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# Persistent organic pollutants in the Atlantic and southern oceans and oceanic atmosphere

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1 **Persistent Organic Pollutants in the Atlantic and Southern Oceans and Oceanic**  
2 **Atmosphere**

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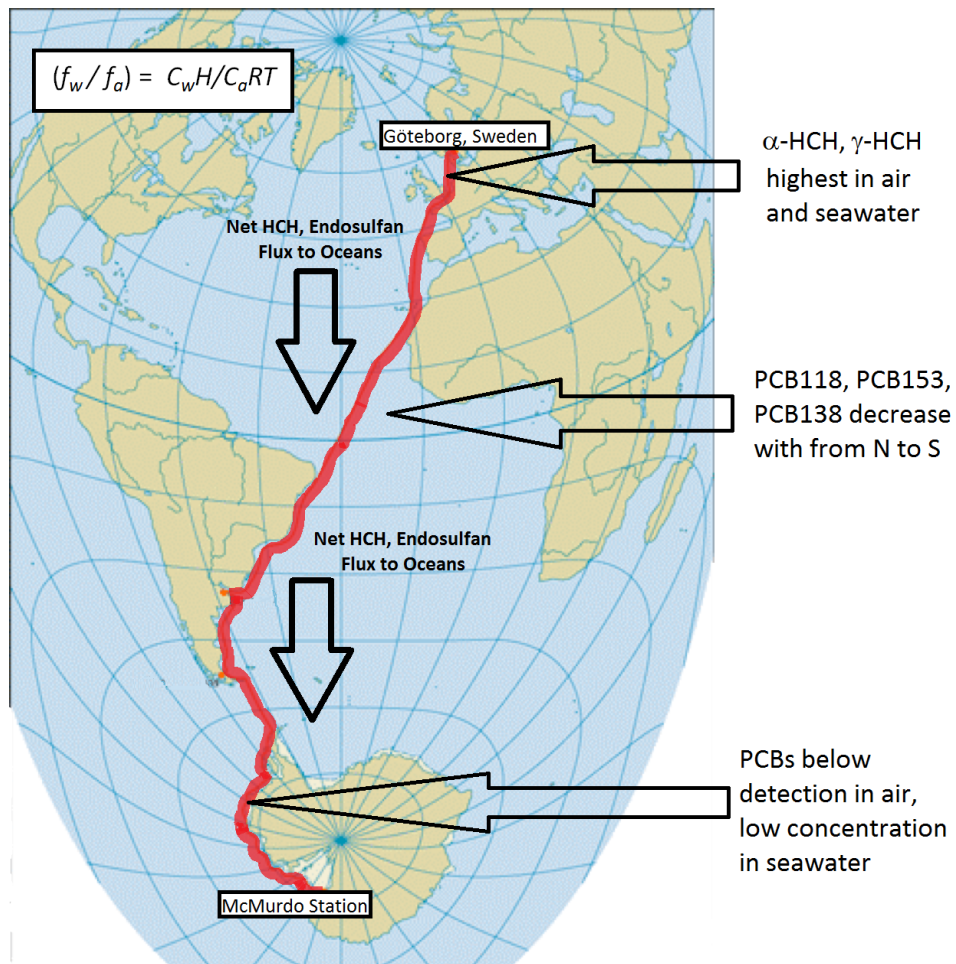
29 **Highlights**

- 30 • Samples were collected between Sweden and Antarctica about R/V Oden in 2007
- 31 • Air and seawater samples were analyzed for persistent organic pollutants (POPs)
- 32 • Air and seawater POP concentrations were higher in the northern hemisphere
- 33 • Net fluxes for  $\alpha$ -HCH,  $\gamma$ -HCH, and Endosulfan were from air to seawater
- 34 • Ocean continues to act as a sink for legacy pesticides

35

36

## 36 Graphical Abstract



**38 Abstract**

39 Persistent organic pollutants (POPs) continue to cycle through the atmosphere and  
40 hydrosphere despite banned or severely restricted usages. Global scale analyses of POPs are  
41 challenging, but knowledge of the current distribution of these compounds is needed to  
42 understand the movement and long-term consequences of their global use. In the current study,  
43 air and seawater samples were collected Oct. 2007- Jan. 2008 aboard the Icebreaker Oden en  
44 route from Göteborg, Sweden to McMurdo Station, Antarctica. Both air and surface seawater  
45 samples consistently contained  $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH),  $\gamma$ -HCH, hexachlorobenzene  
46 (HCB),  $\alpha$ -Endosulfan, and polychlorinated biphenyls (PCBs). Sample concentrations for most  
47 POPs in air were higher in the northern hemisphere with the exception of HCB, which had high  
48 gas phase concentrations in the northern and southern latitudes and low concentrations near the  
49 equator. South Atlantic and Southern Ocean seawater has a high ratio of  $\alpha$ -HCH to  $\gamma$ -HCH,  
50 indicating persisting levels from technical grade sources. The Atlantic and Southern Ocean  
51 continue to be net sinks for atmospheric  $\alpha$ -,  $\gamma$ -HCH, and Endosulfan despite declining usage.

52

**53 Key words**

54 POPs, organochlorine pesticides, air-sea flux, hexachlorocyclohexane, Endosulfan

55

## 55 **Introduction**

56 International regulation of persistent organic pollutants (POPs) is controlled by the  
57 Stockholm Convention of the United Nations Environment Programme (UNEP, 2016), which  
58 originally identified twelve pollutants to be monitored globally and their emissions to the  
59 environment reduced. This list included organochlorine pesticides including chlordane,  
60 hexachlorobenzene, and DDT, as well as polychlorinated biphenyls and polychlorinated dibenzo-  
61 *p*-dioxins and –furans. Additional chemicals identified as POPs continue to be added to this  
62 international treaty, including hexachlorocyclohexane (HCH) and Endosulfan (UNEP, 2016).  
63 POPs are distributed worldwide by various partitioning processes across interfaces between, e.g.,  
64 air, water, and biota in aquatic and terrestrial environments (Jones and De Voogt, 1999; Wania  
65 and Mackay, 1996). Global scale studies of the atmospheric transport and air-sea exchange of  
66 POPs have had a major impact on our understanding of POP movement in the environment and  
67 the impact of POPs on remote locations (Dachs et al., 2002; Iwata et al., 1993; Pozo et al., 2009,  
68 2006). According to the hypothesis of cold condensation, semi-volatile organic pollutants are  
69 constantly cycled from the gaseous phase in warmer latitudes to the cooler polar regions and  
70 deposited in aquatic and terrestrial environments where revolatilization is minimal (Wania and  
71 Mackay, 1996). Such chemicals have been found to accumulate in polar regions where they  
72 bioaccumulate in biota and may reach concentrations in top predators that potentially have  
73 adverse effects (Braathen et al., 2004; Brault et al., 2013; Goerke et al., 2004; Oskam et al.,  
74 2004; Sonne, 2010). Although substantial work has been done in the Arctic to monitor these  
75 compounds and their impacts, studies on POP distribution and movement in the Southern  
76 hemisphere and particularly the Antarctic have been much more limited. Changes in polar  
77 regions are of particular interest as legacy use compounds may be released to the aquatic

