Cycling of PCBs and HCB in the Surface Ocean-Lower Atmosphere of the Open Pacific

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Surface ocean and lower atmosphere samples were collected on the R/V *Revelle* during a scientific cruise from San Diego, CA to New Zealand via Samoa and the South Pacific Gyre (SPG) from 12/2006 to 1/2007. Samples were analyzed for polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB). $\sum_{ICES}$PCBs gaseous concentrations (ICES: International Council for the Exploration of the Sea) ranged from 28–103 pg m^{-3} in the northern hemisphere (NH) and 1.5–36 pg m^{-3} in the southern hemisphere (SH), whereas dissolved seawater concentrations were between 0.2–15 pg L^{-1} in the NH and 0.3–7.8 pg L^{-1} in the SH. Both gas ($[PCBs]_{gas}$) and dissolved phase concentrations ($[PCBs]_{sw\_dis}$) displayed highest concentrations near North America and lowest in the SPG. In the NH, $[HCB]_{gas}$ ranged from 42–89 pg m^{-3}, higher than the average in the SH (31 pg m^{-3}), while $[HCB]_{sw\_dis}$ were comparable in both hemispheres (NH: 0.4–1.6 pg L^{-1}, SH: 0.4–0.8 pg L^{-1}). Fugacity ratio calculations suggest PCBs were volatilizing from surface waters to the overlying atmosphere, and air–water exchange fluxes were ~0.5 to ~30.4 ng m^{-2} d^{-1}. This is the first study reporting the degassing of PCBs from the open ocean into the air. Previous studies deduced net deposition of PCBs into the Atlantic and Arctic Oceans. As has been observed for other oceans, HCB was at/near air–water equilibrium. A mass balance model was used to interpret the short-term variations in $[PCBs]_{gas}$ in the SPG, which was not observed for HCB. It is suggested that hydroxyl radical depletion reaction and air–water gas exchange together controlled the variation in $[PCBs]_{gas}$.

Introduction

It has been several decades since the production of polychlorinated biphenyls (PCBs) ended in most industrialized countries. Several international treaties were established to ensure their worldwide ban (*1, 2*). The implementation of these treaties has demanded improved understanding and characterization of the global fate and behavior of PCBs and other persistent organic pollutants (POPs) to better assess the continuous threat posed by them. During the peak usage of PCBs, high gaseous concentrations resulted in air-to-water fugacity gradients and hence net air to water transport of PCBs. A relatively small portion of PCBs could be removed from the gas phase by sorption to particles and scavenging by rain drops. Hydroxyl (OH) radical depletion reaction in the atmosphere is recognized as one of the few permanent sinks of PCBs (*3, 4*). There is scant field evidence for its impact

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on the cycling of PCBs, however (*5*). In contrary to the atmosphere, photochemical degradation of PCBs happens much slower in the water (*6*). Besides, PCBs can be removed from the surface water and delivered below the thermocline through intermediate/deep water formation at few locations and/or sorption to sinking particles where surface biological production is high (*7, 8*). Historically large water bodies such as the Great Lakes and oceans are considered as sinks receiving PCBs and other POPs via air–water gas exchange, dry and wet deposition (*9–13*). It has been suggested that these large water bodies may likely play a different role lately, with reduced primary atmospheric emissions and global warming. A recent model study suggested that the world oceans are returning pollutants to the atmosphere instead of being a sink (*13*). It was earlier shown that the Great Lakes have been acting as a secondary source supplying PCBs to the atmosphere. This volatilization flux could be supported by release of PCBs from previously contaminated sediments (*9*).

While the occurrence and cycling of POPs in the Atlantic has been the subject of several large-scale cruises over the past few years, little is known about other major ocean basins. In the Atlantic, the depositional flux of PCBs observed is probably the result of an air-to-water fugacity gradient caused by the removal of PCBs from surface waters via settling particles (*11*). In the remote South Atlantic, a diurnal cycle of gaseous PCBs concentrations was observed, with high daytime concentrations and low nighttime concentrations (*14*). Though the mechanisms responsible for this diurnal pattern are still under debate, it is clearly not caused by OH radical depletion reactions. OH radical only exists during the daytime so that if this removal process dominated other processes, it would result in depletion of $[PCB]_{gas}$ during the daytime. Only a few studies reported field evidence of OH-radical depletion of PCBs on land (*3, 4*). The open ocean has been suggested as the best location to find the evidence of atmospheric depletion reactions, if air–water exchange fluxes of PCBs are known (*15*). However, reports on simultaneously taken air and water samples for the open ocean in the literature are sparse, especially outside of the Atlantic/Arctic Oceans (*16*).

We were interested in the presence and fate of POPs in the Pacific Ocean, the largest water body on Earth. Of particular interest is the behavior of POPs in the remote Pacific such as the South Pacific Gyre (SPG). The surface biological production is extremely low at the SPG as inferred from low surface chlorophyll concentrations (Figure 1), resulting in low sedimentation rates. A lack of deep water formation and low sedimentation removal rates could result in a situation where OH radical depletion reaction in the atmosphere was the only significant removal process of POPs such as PCBs in the surface ocean–lower atmosphere over the SPG.

