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Levels, Sources and Chemical Fate of Persistent Organic Pollutants in the Atmosphere and Snow along the Western Antarctic Peninsula

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1 **Levels, Sources and Chemical Fate of Persistent Organic Pollutants in the**
2 **Atmosphere and Snow along the Western Antarctic Peninsula**

3
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19
20
21 **Abstract**

22
23 The Antarctic continent is among the most pristine regions; yet various organic
24 contaminants have been measured there routinely. Air and snow samples were collected
25 during the austral spring (October - November, 2010) along the western Antarctic
26 Peninsula and analyzed for organochlorine pesticides (OCPs), polychlorinated biphenyls
27 (PCBs) and polybrominated diphenyl ethers (PBDEs) to assess the relative importance of
28 long-range transport versus local primary or secondary emissions. Highest concentrations
29 of PCBs, PBDEs and DDTs were observed in the glacier's snow sample, highlighting the
30 importance of melting glaciers as a possible secondary source of legacy pollutants to the
31 Antarctic. In the atmosphere, contaminants were mainly found in the vapor phase (> 65
32 %). Hexachlorobenzene (33.6 pg/m³), PCBs (11.6 pg/m³), heptachlor (5.64 pg/m³),
33 PBDEs (4.22 pg/m³) and cis-chlordane (2.43 pg/m³) were the most abundant
34 contaminants. In contrast to other compounds, PBDEs seem to have originated from local

35 sources, possibly the research station itself. Gas-particle partitioning for analytes were
36 better predicted using the adsorption partitioning model than an octanol-based absorption
37 approach. Diffusive flux calculations indicated that net deposition is the dominant
38 pathway for PBDEs and chlordanes, whereas re-volatilization from snow (during melting
39 or metamorphosis) was observed for PCBs and some OCPs.

40

41 **0. Capsule**

42 Highest concentrations of organic pollutants were observed in an Antarctic glacier's snow
43 sample, highlighting their importance as a possible secondary source of legacy pollutants.

44

45 **1. Introduction**

46

47 Polar regions have been regarded as clean environments with no significant pollution
48 sources. The Antarctic in particular has been considered more pristine since it is far away
49 from any urbanization, and the southern hemisphere is mainly covered by oceans and is
50 less populated. Nonetheless, starting from 1960s, persistent organic pollutants (POPs)
51 were detected in the Antarctic Peninsula (Baek et al., 2011; Bidleman et al., 1993;
52 Montone et al., 2003; Risebrough et al., 1976, 1968). It was assumed that global cold-
53 trapping, fractionation (Wania et al., 1999) and long range atmospheric transport
54 processes are the major source of POPs to the polar regions (Larsson et al., 1992;
55 Montone et al., 2003; Tanabe et al., 1983). Additionally, research stations have been
56 identified as local point sources of POPs in the Antarctic (Hale et al., 2008; Larsson et
57 al., 1992).

58 Due to its large surface area, snow can sorb significant quantities of POPs (Roth et al.,
59 2004). During aging, the snowpack can release scavenged pollutants or take up
60 compounds present in the lower layers of the atmosphere (Roth et al., 2004). The
61 degradation of POPs in the Antarctic is slow due to the low temperatures and winter
62 darkness (Corsolini, 2009). However, trapped POPs in the ice can be released to the
63 environment during spring melt causing them to bioaccumulate in the Antarctic
64 organisms (Geisz et al., 2008). Release of POPs to the atmosphere could also occur when
65 snow melts (Burniston et al., 2007). Accordingly, quantitation of the snow-air exchange
66 is deemed important to better understand the environmental fate of POPs in the polar
67 regions.

68
69 The capacity of snow to bind pollutant has also resulted in glaciers accumulating POPs
70 over time. Melting glaciers have hence been identified as potentially important secondary
71 sources of legacy pollutants. For instance, melting of Alpine glaciers have been found to
72 be a major source of OCPs in sediments and mussels (during 2005) of lakes in Italy
73 (Bettinetti et al., 2011, 2008) and Switzerland (Bogdal et al., 2009; Schmid et al., 2011).
74 Sediment cores taken from Lake Iseo, Italy and Lake Stein, Switzerland indicated that
75 although DDT was heavily used in the period from 1950 - 1970s, a peak increase was
76 observed at sediment intervals corresponding to 1990s (long after its ban) due to
77 accelerated melting of glaciers. Additionally, melting glaciers supply 50 to 97% of the
78 OCP inputs to Bow lake in Alberta, Canada (Blais et al., 2001), and were found to be a
79 probable source of DDTs in the Antarctic marine ecosystem (Geisz et al., 2008). As the
80 melting of glaciers is significantly accelerated nowadays because of the increased effect

81 of global warming, loads of POPs to the surrounding environment is expected to greatly
82 increase.