78 environment and atmosphere during the melting of ice sheets and general warming (Cabrerizo et  
79 al., 2013; Cincinelli et al., 2016; Geisz et al., 2008; Goerke et al., 2004).

80 Information on air-sea fluxes of individual POPs is important to understand if a particular  
81 area of the sea acts as a sink or a source, which, in turn, is essential for the understanding of the  
82 global distribution and environmental fate of these contaminants. Without environmental  
83 distribution and fate information, environmental risks cannot be estimated. A particular  
84 advantage of long geographical transects is that information from a wide range of environmental  
85 conditions and distances from anthropogenic sources can be collected.

86 This study took place during the expedition “Oden Southern Ocean 2007-2008” (OSO  
87 07-08). The objective was to collect information on the distribution and air-sea fluxes of several  
88 POPs in a north-south transect of the Atlantic Ocean and a west-east transect in the Southern  
89 Ocean between the Western Antarctic Peninsula and the Ross Sea.

90

## 91 **Methods**

92 **Sample Collection.** Air and surface seawater samples were collected aboard the Swedish  
93 Icebreaker Oden on a transect between Göteborg, Sweden and McMurdo Station, Antarctica  
94 from 23 October through 4 January 2008 (**Figure 1, Table S1**). Samples were analyzed for 26  
95 current and past-use organochlorine pesticides and 21 polychlorinated biphenyls (PCBs) using  
96 gas chromatography combined with mass spectrometry (**Table S2**). Gas and dissolved phase  
97 concentrations were then used to calculate air-sea fluxes.



98

99 **Figure 1.** Cruise track for the Swedish Icebreaker Oden, Oct. 2007 – Jan. 2008.

100

101 Air samples were collected using two high volume samplers consisting of 150 mm diameter  
102 glass fiber filters (GFFs) to collect aerosol samples and two polyurethane foam (PUF) plugs (8  
103 cm diameter x 7.6 cm) to collect gas phase samples of approximately 500 m<sup>3</sup>. The air samplers  
104 were deployed in front of Deck 5, approximately 18 m above the sea surface with the bulk of the  
105 bridge shielding the samplers from the stack and, except during storms, out of the sea spray.  
106 Sampling took place only while under way, but regardless of wind direction. Prior to use, the  
107 GFFs were baked for 4 h at 400 °C and the PUFs Soxhlet extracted with acetone and petroleum



108 ether (24 h each). GFFs were stored in envelopes of aluminum foil baked at 400 °C and PUF  
109 plugs were stored in precleaned glass jars, both at -20 °C after sampling, until extraction.

110 To increase sample volume, some PUF gas phase samples were composited such that  
111 sample volumes ranged from ~500-1400 m<sup>3</sup> for Atlantic samples and ~600-2000 m<sup>3</sup> for Antarctic  
112 samples. Only Atlantic aerosol samples were analyzed as part of this study and were also  
113 composited prior to extraction to increase sample volumes (3500 - 6500 m<sup>3</sup>). Antarctic aerosol  
114 analyses have been reported previously (Dickhut et al., 2012). A surrogate standard mixture of  
115 perdeuterated  $\alpha$ -hexachlorocyclohexane (d<sub>6</sub>- $\alpha$ -HCH) and PCB 204 was added and PUF plugs  
116 were Soxhlet extracted with acetone and petroleum ether (24 h each). Anhydrous sodium sulfate  
117 was added to the sample extracts to remove residual water, and extracts were reduced to 10 mL  
118 using rotary evaporation (Buchi) and/or a Turbovap II (Zymark), exchanged into hexane, and  
119 further reduced to 3 mL using a gentle stream of ultra-high purity N<sub>2</sub>. Aerosol extracts and  
120 approximately half the gas phase extracts were acid treated using concentrated sulfuric acid. The  
121 sample extracts were then cleaned up using silica column chromatography (Chiuchiolo et al.,  
122 2004), and an internal standard (d<sub>6</sub>- $\gamma$ -HCH) was added prior to volume reduction to ~100  $\mu$ L  
123 using ultra high purity N<sub>2</sub>.

124 Seawater samples were collected via a direct inlet line from the bottom of the ship (app. 8  
125 m depth) into the laboratory. The entire inlet system was made of acid resistant stainless steel  
126 with the exception of PTFE pump impellers. Large volume seawater samples (~110 L for  
127 Atlantic Ocean and ~150-160 L for Southern Ocean) were collected in steel holding tanks and  
128 treated according to Dickhut et al., 2005. The water was extracted by passing through a column  
129 (35 cm x 25 mm i.d.) of Amberlite XAD-2 resin (Sulpeco, Bellefonte, PA). The XAD-2 resin  
130 columns were stored at 4 °C until extraction. For analyses, the XAD-2 resin was Soxhlet

131 extracted with acetone and hexane (24 h each) after the addition of the surrogate standard  
132 mixture described above. The acetone fractions were back-extracted using hexane and hexane-  
133 extracted water three times via agitation for three minutes, and the resulting hexane was  
134 combined with the hexane extract and reduced in volume by rotary evaporation. The hexane  
135 extracts were then cleaned and analyzed as described above.

