

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

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Abstract

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 to 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.

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

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

1. Introduction

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

The usage patterns of OCPs differed between both hemispheres. Many developed and developing countries located in the temperate and tropical regions in the northern hemisphere (NH) were considered

to be the major sources of the legacy OCPs production and usage (Breivik et al., 2004). The Southern hemisphere (SH), mainly covered by oceans, is considered to be less polluted. The distribution patterns of OCPs in NH may indicate historical usage, while the residue levels in SH may show ongoing usage of certain OCPs such as DDTs in Africa for control of Malaria (Huang et al., 2016). Comparisons of occurrences between the SH and the NH can also show the magnitudes of potential sources and efficiency of long-range transport (Zhang and Lohmann., 2010; Galbán-Malagón et al., 2013a; Shunthirasingham et al., 2016;). However, most of the previous assessment of organic pollution focused in the NH, especially the North Atlantic (Zhang et al., 2012; Lohmann et al., 2012), Arctic (Harner et al., 1999; Lohmann et al., 2009; Bidleman et al., 2015), and N Pacific (Ding et al., 2007; Wu et al., 2010). There were only a few studies in the SH (Bigot et al., 2016), the major one was conducted a few decades ago (Iwata et al., 1993;). There was a long history of scientific assessment of organic pollution in polar regions and coastal areas (Zhang et al., 2007; Xie et al., 2011; Lin et al., 2012; Jantunen et al., 2015; Ma et al., 2018), but less frequently in the open ocean. As the largest water body on Earth, the Pacific Ocean plays a critical role in the cycling of OCPs in the environment. However, studies on OCPs in the Pacific are scarce, furthermore, the reports on air-water exchange studies of OCPs in the Pacific are even fewer.

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

2. Methods and materials

2.1 Cruise Track and Sample Collection

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

2.2 Sample Treatment and Analytical Protocol

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

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

2.3 Air Mass Back Trajectories

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

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

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

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

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

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 L^{-1}) concentrations of OCPs, and $K_{aw}(T, Sal)$ is the K_{aw} corrected with *in situ* temperature and salinity. According to the uncertainty assessment in FR calculation conducted by Zhang et al., (2012), the significant FRs for net volatilization ($FR_{Volatilization}$) were 0.57 for α -HCH, 0.58 for γ -HCH, and 0.46 for HEPX, respectively. The significant FRs for net deposition ($FR_{Deposition}$) were 1.56 for α -HCH, 1.55 for γ -HCH, and 1.66 for HEPX, respectively. Only $FRs > FR_{deposition}$ were treated as net deposition and $FR < FR_{volatilization}$ as net volatilization with 95% certainty. FRs in between were deemed not significantly different from air-water equilibrium.

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

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

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

3. Results and discussion

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

3.1.1 HCH.

In the atmosphere, the sum of the α - β - and γ - HCH (Σ HCH) ranged from 2.1 to 12.0 pg m⁻³ (avg. =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 were the most abundant HCH isomers detected in the atmosphere in both NH and SH. Highest levels were observed at the beginning of the cruise where the air mass originated from the west coast of North America (Fig.1). The lowest air concentration of Σ HCH was observed at the southmost end of the cruise track in SH, and back trajectories indicated the air mass was transported from the Southern Ocean without contact with land for more than 10 days. In general, the average [Σ HCH]_{gas} in the NH was about 5 times higher than that in the SH, which was consistent with the distribution trends of HCH observed in the Atlantic Ocean (Xie et al., 2011).