83
84 Although numerous studies investigated the levels of POPs in the Arctic atmosphere and
85 snow (Baek et al., 2011; Barrie et al., 1992; Bidleman et al., 1989; Eckhardt et al., 2007;
86 Halsall et al., 1998; Herbert et al., 2005; Hung et al., 2005, 2002, 2001), similar studies in
87 the Antarctic are limited (Baek et al., 2011; Bidleman et al., 1993; Dickhut et al., 2005;
88 Kallenborn et al., 1998; Li et al., 2012; Montone et al., 2003). Accordingly, we
89 performed this study to determine concentrations, distribution and potential sources of
90 OCPs, PCBs and PBDEs in the Antarctic atmosphere and snow. The air-snow exchange
91 of the gaseous POPs was also evaluated to determine whether atmospheric deposition is
92 still a major source of POPs to snow or the snow is currently the source of POPs to the
93 atmosphere.

94

95 **2. Materials and Methods**

96 Detailed description of the air and snow sampling, extraction and cleanup, instrumental
97 analysis and quality assurance are given in the Supplementary data. A summary is given
98 below.

99

100 **2.1. Air and Snow Sampling**

101

102 Two air samplers were used to collect 12 air samples (using GFF filters and PUF plugs)
103 during the spring (October 19 – November 11) from Palmer Station (USA) located to the
104 west of Palmer Peninsula (Figure 1). The average volume of air samples was 3082 m³,
105 which was higher than air volumes previously sampled in the Antarctica (Dickhut et al.,

106 2005; Galbán-Malagón et al., 2013; Piazza et al., 2013). Seven snow samples were
107 collected from five different locations (including two duplicates) during the same air
108 sampling period (Figure 1) from Palmer Station (n = 4), Jacob's Island, and Torgerson (n
109 = 2). See Supplementary data, Tables A1 and A2 for more information about sampling
110 periods and volumes.

111

112 **2.2. Extraction, Instrumental Analysis and Quality Assurance**

113

114 PUF plugs and GFF filters (both air and snow) were separately extracted in a Soxhlet
115 extractor after spiking with surrogates, and purified on a glass chromatographic column
116 as described in (Khairy and Lohmann, 2012). The breakthrough of the analytes from the
117 upper to the bottom PUF was corrected using the PUF-Air equilibrium partitioning
118 approach as detailed in (Zhang et al., 2012).

119

120 Extraction of the XAD-2 resin was done according to (Dickhut et al., 2005) and cleanup
121 was performed as described above for the PUFs and filters.

122

123 Twenty nine PCB congeners (PCB-8, 11, 18, 28, 44, 52, 66, 77, 81, 101, 105, 114, 118,
124 123, 126, 128, 138, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209), and
125 27 OCPs (hexachlorobenzene (HCBz), α -, β -, γ - and δ - hexachlorocyclohexane (HCH),
126 heptachlor and its epoxide, aldrin, dieldrin, oxychlordan, trans- and cis-chlordane, trans-
127 and cis-nonachlor, α - and β - endosulfan, endosulfan sulfate, endrin, endrin aldehyde,
128 endrin ketone, methoxychlor, o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDE, p,p'-DDD and
129 p,p'-DDT), and 12 PBDE congeners (BDE-2, 8, 15, 28, 30, 47, 49, 99, 100, 153, 154,

130 183) were investigated in the current study. Detailed description of the instrument
131 operational conditions can be found in the Supplementary data.

132
133 Procedural blanks and matrix spikes were included with each sample batch and were
134 carried throughout the entire analytical procedure in a manner identical to the samples.

135 Recoveries of the surrogate standards in the air filters, PUFs, snow filters and XAD-2
136 resin generally ranged from 68 to 96 %. Matrix spikes recoveries were always > 90 %
137 and relative standard deviation < 20 % (Tables A 5-6). Results of the replicate analysis of
138 the snow samples indicated that the reproducibility of the analysis ranged from 6.0 to 15
139 % for PCBs, 9.0– 19 % (OCPs), and 4.9–12 % for PBDEs. Method detection limit
140 calculations are detailed in the Supplementary data and Tables A7 - 8. The majority of
141 the congeners were not detected in the lower PUF of the air samples. Accordingly, these
142 PUFs were used as the field blanks (Dickhut et al., 2005), and this indicates that no cross
143 contamination occurred during the transportation and storage of the samples.

144
145 **2.3. Snow Properties**

146 Snow specific surface area (SSA) was calculated (Table A2) according to the following
147 equation (Burniston et al., 2007) (equation 1):

148
149
$$\text{SSA (m}^2\text{/kg)} = 2030 \exp (-4.1 \times \rho) \quad (1)$$

150
151 where ρ is the density of the snow (kg/m³). Density was calculated according to the
152 weight and volume of the snow samples (Table A2).

153
154 **2.4. Air-Snow Gas Exchange Flux**

155 The dry gas exchange flux at the surface was derived as follows (equation 2) (Hansen et
156 al., 2006; Thibodeaux and Mackay, 2010):

157

$$158 \quad F \text{ (pg/m}^2\text{/day)} = K_m \left(\frac{C_s}{K_{SA}} - C_g \right) \quad (2)$$

159

160 where K_m is the overall mass transfer coefficient (m/day), K_{SA} is the snow-air
161 partitioning coefficient (dimensionless), C_s is the measured snow concentration (pg/m³)
162 and C_g is the gaseous atmospheric concentration of POPs (pg/m³). C_s/K_{SA} calculates the
163 concentration of POPs in the snow pore space. See Supplementary Data for more details
164 on the flux calculations.