136 **Quantification.** Samples were analyzed on a Hewlett-Packard 6890 Gas Chromatograph  
137 with a 5973 Mass-Selective Detector in negative chemical ionization mode using a J&W DB-  
138 35MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) and selective ion  
139 monitoring. Method parameters for analysis were as follows: 70 °C initial hold time of 1 min;  
140 70-150 °C at 20 °C min<sup>-1</sup>; 150-280 °C at 4 °C min<sup>-1</sup>, hold for 15 min; 280-295 °C at 5 °C min<sup>-1</sup>,  
141 hold for 2 min; source temperature 150 °C. The carrier gas for both methods was helium at 1.0  
142 mL min<sup>-1</sup> with a velocity of 39 cm s<sup>-1</sup> (Chiuchiolo et al., 2004).

143 **Quality Assurance and Quality Control.** Quality control procedures included the  
144 collection and analysis of laboratory and field blanks, selected duplicate samples, and  
145 breakthrough on PUF plugs, non-sequential sample extraction ordering, quantitation of surrogate  
146 standard and internal standard recoveries, and the use of a conservative method detection limit.

147 Laboratory and field blanks were collected and analyzed as quality control procedures.  
148 One laboratory blank of baked GFF filters was extracted alongside composite particulate filters  
149 (1 laboratory blank to eight samples), as were two laboratory blanks of cleaned PUF not taken in  
150 the field. Paired air and seawater field blanks were collected across the Atlantic leg every seven  
151 samples (three total), and four air field blanks (30s on high volume air sampler) and two  
152 seawater field blanks were collected during the Antarctic leg. Field duplicate Antarctic PUF  
153 samples were collected, but most were combined to increase sample volume. Two PUF field

154 duplicates were analyzed separately, and for one pair analytes agree well (most NQ,  $\gamma$ -HCH 0.99  
155  $\text{pg m}^{-3}$  vs. 0.83  $\text{pg m}^{-3}$ ; HCB 23  $\text{pg m}^{-3}$  vs. 24  $\text{pg m}^{-3}$ ). For the second pair, the values are similar  
156 for  $\alpha$ -HCH - NQ (MDL 0.11  $\text{pg m}^{-3}$ ) vs. 0.12  $\text{pg m}^{-3}$ , but  $\gamma$ -HCH and HCB concentrations were  
157 not similar ( $\gamma$ -HCH 1.9  $\text{pg m}^{-3}$  vs. <MDL; HCB 99  $\text{pg m}^{-3}$  vs. 20  $\text{pg m}^{-3}$ ). Two duplicate seawater  
158 samples were collected during the Atlantic leg, but unfortunately one of these had no surrogate  
159 standard recovery so analytes could not be quantified.

160 Sample extractions were performed in a non-sequential order to prevent laboratory  
161 changes over time from imitating geographic trends, and at least every other set of four soxhlet  
162 extractions included either a laboratory or field blank control sample. The front and back PUF  
163 plugs were analyzed and quantified separately to determine the breakthrough of individual  
164 analytes. The average breakthrough of  $\alpha$ -HCH and  $\gamma$ -HCH from the front to the back PUF was  
165  $21\pm 18$  and  $24\pm 11\%$ , respectively. Breakthrough for hexachlorobenzene (HCB) was highest  
166 ( $33\pm 8\%$ ) and  $\alpha$ -Endosulfan was lowest ( $13\pm 11\%$ ). As expected, breakthrough was greater for  
167 lower molecular weight compounds and more volatile compounds. Breakthrough was also higher  
168 at lower latitudes and warmer temperatures compared to higher latitudes, which should be  
169 considered when sampling over a wide range of latitudes or during a variety of seasons. The PUF  
170 had also been used once prior to sampling, which may have degraded its ability to collect.  
171 Alternatively, a longer PUF column length may be necessary to improve the extraction efficiency  
172 for more volatile compounds.

173 Surrogate standard recovery of  $d_6$ - $\alpha$ -HCH in gas phase air samples was  $65\pm 6\%$  and  
174  $81\pm 8\%$  for PCB 204 (average  $\pm$  confidence interval,  $\alpha = 0.05$ ). Surrogate standard recovery of  
175 aerosol samples was  $89\pm 33\%$  for PCB 204. Surrogate standard recoveries in seawater samples

176 were 85±4% for d<sub>6</sub>-α-HCH and 115±5% for PCB 204. Reported sample concentrations are not  
177 corrected for surrogate standard recoveries.

178 Method detection limits (MDLs) were conservatively calculated as three times the  
179 average field and lab amount in pg and divided by the average sample volume in m<sup>3</sup> or L  
180 (Dickhut et al., 2012). In cases where no quantifiable peak was identified for a given compound  
181 in any blanks, the MDL was set to 0.05 pg m<sup>-3</sup> (air) and 0.13 pg L<sup>-1</sup> (seawater) as these were on  
182 the low end of calculated MDLs for individual analytes.