In the NH, the average atmosphere concentrations of α -HCH ([α -HCH]_{gas}) and γ -HCH ([γ -HCH]_{gas}) 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 4-7 times higher than the mean value of [α -HCH]_{gas} (0.4 pg m⁻³) and [γ -HCH]_{gas} (0.7 pg m⁻³) in the SH (Table1, Fig. 2). Such hemispheric differences for both isomers were also observed by Iwata et al (1993) and still existed during this study in 2006-2007, suggesting a much larger inventory for HCHs in the NH. . Comparing to other oceans (Table S6), the average [α -HCH]_{gas} and [γ -HCH]_{gas} in this study were about 7 times and 3 times lower than N Atlantic and Arctic Ocean (55-84°N) in 2004 (Lohmann et al., 2009), and 12 times and 3 times lower than N Atlantic (58-64°N) in 2008 (Zhang et al., 2012), respectively, but were in line with those reported in the lower latitudes of the Indian Ocean (0-6°N) (Huang et al., 2013). Although open ocean studies would provide an insight on the global distribution of POPs including OCPs (Wurl et al., 2006), very few studies have investigated OCPs in the S Pacific Ocean. [α -HCH]_{gas} and [γ -HCH]_{gas} detected in the S Pacific (Figure 2, Table S6) were in line with those reported in the South Atlantic (1.6-41.4°S) in similar latitudes (Xie et al., 2011) and those in the South

Ocean at higher latitudes (47-74°S) (Galbán-Malagón et al., 2013a). In the SH, β -HCH was the most abundant isomer ranging from 0.2-5.9 pg m⁻³ with an average value of 1.4 pg m⁻³.

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

half-life ($t_{1/2}$) can be estimated 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 concentration measured in 2007 in the Pacific and $[HCH]_0$ is the concentration reported by Iwata et al (1993). The half-lives for α -HCH were about 3.0 years both in the NH and SH, which were similar to those estimated in Great Lakes (3.3-4.4 years, Cortes and Hites 2000) but were lower than those for Canadian Arctic (9.1 years, Hung et al., 2005), presumably because the α -HCH emitted in the lower latitudes would deposit in the Arctic region due to its high volatility, then re-emit to the atmosphere from Arctic Ocean and glacial/ice loss (Dachs 2011, Galbán-Malagón et al., 2013, Cabrerizo et al., 2013), which slowed down the decline in higher latitudes. The half-lives for γ -HCH derived here were 4.5 and 4.4 years in NH and SH, respectively, which are similar to those in Great Lakes (4.6-5.4 years, Cortes and Hites 2000) and Canadian Arctic (4.9-5.7 years, Hung et al., 2005). The longer half-lives of γ -HCH compared to α -HCH were probably due to the continued usage of lindane (γ -HCH) after the ban of technical HCHs.

The ratio of the α/γ -HCH has been suggested as a method of characterizing local lindane (mainly γ -HCH) releases (near or less than 1) versus global transport of technical HCH residues (α/γ -HCH >1) (Willett et al., 1998; Lakaschus et al., 2002; Dickhut et al., 2005). Variation of the α/γ -HCH ratios in space and time were influenced by the historical usage of technical HCH and lindane and the environmental behaviors of the two isomers during the LRT (Iwata et al., 1993). In this study, the average ratio of α/γ -HCH was 1 in the N Pacific which was comparable with the value reported in the Equatorial Indian Ocean (1.3) in 2011 (Huang et al., 2013), but was lower than those in the N Pacific (4) (Iwata et al., 1993) in 1989-1990, the Northern N Pacific (9.4) in 2003 (Ding et al., 2007) and (2.6) in 2008 (Wu et al., 2010), and the North Atlantic (3.3) in 2008 (Zhang et al., 2012) and Arctic Ocean (2.3) in 2004 (Lohmann et al., 2009). It is reasonable to have α/γ -HCH >1 in the NH, as technical HCHs were heavily used in the NH until 2000 (Lakaschus et al., 2002) and photochemical reactions during the LRT could also convert γ -HCH to α -HCH to make the ratio higher than 1 (Iwata 1993 and Willett et al., 1998). To the contrary, the average α/γ -HCH ratio is 0.5 in the S Pacific, in line with the value reported in the Southern Ocean (0.6) in 2008-2009 (Galbán-Malagón et al., 2013). There was also a declining trend of the ratio (1.8-0.3)

206 along the cruise track (Spearman's $F_{25} = 0.697$, $p = 0.01$) from NH to SH. The temporal and spatial
207 declining trend of this ratio together with the distribution patterns of HCHs observed in this study indicate
208 a reduction in usage of technical HCHs from NH to SH ([Dicknut et al., 2005](#)) and a greater usage of
209 lindane in the SH ([Voldner and Li, 1995](#); [Jantunen et al., 2004](#)).

