-ECD): tri-PCB 18, 17, 31, 28; tetra-PCB 52, 49, 44, 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

Table 1. Literature-Available POP Concentrations for Antarctic Vegetation and Comparison with This Study

sample type	Antarctic sector	PCBs (ng g^{-1} dw)	HCB (ng g^{-1} dw)	p,p'-DDE (ng g^{-1} dw)	PAHs (ng g^{1} dw)	ref
mosses	East Antarctica	Σ_{21}PCBs = 23−34	0.85−1.90	1.10−7.90		21
mosses	East Antarctica	Σ_{21}PCBs < 5−16	0.30−0.80	0.20		22
lichens	West Antarctica	Σ_{12}PCBs = 0.005−0.04				24
lichens	East Antarctica	Σ_{28}PCBs = 3.30	0.30	0.40		23
lichens	West Antarctica	Aroclor1242 < 5−12	0.32−2.16	0.10−0.60		26
mosses	West Antarctica	Aroclor1242 < 5−12	0.30−0.68	0.17−0.53		26
macroalgae	West Antarctica	Σ_{12}PCBs = 0.46−3.86				25
mosses	West Antarctica	Σ_{38}PCBs = 0.04−0.76	0.021−0.12	0.005−0.04	4.4−34	this study
lichens	West Antarctica	Σ_{38}PCBs = 0.043−0.61	0.002−0.31	0.003−0.01	15−40	this study
hair grass	West Antarctica	Σ_{38}PCBs = 0.39−2.40	0.080−0.20	0.061−0.09	6−10	this study
pearl-wort	West Antarctica	Σ_{38}PCBs = 0.31	0.04	0.04	9.5	this study
green algae	West Antarctica	Σ_{38}PCBs = 0.86	0.033	0.08	7	this study
red snow algae	West Antarctica	Σ_{38}PCBs = 3.07	0.67	0.28	141	this study

206, 209; HCB, and DDT and its metabolites (p,p'-DDT, p,p'-DDE). All samples were analyzed for the following parent PAHs: phenanthrene (Phe), anthracene (Ant), fluoranthrene (Flu), pyrene (Pyr), benzo(a)anthracene (B(a)ant), chrysene (Cry), benzo(b&k)fluoranthene (B(b+k)f), benzo(e)pyrene (B(e)pyr), benzo(a)pyrene (B(a)pyr), perylene (Pery), dibenzo(a,h)anthracene (Dib(a,h)ant), benzo(g,h,i)perylene (B(g,h,i)pery), indeno(1,2,3-cd)pyrene (In(1,2,3-cd)pyr), dibenzonthiophene (DBT) and alkyl homologues, methyldibenzonthiophenes (ΣMDBT), methylphenanthrenes (ΣMP), and dimethylphenanthrenes (ΣDMPD) by gas chromatography coupled to mass spectrometry (GC/MS) with a EI+ source operating in selected ion mode (SIM). Details of the temperature programs and monitored ions are given elsewhere.[13−15] Reference to the sum of homologue groups or the total sum of PCBs (ΣPCBs), and PAHs (ΣPAHs) considers the aforementioned congeners.

Quality Assurance/Quality Control. To minimize analysis contamination, samples were handled and extracted in a dedicated clean laboratory at Lancaster University which has filtered, charcoal-stripped air, and positive pressure conditions. All analytical procedures were monitored using strict quality assurance and control measures. Laboratory blanks constituted 20% of the total number of samples processed. PCB congeners 95, 110, 118, 187 and Flu and Pyr were detected in blanks at low concentrations, ranging between 2 and 9% of levels found in samples, indicating minimal contamination during processing. Therefore, samples were not blank corrected. PCBs, OCPs, and PAHs method quantification limits were derived from the lowest standard in the calibration curve; they ranged from 0.015 to 0.12 pg g^{-1} and 0.018−0.15 pg g^{-1}, 0.20 and 0.25 pg g^{-1} and 2 and 2.5 pg g^{-1} for PCBs, OCPs, and PAHs in vegetation and soil expressed as dry weight (dw) respectively. Recoveries were routinely monitored using PCB65 and PCB200 and phenanthrene−d_{10}, chrysene−d_{12}, and perylene−d_{12} and they ranged from 70 to 110% and from 50 to 120% for soil and vegetation, respectively, so samples were not corrected by recoveries.