183

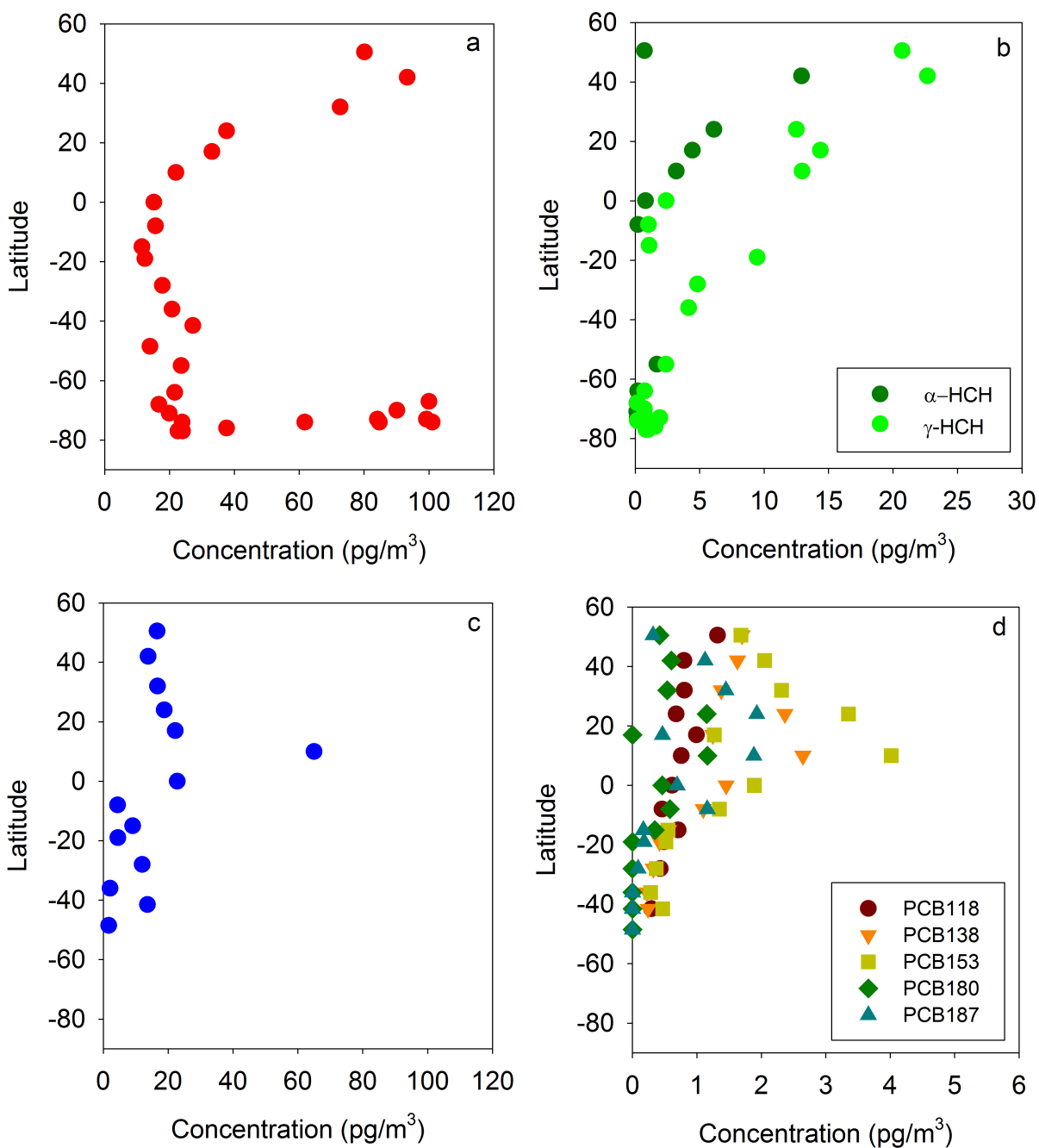
## 184 **Results and Discussion**

185 The most frequently identified compounds in the gas phase and seawater were α-HCH, γ-  
186 HCH, HCB, α-Endosulfan, heptachlor, and PCB congeners 118, 138, 153, 180, and 187 (**Figure**  
187 **2, Figure 3, Table S3, Table S4**). α-HCH, γ-HCH, HCB, α-Endosulfan, and heptachlor were  
188 also detected in the eight composite aerosol samples (**Figure S1, Table S5**). High concentrations  
189 of heptachlor were identified in both aerosol and gas phase blanks and are therefore not reported.  
190 In samples collected while the ship was breaking ice, with frequent backing up and ramming, a  
191 grey color was observed on the filters indicating influence from the smoke stack. But even when  
192 ship contamination was expected (e.g., Dec. 29-Jan. 1), most compounds were not quantifiable in  
193 field blanks. Thus, although ship influence is possible, it is not expected to contribute to the  
194 specific analytes or influence the interpretation of the results with the exception of Antarctic  
195 HCB concentrations.

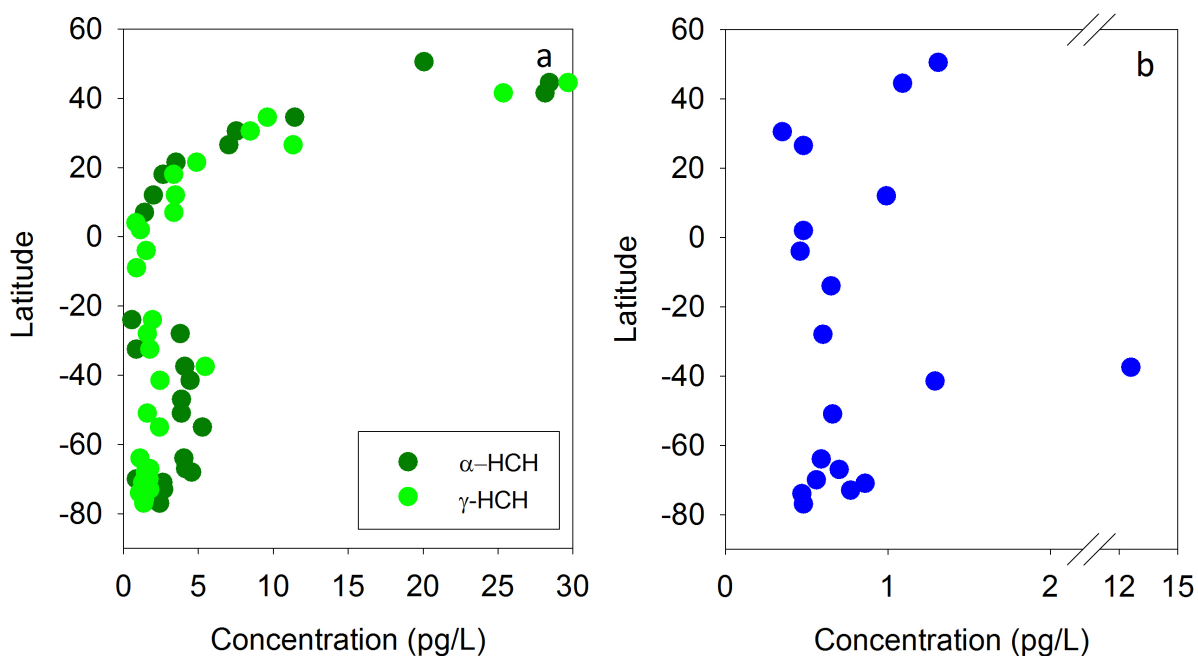
196

197 **Hexachlorocyclohexane.** α-HCH and γ-HCH concentrations in gas phase samples  
198 ranged from below method detection limits (MDLs) (0.11 pg m<sup>-3</sup> and 0.18 pg m<sup>-3</sup>) to 13 and 23