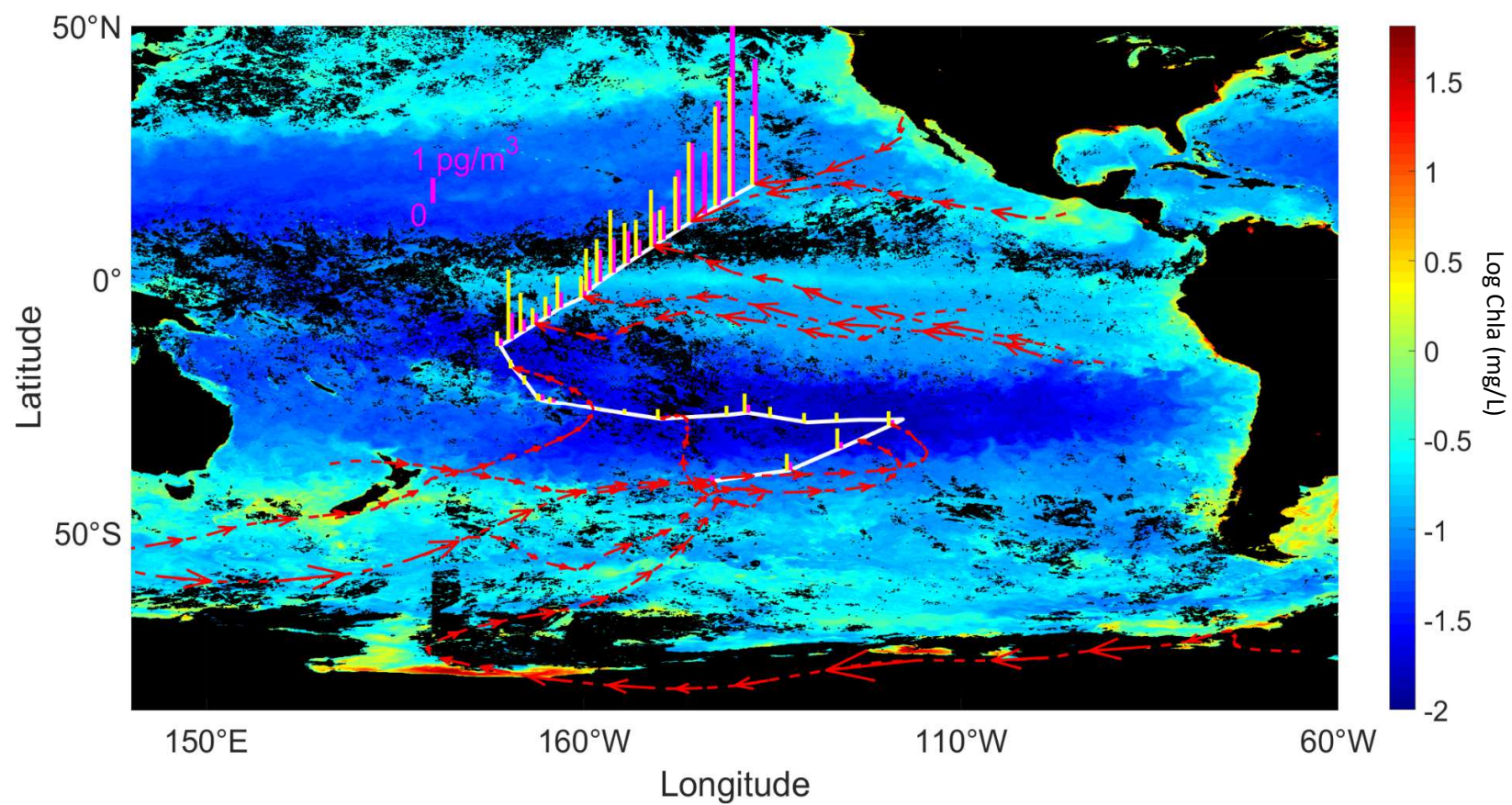


Figure 1 Gaseous HCH concentrations (magenta bars stand for α -HCH; yellow bars stand for γ -HCH) and back trajectories (red dash arrows) during the sampling track. Color bar indicates chlorophyll a (Chla) concentration of Jan-2007 in the Pacific Ocean.

