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## Air-water exchange and distribution pattern of organochlorine pesticides in the atmosphere and surface water of the open

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Surface seawater and lower atmosphere gas samples were collected simultaneously between 18°N and 40°S in the open Pacific Ocean in 2006–2007. Samples were analyzed for organochlorine pesticides (OCPs) to assess their distribution patterns, the role of ocean in the long-range transport (LRT), and the air-water exchange directions in the open Pacific Ocean. Such open ocean studies can yield useful information such as establishing temporal and spatial trends and assessing primary vs secondary emissions of legacy OCPs. Target compounds included hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethanes (DDTs) and its derivatives, and chlordane compounds. Concentrations for  $\alpha$ -HCH,  $\gamma$ -HCH, trans-chlordane (TC), and cis-chlordane (CC) were higher in the Northern Hemisphere (NH) than the Southern Hemisphere (SH) in both gaseous and dissolved phases, while the distribution patterns of DDTs and heptachlor *exo*-epoxide (HEPX) showed a reversed pattern. In the N Pacific, concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH in the present work were lower by 63 and 16 times than those observed in 1989–1990. The distribution patterns of DDT suggested there was usage in the SH around 2006. Calculated fugacity ratios suggested that  $\gamma$ -HCH was volatilizing from surface water to the atmosphere, and the air-water exchange fluxes were 0.3–11.1 ng m<sup>-2</sup> day<sup>-1</sup>. This is the first field study that reported the open Pacific Ocean has become the secondary source for  $\gamma$ -HCH and implied that ocean could affect LRT of OCPs by supplying these compounds via air-sea exchange.

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1 Air-water exchange and distribution pattern of organochlorine pesticides  
2 in the atmosphere and surface water of the open Pacific Ocean

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10 **Abstract**

11 Surface seawater and lower atmosphere gas samples were collected simultaneously between 18°N and 40°S  
12 in the open Pacific Ocean in 2006-2007. Samples were analyzed for organochlorine pesticides (OCPs) to  
13 assess their distribution patterns, the role of ocean in the long-range transport (LRT), and the air-water  
14 exchange directions in the open Pacific Ocean. Such open ocean studies can yield useful information such  
15 as establishing temporal and spatial trends and assessing primary vs secondary emissions of legacy OCPs.  
16 Target compounds included hexachlorocyclohexanes (HCHs), dichlorodiphenyltrichloroethanes (DDTs)  
17 and its derivatives, and chlordane compounds. Concentrations for  $\alpha$ -HCH,  $\gamma$ -HCH, trans-chlordane (TC),  
18 and cis-chlordane (CC) were higher in the Northern Hemisphere (NH) than the Southern Hemisphere (SH)  
19 in both gaseous and dissolved phases, while the distribution patterns of DDTs and heptachlor *exo*-epoxide  
20 (HEPX) showed a reversed pattern. In the N Pacific, concentrations of  $\alpha$ -HCH and  $\gamma$ -HCH in the present  
21 work were lower by 63 and 16 times than those observed in 1989-1990. The distribution patterns of DDT  
22 suggested there was usage in the SH around 2006. Calculated fugacity ratios suggested that  $\gamma$ -HCH was  
23 volatilizing from surface water to the atmosphere, and the air-water exchange fluxes were 0.3 to 11.1 ng m<sup>-2</sup>  
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25 for  $\gamma$ -HCH and implied that ocean could affect LRT of OCPs by supplying these compounds via air-sea  
26 exchange.

27 Keyword: Pacific Ocean, organochlorine pesticides, atmosphere, seawater, air-water exchange

28 Capsule: Most organochlorine pesticides levels were higher in N Pacific and S Pacific and declined  
29 compared to three decades ago,  $\gamma$ -HCH was found to volatilize from surface water to the atmosphere.

## 30 **1. Introduction**

31 Persistent organic pollutants (POPs) are ubiquitous in the environment and can be detected in various  
32 biotic and abiotic matrices, even in the remote environments such as polar regions (Zhang et al., 2013; Muir  
33 et al., 2013; Galbán-Malagón et al., 2013a, c; Khairy et al., 2016; Ruge et al., 2018;). Most semi-volatile  
34 POPs, such as organochlorine pesticides (OCPs), can be transported globally and deposited in remote  
35 regions far from the primary emission areas (Ding et al., 2007; Wu et al., 2010; Zhang et al., 2012; Galbán-  
36 Malagón et al., 2013a), which has caused extensive concerns due to their persistence, toxicity, and high  
37 bioaccumulative potentials (Berrojalbiz et al., 2014; Wang et al., 2017; Ma et al., 2018; Li et al., 2018;  
38 Lohmann et al., 2019). Long-range oceanic current transport, air-sea exchange, and biological pump and  
39 sedimentation processes greatly affect the distribution and fate of POPs in the ocean, which were once  
40 believed to be the ultimate sink of these contaminants (Iwata et al., 1993; Harner et al., 2000; Lohmann et  
41 al., 2009; Nizzetto et al., 2010; Xie et al., 2011, Zhang et al., 2012; Galbán-Malagón et al., 2013b). However,  
42 because of the declined emission of most legacy POPs after the bans on the usage of these contaminants  
43 and together with the warming of seawater (Yao et al., 2019), the ocean became the secondary source of  
44 certain POPs by returning to the atmosphere (Lohmann et al., 2009; Zhang and Lohmann, 2010; Huang et  
45 al., 2013). The outgassing phenomena have been reported for PCBs in the Pacific Ocean (Zhang and  
46 Lohmann, 2010;), in the Atlantic Ocean (Lohmann et al., 2012), and in the Great Lakes (Ruge et al., 2018),  
47 DDTs in the Equatorial Ocean (Huang et al., 2013), and  $\alpha$ -HCH in the Arctic Ocean (Harner et al., 1999; Li  
48 et al., 2003; Bidleman et al., 2015). The distributions of POPs are different in various oceanic environments,  
49 so it is important to assess the air-water exchange directions and calculate the fluxes for all major POPs in  
50 the oceans, particularly the largest one, the Pacific Ocean, to better understand the global fate of POPs.

51 The usage patterns of OCPs differed between both hemispheres. Many developed and developing  
52 countries located in the temperate and tropical regions in the northern hemisphere (NH) were considered to  
53 be the major sources of the legacy OCPs production and usage (Breivik et al., 2004). The Southern

54 hemisphere (SH), mainly covered by oceans, is considered to be less polluted. The distribution patterns of  
55 OCPs in NH may indicate historical usage, while the residue levels in SH may show ongoing usage of  
56 certain OCPs such as DDTs in Africa for control of Malaria (Huang et al., 2016). Comparisons of  
57 occurrences between the SH and the NH can also show the magnitudes of potential sources and efficiency  
58 of long-range transport (Zhang and Lohmann., 2010; Galbán-Malagón et al., 2013a; Shunthirasingham et  
59 al., 2016;). However, most of the previous assessment of organic pollution focused in the NH, especially  
60 the North Atlantic (Zhang et al., 2012; Lohmann et al., 2012), Arctic (Harner et al., 1999; Lohmann et al.,  
61 2009; Bidleman et al., 2015), and N Pacific (Ding et al., 2007; Wu et al., 2010). There were only a few  
62 studies in the SH (Bigot et al., 2016), the major one was conducted a few decades ago (Iwata et al., 1993;).  
63 There was a long history of scientific assessment of organic pollution in polar regions and coastal areas  
64 (Zhang et al., 2007; Xie et al., 2011; Lin et al., 2012; Jantunen et al., 2015; Ma et al., 2018), but less  
65 frequently in the open ocean. As the largest water body on Earth, the Pacific Ocean plays a critical role in  
66 the cycling of OCPs in the environment. However, studies on OCPs in the Pacific are scarce, furthermore,  
67 the reports on air-water exchange studies of OCPs in the Pacific are even fewer.

