

6-10-2020

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

Follow this and additional works at: <https://digitalcommons.uri.edu/gsofacpubs>

The University of Rhode Island Faculty have made this article openly available.
Please let us know how Open Access to this research benefits you.

Rainer Lohmann

University of Rhode Island, rlohmann@uri.edu

This article is made available under the terms and conditions applicable towards Open Access Policy Articles, as set forth in our [Terms of Use](#).

Chenglong Wang

Citation/Publisher Attribution

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 α -HCH, γ -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 α -HCH and γ -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 γ -HCH was volatilizing from surface water to the atmosphere, and the air-water exchange fluxes were 0.3–11.1 ng m⁻² day⁻¹. This is the first field study that reported the open Pacific Ocean has become the secondary source for γ -HCH and implied that ocean could affect LRT of OCPs by supplying these compounds via air-sea exchange.

This Article is brought to you for free and open access by the Graduate School of Oceanography at DigitalCommons@URI. It has been accepted for inclusion in Graduate School of Oceanography Faculty Publications by an authorized administrator of DigitalCommons@URI. For more information, please contact digitalcommons-group@uri.edu.

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

The University of Rhode Island Faculty have made this article openly available.
Please let us know how Open Access to this research benefits you.

This is a pre-publication author manuscript of the final, published article.

Terms of Use

This article is made available under the terms and conditions applicable towards Open Access Policy Articles, as set forth in our [Terms of Use](#).

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

3 Yali Li^{a,b,c,d}, Rainer Lohmann^e, Xinqing Zou^{b,c}, Chenglong Wang^b, Lin Zhang^{d*}

4 ^a School of Marine Sciences, Sun Yat-sun University, Zhuhai 519082, China

5 ^b Ministry of Education Key Laboratory for Coastal and Island Development, Nanjing University, Nanjing 210093,
6 China

7 ^c Southern Marine Science and Engineering Guangdong Laboratory, Zhuhai, 519080, China

8 ^d Department of Physical and Environmental Science, Texas A&M University Corpus Christi, 78412, USA

9 ^e Graduate school of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA

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 α -HCH, γ -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 α -HCH and γ -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 γ -HCH was
23 volatilizing from surface water to the atmosphere, and the air-water exchange fluxes were 0.3 to 11.1 ng m⁻²
24 day⁻¹. This is the first field study that reported the open Pacific Ocean has become the secondary source
25 for γ -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, γ -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 α -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 (α , β , γ -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 α , β , γ -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 α , β , γ - 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 (pg m^{-3}) and dissolved (pg
112 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 α -HCH, 0.58 for γ -HCH, and 0.46 for HEPX,
115 respectively. The significant FRs for net deposition ($FR_{Deposition}$) were 1.56 for α -HCH, 1.55 for γ -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 α - β - and γ - HCH (\sum HCH) ranged from 2.1 to 12.0 pg m^{-3} (avg.
131 =5.1 pg m^{-3}) in the NH, and from 0.1 to 8.9 pg m^{-3} (avg. =1.1 pg m^{-3}) in the SH (Table 1). α - and γ -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 α -HCH ($[\alpha\text{-HCH}]_{\text{gas}}$) and γ -HCH ($[\gamma\text{-HCH}]_{\text{gas}}$)
140 were 2.7 pg m^{-3} (range 0.6-7.2 pg m^{-3}) and 2.6 pg m^{-3} (range 1.2-4.7 pg m^{-3}), respectively, which were about
141 4-7 times higher than the mean value of $[\alpha\text{-HCH}]_{\text{gas}}$ (0.4 pg m^{-3}) and $[\gamma\text{-HCH}]_{\text{gas}}$ (0.7 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, β -HCH was the most abundant isomer ranging from 0.2-5.9 pg
153 m^{-3} with an average value of 1.4 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 α -HCH and γ -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), α -HCH and γ -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 α -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 α -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 α -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 α -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 γ -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 γ -HCH compared to α -HCH were
188 probably due to the continued usage of lindane (γ -HCH) after the ban of technical HCHs.

189 The ratio of the α/γ -HCH has been suggested as a method of characterizing local lindane (mainly γ -
190 HCH) releases (near or less than 1) versus global transport of technical HCH residues (α/γ -HCH >1) (Willett
191 et al., 1998; Lakaschus et al., 2002; Dickhut et al., 2005). Variation of the α/γ -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 α/γ -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 α/γ -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 γ -HCH to α -HCH
200 to make the ratio higher than 1 (Iwata 1993 and Willett et al., 1998). To the contrary, the average α/γ -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](#)).