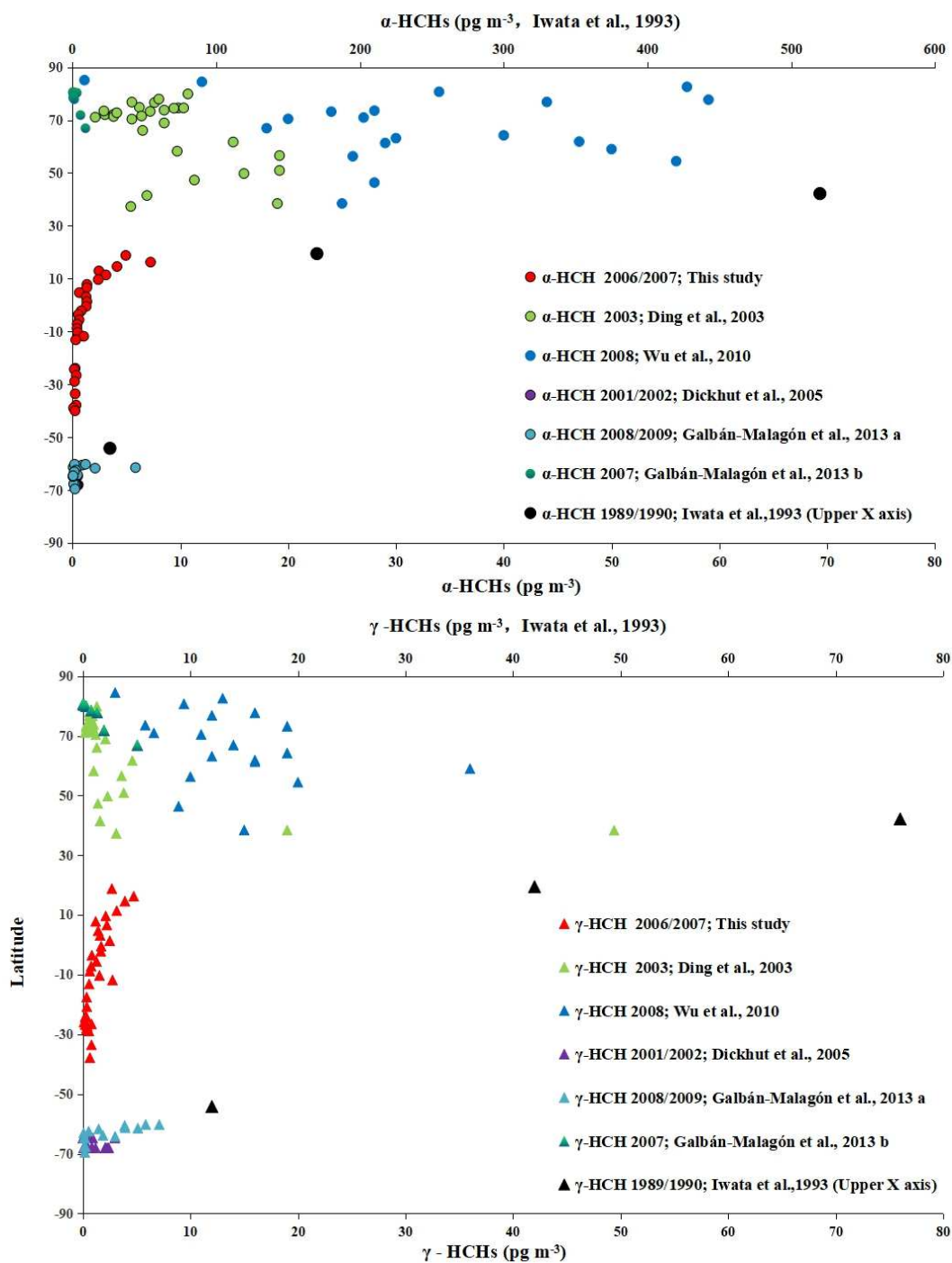


Figure.2 Temporal and latitudinal distribution of gaseous α - HCH (A) and γ - HCH (B) in the Pacific. Data were obtained from this study and previous studies cited in the legend.