The following physicochemical characteristics of samples were measured by standard methods described in Annex II of SI: soil temperature (Soil T), ambient air temperature (Air T), soil−water content (SWC), soil organic carbon (TOC) or organic carbon fraction (f_{OC}) and lipid content, soil redox potential, and soil pH.

RESULTS AND DISCUSSION

Occurrence of PCBs, OCPs, and PAHs in Antarctic Vegetation. All the measured concentrations and % lipid content, Σ_{38}PCBs, ICES congeners (Σ_7PCBs), individual PAHs, and ΣPAHs are listed in Annex III SI. Overall, low molecular weight PCB congeners groups dominate the vegetation profile in all vegetation types (Figure 2 left panel). Σ_{38}PCB concentrations were in the range of 0.04−0.61 ng g^{-1} dw in lichen, 0.04−0.76 ng g^{-1} dw in mosses, 0.39−2.40 ng g^{-1} dw in grass, 0.31 in the Antarctic pearl-wort, and between 0.86 and 3.07 for green algae and red snow algae, respectively. There are few studies which have reported data on terrestrial Antarctic vegetation (Table 1). Some have used mosses and lichens for biomonitoring of heavy metals in the Arctic and Antarctic,[18−20] but there is a lack of data regarding POPs in the different vegetation types. In general, concentrations of ΣPCBs, HCB, and p,p'-DDE for mosses and lichens in this study are comparable but in lower ranges than those previously reported in East Antarctica.[21−23] A most recent study[24] in lichens from a King George Island (South Shetland Island) reported ΣPCBs in the range of 0.005−0.04 ng g^{-1} dw which is lower than previous studies but in agreement with our results. No previous reports exist for POPs in Antarctic grass and pearl-wort, so this study is unique in providing comparative data on the Antarctic terrestrial vegetation. A previous study[25] reported data for ΣPCBs in a macroalgae in western Antarctica in the range of 0.46−3.86 ng g^{-1} dw, which is in agreement with our reported concentration in algae, although algae species are different. Concentrations of HCB (0.002−0.67 ng g^{-1} dw) and p,p'-DDE (0.003 and 0.28 ng g^{-1} dw) are in the range reported in previous studies,[23,26] with p,p'-DDE being the main contributor, up to 60%, to the ΣDDT for most vegetation samples, consistent with the fact that DDT is subject to microbial degradation to more stable and toxic metabolites such as p,p'-DDE. The ratios p,p'-DDE/p,p'-DDT have been used successfully to distinguish the source of DDT.[27−29] Therefore, if the ratio of p,p'-DDE/p,p'-DDT is >1, it indicates aged DDT, while ratios <1 indicate fresh inputs. From the data set reported here (n = 18), vegetation samples had always ratios of p,p'-DDE/p,p'-DDT >1, indicating aged DDT.

The PAH profile in vegetation samples (Figure 2 right panel) was dominated, as in the case of PCBs, by low molecular weight (LMW) compounds. The most abundant compounds are those having 3 (Phe) and 4 aromatic rings (Flu, Pyr, and Cry). On average, Phe, ΣMP, ΣDMP were the most abundant compounds in all samples, independent of the vegetation