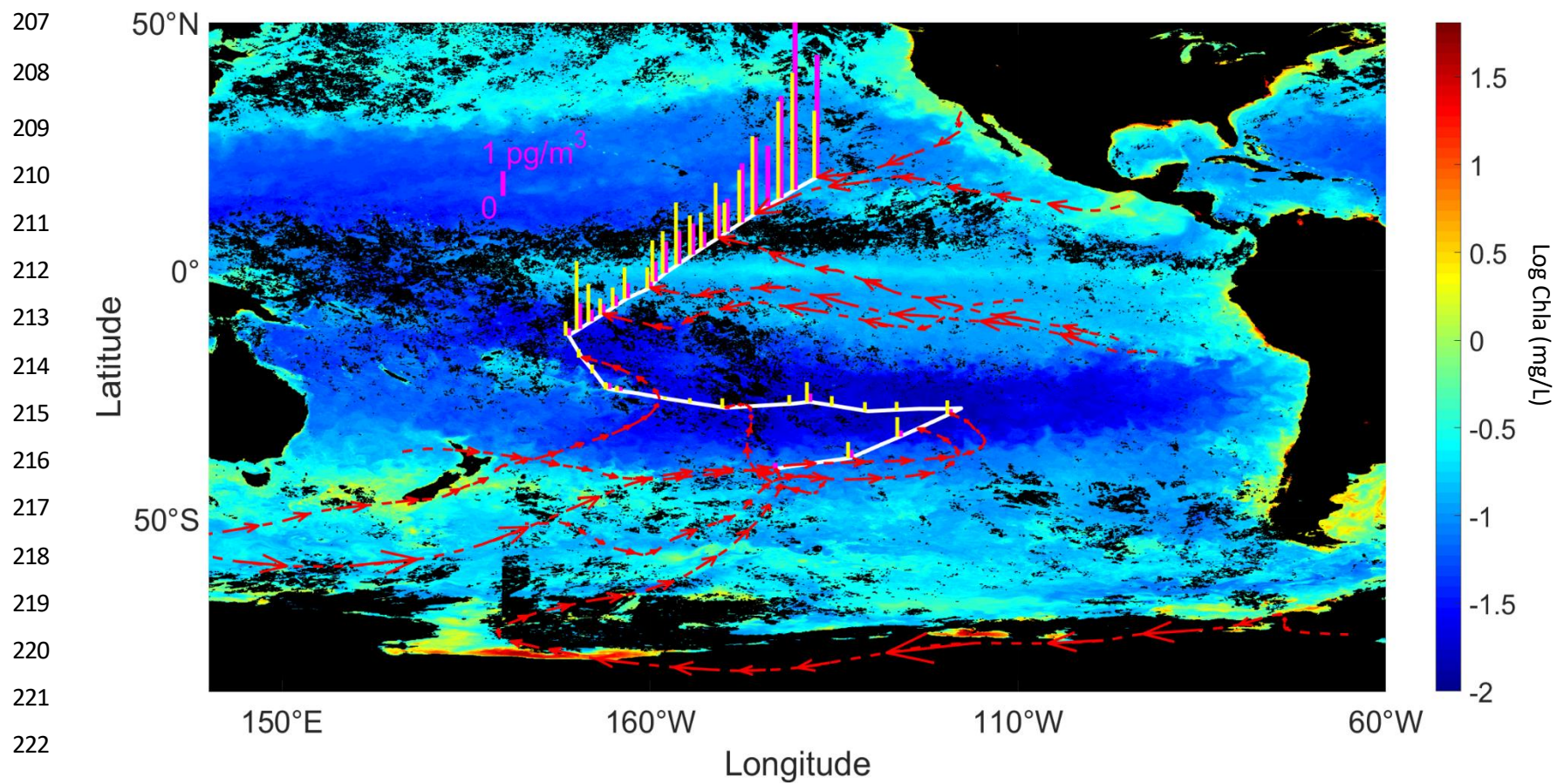