199  $\text{pg m}^{-3}$ , respectively.  $\alpha$ -HCH and  $\gamma$ -HCH concentrations in aerosol samples were low and close to  
200 MDLs ( $0.06 \text{ pg m}^{-3}$  and  $0.10 \text{ pg m}^{-3}$ , respectively), with only  $\gamma$ -HCH detected above the method  
201 detection limit at one site. The highest concentrations of gas phase HCHs were found in the  
202 northern hemisphere with a sharp drop off below the equator (**Figure 2**). HCHs were  
203 significantly higher (Student's t-test,  $p < 0.01$ ) in the northern versus southern hemisphere. The  
204 highest concentrations of both isomers were observed off the Western European coastline ( $45^\circ$   
205 N,  $8^\circ$  W). In the Southern hemisphere,  $\alpha$ -HCH consistently declined southward but  $\gamma$ -HCH  
206 concentrations increased slightly near 50S, potentially indicating recent South American use.  
207 These values are consistent with the spatial and temporal patterns reported over the past two  
208 decades, including Eastern Atlantic transects in 1999 and 2008 (Lakaschus et al., 2002; Xie et  
209 al., 2011). Since 1987, a clear decline of nearly an order of magnitude has been observed in HCH  
210 concentrations across this transect (Xie et al., 2011).



211  
 212 **Figure 2.** Gas-phase air concentrations of a) hexachlorobenzene b) hexachlorocyclohexanes c)  
 213 Endosulfan I d) polychlorinated biphenyls in the Atlantic and Southern Oceans, Oct. 2007-Jan.  
 214 2008. <MDLs and NQ not shown.



215  
 216 **Figure 3.** Seawater dissolved phase concentrations of a) hexachlorocyclohexanes \*not showing  
 217 point at 50.5N, 77 pg L<sup>-1</sup> for scaling reasons b) Endosulfan I in the Atlantic and Southern  
 218 Oceans, Oct. 2007-Jan. 2008. Samples <MDLs and NQ not shown.

219  
 220 Gas phase samples collected at latitudes below 60° S in the present study had  
 221 concentrations of α-HCH and γ-HCH that ranged from below MDLs to 0.99 and 1.9 pg m<sup>-3</sup>,  
 222 respectively. These are similar to levels reported in 2001- 2002 in the Western Antarctic  
 223 Peninsula (0.05-0.52 pg m<sup>-3</sup> for α-HCH, and 0.06-2.4 pg m<sup>-3</sup> for γ-HCH) (Dickhut et al., 2005).  
 224 Antarctic atmospheric α- and γ-HCH concentrations measured in this study are consistent with  
 225 declines seen over the past twenty-five years (Bidleman et al., 1993; Dickhut et al., 2005;  
 226 Jantunen et al., 2004; Tanabe et al., 1983). Given that HCHs have been shown to have half-lives  
 227 of ~3 years in Antarctic air (Dickhut et al., 2005), the similar levels measured in 2007-2008  
 228 compared to 2001-2001 may indicate that current sources, such as continued agricultural use,

229 may contribute HCHs to the Southern Ocean atmosphere. Alternatively, if agricultural use has  
230 declined, a possible source of HCHs is volatilization from the western Antarctic ice sheet, which  
231 has been shown to be a source of other legacy use pesticides to the aquatic environment  
232 (Cincinelli et al., 2016; Geisz et al., 2008).

233         The ratios of  $\alpha$ -HCH to  $\gamma$ -HCH in the gas phase were computed to investigate the  
234 presence of technical grade HCH versus the purer lindane ( $\gamma$ -HCH) in samples where both  
235 isomers were above method detection limits; a ratio greater than one represents higher amounts  
236  $\alpha$ -HCH isomer associated with technical grade HCH that has been phased out (**Figure S2**).  
237 Atmospheric  $\alpha$ -HCH concentrations are lower than  $\gamma$ -HCH concentrations across the Atlantic  
238 transect, which is consistent with a global reduction in technical HCH usage (Li et al., 1998), but  
239 may also imply continued sources of current use  $\gamma$ -HCH.  $\alpha$ -HCH appears to be longer lived in  
240 the atmosphere ( $t_{1/2}$  of 120 vs. 96 d) (Harner et al., 1999; Li et al., 2004), but  $\gamma$ -HCH may be  
241 degraded to  $\alpha$ -HCH (Walker et al., 1999) complicating the meaning of this ratio.

242         Seawater  $\alpha$ - and  $\gamma$ -HCH concentrations ranged from below MDLs to 28 and 77  $\text{pg L}^{-1}$ ,  
243 respectively (MDL  $\alpha$ -HCH = 0.13  $\text{pg L}^{-1}$ ,  $\gamma$ -HCH = 0.13  $\text{pg L}^{-1}$ ) (**Figure 3, Table S4**). Similar to  
244 HCHs in air, a spatial trend with significantly higher concentrations in the northern hemisphere  
245 and lower concentrations in the southern hemisphere was observed (Student's t-test,  $p < 0.01$ ).  
246 This latitudinal trend has been observed over the past two decades by several researchers (Harner  
247 et al., 1999, 1999; Iwata et al., 1993; Lakaschus et al., 2002; Schreitmueller and Ballschmiter,  
248 1995; Xie et al., 2011). Current concentrations also followed a temporal decline noted by  
249 Lakaschus et al., (2002). A 2008 Eastern Atlantic sampling cruise also observed a slight increase  
250 in  $\alpha$ -HCH near 50S (Xie et al., 2011). This may be caused by regional technical HCH use (Pozo



251 et al., 2006) or by the isomerization of  $\gamma$ -HCH to  $\alpha$ -HCH in the environment (Walker et al.,  
252 1999).