68 In this study, the surface seawater samples and marine boundary layer air samples were collected  
69 simultaneously from the open Pacific Ocean and analyzed for OCPs, specifically HCHs ( $\alpha$ ,  $\beta$ ,  $\gamma$ -HCH),  
70 DDTs (*o,p'*- and *p,p'*-DDT, DDE, and DDD), chlordane including trans-chlordane (TC) and cis-chlordane  
71 (CC), heptachlor (HEPT), and heptachlor *exo*-epoxide (HEPX). The R/V *Revelle* sailed from San Diego,  
72 CA, to Samoa and from Samoa to New Zealand between December 2006 and January 2007, which crossed  
73 the Equatorial Current, North, and South Pacific Gyre. The results of the PCBs from the same cruise have  
74 been published elsewhere (Zhang and Lohmann 2010), this study focuses on the results of OCPs with the  
75 goals to (1) determine the residual levels and distribution patterns of selected OCPs in open Pacific to better  
76 understand the usage patterns in both hemispheres, (2) assess the air-water exchange directions and fluxes  
77 to investigate the role of open ocean in determining the transport and environment fates of selected OCPs.

## 78 **2. Methods and materials**

### 79 2.1 Cruise Track and Sample Collection

80 A total of 27 water samples and 44 air samples were collected every 12 h to 48 h during a cruise on  
81 board R/V *Revelle* from San Diego, CA (32.78 °N, 117.15° W) to New Zealand (40°S, 143.0°W) via Samoa  
82 between December 2006 and January 2007. The cruise track and sampling locations of the surface seawater  
83 and boundary layer air are presented in Supporting Information (SI) Table S1, Table S2 (date, time, volume,  
84 temperature, coordinates, wind speed, and relative humidity).

### 85 2.2 Sample Treatment and Analytical Protocol

86 Detailed sampling treatment and analytical methods have been described elsewhere ([Zhang et al.,](#)  
87 [2012](#)). Briefly, OCPs in the gaseous phase were filtered through Whatman glass fiber filters (GFF) and  
88 retained by two polyurethane foams (PUFs) using a high-volume air sampler installed on the flying bridge  
89 (ca. 17 m above sea level). Three PUFs were used on the water side for collecting OCPs in the dissolved  
90 phase. Whatman GFF (0.7 µm) was used to filter particles and replaced when the flow rate was below 1  
91 L/min. The three PUFs of a few samples were analyzed separately to test if there was any breakthrough.  
92 Only compounds with low  $K_{OWS}$  such as  $\alpha$ ,  $\beta$ ,  $\gamma$ -HCH were detected on the third PUF in the water samples,  
93 which were corrected based on equilibrium partitioning approach following Zhang et al., 2012 (see SI for  
94 more details).

95 Thirteen OCPs including  $\alpha$ ,  $\beta$ ,  $\gamma$ - HCH, TC, CC, HEPT, HEPX, o,p-, and p,p-DDT, and their  
96 degradation products (o,p-, and p,p-DDD and DDE) were determined by a Quattro micro GC-MS/MS  
97 (Waters Corporation, Milford, MA, US) using a quartz capillary DB-5MS column (30 m × 0.25 mm ×  
98 0.25 µm film thickness, Agilent). More detailed information about sample analysis and quality assurance /  
99 quality control is summarized in SI.

### 100 2.3 Air Mass Back Trajectories

101 Back trajectories (BTs) were calculated using NOAA's HYSPLIT model to assess the air mass origins  
102 of each air sample. BTs were retrieved at the beginning and end of each sample collection at 300 m above

103 sea level and traced back for 10 days with 6 h steps (Fig.1). The detailed BTs information was described in  
104 Zhang and Lohmann (2010).

#### 105 2.4 Air-Water Fugacity Ratios and Air-Water Exchange Flux

106 Organochlorine pesticides concentrations of 25 paired air-water samples collected simultaneously  
107 were used to calculate air-water exchange directions and fluxes. The calculation of air-water fugacity ratios  
108 (FRs) and air-water flux ( $F_{a/w}$ ) has been described in more detail in Zhang et al. (2012). FRs were calculated  
109 according to equation (1):

$$\frac{f_{gas}}{f_{water}} = \frac{C_{gas}}{C_{water} \times K_{aw}(T, sal)} \quad (1)$$

110  
111 Where  $f_{gas}$  and  $f_{water}$  are fugacities in air and seawater,  $C_{gas}$  and  $C_{water}$  are gaseous ( $\text{pg m}^{-3}$ ) and dissolved ( $\text{pg}$   
112  $\text{L}^{-1}$ ) concentrations of OCPs, and  $K_{aw}(T, Sal)$  is the  $K_{aw}$  corrected with *in situ* temperature and salinity.  
113 According to the uncertainty assessment in FR calculation conducted by Zhang et al., (2012), the significant  
114 FRs for net volatilization ( $FR_{Volatilization}$ ) were 0.57 for  $\alpha$ -HCH, 0.58 for  $\gamma$ -HCH, and 0.46 for HEPX,  
115 respectively. The significant FRs for net deposition ( $FR_{Deposition}$ ) were 1.56 for  $\alpha$ -HCH, 1.55 for  $\gamma$ -HCH, and  
116 1.66 for HEPX, respectively. Only FRs  $> FR_{deposition}$  were treated as net deposition and FR  $< FR_{volatilization}$  as  
117 net volatilization with 95% certainty. FRs in between were deemed not significantly different from air-  
118 water equilibrium.  
119

120 Air-water gas exchange fluxes ( $F_{a/w}$ ,  $\text{ng m}^{-2} \text{d}^{-1}$ ) were calculated using a modified version of the two-  
121 film model described in Schwarzenbach et al (2003):

$$F_{a/w} = v_{pop, a/w} \times \left( C_{water} - \frac{C_{gas}}{K_{aw}(T, sal)} \right) \quad (2)$$

122  
123 where  $V_{pop, a/w}$  is the air-water gas exchange mass transfer velocity, calculated as described in Zhang et al.,  
124 (2012). A positive value of  $F_{a/w}$  indicates a net flux from water to air, whereas a negative value of  $F_{a/w}$   
125 suggests net deposition of pollutants from air to water.  
126

### 127 3. Results and discussion

#### 128 3.1 Gas phase concentrations and distribution patterns of OCPs in the open Pacific

##### 129 3.1.1 HCH.

130 In the atmosphere, the sum of the  $\alpha$ -  $\beta$ - and  $\gamma$ - HCH ( $\sum$ HCH) ranged from 2.1 to 12.0  $\text{pg m}^{-3}$  (avg.  
131 =5.1  $\text{pg m}^{-3}$ ) in the NH, and from 0.1 to 8.9  $\text{pg m}^{-3}$  (avg. =1.1  $\text{pg m}^{-3}$ ) in the SH (Table 1).  $\alpha$ - and  $\gamma$ -HCH  
132 were the most abundant HCH isomers detected in the atmosphere in both NH and SH. Highest levels were  
133 observed at the beginning of the cruise where the air mass originated from the west coast of North America  
134 (Fig.1). The lowest air concentration of  $\sum$ HCH was observed at the southmost end of the cruise track in SH,  
135 and back trajectories indicated the air mass was transported from the Southern Ocean without contact with  
136 land for more than 10 days. In general, the average  $[\sum\text{HCH}]_{\text{gas}}$  in the NH was about 5 times higher than  
137 that in the SH, which was consistent with the distribution trends of HCH observed in the Atlantic Ocean  
138 (Xie et al., 2011).