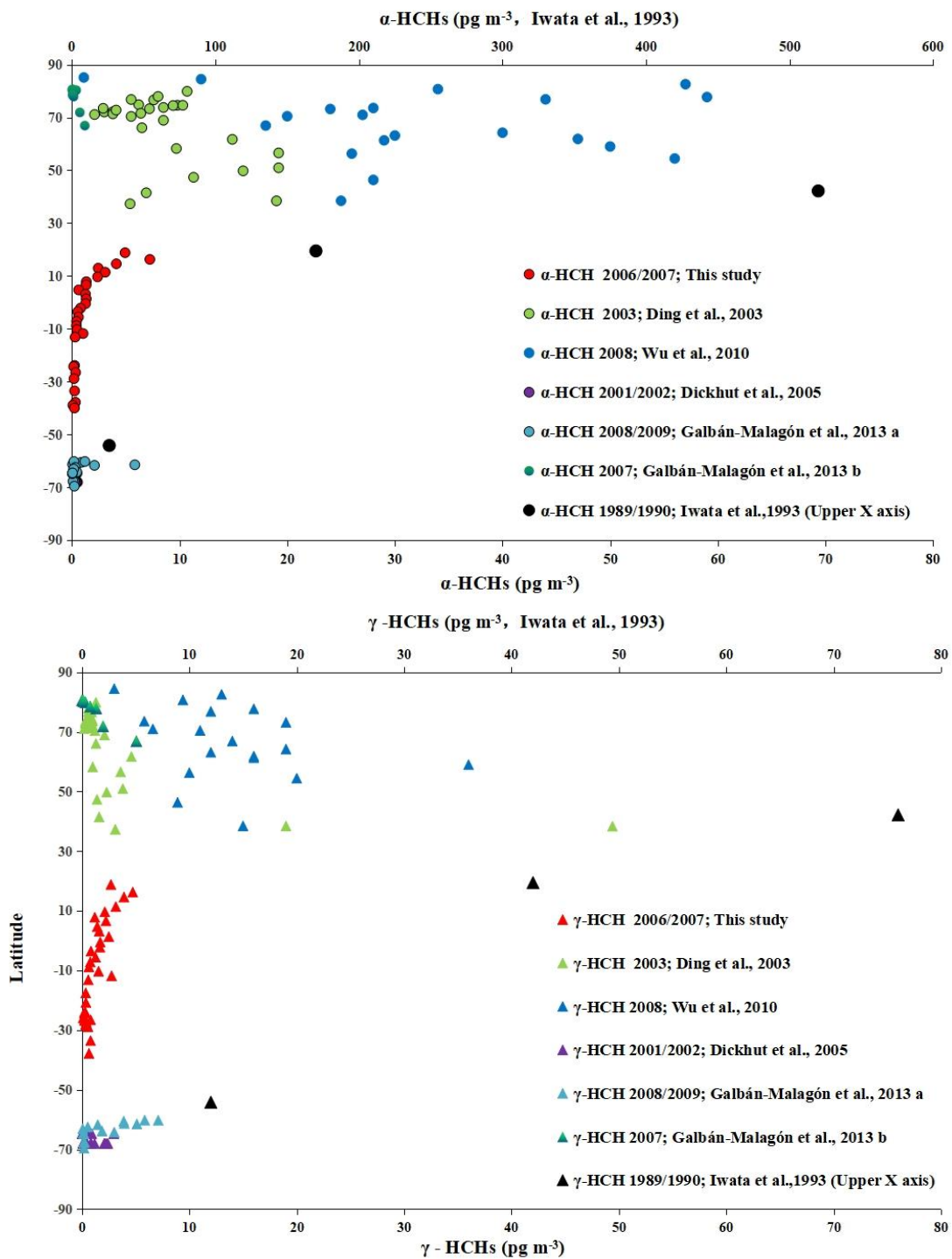