253 A somewhat bimodal distribution was observed in the ratios of  $\alpha$ -HCH to  $\gamma$ -HCH in  
254 seawater samples (**Figure S2**), where the northern and southern latitudes had higher ratios and  
255 tropical latitudes had lower ratios (or were not calculated due to non-detection of one of the two  
256 isomers). However, the southern latitudes had 3.5 times as much  $\alpha$ -HCH as  $\gamma$ -HCH, where as  
257 northern latitudes hover at or below 1. Consistently higher  $\alpha$ - to  $\gamma$ -HCH ratios in Antarctic  
258 seawater versus air indicate that  $\alpha$ -HCH may be longer lived in the seawater environment than  $\gamma$ -  
259 HCH, or represent an older pool of HCH dominated by technical grade containing  $\alpha$ -HCH. The  
260 apparent half-life of  $\Sigma$ HCHs in the Antarctic seawater environment has previously been  
261 estimated as 2 y and 3.4 y in two separate studies (Chiuchiolo et al., 2004; Galbán-Malagón et  
262 al., 2013), which is similar to half-lives reported Antarctic air (3 y) (Dickhut et al., 2005).  
263 However, much longer half-lives of 5.9 years and 23.1 years for the (+) and (-) enantiomers of  $\alpha$ -  
264 HCH and 18.8 years for  $\gamma$ -HCH were reported in the Eastern Arctic Ocean during a 1996 cruise  
265 (Harner et al., 1999). It is unclear why such a high ratio of  $\alpha$ -HCH persists in Southern Ocean  
266 seawater and not in the overlying atmosphere, but is likely driven by current and historical usage  
267 patterns as well as differing degradation rates and isomerization from  $\gamma$ -HCH to  $\alpha$ -HCH (Harner  
268 et al., 1999; Li et al., 1998; Walker et al., 1999).

269

270 **Hexachlorobenzene.** HCB was ubiquitous in gas phase air samples with concentrations  
271 ranging from 12 to 100 pg m<sup>-3</sup> (MDL = 1.3 pg m<sup>-3</sup>). HCB in aerosol samples (MDL = 0.21 pg  
272 m<sup>-3</sup>) was frequently below detection limits with only two samples above the MDL. The highest  
273 concentrations of HCB in the gas phase were observed in the northern Atlantic and Antarctic air

274 while lower concentrations were measured in tropical and South Atlantic air. A comparison of  
275 front and back PUF indicated high levels of HCB breakthrough in the Atlantic samples that were  
276 collected at temperatures greater than 20 °C (54±3%). In a 2009 Atlantic transect (N-S and E-  
277 W), HCB concentrations were lowest near the equator although concentrations were nearly an  
278 order of magnitude lower than reported here for most samples (Lohmann et al., 2012). However,  
279 breakthrough information was not reported for these samples.

280 Southern Ocean HCB concentrations ranged from 17-100 pg m<sup>-3</sup> with no discernible  
281 pattern over the concentration range, slightly higher than the range reported during a 2008 -2009  
282 sampling expedition along the Western Antarctic peninsula (Galbán-Malagón et al., 2013a).  
283 However, air mass back trajectories (Stein et al., 2015) did not indicate unique air masses for  
284 high versus low concentration sampling periods (**Figure S3, Table S6**). Lab and field blanks  
285 extracted and analyzed at the same time are similar and do not indicate a contamination event  
286 during the high HCB concentration sample extractions. It is noteworthy, however, that the high  
287 concentration events all are from the highest latitudes. This opens up for two explanations: 1)  
288 emission of legacy HCB from the melting continental or shelf ice as suggested by (Geisz et al.,  
289 2008) or, 2) contamination from the ship during icebreaking. The second explanation is, perhaps,  
290 the more likely, as release of legacy POPs from melting glaciers would probably also lead to  
291 locally increased air concentrations of, e.g., HCHs, which is not observed. Elevated air  
292 concentrations of HCB during icebreaking have not been observed during previous expeditions  
293 with Oden, but in this case the bunker fuel was from a different source than normally used.

294 A further indication that it might be conditions during icebreaking that caused the high  
295 concentrations of HCB at high latitudes is that in one case, a duplicate pair collected from the  
296 same time and location had vastly different concentrations (20 vs. 99 pg m<sup>-3</sup>). With a strong side

297 wind, it is likely that one of the air samplers picked up more of a locally produced contamination  
298 than the other.

299 An autumn 2001 sampling cruise found atmospheric HCB levels in air that averaged 19  
300 ( $\pm 7.6$ )  $\text{pg m}^{-3}$  on the Western Antarctic Peninsula north of  $68^\circ$  S (Dickhut et al., 2005). More  
301 recently, the Norwegian Troll long term monitoring station in Dronning Maud Land, [Antarctica]  
302 observed consistent  $22 \text{ pg m}^{-3}$  HCB concentrations from 2007-2010, with an austral winter peak  
303 (Kallenborn et al., 2013). The highest recent Antarctic HCB measurements (2008-2009) peaked  
304 at  $49.7 \text{ pg m}^{-3}$  (Galbán-Malagón et al., 2013a) along the Western Antarctic Peninsula, but are not  
305 as high as the highest HCB concentrations observed in this study.

306 A high HCB MDL was calculated for the seawater samples ( $8.0 \text{ pg L}^{-1}$ ) and therefore  
307 HCB was only above the MDL in one seawater sample collected at  $50^\circ$  N ( $11 \text{ pg L}^{-1}$ ). In  
308 previous transects, HCB has only been observed in seawater at concentrations of  $1 \text{ pg L}^{-1}$  or less  
309 (Lohmann et al., 2012, Zhang and Lohmann, 2010, Galbán-Malagón et al., 2013).

310  
311 **Endosulfan.** Endosulfan ( $\alpha$ -Endosulfan) concentrations in gas phase air samples ranged  
312 from below the MDL ( $0.21 \text{ pg m}^{-3}$ ) to  $65 \text{ pg m}^{-3}$  with significantly higher levels in the northern  
313 versus southern hemisphere (Student's t-test,  $p = 0.03$ ). Endosulfan in aerosol samples (MDL =  
314  $0.03 \text{ pg m}^{-3}$ ) was frequently below detection limits with only three samples above the MDL.  
315 High Endosulfan gas phase concentrations were observed off the West African coast, where an  
316 air mass back trajectory indicated air of continental origin. Inland passive air sampling in West  
317 Africa observed extremely high levels of Endosulfan (sum of  $\alpha$ -,  $\beta$ -, and  $-\text{SO}_4$ ) in passive air  
318 sampling ( $\sim 2400 \text{ pg m}^{-3}$  in 2004-2005) indicating that these high levels are likely due to regional  
319 agricultural applications (Pozo et al., 2009, 2006). Although atmospheric Endosulfan peaked off