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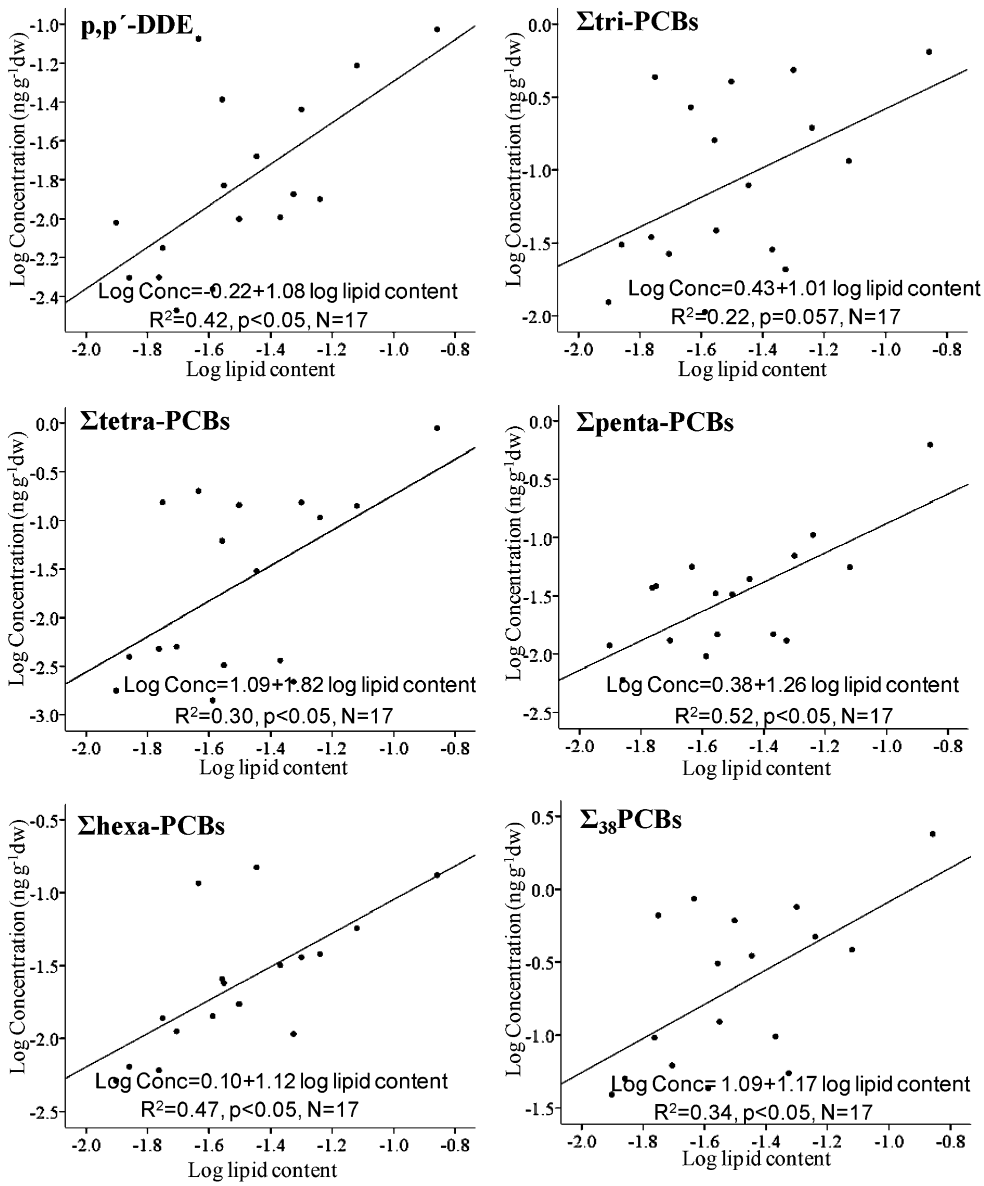

Figure 3. Log concentration (ng g^{-1} dw) in vegetation of *p,p*′-DDE, PCB homologues groups, and Σ_{38}PCBs versus log lipid content.

type, contributing up to 60% of the total PAHs, followed by Flu and Pyr. The ranges of vegetation concentrations of ΣPAHs were 15−40 ng g^{-1} dw in lichens, 4.4−34 ng g^{-1} dw in mosses, 6−10 ng g^{-1} dw in grass, 9.5 ng g^{-1} dw in the Antarctic pearlwort, and between 7 and 141 ng g^{-1} dw for green algae and red snow algae, respectively. To the best of our knowledge, no data regarding PAHs in Antarctic vegetation have previously been reported. Available data for PAHs in remote areas of Andean Mountains,[30] Alaska,[31] Arctic,[32] Poland,[31] and China[10] reported higher values than those presented in this study. Profiles dominated by low molecular PCB congeners and PAHs and the presence of HCB and *p,p*′-DDE in comparison to heavier compounds suggest the importance of LRT of POPs as a main vector for the introduction of POPs to the remote Antarctic region.[33−35]