Figure 1 Gaseous HCH concentrations (magenta bars stand for α -HCH; yellow bars stand for γ -HCH) and back trajectories (red dash arrows) during the sampling track. Color bar indicates chlorophyll a (Chla) concentration of Jan-2007 in the Pacific Ocean.



229
230

231 Figure.2 Temporal and latitudinal distribution of gaseous α -HCH (A) and γ -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 ⁻¹)								air concentration (pg m ⁻³)							
	>% 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

234

235

236

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) pg m^{-3} in the NH, which were in line with
240 the reported values in the N Pacific (0.2-2.5 pg m^{-3}) (Ding et al., 2003) and the Equatorial Indian Ocean
241 (0.4-2.9 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) pg m^{-3} (Fig. S1), which were higher than those reported in East Indian
244 and Southern Ocean in the SH in 1989-1900 (Iwata et al., 1993). For *p,p'*-DDE, the average concentration
245 was 1.3 (0.8-1.9) 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 pg m^{-3} , Ding et al., 2003), N Atlantic (0.3-1.1 pg m^{-3} , Zhang et al., 2012), and Equatorial Indian
247 Ocean (0.2-2 pg m^{-3} , Huang et al., 2013), but was lower than that in the Canadian Arctic (0.7-8.3 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 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 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 pg m^{-3}) among all chlordane compounds,
268 followed by TC (3.0 pg m^{-3}), CC (1.6 pg m^{-3}) and HEPX (1 pg m^{-3} ; Table 1). The chlordane compounds
269 with highest average concentration in the SH was TC (3.0 pgm^{-3}), followed by CC (1.3 pgm^{-3}), HEPX (1.1
270 pg m^{-3}), and HEPT (1.0 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 pg m^{-3} and 0.4 to 8 pg m^{-3} in
274 the NH and SH, respectively, and CC concentration ($[\text{CC}]_{\text{gas}}$) ranged from 1.2 to 2.0 pg m^{-3} and 0.8 to 2.0
275 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 pg m^{-3} in the NH and 0.2 to 3.9 pg m^{-3} in the SH, respectively. HEPX
292 ranged from 0.6 to 1.2 pg m^{-3} in the NH and 0.1 to 2.7 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 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 pg L^{-1} for α -HCH, 79.4 pg L^{-1} for β -HCH, and 21.8 pg L^{-1} for γ -HCH. In
310 the SH, average concentrations for α -, β -, and γ -HCH were 0.8 pg L^{-1} , 17 pg L^{-1} and 8.8 pg L^{-1} , respectively

311 (Table 1). There was about 2-fold decline of the average dissolved γ -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 α -
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 γ -HCH (16.2 years) than α -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⁻¹) did not decrease much compared to two decades ago (8.2 pg L⁻¹ 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 α/γ -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 α/γ -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 α -HCH (Spearman's
329 $F_{12} = 0.979$, $p = 0.01$), β -HCH (Spearman's $F_{17} = 0.880$, $p = 0.01$), and γ -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. β -HCH was found to have higher concentrations in
332 surface seawater than γ -HCH and α -HCH in both NH and SH, which was probably due to the much lower
333 K_{AW} of β -HCH compared to other two HCH isomers (Table S3) and β -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 β -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⁻¹) 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⁻¹) 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⁻¹) 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⁻¹ for *o,p'*-DDT and 1600 pg L⁻¹ 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⁻¹ and from 0.1 to 1.9 pg L⁻¹ for CC in NH, the average dissolved
363 concentration of both isomers was 1.2 pg L⁻¹ 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⁻¹) and
366 0.6 pg L⁻¹ (0.1 to 1.4 pg L⁻¹), respectively. Compared to the reported levels of TC (avg. 3.4 pg L⁻¹) and CC
367 (avg. 3 pg L⁻¹) 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⁻¹ for TC, 0.2 pg L⁻¹ for CC) in 2004 (Lohmann et al., 2009) and the N Atlantic (0.7 pg
371 L⁻¹ 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⁻¹) and
373 CC (6.6 pg L⁻¹) 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 pg L^{-1} in the NH and 0.6 pg L^{-1} in the SH) were higher than HEPT in both
391 hemispheres (0.1 pg L^{-1} in the NH and 0.11 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 1×10^{-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, α -HCH varied between equilibrium
400 and net deposition along the cruise track. Deposition or equilibrium between gaseous and dissolved phase
401 of α -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 β -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 γ -HCH reflected net volatilization from water to air. However, most
406 previous studies reported net deposition and equilibrium for γ -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 γ -HCH to volatilize
410 in the Pacific. To our best knowledge, it is the first time that the volatilization of γ -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 α -HCH in this study ranged from -6.9 to -4.1 ng m⁻²day⁻¹ in the N Pacific,
415 which were about 100 times lower than those during 1989 to 1990 (about -500 ng m⁻²day⁻¹, 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 α -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⁻² day⁻¹) reported by a previous study (Zhang and Lohmann 2010). However,
423 the status for γ -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 γ -
425 HCH in this study with fluxes ranging from 0.3 to 11.1 ng m⁻² day⁻¹ suggested that the tropical Pacific
426 Ocean were acting as a secondary source supplying γ -HCH to the atmosphere.

427

428

429

430

431

432

433

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	α -HCH		β -HCH		γ -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, α -HCH levels
 443 were lowered by a factor of 63 compared to those observed in 1990s (Iwata 1993), but γ -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 γ -HCH was returning to the atmosphere in open oceans. With ongoing volatilization, γ -HCH
 446 may reach equilibrium soon like α -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.