139 In the NH, the average atmosphere concentrations of  $\alpha$ -HCH ( $[\alpha\text{-HCH}]_{\text{gas}}$ ) and  $\gamma$ -HCH ( $[\gamma\text{-HCH}]_{\text{gas}}$ )  
140 were 2.7  $\text{pg m}^{-3}$  (range 0.6-7.2  $\text{pg m}^{-3}$ ) and 2.6  $\text{pg m}^{-3}$  (range 1.2-4.7  $\text{pg m}^{-3}$ ), respectively, which were about  
141 4-7 times higher than the mean value of  $[\alpha\text{-HCH}]_{\text{gas}}$  (0.4  $\text{pg m}^{-3}$ ) and  $[\gamma\text{-HCH}]_{\text{gas}}$  (0.7  $\text{pg m}^{-3}$ ) in the SH  
142 (Table1, Fig. 2). Such hemispheric differences for both isomers were also observed by Iwata et al (1993)  
143 and still existed during this study in 2006-2007, suggesting a much larger inventory for HCHs in the NH. .  
144 Comparing to other oceans (Table S6), the average  $[\alpha\text{-HCH}]_{\text{gas}}$  and  $[\gamma\text{-HCH}]_{\text{gas}}$  in this study were about 7  
145 times and 3 times lower than N Atlantic and Arctic Ocean (55-84°N) in 2004 (Lohmann et al., 2009), and  
146 12 times and 3 times lower than N Atlantic (58-64°N) in 2008 (Zhang et al., 2012), respectively, but were  
147 in line with those reported in the lower latitudes of the Indian Ocean (0-6°N) (Huang et al., 2013). Although  
148 open ocean studies would provide an insight on the global distribution of POPs including OCPs (Wurl et  
149 al., 2006), very few studies have investigated OCPs in the S Pacific Ocean.  $[\alpha\text{-HCH}]_{\text{gas}}$  and  $[\gamma\text{-HCH}]_{\text{gas}}$   
150 detected in the S Pacific (Figure 2, Table S6) were in line with those reported in the South Atlantic (1.6-  
151 41.4°S) in similar latitudes (Xie et al., 2011) and those in the South Ocean at higher latitudes (47-74°S)

152 (Galbán-Malagón et al., 2013a). In the SH,  $\beta$ -HCH was the most abundant isomer ranging from 0.2-5.9 pg  
153  $\text{m}^{-3}$  with an average value of 1.4  $\text{pg m}^{-3}$ .

154 The data from this study and previous studies undertaken between 1989 and 2011 were plotted together  
155 in Figure 2 to assess the temporal and spatial trends of gaseous HCHs in the Pacific Ocean of both  
156 hemispheres, which provides useful insights on global fate of HCHs and ocean's role in long range transport  
157 of OCPs. In the lower latitudes of the N Pacific,  $[\alpha\text{-HCH}]_{\text{gas}}$  and  $[\gamma\text{-HCH}]_{\text{gas}}$  decreased by a factor of 63  
158 and 16 compared to 1989-1990 (Iwata et al., 1993). During the similar period,  $[\alpha\text{-HCH}]_{\text{gas}}$  and  $[\gamma\text{-HCH}]_{\text{gas}}$   
159 in the high latitudes (i.e. Arctic regions) decreased by a factor of 15 and 4 compared to 1984 (Oehme, 1991,  
160 Wu et al., 2010). Even though the levels of HCHs decreased across latitudes in the NH, the concentrations  
161 of HCHs were still much higher than in the SH (Iwata et al., 1993, Table1, Figure 2). A steep gradient of  
162  $[\alpha\text{-HCH}]_{\text{gas}}$  was observed in the Pacific between the Arctic Ocean and the Southern Ocean (Fig. 2a).  
163 Although  $[\gamma\text{-HCH}]_{\text{gas}}$  also decreased from 80°N towards SH, a slight increasing trend was observed near  
164 the Antarctic Continent (Fig.2). Variations in the  $\alpha$ -HCH and  $\gamma$ -HCH distribution patterns are probably  
165 determined by the physiochemical properties of these compounds and usage history of technical HCHs and  
166 lindane. Technical HCHs had been used heavily from 1940s to 2000 in NH (Iwata et al., 1993; Lakaschus  
167 et al., 2002). Due to their high volatility (Table S3),  $\alpha$ -HCH and  $\gamma$ -HCH can also be transported far away  
168 from source regions via long-range atmospheric transport and condensed at high latitudes (i.e. Arctic) due  
169 to global distillation. Relatively uniform distribution of  $\alpha$ -HCH in the SH indicates less usage of technical  
170 HCH in the SH, whereas increasing  $[\gamma\text{-HCH}]_{\text{gas}}$  with latitude in the SH suggests more lindane was used in  
171 the SH (Tanabe and Tatsukawa, 1982). The observed increase of both HCH isomers near Antarctic could  
172 also be that the result of previously deposited HCHs outgassing to the environment resulted from ice  
173 melting (Dachs 2011, Galbán-Malagón et al., 2013, Cabrerizo et al., 2013). Technical HCH was banned  
174 since the 1970s by many countries (Li and Macdonald 2005) resulted in the continuous decline in  $\alpha$ -HCH  
175 levels globally seen in this study and in Canadian Arctic throughout the 1990s (Hung et al., 2005). Since  
176 both HCHs showed decline trends in both hemispheres compared to the 1990s (Iwata et al., 1993)  
177 suggesting no major emission sources since then, an apparent first order half-life ( $t_{1/2}$ ) can be estimated



178 following  $t_{1/2}=t/\log_{1/2}([HCH]_t/[HCH]_0)$ , where  $t$  is the time interval between 1990 and 2007,  $[HCH]_t$  is the  
179 concentration measured in 2007 in the Pacific and  $[HCH]_0$  is the concentration reported by Iwata et al  
180 (1993). The half-lives for  $\alpha$ -HCH were about 3.0 years both in the NH and SH, which were similar to those  
181 estimated in Great Lakes (3.3-4.4 years, Cortes and Hites 2000) but were lower than those for Canadian  
182 Arctic (9.1 years, Hung et al., 2005), presumably because the  $\alpha$ -HCH emitted in the lower latitudes would  
183 deposit in the Arctic region due to its high volatility, then re-emit to the atmosphere from Arctic Ocean and  
184 glacial/ice loss (Dachs 2011, Galbán-Malagón et al., 2013, Cabrerizo et al., 2013), which slowed down the  
185 decline in higher latitudes. The half-lives for  $\gamma$ -HCH derived here were 4.5 and 4.4 years in NH and SH,  
186 respectively, which are similar to those in Great Lakes (4.6-5.4 years, Cortes and Hites 2000) and Canadian  
187 Arctic (4.9-5.7 years, Hung et al., 2005). The longer half-lives of  $\gamma$ -HCH compared to  $\alpha$ -HCH were  
188 probably due to the continued usage of lindane ( $\gamma$ -HCH) after the ban of technical HCHs.

189 The ratio of the  $\alpha/\gamma$ -HCH has been suggested as a method of characterizing local lindane (mainly  $\gamma$ -  
190 HCH) releases (near or less than 1) versus global transport of technical HCH residues ( $\alpha/\gamma$ -HCH >1) (Willett  
191 et al., 1998; Lakaschus et al., 2002; Dickhut et al., 2005). Variation of the  $\alpha/\gamma$ -HCH ratios in space and time  
192 were influenced by the historical usage of technical HCH and lindane and the environmental behaviors of  
193 the two isomers during the LRT (Iwata et al., 1993). In this study, the average ratio of  $\alpha/\gamma$ -HCH was 1 in  
194 the N Pacific which was comparable with the value reported in the Equatorial Indian Ocean (1.3) in 2011  
195 (Huang et al., 2013), but was lower than those in the N Pacific (4) (Iwata et al., 1993) in 1989-1990, the  
196 Northern N Pacific (9.4) in 2003 (Ding et al., 2007) and (2.6) in 2008 (Wu et al., 2010), and the North  
197 Atlantic (3.3) in 2008 (Zhang et al., 2012) and Arctic Ocean (2.3) in 2004 (Lohmann et al., 2009). It is  
198 reasonable to have  $\alpha/\gamma$ -HCH >1 in the NH, as technical HCHs were heavily used in the NH until 2000  
199 (Lakaschus et al., 2002) and photochemical reactions during the LRT could also convert  $\gamma$ -HCH to  $\alpha$ -HCH  
200 to make the ratio higher than 1 (Iwata 1993 and Willett et al., 1998). To the contrary, the average  $\alpha/\gamma$ -HCH  
201 ratio is 0.5 in the S Pacific, in line with the value reported in the Southern Ocean (0.6) in 2008-2009  
202 (Galbán-Malagón et al., 2013). There was also a declining trend of the ratio (1.8-0.3) along the cruise track  
203 (Spearman's  $F_{25} = 0.697$ ,  $p = 0.01$ ) from NH to SH. The temporal and spatial declining trend of this ratio

204 together with the distribution patterns of HCHs observed in this study indicate a reduction in usage of  
205 technical HCHs from NH to SH ([Dicknut et al., 2005](#)) and a greater usage of lindane in the SH ([Voldner](#)  
206 [and Li, 1995](#); [Jantunen et al., 2004](#)).