If long-range atmospheric transport and deposition is the process dominating the POPs input to the Antarctic ecosystem, the uptake of POPs in Antarctic vegetation may be influenced by the occurrence of relevant sorbing phases at each site (fugacity capacity), which for vegetation is given by the lipid content, even though other factors such as age and growth rate can also play a role. Although there are no available data on the age of Antarctic vegetation in the study area, it is assumed that they are very old organisms since their growth rate is limited to the environmental conditions, which may affect POPs storage. Estimated growth rates on *Usnea antarctica*, in Livingstone Island[36] over an 11-year period, show annual growth rate in length of 2 mm $year^{-1}$ with an increase in the lichen diameter from 50 (1991) to 72 mm (2002). Populations of both vascular plants (*Colobanthus quitensis* and *Deschampsia antarctica*) were observed to increase in the Antarctic Peninsula over the last decades, and other studies[37] have suggested that the changes may be related to rising temperatures and glacier retreat in the area.[38] The influence of vegetation type, for which the lipid content was in the range 1.25−13.85% for the different vegetation types, on PCBs, OCPs, and PAHs concentrations was assessed by regression analysis. Figure 3 shows the significant dependence (*p*-level < 0.05) of PCB homologue groups (r^2 = 0.22−0.52), Σ_{38}PCBs (r^2 = 0.34), and *p,p*′-DDE (r^2 = 0.42) concentrations on lipid content, thus suggesting that

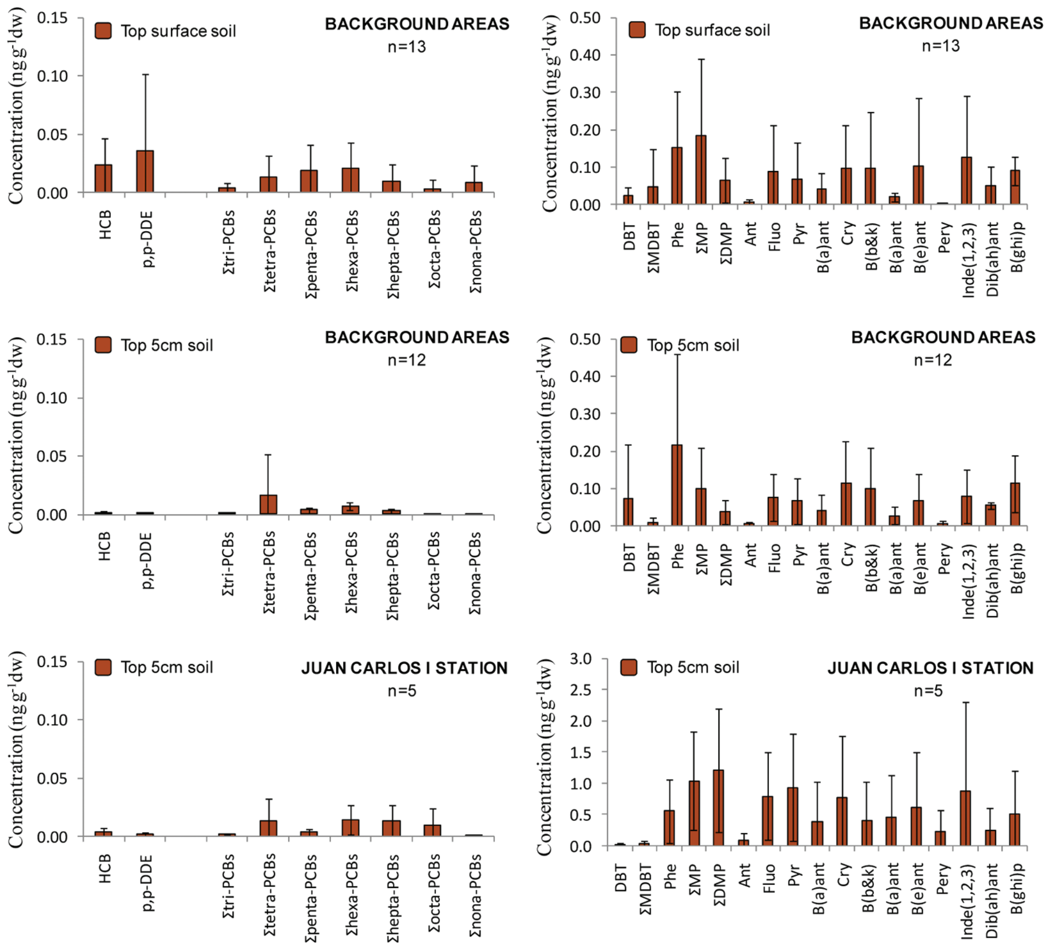

Figure 4. OCPs, PCBs, and PAHs concentrations (ng g^{-1} dw) in top 1 cm and top 5 cm soil samples from background areas of Livingstone and Deception Island (top panels) and from samples collected proximate to Juan Carlos I research station.