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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
<i>α</i> -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
<i>β</i> -HCH	67%	61%	79.4	17.0	33.8	6.2	152.6	26.7	0%	27%	—	1.4	—	0.2	—	5.9
<i>γ</i> -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
<i>α/γ</i> -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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3.1.2 DDT and its metabolites.

In the gas phase, *o,p'*-DDT and *p,p'*-DDE were the most abundant DDT and its derivatives detected. 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 the reported values in the N Pacific (0.2-2.5 pg m⁻³) (Ding et al., 2003) and the Equatorial Indian Ocean (0.4-2.9 pg m⁻³) (Huang et al., 2013), but lower than those measured two decades ago in the N Pacific from 11.62 °N to 43.73 °N (Iwata et al., 1993, Table S6). The concentrations of *o,p'*-DDT were higher in the SH ranging from 0.6 to 11.4 (avg.= 2.7) pg m⁻³ (Fig. S1), which were higher than those reported in East Indian and Southern Ocean in the SH in 1989-1900 (Iwata et al., 1993). For *p,p'*-DDE, the average concentration 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 (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 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, Lohmann et al., 2009) and lower than the samples collected in the N Pacific in 1989-1990 (Table S6) by Iwata et al. (1993). In contrast, the concentrations of *p,p'*-DDE (0.3-7.2 pg m⁻³) in the lower and mid latitudes in the SH were higher than those reported two decades ago in the SH (Iwata et al., 1993), and higher than the values reported in the western Antarctic peninsula (0.29 pg m⁻³, Khairy et al., 2016). This temporal declining trend in the N Pacific and relative uniform distribution across different oceans in the NH suggest a reduced usage of DDTs in the NH, even though there was higher historical DDT use in the NH (Li and Macdonald, 2005). The concentrations of both *o,p'*-DDT and *p,p'*-DDE in the SH were higher than the NH, probably reflecting the existence of unknown sources of DDTs besides the residues of technical DDT (Voldner and Li, 1995; Channa et al., 2012) at the sample of sampling. Highest levels of gaseous DDTs in this study were located in the S Pacific gyre with 10-day back trajectory tracing the air back to New Zealand (about 40° S). However, the average wind speed of circumpolar westerly was about 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 current source of DDT usage could be from any countries around this latitude in the SH. Another possibility is that these relatively high levels DDTs were resulted

from outgassing of previously deposited DDTs due to glacial melting/ice loss (Dachs 2011, Galbán-Malagón et al., 2013, Cabrerizo et al., 2013).

3.1.3 Chlordane.

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

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

Mattina et al., 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 technical mixture, but a similar TC/CC value (2) in the dissolved phase was reported in the Arctic in 1993/1994 (Jantunen and Bidleman 1998). The apparent half-lives estimated in this study for TC is 15 years and 9.6 years for CC, respectively. Therefore, it is reasonable that the TC/CC ratio in the air exceed the ratio in the technical mixture.

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

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

3.2.1 HCH

Reports on dissolved HCH isomers in seawater are much more limited than measurements for gas phase, especially in the S Pacific Ocean. Similar to the distribution pattern in the gas phase, the concentrations of dissolved HCH isomers in NH were much higher (2-24 folds) than in the SH, which is in consistent with the higher historical usage of technical HCH in the NH (Xie et al., 2011). Average 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

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

This pattern was also observed by Huang et al. (2013) in the Equatorial Indian Ocean. The average dissolved concentration of β -HCH in SH was about 5-fold lower than NH, the latter was much higher than other oceans (Table S7) such as the Atlantic Ocean (Zhang et al., 2012; Xie et al., 2011), the Equatorial Indian Ocean (Huang et al., 2013) and Southern Ocean (Dicknut et al., 2005; Galbán-Malagón et al., 2013b). This was probably due to the fact that most of the sampling in this study was in the middle of the N and S Pacific Gyres, the current circulation in the central gyre is slower than those in the boundary currents, which may lead to the accumulation of plastics, garbage, and POPs.