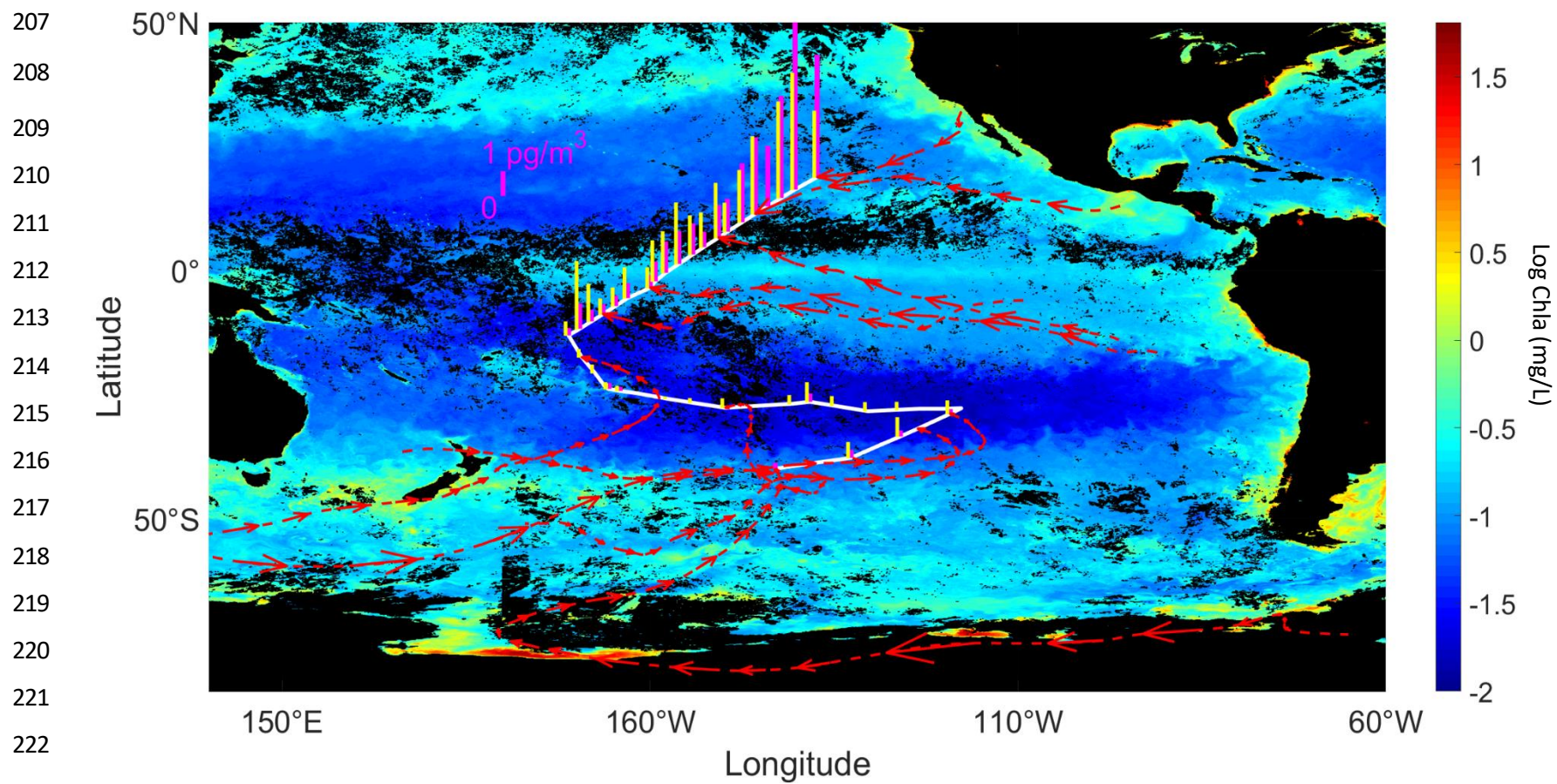
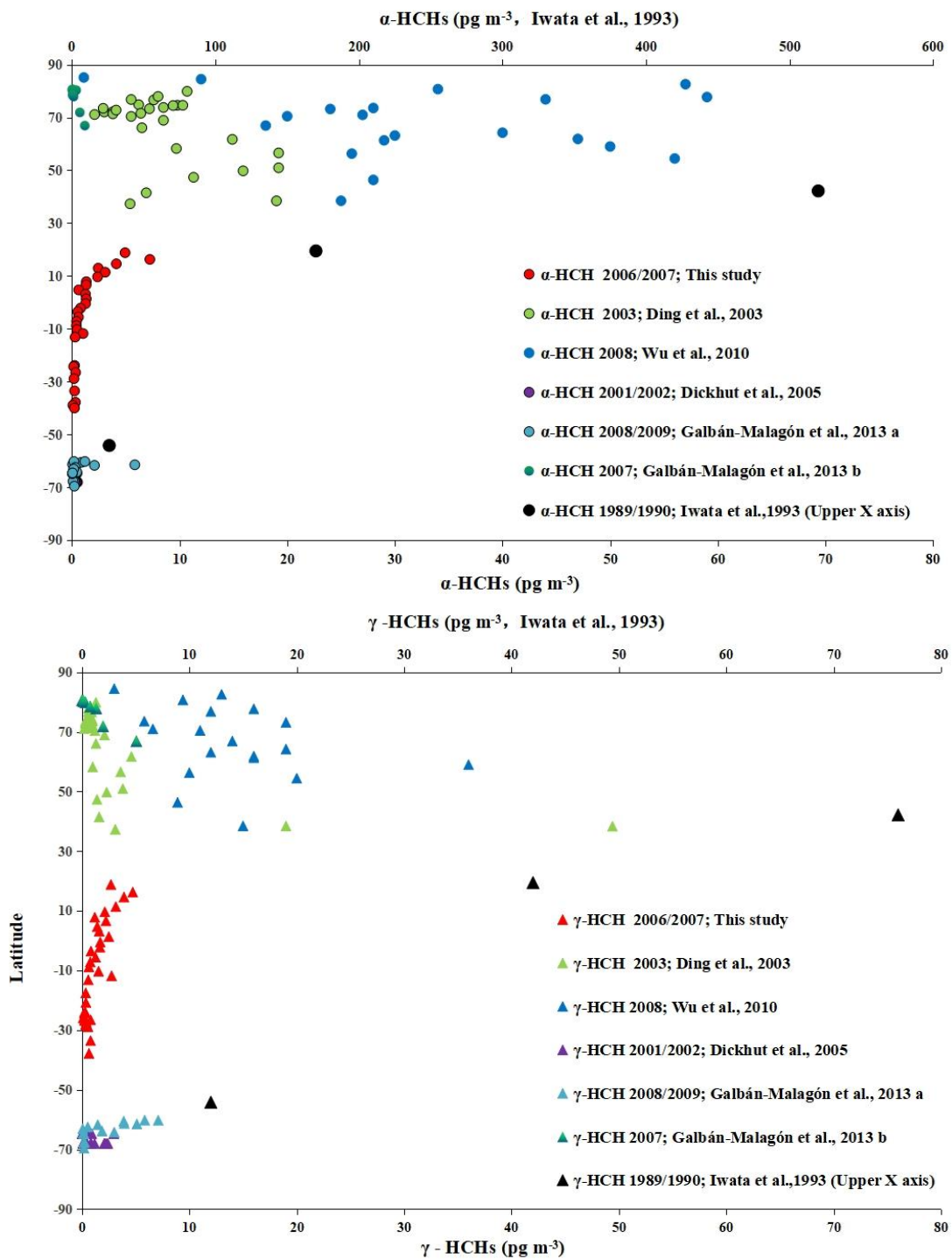


Figure 1 Gaseous HCH concentrations (magenta bars stand for  $\alpha$ -HCH; yellow bars stand for  $\gamma$ -HCH) and back trajectories (red dash arrows) during the sampling track. Color bar indicates chlorophyll a (Chla) concentration of Jan-2007 in the Pacific Ocean.