Table 2. Literature Available POP Concentrations for Antarctic Soils and Comparison with This Study[a]

sample type	Antarctic sector	PCBs (ng g^{-1} dw)	HCB (ng g^{-1} dw)	*p,p′*-DDE (ng g^{-1} dw)	PAHs (ng g^{-1} dw)	ref
soil	West Antarctica	Σ_{32}PCBs = 0.008–0.03				24
		Σ_{12}PCBs = 0.0006–0.01				
soil 0–5 cm	West Antarctica				<lod	42
soil 0–5 cm	West Antarctica				19–42	44
soil 0–2 cm	West Antarctica				46–1844	42
soil 0–5 cm	East Antarctica	Σ_{21}PCBs = 0.36–0.56	0.03–0.17	0.05–0.08		21
soil 0–5 cm	East Antarctica	Σ_{28}PCBs = 0.30–0.41	0.02–0.03	0.03–0.19		23
soil 0–5 cm	East Antarctica	Σ_{28}PCBs = 1.98–6.94	0.25–1.16	0.32–3.19		23
soil 0–5 cm	East Antarctica	Σ_{28}PCBs = 90–157	0.09–25	0.38–2.13		23
soil 0–10 cm	East Antarctica	Σ_{7}PCBs = 0.51–1.82	2.41–7.75	ΣDDTs = 0.51–4	34.9–171	43
soil surface	East Antarctica				71.000	56
soil surface	East Antarctica				841–85659	57
soil surface	East Antarctica				5.3–88452	58
soil surface 1 cm	West Antarctica	Σ_{38}PCBs = 0.012–0.32	loq–0.07	loq–0.20	0.30–4.6	this study 2009 background
soil 0–5 cm	West Antarctica	Σ_{38}PCBs = 0.005–0.14	loq–0.004	loq–0.002	0.16–3.51	this study 2009 background
soil 0–5 cm	West Antarctica	Σ_{38}PCBs = 0.07–0.12	loq–0.004	0.003–0.008	0.62–2.2	this study 2005 background
soil 0–5 cm	West Antarctica	Σ_{38}PCBs = 0.012–0.15	0.002–0.01	loq–0.005	0.59–3718	this study 2009 at Juan Carlos I

[a]loq: quantification limit; lod: detection limit.

lipid content is a key factor controlling PCBs and *p,p′*-DDE in Antarctic terrestrial vegetation, and lipid content explain the higher PCBs and *p,p′*-DDE concentrations found in grass in comparison to other vegetation types. However, no statistically significant regression was observed between individual PAHs and HCB and lipid content when considering all samples. However, there is a positive statistically significant regression for more volatile PAHs (Annex III SI) when excluding the vascular plants and algae and considering only moss and lichen samples. PAHs are not as persistent of pollutants as PCBs and