165

166 **3. Results and Discussion**

167 **3.1. Concentrations of POPs in the Snow Samples**

168 Two fractions were analyzed for the snow samples – particle-bound POPs, and the
169 ‘snowmelt’ fraction (melting the snow and passing the snow melt on XAD-2 resin
170 column). The latter combines POPs adsorbed to the crystal surface of the snow, absorbed
171 in the quasi liquid layer or incorporated in the solid ice.

172

173 Overall, concentrations of all POPs in the snowmelt samples were significantly higher in
174 the glacier sample (Kruskal-Wallis One Way ANOVA on Ranks, $p < 0.05$).

175 Concentrations of HCHs, HCBz, DDTs, PCBs and PBDEs were 1.4-23 times greater than
176 at the other locations. This confirms earlier suspicions that melting glaciers could have
177 become an important secondary source of legacy pollutants to the western Antarctic
178 Peninsula. For the other locations, higher concentrations (after the glacier sample) of
179 POPs were observed at Torgerson Island and Old Palmer located to the northwest of

180 Palmer Station. The least OCP concentrations were always observed at Jacob Island
181 located to the south of the Palmer Station (Figure 1), whereas the backyard of the
182 research station showed the lowest concentrations of PCBs and PBDEs in the snowmelt
183 samples. In the particulate phase samples, concentrations of HCBz, p,p'-DDT and PCBs
184 at Torgerson Island were 2.0-14 times greater than concentrations detected at all the other
185 locations including the glacier. Torgerson is a rocky Island and could possibly be richer
186 in organic matter compared to the other locations. In contrast, concentration of p,p'-DDE
187 at the glacier was 3.0-16 times greater than concentrations detected at the other samples.
188 Chlordanes and PBDEs showed comparable concentrations at all the locations. Most of
189 the OCPs, and PCBs were found in the snowmelt as was previously observed for OCPs
190 in the Canadian melting glaciers (Blais et al., 2001) due to the poor organic matter in the
191 glacial clay. In contrast, a significant portion of PBDEs was bound to particles indicating
192 either their different emission sources and/or a different particle-snowmelt partitioning
193 behavior than PCBs. Ratios of OCPs confirmed their legacy origin whereas for PBDEs,
194 the existence of possible local sources was indicated (see discussion below and
195 Supplementary data for more details).

196

197 **3.1.1. OCPs**

198 DDTs (sum of the six isomers) showed the highest concentrations among all the
199 investigated OCPs at all the locations with concentrations ranging from 30 pg/L (Jacob's
200 Island) to 412 pg/L (glacier). Aldrin, dieldrin, oxychlordane, endosulfans, endrin, endrin
201 aldehyde, endrin ketone and methoxychlor were <LOD in all the samples. Snowmelt
202 concentrations (in pg/L water) of OCPs are given in Table A9.

203

204 HCBz, trans-chlordane, cis-chlordane, p,p'-DDE, p,p'-DDD and p,p'-DDT were the only
205 detected OCPs in the particulate phase. HCBz showed the highest concentrations among
206 the other detected OCPs in all the samples with values ranging from 10 pg/L (Palmer
207 Backyard) to 46 pg/L (Torgerson Island) followed by p,p'-DDE (3.5 - 55 pg/L), p,p'-DDD
208 (<LOD - 20 pg/L) and cis-chlordane (7.0 - 19 pg/L). Particulate phase concentrations of
209 OCPs in the snow samples are given in Table (A10).

210

211 **3.1.2. PCBs**

212 Snowmelt PCB concentrations ranged from 300 pg/L (Palmer Backyard) to 1,100 pg/L
213 (glacier) with an average concentration of 770 pg/L (Table A11). The most abundant
214 PCB congeners were PCB 8, 11, 28, 44, 52, 66, 101, 153, 138, 180, 187 and 206 (Table
215 A11). Except for the glacier sample, all the other samples were dominated by tri- through
216 penta-chlorinated biphenyls comprising 63 - 72 % of the total detected snowmelt
217 concentrations (Figure 2A). In the glacier sample, comparable contributions from di-
218 through hepta-chlorinated biphenyls were observed (14 - 20 %).

219

220 Particulate phase concentrations of PCBs ranged from 78 pg/L (Jacob Island) to 860 pg/L
221 (Torgerson Island) with an average concentration of 270 pg/L. Detected concentrations of
222 PCB congeners at Torgerson Island (Table A12) were significantly higher (Kruskal-
223 Wallis One Way ANOVA on Ranks, $p < 0.05$) than detected concentrations at the other
224 samples. Samples were dominated by tetra-through hepta-chlorinated biphenyls
225 comprising 67 - 91 % of the total detected concentrations (Figure 2B). Unlike the
226 snowmelt samples, significant contribution from the hepta-chlorinated biphenyls was
227 observed in the particulate samples.