229  
230

231 Figure.2 Temporal and latitudinal distribution of gaseous  $\alpha$ -HCH (A) and  $\gamma$ -HCH (B) in the Pacific. Data were  
232 obtained from this study and previous studies cited in the legend.

233

Table 1 Concentration of OCPs in Water and Air of the Pacific Ocean.

Compound	water concentration (pg L <sup>-1</sup> )								air concentration (pg m <sup>-3</sup> )							
	>% DL		Average		Minimum		Maximum		>% DL		Average		Minimum		Maximum	
	N.H	S.H	N.H	S.H	N.H	S.H	N.H	S.H	N.H	S.H	N.H	S.H	N.H	S.H	N.H	S.H
α-HCH	78%	28%	18.8	0.8	1.3	0.2	37.2	2.9	100%	52%	2.7	0.4	0.6	0.1	7.2	1.3
β-HCH	67%	61%	79.4	17.0	33.8	6.2	152.6	26.7	0%	27%	–	1.4	–	0.2	–	5.9
γ-HCH	67%	61%	21.8	8.8	0.8	5.5	50.6	11.3	91%	76%	2.6	0.7	1.2	0.1	4.7	2.8
α/γ-HCH	67%	28%	1.4	0.3	0.8	0.3	2.0	0.3	91%	45%	1.0	0.5	0.4	0.3	1.8	1.0
<i>o,p'</i> -DDT	22%	33%	0.8	0.7	0.6	0.0	1.0	1.8	45%	27%	2.0	2.7	1.1	0.6	3.6	11.4
<i>o,p'</i> -DDD	22%	6%	0.4	1.2	0.3	1.2	0.4	1.2	–	–	–	–	–	–	–	–
<i>o,p'</i> -DDE	22%	22%	0.2	0.3	0.1	0.2	0.2	0.5	–	–	–	–	–	–	–	–
<i>p,p'</i> -DDT	22%	6%	0.4	0.6	0.4	0.6	0.5	0.6	–	–	–	–	–	–	–	–
<i>p,p'</i> -DDD	22%	17%	2.0	2.8	1.3	1.3	2.7	4.7	–	–	–	–	–	–	–	–
<i>p,p'</i> -DDE	33%	33%	0.9	1.0	0.4	0.6	1.5	1.7	64%	21%	1.3	2.3	0.8	0.3	1.9	7.2
TC	33%	22%	1.2	0.9	0.7	0.7	1.6	1.0	64%	39%	3.0	3.0	1.8	0.4	4.9	8.0
CC	33%	17%	1.2	0.6	0.1	0.1	1.9	1.4	36%	15%	1.6	1.3	1.2	0.8	2.0	2.0
TC/CC	33%	6%	2.1	0.7	0.8	0.7	4.6	0.7	36%	12%	2.3	2.0	2.0	0.5	2.5	3.0
HEPT	22%	11%	0.1	0.1	0.1	0.0	0.1	0.2	100%	76%	3.3	1.0	1.2	0.2	6.1	3.9
HEPX	67%	39%	0.4	0.6	0.2	0.1	0.8	3.1	91%	36%	0.9	1.1	0.6	0.1	1.2	1.9
HEPX/HEPT	22%	6%	4.4	1.8	3.0	1.8	5.8	1.8	91%	36%	0.4	1.0	0.1	0.1	0.9	2.7

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237 3.1.2 DDT and its metabolites.

238 In the gas phase, *o,p'*-DDT and *p,p'*-DDE were the most abundant DDT and its derivatives detected.  
239 The concentration of *o,p'*-DDT ranged from 1.1 to 3.6 (avg.= 2.0)  $\text{pg m}^{-3}$  in the NH, which were in line with  
240 the reported values in the N Pacific (0.2-2.5  $\text{pg m}^{-3}$ ) (Ding et al., 2003) and the Equatorial Indian Ocean  
241 (0.4-2.9  $\text{pg m}^{-3}$ ) (Huang et al., 2013), but lower than those measured two decades ago in the N Pacific from  
242 11.62 °N to 43.73 °N (Iwata et al., 1993, Table S6). The concentrations of *o,p'*-DDT were higher in the SH  
243 ranging from 0.6 to 11.4 (avg.= 2.7)  $\text{pg m}^{-3}$  (Fig. S1), which were higher than those reported in East Indian  
244 and Southern Ocean in the SH in 1989-1990 (Iwata et al., 1993). For *p,p'*-DDE, the average concentration  
245 was 1.3 (0.8-1.9)  $\text{pg m}^{-3}$  in the NH, which were similar to those reported in the same decade in the N Pacific  
246 (0.2-1.1  $\text{pg m}^{-3}$ , Ding et al., 2003), N Atlantic (0.3-1.1  $\text{pg m}^{-3}$ , Zhang et al., 2012), and Equatorial Indian  
247 Ocean (0.2-2  $\text{pg m}^{-3}$ , Huang et al., 2013), but was lower than that in the Canadian Arctic (0.7-8.3  $\text{pg m}^{-3}$ ,  
248 Lohmann et al., 2009) and lower than the samples collected in the N Pacific in 1989-1990 (Table S6) by  
249 Iwata et al. (1993). In contrast, the concentrations of *p,p'*-DDE (0.3-7.2  $\text{pg m}^{-3}$ ) in the lower and mid  
250 latitudes in the SH were higher than those reported two decades ago in the SH (Iwata et al., 1993), and  
251 higher than the values reported in the western Antarctic peninsula (0.29  $\text{pg m}^{-3}$ , Khairy et al., 2016). This  
252 temporal declining trend in the N Pacific and relative uniform distribution across different oceans in the  
253 NH suggest a reduced usage of DDTs in the NH, even though there was higher historical DDT use in the  
254 NH (Li and Macdonald, 2005). The concentrations of both *o,p'*-DDT and *p,p'*-DDE in the SH were higher  
255 than the NH, probably reflecting the existence of unknown sources of DDTs besides the residues of  
256 technical DDT (Voldner and Li, 1995; Channa et al., 2012) at the sample of sampling. Highest levels of  
257 gaseous DDTs in this study were located in the S Pacific gyre with 10-day back trajectory tracing the air  
258 back to New Zealand (about 40°S). However, the average wind speed of circumpolar westerly was about  
259 9-12 m/s (Sun et al., 2012), the shortest time needed for it to circle the earth is 30 days at 40°S, so the  
260 current source of DDT usage could be from any countries around this latitude in the SH. Another possibility



261 is that these relatively high levels DDTs were resulted from outgassing of previously deposited DDTs due  
262 to glacial melting/ice loss (Dachs 2011, Galbán-Malagón et al., 2013, Cabrerizo et al., 2013).