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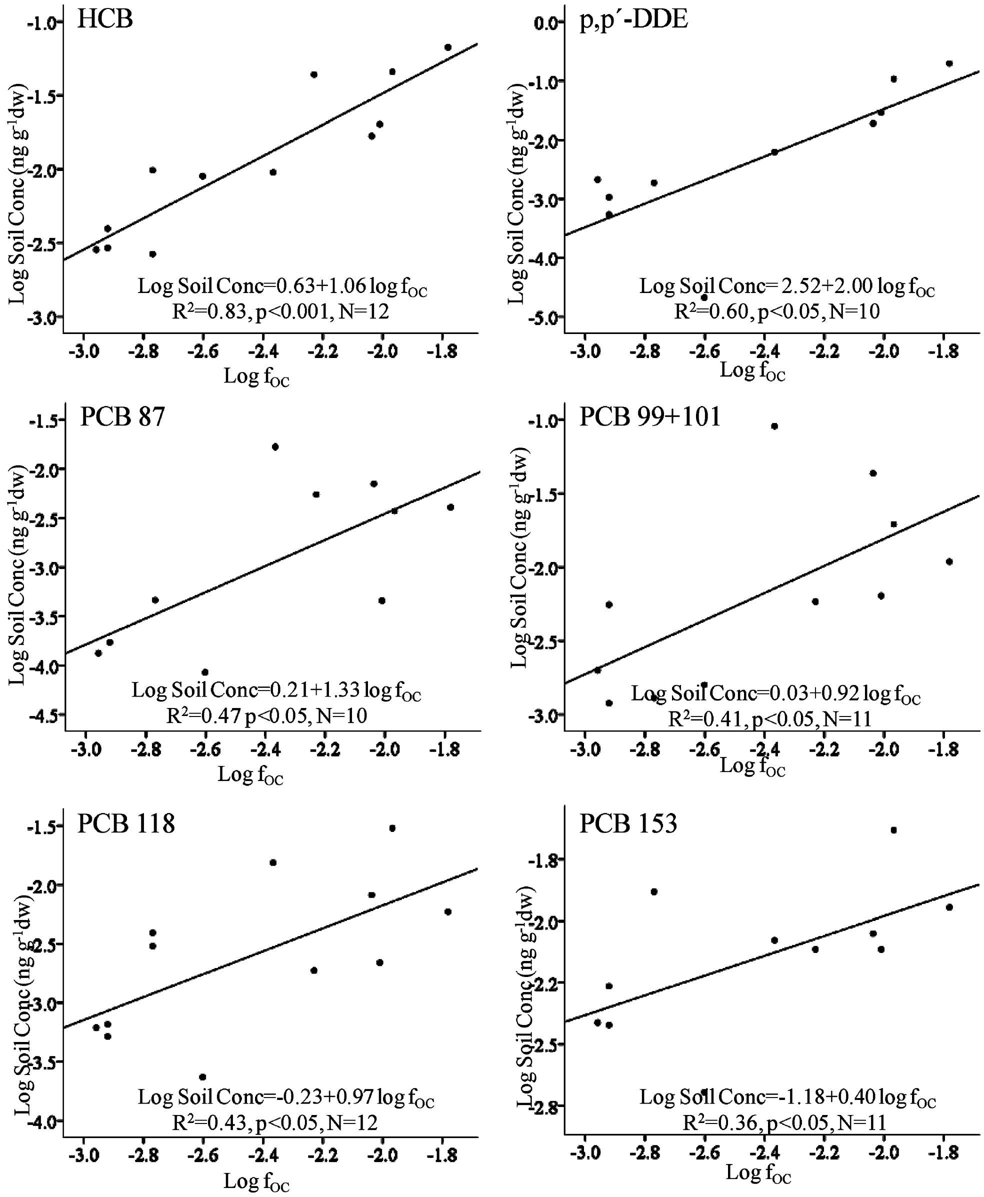

Figure 5. Log soil concentration (ng g^{-1} dw) of OCPs and selected PCB congeners versus log f_{OC}.

may potentially be degraded before deposition on the surface cuticle in the case of vascular plants and mosses, or in cell walls in the case of lichens, or they can be potentially biogenically produced from degradation of organic matter, mainly triterpens.[14,39−41]