458 **Acknowledgments**

459 This study was supported by NSF Atmospheric Chemistry award (0646574), the Collaborative
460 Innovation Center of South China Sea Studies of Nanjing University, the Natural Science Foundation of
461 Jiangsu Province (BK20130056), and Fundamental Research Funds for the central Universities.

462 **References**

- 463 Berrojalbiz, N., Castro-Jiménez, J., Mariani, G., Wollgast, J., Hanke, G., Dachs, J., 2014. Atmospheric
464 occurrence, transport and deposition of polychlorinated biphenyls and hexachlorobenzene in the
465 Mediterranean and Black Seas. *Atmos. Chem. Phys.* 14, 8947-8959.
- 466 Bidleman, T.F., Jantunen, L.M., Helm, P.A., Brorström-Lundén, E., Juntto, S., 2002. Chlordane
467 enantiomers and temporal trends of chlordane isomers in arctic air. *Environ. Sci. Technol.* 36, 539-
468 544.
- 469 Bidleman, T.F., Jantunen, L.M., Hung, H., Ma, J., Stern, G.A., Rosenberg, B., Racine, J., 2015. Annual
470 cycles of organochlorine pesticide enantiomers in Arctic air suggest changing sources and pathways.
471 *Atmos. Chem. Phys.* 15, 1411-1420.
- 472 Bigot, M., Muir, D.C.G., Hawker, D.W., Cropp, R., Dachs, J., Teixeira, C.F., Bengtson, N.S., 2016. Air-
473 seawater exchange of organochlorine pesticides in the Southern Ocean between Australia and
474 Antarctica. *Environ. Sci. Technol.* 50, 8001-8009
- 475 Breivik, K., Alcock, R., Li, Y., Bailey, R.E., Fiedler, H., Pacyna J.M., 2004. Primary sources of selected
476 POPs: regional and global scale emission inventories. *Environ. Pollut.* 128, 3-16.
- 477 Bruhn, R., Soenke, L., Michael, S.M., 2003. Air/sea gas exchange of PCBs in the southern Baltic
478 Sea. *Atmos. Environ.* 37, 3445-3454.
- 479 Cabrerizo, A.; Dachs, J.; Barceló, D.; Jones, K. C. Climatic and biogeochemical controls on the
480 remobilization and reservoirs of persistent organic pollutants in Antarctica. *Environ. Sci. Technol.*
481 2013, 47, 4299–4306,
- 482 Channa, K.R., Röllin, H.B., Wilson, K.S., Nøst, T.H., Odland, J.Ø., Naik, I., Sandanger, T.M., 2012.
483 Regional variation in pesticide concentrations in plasma of delivering women residing in rural indian
484 ocean coastal regions of South Africa. *J. Environ. Monitor.* 14, 2952-2960.

485 Dachs, J., Eisenreich, S.J., Baker, J.E., Ko, F.C. and Jeremiason, J.D., 1999. Coupling of phytoplankton
486 uptake and air-water exchange of persistent organic pollutants. *Environ. Sci. Technol.* 33, 3653-
487 3660.

488 Dachs, J., Lohmann, R., Ockenden, W.A., Méjanelle, L., Eisenreich, S.J. and Jones, K.C., 2002. Oceanic
489 biogeochemical controls on global dynamics of persistent organic pollutants. *Environ. Sci. Technol.*
490 36, 4229-4237.

491 Dachs, J. Coming in from the cold *Nat. Clim. Change* 2011, 1, 247–248

492 D'Hondt, S., Spivack, A.J., Pockalny, R., Ferdelman, T.G., Fischer, J.P., Kallmeyer, J., Abrams, L.J., Smith,
493 D.C., Graham, D., Hasiuk, F., Schrum, H., Stancin A.M., 2009. Subseafloor sedimentary life in the
494 south pacific gyre. *Proc. Natl. Acad. Sci. U.S.A.* 106, 11651-11656.

495 Dickhut, R.M., Cincinelli, A., Cochran, M., Ducklow, H.W., 2005. Atmospheric concentrations and air-
496 water flux of organochlorine pesticides along the Western Antarctic Peninsula. *Environ. Sci. Technol.*
497 39, 465-470.

498 Ding, X., Wang, X., Xie, Z., Xiang, C., Mai, B., Sun, L., Zheng, M., Sheng, G., Fu, J., 2007. Atmospheric
499 hexachlorocyclohexanes in the North Pacific Ocean and the adjacent arctic region: spatial patterns,
500 chiral signatures, and sea-air exchanges. *Environ. Sci. Technol.* 41, 5204-5209.