### 263 3.1.3 Chlordane.

264 Technical chlordane including two abundant isomers: TC (8-15%) and CC (8-13%), and other  
265 components with different numbers of chlorines, such as heptachlor (Dearth, 1991) were banned by the  
266 Stockholm Convention on Persistent Organic Pollutants in 2001. In the atmosphere over Pacific, HEPT  
267 displayed the highest average concentration in the NH (mean 3.3  $\text{pg m}^{-3}$ ) among all chlordane compounds,  
268 followed by TC (3.0  $\text{pg m}^{-3}$ ), CC (1.6  $\text{pg m}^{-3}$ ) and HEPX (1  $\text{pg m}^{-3}$ ; Table 1). The chlordane compounds  
269 with highest average concentration in the SH was TC (3.0  $\text{pgm}^{-3}$ ), followed by CC (1.3  $\text{pgm}^{-3}$ ), HEPX (1.1  
270  $\text{pg m}^{-3}$ ), and HEPT (1.0  $\text{pg m}^{-3}$ ). The different distribution patterns between the NH and the SH probably  
271 attribute to the isomer-specific behavior during the long-range transport (Iwata et al., 1993) and different  
272 usage history in different hemispheres.

273 The concentration of TC in the gas phase ( $[\text{TC}]_{\text{gas}}$ ) ranged from 1.8 to 4.9  $\text{pg m}^{-3}$  and 0.4 to 8  $\text{pg m}^{-3}$  in  
274 the NH and SH, respectively, and CC concentration ( $[\text{CC}]_{\text{gas}}$ ) ranged from 1.2 to 2.0  $\text{pg m}^{-3}$  and 0.8 to 2.0  
275  $\text{pg m}^{-3}$  in the NH and SH, respectively (Table 1). TC was more frequently detected than CC in both  
276 hemispheres (Table 1). These gaseous concentration levels in the N Pacific were about 2 to 5-fold lower  
277 than those measured in 1989-1990 (Iwata et al., 1993), showing that both TC and CC were declining over  
278 the N Pacific Ocean in the past 2 decades. However, much higher values of TC and CC were reported in  
279 the Equatorial Indian Ocean in 2011, suggesting possible continue usage of chlordane in Sri Lanka (Huang  
280 et al., 2013). Back trajectories of the air samples collected in the NH suggest the air mass mainly coming  
281 from the east from American continents transported by Trade Winds (Fig S2 and Fig 1), which may have  
282 caused the relatively higher levels of TC and CC in this study compared to reports in the Arctic Ocean in  
283 2004 (Lohmann et al., 2009), N Atlantic in 2008 (Zhang et al., 2012), and Antarctic in 2010 (Khairy et al.,  
284 2016). Technical chlordane has a TC/CC range of 0.76-0.87 in China (Li et al., 2006) and ~1.16 in North  
285 America and other places in the world (Shunthirsingham et al., 2010; Jantunen et al., 2000; Mattina et al.,

286 1999). The mean value of TC/CC was 2.3 in NH, 2 in SH in this study, which were higher than those in the  
287 technical mixture, but a similar TC/CC value (2) in the dissolved phase was reported in the Arctic in  
288 1993/1994 (Jantunen and Bidleman 1998). The apparent half-lives estimated in this study for TC is 15 years  
289 and 9.6 years for CC, respectively. Therefore, it is reasonable that the TC/CC ratio in the air exceed the  
290 ratio in the technical mixture.

291 HEPT ranged from 1.2 to 6.1  $\text{pg m}^{-3}$  in the NH and 0.2 to 3.9  $\text{pg m}^{-3}$  in the SH, respectively. HEPX  
292 ranged from 0.6 to 1.2  $\text{pg m}^{-3}$  in the NH and 0.1 to 2.7  $\text{pg m}^{-3}$  in the SH, which was similar to those reported  
293 in the Atlantic Ocean in 2008 (Zhang et al., 2012), suggesting HEPX as the metabolite of HEPT may have  
294 a uniform distribution in the open ocean. HEPT, on the other hand may still be used in some countries at  
295 the time of sampling (2006-2007) as high levels (27  $\text{pg m}^{-3}$ ) were observed in the Equatorial Indian Ocean  
296 in 2011 (Huang et al., 2013). In addition, HEPT was the most frequently detected isomers in the air and has  
297 higher concentrations than HEPX in the NH. This could be due to the larger historical emissions in the NH  
298 (Iwata et al., 1993) and continuous usage in some countries (Huang et al., 2013), and also due to the much  
299 higher  $K_{AW}$  of HEPT than other chlordane compounds (Table S3), which results a relatively low HEPX/  
300 HEPT ratio in the NH (0.4). The HEPX/ HEPT ratio in the SH averaged at 1, which may suggest no current  
301 usage of HEPT in the SH and further confirmed by a declining trend of HEPT gaseous concentrations along  
302 the ship track observed in this study (Fig. S3, Spearman's  $F_{36}=0.82$ ,  $p=0.01$ ).

### 303 3.2 Dissolved phase concentration level and distribution pattern of OCPs in open Pacific

#### 304 3.2.1 HCH

305 Reports on dissolved HCH isomers in seawater are much more limited than measurements for gas  
306 phase, especially in the S Pacific Ocean. Similar to the distribution pattern in the gas phase, the  
307 concentrations of dissolved HCH isomers in NH were much higher (2-24 folds) than in the SH, which is in  
308 consistent with the higher historical usage of technical HCH in the NH (Xie et al., 2011). Average  
309 concentrations in NH were 18.8  $\text{pg L}^{-1}$  for  $\alpha$ -HCH, 79.4  $\text{pg L}^{-1}$  for  $\beta$ -HCH, and 21.8  $\text{pg L}^{-1}$  for  $\gamma$ -HCH. In  
310 the SH, average concentrations for  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HCH were 0.8  $\text{pg L}^{-1}$ , 17  $\text{pg L}^{-1}$  and 8.8  $\text{pg L}^{-1}$ , respectively



311 (Table 1). There was about 2-fold decline of the average dissolved  $\gamma$ -HCH ( $[\gamma\text{-HCH}]_{\text{diss}}$ ) concentration in  
312 the N Pacific in this study compared to those measured in 1989-1990 (Iwata et al., 1993), and dissolved  $\alpha$ -  
313 HCH ( $[\alpha\text{-HCH}]_{\text{diss}}$ ) decreased about 10 times compared to two decades ago (Table S7). Such disproportional  
314 reductions in dissolved concentrations lead to higher  $[\gamma\text{-HCH}]_{\text{diss}}$  than  $[\alpha\text{-HCH}]_{\text{diss}}$ , and higher half-life of  
315  $\gamma$ -HCH (16.2 years) than  $\alpha$ -HCH (5.28 years) in the N Pacific, which could also be attributed to higher  
316 lindane usage after the volunteered ban of technical HCHs before the 2000. This pattern was also observed  
317 in the Southern Ocean near the Western Antarctic Peninsula (Dickhut et al., 2005; Galbán-Malagón et al.,  
318 2013c).  $[\gamma\text{-HCH}]_{\text{diss}}$  and  $[\alpha\text{-HCH}]_{\text{diss}}$  in the N Pacific were in line with those observed in the N Atlantic  
319 (Zhang et al., 2012) and N Atlantic (Lohmann et al., 2009), but were still lower than those in the Canadian  
320 Arctic (Wong et al., 2011).  $[\alpha\text{-HCH}]_{\text{diss}}$  in the SH decreased strongly compared to Iwata reported in the East  
321 Indian Ocean (9.6-36.6 °S) and Southern Ocean (44.2-64.7 °S) in 1989-1990 (Iwata et al., 1993), but the  
322  $[\gamma\text{-HCH}]_{\text{diss}}$  (8.8 pg L<sup>-1</sup>) did not decrease much compared to two decades ago (8.2 pg L<sup>-1</sup> in the Southern  
323 Ocean, Table S7), suggesting the possible usage of lindane in the SH (Jantunen et al., 2004) and no first-  
324 order half-life can be derived. Such declining in seawater resulted in an average  $\alpha/\gamma$ -HCH ratio of 1.4 in the  
325 NH, which was in line with the reported values in Equatorial Indian Ocean (1.46, Huang et al., 2013) but  
326 was lower than those from two decades ago and those in the higher latitudes in the Atlantic (Lohmann et  
327 al., 2009, Zhang et al., 2012). and the  $\alpha/\gamma$ -HCH ratio was 0.3 in the SH, which was similar to those reported  
328 in the Southern Ocean (0.27) in 2008-2009 (Galbán-Malagón et al., 2013b). Dissolved  $\alpha$ -HCH (Spearman's  
329  $F_{12} = 0.979$ ,  $p = 0.01$ ),  $\beta$ -HCH (Spearman's  $F_{17} = 0.880$ ,  $p = 0.01$ ), and  $\gamma$ -HCH (Spearman's  $F_{11} = 0.645$ ,  $p$   
330  $= 0.05$ ) concentrations also exhibited a strong decreasing gradient with latitudes along the cruise track,  
331 while no correlation with temperature was founded.  $\beta$ -HCH was found to have higher concentrations in  
332 surface seawater than  $\gamma$ -HCH and  $\alpha$ -HCH in both NH and SH, which was probably due to the much lower  
333  $K_{\text{AW}}$  of  $\beta$ -HCH compared to other two HCH isomers (Table S3) and  $\beta$ -HCH is also more stable than other  
334 isomers, making it accumulate in the dissolved phase. This pattern was also observed by Huang et al. (2013)  
335 in the Equatorial Indian Ocean. The average dissolved concentration of  $\beta$ -HCH in SH was about 5-fold