3.2.2 DDT and its metabolites.

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

3.2.3 Chlordane.

As the most abundance compounds in the technical chlordane, TC and CC had higher average concentrations than HEPT and HEPX (Table S7) both in the NH and SH. The dissolved concentration of 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 concentration of both isomers was 1.2 pg L⁻¹ in the NH. Similar to the HCH distribution pattern, the concentrations of TC and CC in the NH are higher than those in the SH, which is probably attributed to the usage history. The average dissolved concentrations in the SH for TC and CC were 0.9 (0.7 to 1 pg L⁻¹) and 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 (avg. 3 pg L⁻¹) in 1989-1990 in the N Pacific and those in the SH (Table S7), the present concentration levels were about 2-3 times lower, and this declining trend reflected the decline usage of chlordane globally in the past two decades. However, these values from the Pacific were still higher than those in the Northern 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 L⁻¹ for both isomers) in 2008 (Zhang et al., 2012), which was likely due to two reason. First of all, there are still ongoing usage of Chlordane compounds in the lower latitudes, for example, the TC (9.4 pg L⁻¹) and CC (6.6 pg L⁻¹) concentrations in the Equatorial Indian Ocean were significantly higher (Huang et al., 2013). Secondly, the sampling tracks in this study mainly crossed N and S Pacific gyres with very little biological activities (low chlorophyll a concentrations in Figure 1), the removal of these hydrophobic large-molecular-weight pesticides by sinking particles produced by plankton would be very little, evidenced by extremely low chlorophyll-a concentration (Fig 1) and low sedimentation rates reported by D'Hondt et al., (2009). Therefore, the derived first-order half-lives for TC (12.0 years in NH and 18.0 years in SH) and CC (13.6 years in NH and 12.7 years in SH) were relatively long.

TC/CC ratio has been used to distinguish between aged and new sources of chlordane (Bidleman et al., 2002; Shunthirisingham et al., 2010). In this study, the mean ratio of TC/CC was 2.1 in the NH and 0.7 in the SH. Long-range atmospheric transport likely supply chlordane with a lower TC/CC ratio than freshly evaporated chlordane (Bidleman et al., 2002). The TC/CC value in the NH (2.1) was very similar

to what was reported in the Arctic Ocean (Jantunen and Bidleman 1998). The ratio in the S Pacific Ocean was much lower than the technical grade (~1.16), which was in line with that in the N Atlantic Ocean (avg. 0.53 ± 0.22) in 2004 (Lohmann et al., 2009). The lower ratio in the dissolved phase in the S Pacific Ocean together with the lower concentration of chlordane in the SH than in the NH, indicating that study area had received aged chlordane by long-range atmospheric transport from the source areas (Shunthirasingham et al., 2010).

HEPX is the most detected chlordane compounds in the dissolved phase. The average dissolved 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 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 in their physiochemical properties (Table S3). HEPX has lower K_{AW} value than HEPT, thus, the latter prefers to stay in the gas phase. Their K_{OW} values are similar which is higher than HCHs but lower than DDTs. HEPX would tend to accumulate more in the dissolved phase due to less removal by sinking particles, resulting in relatively higher dissolved concentrations observed in this study.

3.3 Directions and fluxes of air-water exchange

The FRs and $F_{a/w}$ for four OCP compounds were calculated and summarized in Table 2. All of four OCPs have K_{aw} values smaller than 1×10^{-3} (Table 2) suggesting the limiting step for air-water exchange is on the water side (Schwarzenbach et al., 2003). According to the FRs, α -HCH varied between equilibrium and net deposition along the cruise track. Deposition or equilibrium between gaseous and dissolved phase of α -HCH were also observed in the North Atlantic Ocean (Lohmann et al., 2009; Zhang et al., 2012), the Southern Ocean during 2008 to 2009 (Galbán-Malagón et al., 2013a), and the Western Antarctic Peninsula in 2001-2002 (Dickhut et al., 2005). The FRs suggested that the air-water exchange of β -HCH was at the equilibrium or deposition in the S Pacific, which was also reported in the Atlantic Ocean in 2008 (Xie et al., 2011). In contrast, all FRs for γ -HCH reflected net volatilization from water to air. However, most previous studies reported net deposition and equilibrium for γ -HCH in other water bodies (Lohmann et al., 2009; Zhang et al., 2012; Dickhut et al., 2005; Galbán-Malagón et al., 2013). Less