320 the African coast, seawater concentrations did not, yielding further support that atmospheric  
321 conditions were influenced by a continental air mass rather than long-term equilibration with  
322 seawater and the overlying air masses. Although banned in more than fifty countries, Endosulfan  
323 continues to be used on major crops including coffee, soy, cotton, and tobacco, but will be  
324 phased out over the next decade due to inclusion on the Stockholm Convention (UNEP, 2016).  
325 In the Antarctic atmosphere, low Endosulfan levels ( $0.2\text{-}0.8\text{ pg m}^{-3}$ ) were detected with only  
326 three of thirteen samples above the method detection limit. On King George Island, Endosulfan  
327 was found to be the most prevalent and abundant organochlorine pesticide (average  $27\text{ pg/m}^3$ )  
328 during multi-year monitoring (2005-2007) (Baek et al., 2011). Prior to that study, Endosulfan  
329 had not been detected in Antarctic air, but may be because Endosulfan was rarely included as an  
330 analytes (Pozo et al., 2006). Based on these results and similar Arctic findings (Weber et al.,  
331 2010), Baek and colleagues suggested that Endosulfan is extensively transported to polar regions  
332 (Baek et al., 2011). However, air mass back trajectories in the current study indicate air of  
333 oceanic origin, potentially explaining why low of Endosulfan was observed in the present study  
334 rather than at levels similar to King George Island which is more likely influenced by direct  
335 South American air masses.

336 Seawater Endosulfan concentrations (**Figure 3**) were consistently low and showed no  
337 clear latitudinal trends. No clear hemispheric difference is consistent with approximately  
338 equivalent northern and southern hemisphere applications and continued Endosulfan use (Weber  
339 et al., 2010). Concentrations ranged from below the MDL ( $0.13\text{ pg L}^{-1}$ ) to  $1.3\text{ pg L}^{-1}$  with a  
340 single outlier of  $13\text{ pg L}^{-1}$  measured at  $37^\circ\text{ S}$ . This outlier was collected near shore in the Rio de  
341 la Plata estuary, the second largest drainage basin in South America, draining large agricultural  
342 and urban regions where Endosulfan have been used recently and continue to persist at high

343 concentrations in agricultural stream beds (Hunt et al., 2016). Endosulfan concentrations in  
344 seawater have not been previously reported along an Atlantic transect or in the Antarctic. Arctic  
345 sampling has shown low Endosulfan concentrations (mean  $2.3 \text{ pg L}^{-1}$ ) similar in magnitude to  
346 these findings (Weber et al., 2010).

347

348 **Polychlorinated Biphenyls.** Twenty different PCB congeners were analyzed in the gas  
349 phase samples, but only congeners 118, 138, 153, 180, and 187 were consistently detected  
350 (**Figure 2**). PCBs were quantified in two aerosol samples but all were below MDLs. Gas phase  
351 concentrations were highest in the northern hemisphere and were nearly undetectable in the air  
352 over the South Atlantic and Southern Ocean (MDLs ranged from  $0.05 \text{ pg m}^{-3}$  to  $0.26 \text{ pg m}^{-3}$  for  
353 individual congeners). In an Atlantic sampling cruise in 2008, PCBs 153 and 180 were reported  
354 to have concentrations similar to those observed for the tropical Atlantic (Lohmann et al., 2012).  
355 In the present study, PCB153 and PCB180 levels were approximately twice those reported by  
356 Lohmann north of the equator, likely because sampling occurred on the Western Atlantic  
357 (present study) versus the Eastern Atlantic (Lohmann et al., 2012). Previous studies have shown  
358 high atmospheric PCB concentrations in these coastal waters (including those identified here,  
359 PCB118, 138, 153, and 180), with mass back trajectories indicative of a known West Africa  
360 source (Gioia et al., 2011, 2008).

361 Four of the five PCB congeners consistently observed in samples (118, 138, 153, 180)  
362 were reported by Lohmann (Lohmann et al., 2004) as congeners which concentrations may  
363 potentially be influenced by shipboard contamination. It is possible that some PCBs found in the  
364 samples were due to shipboard contamination, as PCBs were detected in some field blanks at low  
365 levels. However, shipboard contamination would be expected to impact air samples collected

366 throughout the cruise, and the consistently low levels (<MDL) of PCBs found in the gas phase  
367 samples collected throughout the South Atlantic indicates that the measured concentrations are  
368 likely representative of actual atmospheric levels with a clear decline from northern to southern  
369 latitudes. It should be noted that Oden was built and commissioned 16 years after all uses of PCB  
370 were banned in Sweden. As far as has been possible to check among ship documents, no PCB  
371 containing equipment has ever been taken aboard. Also, H. Kylin has repeatedly investigated  
372 various parts of the ship for contamination of PCB and organochlorine pesticides. This has  
373 included screening all batches of paints, etc. used for the ship (particularly those used in the  
374 laboratory/sampling areas) prior to application. To date, no sources of contaminants have been  
375 identified on board, but there is a risk for contamination with incineration-derived compounds  
376 (e.g., HCB) from the industrial activities around the shipyard where Oden is refurbished prior to  
377 each expedition.

378         Similar to air samples, PCB118 and PCB153 were most commonly detected PCBs in  
379 seawater. However, these analytes also had high MDLs (**Table S4**) and therefore PCB118 was  
380 below MDLs in all samples and PCB153 was below MDLs in all but three samples. PCBs 137,  
381 180, and 187 were also detected in several seawater samples and were above MDLs, where  
382 concentrations ranged from below MDLs to 2.6 pg L<sup>-1</sup> (PCB138) at 7° N. The highest PCB187  
383 and PCB180 concentrations (0.50 pg L<sup>-1</sup> and 1.1 pg L<sup>-1</sup>) were also detected in this sample. PCBs  
384 in seawater were only detected in the tropics, likely related to the local West Africa source  
385 (Gioia et al., 2011). Peak concentrations in seawater PCBs near the equator with very low overall  
386 PCB concentrations have also been reported previously in a north-south Atlantic transect,  
387 although within the Eastern South Atlantic (Gioia et al., 2008). The only exception was the  
388 detection of PCB138 at 78 degrees south (0.98 pg L<sup>-1</sup>), perhaps influenced by McMurdo Station.

389 In multiple Antarctic cruises, PCB118 and 153 concentrations ranged from 0.02-0.64 and 0.03-  
 390 0.46  $\text{pg L}^{-1}$ , and PCB99/101 had the highest observed concentrations (Galbán-Malagón et al.,  
 391 2013). PCB concentrations in the Antarctic are decreasing with an apparent half-life of 5.7 years,  
 392 likely driven by loss to depth via the biological pump (Dachs et al., 2002; Galbán-Malagón et al.,  
 393 2013).