501 Galbán-Malagón, C., Berrojalbiz, N., Ojeda, M.J., Dachs, J., 2012. The oceanic biological pump modulates
502 the atmospheric transport of persistent organic pollutants to the Arctic. *Nat. Commun.* 3, 862.

503 Galbán-Malagón, C., Cabrerizo, A., Caballero, G., Dachs, J., 2013. Atmospheric occurrence and deposition
504 of hexachlorobenzene and hexachlorocyclohexanes in the Southern Ocean and Antarctic Peninsula.
505 *Atmos. Environ.*, 80, 41-49.

506 Galbán-Malagón, C., Berrojalbiz, N., Gloia, R., Dachs, J., 2013. The "degradative" and "biological" pumps
507 controls on the atmospheric deposition and sequestration of hexachlorocyclohexanes and
508 hexachlorobenzene in the north atlantic and arctic oceans. *Environ. Sci. Technol.* 47, 7195-7203.

509 Galbán-Malagón, C., Del Vento, S., Berrojalbiz, N., Ojeda, M., Dachs, J., 2013. Polychlorinated biphenyls,
510 hexachlorocyclohexanes and hexachlorobenzene in seawater and phytoplankton from the Southern
511 Ocean (Weddell, South Scotia, and Bellingshausen Seas). *Environ. Sci. Technol.* 47, 5578-5587.

512 Harner, T., Jantunen, L.M., Bidleman, T.F., Barrie, L.A., Kylin, H., Strachan, W.M., Macdonald, R.W.,
513 2000. Microbial degradation is a key elimination pathway of hexachlorocyclohexanes from the Arctic
514 Ocean. *Geophys. Res. Lett.* 27, 1155-1158.

515 Harner, T., Kylin, H., Bidleman, T.F., Strachan, W.M., 1999. Removal of α - and γ -hexachlorocyclohexane
516 and enantiomers of α -hexachlorocyclohexane in the Eastern Arctic Ocean. *Environ. Sci. Technol.* 33,
517 1157-1164.

518 Huang, Y., Xu, Y., Li, J., Xu, W., Zhang, G., Cheng, Z., Liu, J., Wang, Y., Tian, C., 2013. Organochlorine
519 pesticides in the atmosphere and surface water from the equatorial Indian Ocean: enantiomeric
520 signatures, sources, and fate. *Environ. Sci. Technol.* 47, 13395-13403.

521 Hung, H., Blanchard, P., Halsall, C.J., Bidleman, T.F., Stern, G.A., Fellin, P., Muir, D.C.G., Barrue, L.A.,
522 Jantunen, L.M., Helm, P.A., Ma, J., Konoplev, A., 2005. Temporal and spatial variabilities of
523 atmospheric polychlorinated biphenyls (PCBs), organochlorine (OC) pesticides and polycyclic
524 aromatic hydrocarbons (PAHs) in the canadian arctic: results from a decade of monitoring. *Sci. Total*
525 *Environ.* 342, 119-144.

526 Iwata, H., Tanabe, S., Sakai, N., Tatsukawa, R., 1993. Distribution of persistent organochlorines in the
527 oceanic air and surface seawater and the role of ocean on their global transport and fate. *Environ. Sci.*
528 *Technol.* 27, 1080-1098.

529 Jantunen, L. M. M.; Bidleman, T. F. Organochlorine pesticides and enantiomers of chiral pesticides in
530 Arctic Ocean water. *Archives of Environmental Contamination and Toxicology* 1998, 35, 218-228.

531 Jantunen, L.M., Kylin, H., Bidleman, T.F., 2004. Air-water gas exchange of alpha-hexachlorocyclohexane
532 enantiomers in the South Atlantic Ocean and Antarctica. *Deep Sea Res.* 51, 2661-2672.

533 Jantunen, L.M., Wong, F., Gawor, A., Kylin, H., Helm, P.A., Stern, G.A., Strachan, W.M., Burniston, D.A.,
534 Bidleman, T.F., 2015. 20 years of air-water gas exchange observations for pesticides in the Western
535 Arctic Ocean. *Environ. Sci. Technol.* 49, 13844-13852.

536 Li, J., Zhang, G., Qi, S., Li, X., Peng, X., 2006. Concentrations, enantiomeric compositions, and sources of
537 HCH, DDT and chlordane in soils from the Pearl River Delta, South China. *Sci. Total Environ.*
538 372(1):215-24.

539 Khairy, M.A., Luek, J.L., Dickhut, R., Lohmann, R., 2016. Levels, sources and chemical fate of persistent
540 organic pollutants in the atmosphere and snow along the western Antarctic Peninsula. *Environ. Pollut.*
541 216, 304-313.