Occurrence of PCBs, OCPs, and PAHs in soils. Soil concentrations of PCBs, OCPs, and PAHs and soil physicochemical properties (TOC, soil T, ambient air T, soil pH, and soil redox potential) are listed in Annex IV. Soil patterns for PCBs and OCPs are shown in Figure 4 (top left panels). Overall, Σhexa-PCB homologue group was the most abundant, followed by the Σpenta-, Σhepta-, and tetra-PCBs, consistent with previously reported studies.[24] In general, concentration of PCBs tends to decrease from the surface to deeper layers in background soils. Σ_{38}PCBs in the top surface soil (top 1 cm) ranges from 0.012 to 0.32 ng g dw^{-1}, in comparison to Σ_{38}PCBs for soils at top 5 cm which are in the range of 0.005−0.14 ng g dw^{-1}. HCB and *p,p*′-DDE were also detected in most of the samples, with a concentration range of loq−0.07 ng g^{-1} dw for HCB and loq−0.20 ng g^{-1} dw for *p,p*′-DDE in top soil, between loq−0.004 ng g^{-1} dw for HCB and loq−0.002 ng g^{-1} dw for *p,p*′-DDE in top 5 cm soils. The levels of PCBs, HCB, and *p,p*′-DDE concentrations reported here were comparable but slightly lower than previously reported values at other Antarctic regions, although our study reports the highest number of PCB congeners (Table 2). These differences among reported soil concentrations are in agreement with the trends described above for vegetation. Levels of HCB and *p,p*′-DDE in this study are in the same order of magnitude as previously reported for Antarctica.[21,23] PAH soil profile at background areas is shown in Figure 4 (top right panels). Overall, the profile was dominated by low−medium molecular weight compounds. The most abundant compounds are those having 3 rings (especially Phe, ΣMP, ΣDMP) followed by those with 4 rings (Flu, Pyr, and Cry). ΣPAHs in soil surface samples are in the range of 0.30−4.6 ng g^{-1} dw and slightly lower in deeper soil, in the range 0.16−3.51 ng g^{-1} dw. Overall, soil PAH content at other areas (soils and sediments) of Western

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Antarctica has been reported to be below detection limit[42] or higher than our reported values in soil.[43−45] For the soils collected in 2005 concentrations were in the range of 0.07−0.12 ng g^{-1} dw for Σ_{38}PCBs, loq−0.004 ng g^{-1} dw for HCB, 0.003−0.008 ng g^{-1} dw for *p,p*′-DDE, and 0.62−2.20 ng g^{-1} dw for ΣPAHs. These concentrations are not significantly different from those found at soil samples collected during the 2009 campaign at the same sites (see Annex IV), suggesting, as expected, that soil concentrations of these pollutants are not increasing or decreasing at a fast rate.

Soil organic matter quantity is generally considered as the main descriptor of the concentration of hydrophobic pollutants in soils[7,8] at local, regional, and global scales. In this study, and to a larger extent in other studies, Antarctic soils are characterized by low SOM, in the range from detection limit (DL 0.1%) to 1.66% for top 1 cm surface soil. SOM content was always below 0.1% for all the top 5 cm soil samples, with the exception of samples with vegetation cover (0.12−0.43%) and samples collected proximate to the main research buildings of Juan Carlos I research station, which shows values of 0.17%. To study the influence of SOM on POPs concentration in soils, only those samples having SOM values above detection limit were considered for statistical analysis. Overall, a strong significant dependence of HCB and *p,p*′-DDE on f_{OC} was observed (r^2 of 0.83 and 0.60 respectively, p-level < 0.05). Less strong but statistically significant dependence (p-level < 0.05) was also observed for most PCB congeners with r^2 of 0.36−0.47 (Figure 5), which suggests the important role of SOM, even at low amounts, in the retention of PCBs and OCPs in Polar Regions. The mineral phase (not determined in this study) may be an important sorbing phase for those samples with TOC values <0.1%, as has been pointed out elsewhere.[46,47] On the other hand, no statistically significant correlation was found between SOM and PAHs concentrations. The lower affinity of PAHs in comparison with PCBs or OCPs has also been reported in the literature,[48,49] and a number of potential factors such as degradation or autochthonous biogenic production,[39] potential contamination from scientific stations, research vessels, or tourism ships, have been suggested to explain the lack of or weak correlation of PAHs and SOM found in literature studies.