228

229 3.1.3. PBDEs

230 Snowmelt concentrations of PBDEs in the snow samples are given in Table (A13).
231 Concentrations ranged from 20 pg/L (Palmer Backyard) to 470 pg/L (glacier) with an
232 average concentration of 161 pg/L. BDE-2 and 49 were <LOD in the samples. The most
233 abundant PBDE congeners (Figure 2C) were BDE 47 (11 - 293 pg/L) and BDE 99 (3.0 -
234 106 pg/L). Both comprised 68 - 85 % of the total detected PBDE concentrations in the
235 snow samples.

236
237 Particulate phase concentrations of PBDEs are shown in Table (A14). Concentrations
238 generally ranged from 94 pg/L (Jacob Island) to 213 pg/L (glacier) with an average
239 concentration of 180 pg/L. BDE 2, 8 and 15 were <LOD in all the samples. All the
240 samples were dominated by BDE 47 and 99 comprising 74 - 78 % of the total
241 concentrations (Figure 2D). However, in contrast to the snowmelt samples,
242 concentrations of BDE 99 (51 - 89 pg/L) in the particulate phase were higher than BDE
243 47 (22 - 80 pg/L).

244
245 Of the penta BDE congeners, BDE-100 has the longest photodegradation half-life
246 followed by BDE-47 and BDE-99, which is the most photodegradable congener (Dickhut
247 et al., 2012; Eriksson et al., 2004; Fang et al., 2008). Accordingly, calculated ratios for
248 these three congeners could indicate whether the source of PBDE is long range transport
249 or from local emissions. Calculated ratios of BDE-47/BDE-100 (snowmelt: 8.0 - 49;
250 particulate phase: 3.0 - 5.0) and BDE-99/BDE-100 (snowmelt: 4.0 - 13; particulate phase:
251 5.0 - 8.0) in the snow samples were within or higher than values calculated for the penta
252 BDE commercial formulations (Dickhut et al., 2012; La Guardia et al., 2006) (BDE-

253 47/BDE-100: 2.9-5.5; BDE-99/BDE-100: 3.7-5.4) implying that PBDEs were emitted
254 from local sources (research stations) and did not undergo long range transport.

255

256 **3.2. Atmospheric Concentrations of POPs**

257 Gaseous concentrations of OCPs, PCBs and PBDEs detected at the Palmer station
258 sampling site are given in Tables A15, A16 and A17 respectively. Based on average
259 gaseous concentrations, the following descending order was observed: HCBz (34 pg/m³)
260 > Σ PCBs (12 pg/m³) > heptachlor (5.6 pg/m³) > Σ PBDEs (4.2 pg/m³) > cis-chlordane
261 (2.4 pg/m³). All the other detected OCPs showed concentrations < 2.0 pg/m³. Aldrin,
262 dieldrin, methoxychlor, endrin, endrin aldehyde, endrin ketone, DDD (o,p'- and p,p'-
263 isomers), β - and δ -HCH and β - endosulfan were <LOD in all the samples (Table A15).

264

265 In the particulate phase, PCBs showed the highest average concentrations among all the
266 investigated POPs at the two sites (S1: 4.2 pg/m³; S2: 3.1 pg/m³) followed by PBDEs (0.8
267 pg/m³). All the other detected OCPs in both samples showed comparable concentrations
268 (Table A18) with values always < 0.3 pg/m³. Particle-bound concentrations are given in
269 Tables A18, A19 and A20 respectively.

270

271 Ratios of OCPs calculated for the gaseous and particulate phase samples indicated aged
272 sources, whereas PBDE ratios indicated local sources possibly from the research stations.

273

274 **3.2.1. OCPs**

275 Concentrations of gaseous HCBz were significantly higher than concentrations of all the
276 other detected OCPs ($p < 0.001$). A similar finding was previously observed in the
277 Antarctic Peninsula (Dickhut et al., 2005) and at the Norwegian Troll research station
278 (Kallenborn et al., 2013). α - and γ -HCH were the only detected isomers in the gas phase.

279 No statistical significant difference was observed between detected concentrations of α -
280 and γ -HCH isomers.

281
282 Unlike for the Arctic air, few studies have reported concentrations of endosulfans in the
283 Antarctic atmosphere (Baek et al., 2011; Pozo et al., 2006). α -endosulfan was the only
284 detected isomer in the gaseous samples at Palmer station at concentrations ranging from
285 1.1 pg/m^3 to 3.4 pg/m^3 (Table A9), which was similar to the finding at King George
286 Island (Baek et al., 2011).

287
288 Chlordanes include trans- and cis-chlordane, cis- and trans-nonachlor, oxychlordane,
289 heptachlor and its epoxide. Concentrations of chlordanes ranged from 10 pg/m^3 to 18
290 pg/m^3 with an average concentration of 13 pg/m^3 . Based on average concentrations,
291 heptachlor was the second most abundant OCP in the gaseous samples with
292 concentrations significantly higher than concentrations of trans- and cis-chlordane ($p <$
293 0.001) suggesting the use of heptachlor as a pesticide (not as a component of the
294 technical chlordane mixture) (see Supplementary data for comparison with gaseous POP
295 concentrations previously reported for the Antarctic) (Shunthirasingham et al., 2010).