hydrophobicity of HCHs lead to less removal by sinking particles in the ocean and enable them to actively exchange through the air-water interface, which together with the relatively high dissolved concentrations cause γ -HCH to volatilize in the Pacific. To our best knowledge, it is the first time that the volatilization of γ -HCH in the open ocean was observed, this could be due to the delayed ban of lindane, which was not incorporated into the Stockholm Convention until 2009 (Wong et al., 2010). Most of the FRs for HEPX were found to be deposited.

The net deposition fluxes of α -HCH in this study ranged from -6.9 to -4.1 ng m²day⁻¹ in the N Pacific, which were about 100 times lower than those during 1989 to 1990 (about -500 ng m²day⁻¹, Iwata et al., 1993). While technical HCHs were still used, many water bodies probably acted as a sink for HCHs such as observed in 1989-1990 (Iwata et al., 1993). However, after the primary emission sources of POPs were banned in most of the countries, the air-water exchange was at equilibrium or evaporating from water to air for certain POPs in some water bodies, turning them secondary sources of these POPs. For example, Zhang et al. (2012) found that α -HCH in the N Atlantic varied between deposition and equilibrium between gas and dissolved phases. The Pacific Ocean has also become the secondary source for PCBs (air-water exchange flux 0.5-30.4 ng m⁻² day⁻¹) reported by a previous study (Zhang and Lohmann 2010). However, the status for γ -HCH has been dominated by net deposition in water bodies reporting by previous studies (Lohmann et al., 2009; Zhang et al., 2012; Xie et al., 2011; Huang et al., 2013). The volatilization of γ -HCH in this study with fluxes ranging from 0.3 to 11.1 ng m⁻² day⁻¹ suggested that the tropical Pacific Ocean were acting as a secondary source supplying γ -HCH to the atmosphere.

Table 2 Summary of Fugacity (FR) and Air-Water Gas Exchange Fluxes ($\text{ng m}^{-2} \text{d}^{-1}$) for different OCPs (Negative values indicates net deposition fluxes, underlined italic values indicate net evaporation fluxes, and blanks next to FR 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						

4. Conclusion

The distribution patterns and air-water exchange status of OCPs in air and seawater samples in the Pacific Ocean in 2006-2007 were assessed in this study. Both gaseous and dissolved phases concentration for most OCPs were higher in the North than in the South Pacific. Higher OCPs levels were observed in gas samples affected by Trade Winds coming from the American continents. In the N Pacific, α -HCH levels were lowered by a factor of 63 compared to those observed in 1990s (Iwata 1993), but γ -HCH's reduction was not as strong, probably because lindane was still used after banning technical HCHs. This is the first report that γ -HCH was returning to the atmosphere in open oceans. With ongoing volatilization,

γ -HCH may reach equilibrium soon like α -HCH if there is no further lindane usage. DDTs in S Pacific were as high as they were in 1990s which may indicate recent usage in the SH during the time of sample collection. HEPT has higher gaseous concentrations than HEPX due to its higher K_{AW} whereas HEPX accumulated to higher levels in the dissolved phase due to its low K_{AW} and intermediate K_{OW} . The four different groups of OCPs showed different distribution patterns, suggesting such open ocean studies are very useful to reveal historical usage patterns, detect any new usages of OCPs, and predict their environmental fate through air-water exchange assessment. It is essential to continue monitoring POPs in the open oceans, even though there may not be any primary emission sources for legacy POPs, garbage and/or plastics in the ocean may slow down the reduction of these pollutants. Deploying polyethylene passive samplers (Lohmann et al. 2017) on cargo ships could potentially provide an easy way of monitoring POPs in the open ocean, which can help distinguish between background concentrations of legacy POPs likely transported over long distances through atmospheric and oceanic currents and primary inputs of current usage in certain countries.

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