336 lower than NH, the latter was much higher than other oceans (Table S7) such as the Atlantic Ocean (Zhang  
337 et al., 2012; Xie et al., 2011), the Equatorial Indian Ocean (Huang et al., 2013) and Southern Ocean (Dicknut  
338 et al., 2005; Galbán-Malagón et al., 2013b). This was probably due to the fact that most of the sampling in  
339 this study was in the middle of the N and S Pacific Gyres, the current circulation in the central gyre is slower  
340 than those in the boundary currents, which may lead to the accumulation of plastics, garbage, and POPs.

### 341 3.2.2 DDT and its metabolites.

342 *o,p'*- and *p,p'*-DDT and all their metabolites (*o,p'*- and *p,p'*-DDE and DDD) were detected in the  
343 dissolved phase (Table S7). *p,p'*-DDT levels in lower latitudes of the N Pacific (0.4-0.5 pg L<sup>-1</sup>) were lower  
344 than the value reported in 1989-1990 (Iwata et al., 1993), but were higher than the measurements (0.02-0.2  
345 pg L<sup>-1</sup>) in Northern N Atlantic Ocean in 2004 (Lohmann et al., 2009), which suggests a greater reduction  
346 in DDT usage in the N Atlantic surrounding countries. On the contrary, the average concentrations of both  
347 *o,p'*- and *p,p'*-DDT (0.7 and 0.6 pg L<sup>-1</sup>) were close to the values reported in the SH two decades ago (Iwata  
348 et al., 1993), suggesting ongoing usage of DDT products in lower latitudes of N Pacific and in the SH.  
349 Indeed, much higher levels of DDT (avg. 330 pg L<sup>-1</sup> for *o,p'*-DDT and 1600 pg L<sup>-1</sup> for *p,p'*-DDT) and its  
350 derivatives were detected in the Equatorial Ocean in 2011 (Huang et al., 2013). Technical DDT was still  
351 used in India (Huang et al., 2013) and some African countries (Voldner and Li, 1995; Channa et al., 2012)  
352 for agricultural and public health purposes at the time of sample collection in this study, which probably  
353 lead to the increase in the background concentrations of dissolved DDTs in the lower latitudes of the NH  
354 and SH. The dissolved concentrations of  $\sum$ DDTs were significantly lower than those of dissolved  $\sum$ HCHs,  
355 reflecting lower global production of  $\sum$ DDTs than  $\sum$ HCHs (Li and Macdonald, 2005), coupled with the  
356 different physiochemical properties. DDTs are more hydrophobic with much higher  $K_{ow}$  values than HCHs  
357 (Shen and Wania, 2005), thus are removed from the seawater quickly by sinking particles (Lohmann et al.,  
358 2007).

### 359 3.2.3 Chlordane.

360 As the most abundance compounds in the technical chlordane, TC and CC had higher average  
361 concentrations than HEPT and HEPX (Table S7) both in the NH and SH. The dissolved concentration of

362 TC ranged from 0.7 to 1.6 pg L<sup>-1</sup> and from 0.1 to 1.9 pg L<sup>-1</sup> for CC in NH, the average dissolved  
363 concentration of both isomers was 1.2 pg L<sup>-1</sup> in the NH. Similar to the HCH distribution pattern, the  
364 concentrations of TC and CC in the NH are higher than those in the SH, which is probably attributed to the  
365 usage history. The average dissolved concentrations in the SH for TC and CC were 0.9 (0.7 to 1 pg L<sup>-1</sup>) and  
366 0.6 pg L<sup>-1</sup> (0.1 to 1.4 pg L<sup>-1</sup>), respectively. Compared to the reported levels of TC (avg. 3.4 pg L<sup>-1</sup>) and CC  
367 (avg. 3 pg L<sup>-1</sup>) in 1989-1990 in the N Pacific and those in the SH (Table S7), the present concentration  
368 levels were about 2-3 times lower, and this declining trend reflected the decline usage of chlordane globally  
369 in the past two decades. However, these values from the Pacific were still higher than those in the Northern  
370 N Atlantic (0.5 pg L<sup>-1</sup> for TC, 0.2 pg L<sup>-1</sup> for CC) in 2004 (Lohmann et al., 2009) and the N Atlantic (0.7 pg  
371 L<sup>-1</sup> for both isomers) in 2008 (Zhang et al., 2012), which was likely due to two reasons. First of all, there are  
372 still ongoing usage of Chlordane compounds in the lower latitudes, for example, the TC (9.4 pg L<sup>-1</sup>) and  
373 CC (6.6 pg L<sup>-1</sup>) concentrations in the Equatorial Indian Ocean were significantly higher (Huang et al., 2013).  
374 Secondly, the sampling tracks in this study mainly crossed N and S Pacific gyres with very little biological  
375 activities (low chlorophyll a concentrations in Figure 1), the removal of these hydrophobic large-molecular-  
376 weight pesticides by sinking particles produced by plankton would be very little, evidenced by extremely  
377 low chlorophyll-a concentration (Fig 1) and low sedimentation rates reported by D'Hondt et al., (2009).  
378 Therefore, the derived first-order half-lives for TC (12.0 years in NH and 18.0 years in SH) and CC (13.6  
379 years in NH and 12.7 years in SH) were relatively long.

380 TC/CC ratio has been used to distinguish between aged and new sources of chlordane (Bidleman et  
381 al., 2002; Shunthirsingam et al., 2010). In this study, the mean ratio of TC/CC was 2.1 in the NH and 0.7  
382 in the SH. Long-range atmospheric transport likely supply chlordane with a lower TC/CC ratio than freshly  
383 evaporated chlordane (Bidleman et al., 2002). The TC/CC value in the NH (2.1) was very similar to what  
384 was reported in the Arctic Ocean (Jantunen and Bidleman 1998). The ratio in the S Pacific Ocean was much  
385 lower than the technical grade (~1.16), which was in line with that in the N Atlantic Ocean (avg. 0.53±0.22)  
386 in 2004 (Lohmann et al., 2009). The lower ratio in the dissolved phase in the S Pacific Ocean together with

387 the lower concentration of chlordane in the SH than in the NH, indicating that study area had received aged  
388 chlordane by long-range atmospheric transport from the source areas (Shunthirasingham et al., 2010).