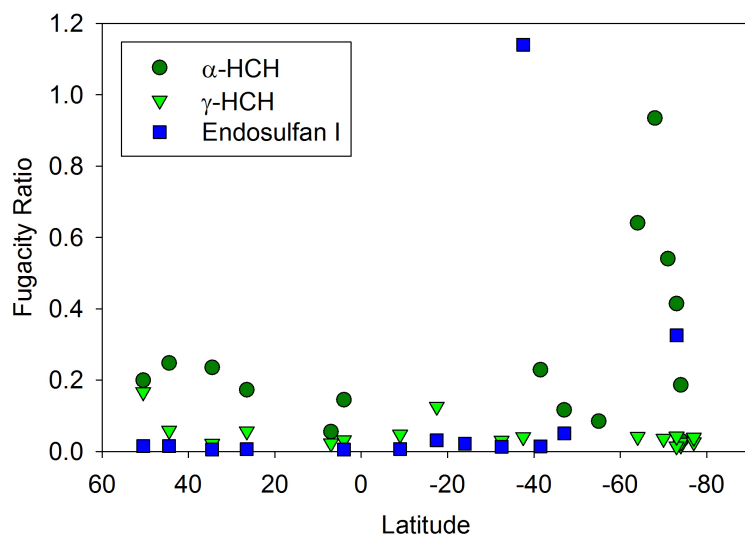
394

395 **Air/Seawater Exchange.** The relative concentrations of air and seawater were examined by  
 396 calculating the water/air fugacity ratios ( $f_w/f_a$ ) as shown below (Mackay and Paterson, 1981):

$$397 \quad f_w/f_a = C_w H / C_a R T$$

398 where water ( $C_w$ ) and air ( $C_a$ ) concentrations are in  $\text{pg m}^{-3}$ , H is the Henry's law constant [ $\text{Pa m}^3$   
 399  $\text{mole}^{-1}$ ], R is the gas constant [ $8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mole}^{-1}$ ], and T is the temperature in K.

400 Calculations were done using average daily air and seawater temperatures measured during  
 401 individual sample collection and temperature appropriate Henry's Law constants (Cetin et al.,  
 402 2006; Sahuvar et al., 2003; Shen and Wania, 2005).



403

404 **Figure 4.** Fugacity ratios of  $\alpha$ -HCH,  $\gamma$ -HCH, and Endosulfan I

405            Calculated HCH fugacity ratios indicated that the Atlantic and Southern Oceans continue  
406 to act as a sink for  $\alpha$ - and  $\gamma$ -HCH ( $F < 1$ ) (**Figure 4, Table S7**). Fugacity ratios were not  
407 calculated for some tropical regions as where one or both isomers were below detection in  
408 seawater, still supporting continued net deposition in this region. Similarly, a 2008 Atlantic  
409 cruise observed consistent HCH deposition from 45° N to 67° S (Xie et al., 2011). A 1990-1991  
410 cruise observed net deposition of  $\Sigma$ HCHs in the North Atlantic (Schreitmüller and Ballschmiter,  
411 1995); however a 1999-2000 cruise found that  $\Sigma$ HCHs were near air-sea equilibrium in the North  
412 Atlantic (Lakaschus et al., 2002). Over a series of Atlantic cruises during the 1990s,  $\gamma$ -HCH was  
413 found to be near equilibrium in the tropical Atlantic, but depositing in the northern and southern  
414 Atlantic (Weber et al., 2006). A portion of Southern Ocean samples observed near equilibrium  
415 ( $0.3 > F < 3$ ) conditions for  $\alpha$ -HCH, similar to reports in Arctic Ocean samples (Bruhn et al., 2003;  
416 Lohmann et al., 2009). However, a similar trend is not observed for  $\gamma$ -HCH in the Southern  
417 Ocean, consistent with recent observations of net deposition of  $\gamma$ -HCH in the Southern Ocean  
418 (Bigot et al., 2016).

419            The fugacity ratio of Endosulfan indicates net deposition is occurring across the Atlantic,  
420 with the exception of the Rio de la Plata sample outlier (**Figure 4**). Although now being phased  
421 out, Endosulfan was still in use during the time of sampling and air concentrations were still  
422 relatively high in Endosulfan (Pozo et al., 2009, 2006). Data collected between 1990 and 2004  
423 noted a net deposition of Endosulfan throughout the Atlantic (Lohmann et al., 2009; Weber et  
424 al., 2006), and the lack of quantifiable concentrations of Endosulfan in a number of surface  
425 seawater samples supports continued deposition from air to water. Fugacity ratios were not  
426 calculated for PCBs or HCBs due to the high MDLs in seawater and therefore few gas phase and  
427 seawater overlapping data points. Errors associated with these calculated fugacity ratios (Bigot et



428 al., 2016) were not computed due to a lack of replication in individual air/sea water values.  
429 Although the error associated with individual values may be considerable, the consistency across  
430 samples gives further support to the conclusions reported of continued net deposition of these  
431 POPs.

432 Although previous studies have suggested that the open ocean will move towards being a  
433 source of POPs to the atmosphere (Bruhn et al., 2003; Schreitmüller and Ballschmiter, 1995;  
434 Weber et al., 2006; Xie et al., 2011), removal of these compounds to the deep ocean bound to  
435 particles or organisms, or via the degradative pump (Galbán-Malagón et al., 2012; Goerke et al.,  
436 2004; Lohmann et al., 2004; Zhang et al., 2013) may continue to keep surface water  
437 concentrations low and indicate net deposition from the atmosphere. Future trends in  
438 atmospheric and open ocean concentrations and fluxes of legacy use organochlorines will likely  
439 be affected by a number of issues. Changing wind patterns and warming surface water  
440 temperatures, as well as new sources of legacy pesticides from melting ice sheets (Cincinelli et  
441 al., 2016; Dickhut and Gustafson, 1995; Geisz et al., 2008) all have the potential to alter the  
442 predicted decline of phased out POPs. How exactly these physical, chemical, and biological  
443 climate change factors will affect this equilibrium has yet to be understood.

444

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456

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