296
297 p,p'-DDE, o,p'-DDE and p,p'-DDT were the only detected isomers in the current study.
298 Concentrations of p,p'-DDE (0.3 - 1.4 pg/m^3) were significantly higher ($p <$ 0.001) than
299 detected concentrations of gaseous o,p'-DDE (0.05 - 0.2 pg/m^3) and p,p'-DDT (0.05 - 0.1
300 pg/m^3) indicating aged DDT sources.

301
302 In the particulate phase, only α -HCH, γ -HCH, HCBz, trans-chlordane, cis-chlordane and
303 p,p'-DDE were detected in the samples (Table A18). For sample 1 (S1; gaseous phase

304 and particulate phase), > 90 % of the total concentrations for the detected OCPs were
305 found in the gaseous phase.

306

307 **3.2.2. PCBs**

308 \sum_{29} PCB concentrations in the gaseous samples ranged from 5.4 pg/m³ to 16 pg/m³ with
309 an average concentration of 12 pg/m³. Detected concentrations of PCBs in the current
310 study were lower than concentrations previously reported for the Antarctic (see
311 Supplementary data for more details). Gaseous concentrations of PCBs are shown in
312 Table A16.

313

314 The most abundant congeners in the gas phase samples were PCB 11 (2.0 pg/m³), PCB 8
315 (1.4 pg/m³), and PCB 28 (1.2 pg/m³). PCB 11 concentrations (1.1 - 3.1 pg/m³) were the
316 highest among all the detected congeners comprising on average 21 % of the total PCB
317 concentrations. Similarly, PCB 11 exhibited the highest concentrations among the
318 investigated PCB congeners in King George Island during 2005-2007 (Baek et al., 2011),
319 and comprised on average 16 % of the total atmospheric PCB concentrations measured in
320 the Antarctic (Vecchiato et al., 2015). However, contributions in the Arctic were much
321 lower (Baek et al., 2011) indicating that the sources of this non-Aroclor congener may be
322 concentrated in the Southern Hemisphere. PCB 11 is found in paints/pigments (Hu et al.,
323 2008) and has been detected in the atmospheric environments of urban centers and the
324 Great Lakes (Hu et al., 2008; Khairy et al., 2015). PCB 11 can also be generated from the
325 degradation of higher chlorinated PCB congeners such as PCB 77, 12 and 169 (Vecchiato
326 et al., 2015), which were all <LOD in the present study. Accordingly, we assume that
327 PCB 11 is emitted from local sources probably from the research station. More
328 investigation is needed to support our assumption. Gaseous samples were dominated by

329 di-, tri- and tetra-chlorinated biphenyls (Figure A1A) comprising on average 38, 20 and
330 15 % respectively of the total PCB concentrations. Penta-, hexa- and hepta-chlorinated
331 biphenyls showed lower contributions (7.5 - 11 %). Octa-, nona- and deca-chlorinated
332 congeners were not detected in the gaseous samples. This observed pattern of the
333 homologue groups indicates that long range atmospheric transport is probably the major
334 source of PCBs (Gambaro et al., 2005). Dominance of the lower chlorinated PCBs was
335 previously observed in the Antarctic at Signy Island (Kallenborn et al., 1998), King
336 George Island (Li et al., 2012), Brazilian Research Station (Montone et al., 2003), Terra
337 Nova Bay (Gambaro et al., 2005) and the Korean Research Station (Choi et al., 2008).

338
339 In the particulate phase (Table A19), a different pattern was observed. Particulate phase
340 PCBs ranged from 2.1 - 5.2 pg/m³ and 1.3 - 4.4 pg/m³ at S1 and S2 respectively. In both
341 samples, PCB 187 (S1: 0.6 - 2.0 pg/m³; S2: 0.4 - 0.9 pg/m³) and 180 (S1: 0.6 - 1.3 pg/m³;
342 S2: 0.4 - 0.8 pg/m³) were the dominant congeners. As for the distribution of the
343 homologous groups, both particulate phase samples showed comparable patterns with
344 slightly higher concentrations of hexa- and hepta-chlorinated biphenyls observed at S1
345 (Figure A1A). Interestingly, octa-chlorinated biphenyls were <LOD in the gas and
346 particulate phases. However, PCB 206 and 209 were only detected in the particulate
347 phase samples. In both samples, hepta-chlorinated biphenyls dominated the profiles
348 comprising on average 44 % and 39 % of the total PCB concentrations at S1 and S2
349 respectively. Di- through hexa-chlorinated biphenyls showed comparable contributions in
350 both samples (Figure A1A), (7.0 % - 12 % at S1 and 8.0 % - 13 % at S2). Nona- and
351 deca-chlorinated biphenyls had only minor contributions (< 5.0 %).