Penguin Colonies and Other Drivers of Higher Soil Organic Carbon Content and POPs in Antarctica. Although Antarctic SOM values are the lowest reported in background soils globally,[7] its presence in slightly higher moderate amounts is limited to localized areas. Higher values of SOM found in this study belong to soils collected at penguin colonies (0.92−1.66%), followed by soils covered by lichen and mosses (0.12−0.98%). This is in agreement with previous studies[24] which have determined important increases in SOM content (up to 26%) in soils collected near penguin colonies or near the habitats with breeding petrels or Skuas. To a minor extent the presence of anthropogenic activities in Antarctica has apparently also contributed to increasing SOM (0.1−0.17%). To elucidate potential sources of pollutants and factors affecting the POP concentrations, different from SOM, soil concentrations of PCBs, HCB, *p,p*′-DDE and PAHs were normalized by organic carbon content. Most reported concentrations of pollutants in Antarctic soils do not show soil concentrations normalized by organic carbon and evaluation of potential sources of POPs are done on dry weight, increasing the uncertainty, since OM is an important parameter affecting the soil POPs repository.[7,8] Background soil samples were divided in samples collected (i) at penguin colonies, (ii) below vegetation communities, (iii) at abandoned old research stations visited by tourists (Deception Island), (iv) at the ongoing research station Juan Carlos I, (v) at Byers Camp, and (vi) at other background soils. Figure S5.1 (Annex V) shows the POPs concentrations normalized by OC. Significantly higher *p,p*′-DDE OC-normalized concentrations were observed in soil samples collected at penguin colonies, suggesting an important *p,p*′-DDE redistribution, resulting in significantly elevated levels. This is consistent with profiles of POPs reported in penguin blood samples[50] and penguin eggs,[51,52] with *p,p*′-DDE being by far the dominant POP followed by HCB and PCBs, and suggests that penguins may redistribute contaminants on a local scale, resulting in significantly elevated POP levels in the soils from penguin colonies. Elevated levels of *p,p*′-DDE normalized by lipid content have also been reported in studies on Antarctic fish, elephant seals, and Weddel Seals.[53−55] Concerning the influence of lichens, grass, and mosses on underlying POP soil concentrations, once normalized by SOM, concentrations of POPs in soils covered by vegetation are not significantly different from those found in bare soils. As pointed out above, close to the research station, slightly higher SOM values were observed. However, the concentrations of some pollutants, especially PAHs, are much higher in soils from the Juan Carlos I Station (bottom panels of Figure 4) than from background soils, even when OC normalized concentrations are considered (Figure S5.1 Annex V).

Local Sources of Organic Pollutants from Research Stations and Other Human Activities. Previously reported PAHs concentrations in Antarctica are often from soils and sediments located in highly contaminated areas where accidental spills have occurred, or close to research stations, with reported concentration up to thousands of ng g^{-1} dw.[56−58] The patterns of OCPs, PCBs, and PAHs for soil collected proximate to the main research buildings of Juan Carlos I (Figure 4 bottom panels) are not significantly different from those found at background sites, but the concentrations of PAHs in soils at Juan Carlos I Station are 1 order of magnitude higher (0.59−25.5 ng g^{-1} dw). An extremely high ΣPAHs concentration (3718 ng g^{-1} dw) was detected in a sample collected where fossil fuel is usually stored, suggesting accidental spillages. Therefore, Juan Carlos I research station is a source of PAHs to the local environment, which suggests that even a small settlement (20 persons during the austral summer) can affect the loading in nearby soils. However, these PAHs levels are still significantly lower when compared with other human-impacted areas.[42,56−58] Conversely, Σ_{38}PCB at Juan Carlos I station was 0.012−0.15 ng g^{-1} dw, which is in the same range as those samples collected at background areas, and OC-normalized concentrations of PCBs and OCPs confirms that the research station has not been a significant local source of PCBs. Levels of PCBs were high at ancient (abandoned) research stations from Deception Island, but in the same range as those samples collected at background sites when normalized by soil OC, indicating that either abandoned stations had not significantly polluted the local environment or PCBs have revolatilized during the last four decades. Higher Σ_{38}PCB (0.45 ng g^{-1}dw) and PAHs (8 ng g^{-1}dw) were detected at Byers Camp, but once these concentrations are normalized by OC, the levels are equal to those of other background sites (Figure S5.1 annex V). The fact that Byers Camp shows no sign of POPs from the human settlement in comparison to Juan Carlos

I Station is an important finding since this research camp is located in an Antarctic Specially Protected Area with special regulation (see Annex I for more details), in order to minimize waste impact. Therefore this study shows that research activities may be possible with a minimal impact to the local environment in terms of chemical pollution, and that despite the scientific research done in Byers Peninsula, regulations are adequately fulfilled.

■ ASSOCIATED CONTENT

Supporting Information

Maps of vegetation and soil sampling sites, sampling details, and soil and vegetation concentration tables. This material is available free of charge via the Internet at http://pubs.acs.org

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