389 HEPX is the most detected chlordane compounds in the dissolved phase. The average dissolved  
390 concentrations of HEPX ( $0.4 \text{ pg L}^{-1}$  in the NH and  $0.6 \text{ pg L}^{-1}$  in the SH) were higher than HEPT in both  
391 hemispheres ( $0.1 \text{ pg L}^{-1}$  in the NH and  $0.11 \text{ pg L}^{-1}$  in the SH), which was probably caused by the differences  
392 in their physiochemical properties (Table S3). HEPX has lower  $K_{Aw}$  value than HEPT, thus, the latter  
393 prefers to stay in the gas phase. Their  $K_{ow}$  values are similar which is higher than HCHs but lower than  
394 DDTs. HEPX would tend to accumulate more in the dissolved phase due to less removal by sinking particles,  
395 resulting in relatively higher dissolved concentrations observed in this study.

### 396 3.3 Directions and fluxes of air-water exchange

397 The FRs and  $F_{a/w}$  for four OCP compounds were calculated and summarized in Table 2. All of four  
398 OCPs have  $K_{aw}$  values smaller than  $1 \times 10^{-3}$  (Table 2) suggesting the limiting step for air-water exchange is  
399 on the water side (Schwarzenbach et al., 2003). According to the FRs,  $\alpha$ -HCH varied between equilibrium  
400 and net deposition along the cruise track. Deposition or equilibrium between gaseous and dissolved phase  
401 of  $\alpha$ -HCH were also observed in the North Atlantic Ocean (Lohmann et al., 2009; Zhang et al., 2012), the  
402 Southern Ocean during 2008 to 2009 (Galbán-Malagón et al., 2013a), and the Western Antarctic Peninsula  
403 in 2001-2002 (Dickhut et al., 2005). The FRs suggested that the air-water exchange of  $\beta$ -HCH was at the  
404 equilibrium or deposition in the S Pacific, which was also reported in the Atlantic Ocean in 2008 (Xie et  
405 al., 2011). In contrast, all FRs for  $\gamma$ -HCH reflected net volatilization from water to air. However, most  
406 previous studies reported net deposition and equilibrium for  $\gamma$ -HCH in other water bodies (Lohmann et al.,  
407 2009; Zhang et al., 2012; Dickhut et al., 2005; Galbán-Malagón et al., 2013). Less hydrophobicity of HCHs  
408 lead to less removal by sinking particles in the ocean and enable them to actively exchange through the air-  
409 water interface, which together with the relatively high dissolved concentrations cause  $\gamma$ -HCH to volatilize  
410 in the Pacific. To our best knowledge, it is the first time that the volatilization of  $\gamma$ -HCH in the open ocean  
411 was observed, this could be due to the delayed ban of lindane, which was not incorporated into the

412 Stockholm Convention until 2009 (Wong et al., 2010). Most of the FRs for HEPX were found to be  
413 deposited.

414 The net deposition fluxes of  $\alpha$ -HCH in this study ranged from -6.9 to -4.1 ng m<sup>-2</sup>day<sup>-1</sup> in the N Pacific,  
415 which were about 100 times lower than those during 1989 to 1990 (about -500 ng m<sup>-2</sup>day<sup>-1</sup>, Iwata et al.,  
416 1993). While technical HCHs were still used, many water bodies probably acted as a sink for HCHs such  
417 as observed in 1989-1990 (Iwata et al., 1993). However, after the primary emission sources of POPs were  
418 banned in most of the countries, the air-water exchange was at equilibrium or evaporating from water to air  
419 for certain POPs in some water bodies, turning them secondary sources of these POPs. For example, Zhang  
420 et al. (2012) found that  $\alpha$ -HCH in the N Atlantic varied between deposition and equilibrium between gas  
421 and dissolved phases. The Pacific Ocean has also become the secondary source for PCBs (air-water  
422 exchange flux 0.5-30.4 ng m<sup>-2</sup> day<sup>-1</sup>) reported by a previous study (Zhang and Lohmann 2010). However,  
423 the status for  $\gamma$ -HCH has been dominated by net deposition in water bodies reporting by previous studies  
424 (Lohmann et al., 2009; Zhang et al., 2012; Xie et al., 2011; Huang et al., 2013). The volatilization of  $\gamma$ -  
425 HCH in this study with fluxes ranging from 0.3 to 11.1 ng m<sup>-2</sup> day<sup>-1</sup> suggested that the tropical Pacific  
426 Ocean were acting as a secondary source supplying  $\gamma$ -HCH to the atmosphere.

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434 Table 2 Summary of Fugacity (FR) and Air-Water Gas Exchange Fluxes ( $\text{ng m}^{-2} \text{d}^{-1}$ ) for different OCPs (Negative  
 435 values indicates net deposition fluxes, underlined italic values indicate net evaporation fluxes, and blanks next to FR  
 436 indicate that air-water was at equilibrium and thus no fluxes were calculated.)

Lat	Long	$\alpha$ -HCH		$\beta$ -HCH		$\gamma$ -HCH		HEPX	
		FR	Flux	FR	Flux	FR	Flux	FR	Flux
20.6	-135.2	0.59				0.06	<u>11.1</u>	0.39	
15.8	-140.8	4.09	-6.9					2.44	
12.5	-144.5	0.98							
9.0	-148.3	3.64	-4.1			0.02	<u>21.0</u>	1.73	
4.4	-153.0					0.04	<u>4.3</u>		
0.9	-156.5							2.07	
-2.6	-159.6			1.74				2.78	
-5.9	-163.4			0.82					
-7.2	-164.7					0.04	<u>1.9</u>		
-9.2	-166.9			1.34				5.48	-1.8
-13.1	-171.1	0.23	<u>0.1</u>			0.04	<u>0.9</u>		
-27.3	-134.9					0.10	<u>0.3</u>		
-28.4	-131.5							0.92	
-28.9	-119.3	1.16		3.10					
-30.5	-121.6								
-32.0	-123.8			2.41					
-33.5	-126.1	3.38	-0.2						

437

#### 438 4. Conclusion

439 The distribution patterns and air-water exchange status of OCPs in air and seawater samples in the  
 440 Pacific Ocean in 2006-2007 were assessed in this study. Both gaseous and dissolved phases concentration  
 441 for most OCPs were higher in the North than in the South Pacific. Higher OCPs levels were observed in  
 442 gas samples affected by Trade Winds coming from the American continents. In the N Pacific,  $\alpha$ -HCH levels  
 443 were lowered by a factor of 63 compared to those observed in 1990s (Iwata 1993), but  $\gamma$ -HCH's reduction  
 444 was not as strong, probably because lindane was still used after banning technical HCHs. This is the first  
 445 report that  $\gamma$ -HCH was returning to the atmosphere in open oceans. With ongoing volatilization,  $\gamma$ -HCH  
 446 may reach equilibrium soon like  $\alpha$ -HCH if there is no further lindane usage. DDTs in S Pacific were as high  
 447 as they were in 1990s which may indicate recent usage in the SH during the time of sample collection.  
 448 HEPT has higher gaseous concentrations than HEPX due to its higher  $K_{AW}$  whereas HEPX accumulated to  
 449 higher levels in the dissolved phase due to its low  $K_{AW}$  and intermediate  $K_{OW}$ . The four different groups of

450 OCPs showed different distribution patterns, suggesting such open ocean studies are very useful to reveal  
451 historical usage patterns, detect any new usages of OCPs, and predict their environmental fate through air-  
452 water exchange assessment. It is essential to continue monitoring POPs in the open oceans, even though  
453 there may not be any primary emission sources for legacy POPs, garbage and/or plastics in the ocean may  
454 slow down the reduction of these pollutants. Deploying polyethylene passive samplers (Lohmann et al.  
455 2017) on cargo ships could potentially provide an easy way of monitoring POPs in the open ocean, which  
456 can help distinguish between background concentrations of legacy POPs likely transported over long  
457 distances through atmospheric and oceanic currents and primary inputs of current usage in certain countries.

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