352

353 3.2.3. PBDEs

354 Gaseous Σ_{12} PBDE concentrations ranged from 1.4 - 7.6 pg/m^3 with an average
355 concentration of 4.2 pg/m^3 (Table A17). BDE-2, 8, 15, 30 and 183 were <LOD in all the
356 samples. > 70 % of the detected PBDE congeners in the present study were found in the
357 gaseous phase. Particulate phase concentrations in the present study ranged from 0.4 - 1.3
358 pg/m^3 (average: 0.8 pg/m^3) and 0.3 - 1.2 pg/m^3 (average: 0.8 pg/m^3) at S1 and S2
359 respectively. BDE-2, 8, 15, 30 and 49 were found <LOD in both samples, whereas BDE-
360 153, 154 and 183 were <LOD only at S1 (Table A20). In the gaseous and particulate
361 phases, BDE-47 was the dominant congener comprising on average 41 - 52 % of the total
362 PBDE concentrations followed by BDE-99 (24 - 35 %). BDE-100 and 28 showed
363 comparable contributions in the gaseous phase (~ 7.0 % each) and the particulate phase
364 of S2 (~ 10 % each). BDE-153, 154 and 183 showed lower contributions (Figure A1B).
365 BDE-47 and 99 were the dominant congeners detected in gaseous phase of the Arctic air
366 (Shen et al., 2006; Su et al., 2007; Wang et al., 2005), whereas BDE-28 and 17 (not
367 included in the present study) were the dominant congeners at King George, Antarctic (Li
368 et al., 2012). BDE-209 (not included in the present study) was the dominant congener in
369 the particulate phase samples collected at Palmer station in 2001 – 2002 (Dickhut et al.,
370 2012). However, average concentrations (S1 and S2) of particulate phase BDE-47 ($0.4 \pm$
371 $0.1 \text{ pg}/\text{m}^3$), 99 ($0.3 \pm 0.1 \text{ pg}/\text{m}^3$) and 100 ($0.07 \pm 0.02 \text{ pg}/\text{m}^3$) were in very good
372 agreement with values observed in 2001 - 2002 (BDE-47: $0.3 \pm 0.08 \text{ pg}/\text{m}^3$; BDE-99: 0.3
373 $+ 0.1 \text{ pg}/\text{m}^3$; BDE-100: $0.06 + 0.03 \text{ pg}/\text{m}^3$) (Dickhut et al., 2012).
374 The average ratio values of BDE-47/BDE-100, BDE-47/BDE-99 and BDE-99/BDE-100
375 in the present study were 7.9, 2.1 and 3.7 respectively for the gaseous phase samples, and

376 5.1, 1.4 and 3.8 for the particulate phase samples. Particulate phase values in the present
377 study were higher than values previously reported for Palmer station during 2001-2002
378 (Dickhut et al., 2012) (BDE-47/BDE-100: 3.6; BDE-99/BDE-100: 2.5) but were within
379 the range observed in the commercial penta BDE formulations (Dickhut et al., 2012; La
380 Guardia et al., 2006) and the Arctic air (BDE-47/BDE-100: 5.9; BDE-47/BDE-99: 1.1;
381 BDE-99/BDE-100: 5.4) (Dickhut et al., 2012). For the gaseous phase samples, the ratio
382 BDE-47/BDE-100 was higher than the commercial formulation, whereas the other two
383 ratios were within the values of the commercial formulation. Based on our findings,
384 PBDEs detected at Palmer Station were not subjected to significant photodegradation. In
385 other words, PBDEs were emitted from local sources and did not undergo long range
386 transport. Accordingly, we suggest that the station itself is the major source of PBDEs
387 which probably overwhelmed the long range transport source. Research stations have
388 been regarded as possible local sources of PBDEs (Hale et al., 2008) and other POPs
389 (Larsson et al., 1992; Risebrough et al., 1990).

390

391 **3.3. Gas- Particle partitioning of POPs**

392 Particle-air partitioning coefficients (K_p) were calculated in the present study based on
393 the Junge - Pankow adsorption partitioning model (using the subcooled liquid vapor
394 pressure, P_L) and the absorption partitioning model (using octanol-air partitioning
395 coefficient, K_{OA}) (Finizio et al., 1997; Harner and Bidleman, 1998). Detailed description
396 of the calculations, sources of K_{OA} and P_L and their temperature correction process can be
397 found in the Supplementary data. As concentrations of the total suspended particulates
398 (TSP) and organic matter content were not measured in the present study, we used

399 literature values measured for Antarctic aerosols (2.4 pg/m^3) (Ali et al., 2015; Mazzera et
400 al., 2001).

401
402 As shown in Figure (3A), particle-bound fractions of PCBs, OCPs and BDE-28 were
403 much higher than the absorption model predicted values, whereas BDE- 47, 99 and 100
404 were generally in better agreement. Measured particle bound fractions of PCBs, OCPs
405 BDE-28 and 47 showed on the other hand better agreement with the predicted values
406 using the adsorption partitioning model (Figure 3B). In contrast, much lower particle-
407 bound fractions were measured for BDE-99 and 100 (pentabrominated diphenyl ether)
408 compared to the predicted curve. This implies that the adsorptive partitioning model (P_L)
409 is generally a better descriptor of particle-air partitioning of POPs in the present study as
410 was previously indicated for some POPs in the UK (Lohmann et al., 2000) (see
411 Supplementary data for more details).