542 Lakaschus, S., Weber, K., Wania, F., Bruhn, R., Schrems, O., 2002. The air-sea equilibrium and time trend
543 of hexachlorocyclohexanes in the Atlantic Ocean between the Arctic and Antarctica. *Environ. Sci.*
544 *Technol.* 36, 138-145.

545 Li, Y., Bidleman, T.F., 2003. Relation between Global Emissions of alpha-hexachlorocyclohexane and its
546 Concentrations in the Arctic Air. *J. Environ. Inform.* 1, 52-57.

547 Li, Y., Wang, C., Zou, X., Feng, Z., Yao, Y., Wang, T., Zhang, C., 2019. Occurrence of polycyclic aromatic
548 hydrocarbons (PAHs) in coral reef fish from the South China Sea. *Mar. Pollut. Bull.* 139, 339-345.

549 Lin, T., Li, J., Xu, Y., Liu, X., Luo, C., Cheng, H., Chen, Y., Zhang, G., 2012. Organochlorine pesticides
550 in seawater and the surrounding atmosphere of the marginal seas of China: spatial distribution, sources
551 and air-water exchange. *Sci. Total Environ.* 435, 244-252.

552 Lohmann, R., Breivik, K., Dachs, J., Muir, D., 2007. Global fate of POPs: current and future research
553 directions. *Environ. Pollut.* 150, 150-165.

554 Lohmann, R., Gioia, R., Jones, K.C., et al., 2009. Organochlorine pesticides and PAHs in the surface water
555 and atmosphere of the North Atlantic and Arctic Ocean. *Environ. Sci. Technol.* 43, 5633-5639.

556 Lohmann, R., Klanova, J., Kukucka, P., Yonis, S., Bollinger, K., 2012. PCBs and OCPs on a east-to-west
557 transect: the importance of major currents and net volatilization for PCBs in the Atlantic Ocean.
558 *Environ. Sci. Technol.* 46, 10471-10479.

559 Lohmann, R., Muir, D., Zeng, E.Y., Bao, L.-J., Allan, I.J., Arinaitwe, K., Booij, K., Helm, P., Kaserzon, S.,
560 Mueller, J.F., Shibata, Y., Smedes, F., Tsapakis, M., Wong, C.S., You, J., 2017. Aquatic global passive
561 sampling (AQUA-GAPS) revisited: first steps toward a network of networks for monitoring organic
562 contaminants in the aquatic environment. *Environ. Sci. Technol.*, 51, 1060-1067.

563 Lohmann, R., Jordi, D., 2019. Polychlorinated Biphenyls in the Global Ocean. *World Seas: An*
564 *Environmental Evaluation.* Academic Press. 269-282.

565 Ma, Y., Adelman, D.A., Bauerfeind, E., CAbererizo, A., Solltwedel, T., Sun, C., Wagner, C.C., Sunderland,
566 E.M., 2018. Concentrations and water mass transport of legacy POPs in the Arctic Ocean. *Geophys.*
567 *Res. Lett.* 45, 12-972.

568 Muir, D., Lohmann, R., 2013. Water as a new matrix for global assessment of hydrophilic POPs. *TrAC,*
569 *Trends Anal. Chem.* 46, 162-172.

570 Nizzetto, L., Lohmann, R., Gioia, R., Dachs, J., Jones, K.C., 2010. Atlantic Ocean surface waters buffer
571 declining atmospheric concentrations of persistent organic pollutants. *Environ. Sci. Technol.* 44, 6978-
572 6984.

573 Oehme, M., 1991. Further evidence for long-range air transport of polychlorinated aromates and pesticides:
574 North America and Eurasia to the Arctic. *Ambio.* 20, 293-297.

575 Remesh, A., Tanabe, S., Iwata, H., Tatsukawa, R., Subramanian, A.N., Mohan, D., et al., 1989. Seasonal
576 variations of organochlorine insecticide residues in air from Porto Novo, South India. *Environ. Pollut.*
577 62, 213-22.

578 Rimondino, G.N., Pepino, A.J., Manetti, M.D., Olcese, L., Argüello, G.A., 2018. Latitudinal distribution
579 of ocps in the open ocean atmosphere between the argentinian coast and antarctic peninsula. *Environ.*
580 *Sci. & Pollu. R.* 25, 13004-13013,

581 Ruge, B.Z., Muir, D., Helm, P. and Lohmann, R., 2018. Concentrations, Trends, and Air-Water Exchange
582 of PCBs and Organochlorine Pesticides Derived from Passive Samplers in Lake Superior in 2011.
583 *Environ. Sci. Technol.* 52, 14061-14069.