412
413 If the major source of POPs in the Antarctic was long range transport, then the gas-
414 particle partitioning should have approached equilibrium [slopes $\log K_{OA} - \log K_p$ and \log
415 $P_L - \log K_p \sim -1(-1)$]. In the present study, slopes (Table A21) were much shallower than -1
416 (~ -0.2 for PBDEs, ~ -0.4 for PCBs and OCPs). We hypothesize that lower chlorinated
417 PCBs and penta- BDEs were emitted from local sources, which needed to re-equilibrate
418 with the clean background particles or those freshly emitted in the Antarctic. This in turn
419 will alter the established gas - particle partitioning causing the slopes to be shallower.
420 The higher measured particle bound fraction of the lower chlorinated biphenyls and the
421 lower measured values for penta- BDEs compared to the predicted ones could be either
422 the reason of the difference in volatility (lower chlorinated biphenyls will re-equilibrate

423 faster with freshly emitted particles than PBDEs) or difference in the local sources. As
424 we suggested earlier, the research activities (station, field work) could be a major source
425 of PBDE at the western Antarctic Peninsula (based on the calculated ratios and the
426 photodegradation half-lives of the penta- BDE congeners). For PCBs and OCPs, we
427 suggest that revolatilization from the snow as it ages and/or melt is a secondary source in
428 the Antarctic at Palmer station, especially for the lower chlorinated congeners which are
429 more volatile. This assumption will be further investigated in the air-snow gaseous
430 exchange section (see below).

431

432 **3.4. Comparison between Atmospheric and Snow Concentrations of POPs**

433 Measured snow concentrations (particulate phase and snowmelt) were compared with the
434 measured atmospheric concentrations in the present study assuming that atmospheric
435 deposition is the major source of POPs present in the snow. To test this assumption, snow
436 concentrations of POPs in the interstitial pore spaces (C_{is}), snowmelt (C_{sm}) and
437 particulates (C_{sp}) were compared to atmospheric gaseous concentrations (C_g ; dry gaseous
438 deposition), scavenged gaseous POPs by snow (wet gaseous deposition) and scavenged
439 particulate phase POPs by snow (wet particle deposition) respectively. Dry gaseous
440 deposition will be discussed later in the flux calculation section. For the wet gaseous
441 deposition, snowmelt concentrations were predicted (C_{psm}) from atmospheric
442 concentrations as follows (equation 1):

$$443 \quad C_{psm} = W_g \times C_g \quad (1)$$

444 where,

445 W_g is the gas scavenging coefficient and

446 C_g is the atmospheric gas phase concentrations of POPs.

447
448 W_g is calculated as (equation 2) (Hansen et al., 2006):

449

$$450 \quad W_g = K_{ia} \times SSA_{in} \times \rho_w \quad (2)$$

451
452 where, SSA_{in} is the specific surface area of fresh snow ($0.12 \text{ m}^2/\text{g}$) (Burniston et al.,
453 2007), and ρ_w is the density of water ($10^6 \text{ g}/\text{m}^3$) (Hansen et al., 2006).

454
455 Similarly, snow particle phase concentrations (C_{psp}) were predicted according to equation
456 3:

$$457 \quad C_{psp} = W_p \times C_{sp} \quad (3)$$

458
459
460 where, W_p is the particle scavenging coefficient (10^5) (Lei and Wania, 2004).

462
463 Results obtained for Palmer Backyard station are shown in Figure (4). Results of the
464 three other locations are presented in the Supplementary Data (Figures A2 - A4).

465
466 Snowmelt concentrations of PBDEs predicted from the wet scavenging process of the
467 atmospheric gas phase were significantly higher ($p < 0.001$) than measured
468 concentrations at all the sampling locations (Figures 4A, A2A, A3A, A4A). Additionally,
469 detected PBDE congeners in the atmospheric samples were different from the snowmelt
470 samples. This implies that either the wet scavenging of gaseous PBDEs is probably not
471 highly efficient or that prolonged snow events caused dilution of contaminant
472 concentration in the snow. Additionally, the difference in the congeners patterns suggest
473 different sources affecting the atmosphere and snow. A similar pattern was observed for
474 the majority of OCPs (Figures 4B, A3B, A4B). However at Old Palmer (Figure A3B),
475 some OCPs (o,p'-DDE, o,p'-DDD, o,p'-DDT, p,p'-DDD, p,p'-DDT, trans-nonachlor,

476 heptachlor and its epoxide) were measured in the snowmelt samples but were <LOD in
477 the atmospheric gas phase samples. This finding is another indication of the different
478 sources of POPs in the atmosphere and the snow. We assume that measured OCPs in the
479 snowmelt that were not detected in the atmospheric samples represents old contamination
480 that was probably incorporated in the crystalline structure of snow as it aged and
481 undergone metamorphosis knowing that the detected OCPs were banned more than three
482 decades ago. In contrast to PBDEs and OCPs, measured snowmelt concentrations of
483 PCBs (Figures 4C, A2C, A3C, A4C), were higher than predicted concentrations
484 especially for the lower chlorinated PCB congeners (di- through penta- chlorinated
485 biphenyls). It is important to mention that the snow analyzed in the current study
486 represent a composite sample of various layers at each sampling location to a depth of 15
487 cm. Snow physical properties (density, specific surface area, porosity) greatly change
488 within hours after snowfall event (Herbert et al., 2005), which will affect the sorbed
489 amount of vapor phase POPs to snow (Herbert et al., 2006). Loss or transformation of
490 analytes in snow could also occur as a result of the photodegradation process (Herbert et
491 al., 2006). Although these processes were not investigated in the present study, it should
492 be considered when comparing between measured and predicted vapor phase POPs in the
493 snow.

494 Wet scavenging of particulate phase PBDEs were found to partially account for the
495 PBDEs found in the snow (particulate phase) as measured concentrations were an order
496 of magnitude higher than predicted values for the majority of the congeners (Figures 4D,
497 A2D, A3D, A4D). Additionally, some PBDEs (BDE-30, 49, 153, 154 and 183) were only
498 found in the snow samples, which as observed in the snowmelt imply the existence of

499 another source other than atmospheric deposition that contributes to the levels of PBDEs
500 in the snow. In contrast, predicted particle bound OCP (except HCBz) (Figures 4E, A2E,
501 A3E, A4E) and PCB concentrations (Figures 4F, A2F, A3F) were significantly higher (p
502 < 0.05) than measured particle bound concentrations. Predicted HCBz concentrations
503 were in good agreement with measured ones. At Torgerson Island, measured particle
504 bound PCBs in snow were higher than predicted concentrations (Figure A4F). W_p was
505 not measured in the present study and estimates available in literature varies greatly
506 (Franz and Eisenreich, 1998; Wania et al., 1999). The process of repartitioning of POPs
507 to particles in snow and the fate of particle bound POPs in snow is also unknown
508 (Herbert et al., 2006). These two points should be considered when performing the
509 comparison between measured and predicted particle bound POP concentrations in snow.

510

511 **3.5. Diffusive Fluxes of Gaseous POPs**

512 Calculated diffusive fluxes ($\text{pg/m}^2/\text{d}$) for gaseous POPs are shown in Figure (5).
513 Calculated fluxes for PBDE (Figure 5A), chlordanes, α -endosulfan (Figure 5C) were
514 negative indicating that these contaminants are depositing from the atmosphere.

515

516 All the PCBs (Figure 5B), HCBz, heptachlor and DDTs (Figure 5C) showed positive
517 fluxes indicating re-volatilization from snow (when it melts or undergo metamorphism)
518 to the atmosphere implying that the Antarctic snow is acting as a source of PCBs and
519 OCPs to the atmosphere. The highest net volatilization flux was calculated for HCBz
520 ($200 - 1040 \text{ pg/m}^2/\text{d}$), followed by PCB 28/31 ($340 - 900 \text{ pg/m}^2/\text{d}$), PCB 5/8 ($200 - 580$
521 $\text{pg/m}^2/\text{d}$) and PCB 11 ($120 - 460 \text{ pg/m}^2/\text{d}$), whereas the highest net depositional flux was
522 calculated for trans-nonachlor (-5.0 to $-15 \text{ pg/m}^2/\text{d}$) followed by cis-chlordane (-3.5 to -

523 7.0 pg/m²/d). All the other contaminants that showed net depositional fluxes had values <
524 -5.0 pg/m²/d. Except for BDE-47, and 99, calculated fluxes for the other congeners were
525 within the uncertainty range, and hence treated as being at or near equilibrium (between
526 snow and air). No great variations (in magnitude and directions) were observed for fluxes
527 calculated for POPs at the four sampling locations (Figure 5). For PCBs (Figure 5B),
528 volatilization fluxes for the lower chlorinated congeners (di- through tetra-) were much
529 higher than fluxes calculated for the higher chlorinated ones (penta- through deca-),
530 which is expected when considering the volatility (vapor pressure) of the PCB congeners.

531

532 **4. Conclusions**

533 We investigated the concentrations of PBDEs, OCPs and PCBs in the atmosphere and
534 snow from the western Antarctic Peninsula. Our results indicated that PBDEs were
535 probably emitted from the research station (local source). However, the atmospheric
536 samples were collected only at one location, which is not enough to support our
537 assumption. Seasonal samples should be collected to have a better image about the
538 temporal variations and chemical fate of POPs in the atmosphere. Due to the difficulties
539 associated with the conventional active sampling technique, the use of passive samplers
540 would be a cost effective way to conduct a long term monitoring of POPs in the Antarctic
541 atmosphere. Although only a few snow samples were investigated in this study, we tried
542 to investigate the wet and dry deposition of gaseous and particle bound POPs and to
543 quantify the diffusive gaseous fluxes of POPs between the air and the snow. Based on
544 the difficulties experienced, the following should be considered in the future studies: a)
545 the fate of POPs in snow should be investigated directly after the snowfall. Additionally,
546 temporal variations in the snow physical properties and the sorbed levels of POPs should

547 also be considered; b) Snow sampling should be performed seasonally in parallel with the
548 atmospheric sampling due to the great variation in the expected levels of POPs both in
549 the atmosphere and snow due to the temperature variations; c) wet scavenging should be
550 investigated with more details to obtain better estimates of the scavenging coefficients; d)
551 Snow cores should be considered in the future studies to investigate and quantify
552 (magnitude and direction) the diffusive transport of POPs in snow.

553

554 **Supplementary material**

555

556 Supplementary data associated with this article can be found in the online version.

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558

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563

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565

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