584 Schwarzenbach, R., Gschwend, P., 2003 *Environmental organic chemistry.* John Wiley & Sons.

585 Shunthirasingham, C., Olyiliagu, C.E., Cao, X., Gouin, T., Wania, F., Lee, S.C., Pozo, K., Harner, T., Muir,
586 D.C.G., 2010 Spatial and temporal pattern of pesticides in the global atmosphere. *J. Environ.*
587 *Monitor.* 12, 1650-1657.

588 Sun, J., Peng H., 2012. *Marine Meteorology*: Sun Yat-sen University Press, 60.

589 Tanabe S., Tatsukawa, R., Kawano, M., Hidaka, H., 1982. Global distribution and atmospheric transport of
590 chlorinated hydrocarbons: HCH (BHC) isomers and DDT compounds in the Western Pacific, Eastern
591 Indian and Antarctic Oceans. *J. Oceanog. Soc. Japan.*

592 Voldner, E.C., Yifan, L.I., 1993. Global usage of selected persistent organochlorines. *Sci. Total Environ.*,
593 160-161, 201-210.

594 Wang, C., Zou, X., Zhao, F., Li, Y., Song, Q.C., Wang, T., Yu, W., 2017. Distribution pattern and mass
595 budget of sedimentary polycyclic aromatic hydrocarbons in shelf areas of the Eastern China Marginal
596 Seas. *J. Geophys. Res.: Oceans* 122, 4990-5004.

597 Wania, F., Donald M., 1993. Global fractionation and cold condensation of low volatility organochlorine
598 compounds in polar regions. *Ambio.* 22. 10-18.

599 Willett, K.L., Ulrich, E. M., Hites, R. A., 1998. Differential toxicity and environmental fates of
600 hexachlorocyclohexane isomers. *Environ. Sci. Technol.* 32, 2197-2207.

601 Wong, F., Jantunen, L.M., Pucko, M., Papakyriakou, T., Staebler, R.M., Stem, G.A., Bidleman, T.F., 2010.
602 Air-water exchange of anthropogenic and natural organohalogenes on International Polar Year (IPY)
603 expeditions in the Canadian Arctic. *Environ. Sci. Technol.* 45, 876-881.

604 Wu, X., Lam, J.C.W., Xia, C., Kang, H., Sun, L., Xie, Z., Lam, P.K.S., 2010. Atmospheric HCH
605 concentrations over the marine boundary layer from Shanghai, China to the Arctic Ocean: role of
606 human activity and climate change. *Environ. Sci. Technol.* 44, 8422-8428.

607 Wurl, O., Potter, J.R., Obbard J.P., 2006. Persistent organic pollutants in the equatorial atmosphere over
608 the open Indian Ocean. *Environ. Sci. Technol.* 40, 1454-1461.

609 Xie, Z., Koch, B.P., Moller, A., Sturm, R., Ebinghaus, R., 2011. Transport and fate of
610 hexachlorocyclohexanes in the oceanic air and surface seawater. *Biogeosciences*, 8, 2621-2633.

611 Yao, Y., Zou, X., Zhao, Y., Wang, T., 2019, Rapid changes in land-sea thermal contrast across China's
612 coastal zone in a warming climate. *J. Geophys. Res.: Atmospheres.* 124, 2049-2067.

613 Zhang, G., Li, J., Cheng, H., Li X., Xu, W., Jones, K.C., 2007. Distribution of organochlorine pesticides in
614 the Northern South China Sea: implications for land outflow and air-sea exchange. *Environ. Sci.*
615 *Technol.* 41, 3884-3890.

616 Zhang, L., Bidlman, T., Perry, M.J., Lomann, R., 2012. Fate of chiral and achiral organochlorine pesticides
617 in the North Atlantic bloom experiment. *Environ. Sci. Technol.* 46, 8106-8114.

618 Zhang, L., Dickhut, R., Demaster, D., Pohl, K., Lohmann, R., 2013. Organochlorine pollutants in western
619 antarctic peninsula sediments and benthic deposit feeders. *Environ. Sci. Technol.* , 47, 5643-5651.

620 Zhang, L., Lohmann, R., 2010. Cycling of PCBs and HCB in the surface ocean-lower atmosphere of the
621 open Pacific. *Environ. Sci. Technol.* 44, 3832-3838.

622