In this study, marine boundary layer air and seawater samples were taken on the R/V *Revelle* from December 2006 to January 2007, during a cruise from San Diego, CA to Samoa, and from Samoa via the SPG to New Zealand. These samples were analyzed for different PCB congeners and HCB to investigate their spatial distribution, diurnal concentration variations, and directions and fluxes of air–water exchange. Finally, a mass balance model was developed to interpret the occurrences of PCBs and HCB in air samples collected every 12 h in the SPG, as well as to elucidate the interaction between air–water exchange and daytime OH depletion reactions.
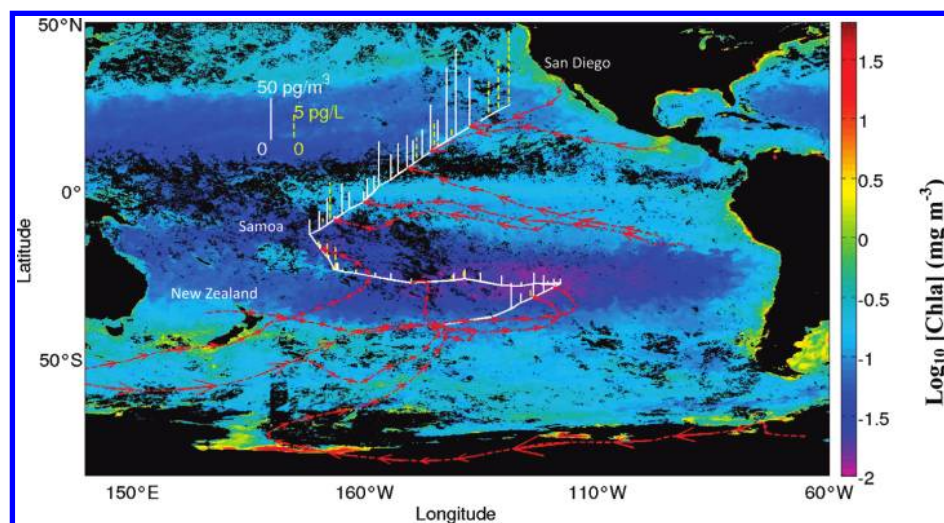
FIGURE 1. Air PCB concentrations (white bar), water PCB concentrations (yellow dash lines), and back trajectories (red arrow dash lines) plotted on aqua MODIS Jan-2007 chlorophyll concentration map in the Pacific.

Materials and Methods

Sample Collection. A total of 23 air samples (air sample nos. 1−23) and 28 water samples (water sample nos. 1−28) were collected every 12 h (400−900 m³ air, 400−700 L seawater) as the ship sailed from San Diego, CA (32.78°N, 117.15°W) to Samoa (13.83°S, 171.75°W) crossing the Equatorial up-welling area as well as Equatorial Current and Equatorial Counter Current systems. Twenty-six air samples (200−1700 m³, air sample nos. 100−125) and 27 water samples (200−1000 L, water sample nos. 100−126) were collected from Samoa to the SPG and New Zealand (41.28°S, 174.45°E). The sampling time during the second part of the cruise varied from 12 to 48 h. Detailed cruise track and sampling conditions are summarized in Supporting Information (SI) Table 1a and b (page S10).

Air samples were taken using a high-volume (Hi-Vol) air sampler installed on the flying bridge (ca. 17 m above sea level), with Whatman glass fiber filters (GFF) collecting particle-bound compounds and two polyurethane foams (PUFs) retaining compounds in the gaseous phase. Whereas, three PUFs were used to trap compounds in the water phase by filtering seawater from the ship's underway seawater intake in a sealed apparatus (see SI page S17). GFFs were used to remove the particles in seawater and replaced as needed to maintain a flow rate of ∼1 L/min.

Sample Processing and Analysis. Detailed analysis methods have been described in the SI (page S2). In brief, $^{13}C_{12}$-labeled PCBs (8, 28, 52, 118, 138, 180, and 209 each at 60 ng) were used as surrogates for PCBs and $^{13}C_{12}$-p,p′-dichlorodiphenyltrichloroethane (DDT) for HCB and other organochlorine pesticides (reported separately). These surrogates were spiked into the receiving flasks underneath soxhlets to account for loss during sample treatment. PUFs were extracted using soxhlets with dichloromethane (DCM) overnight. The extracts were dehydrated using sodium sulfate and passed through a silica gel cartridge (Agilent AccuBOND^{II}). The extracts were solvent exchanged and reduced to ∼100 μL of hexane using a vacuum rotary evaporator (Heidolph Laborota 4003). Prior to analysis, 2,4,6-tribromobiphenyl (143 ng) was added as the internal standard.

PCBs and HCB were analyzed using an Agilent GC 6890N with a DB-5MS capillary column (J&W Scientific) equipped with a Quattro MicroGC tandem MS (Waters). A total of 15 PCB congeners (PCB-3, PCB-8, PCB-18, PCB-28, PCB-44, PCB-52, PCB-66, PCB-101, PCB-118, PCB-138, PCB-153, PCB-180, PCB-189, PCB-206, and PCB-209) and HCB were quantified using an internal standard method.

Quality Assurance/Quality Control. Strict analytical procedures were performed to ensure quality control. For about every 10 samples, a field blank was taken to represent the potential contamination during handling on the ship. A laboratory blank was analyzed along with about every five samples, reflecting possible contamination in the clean laboratory at URI-GSO. Truly dissolved concentrations of PCBs and HCB were calculated by correcting total concentration collected on PUFs for the interference by dissolved organic carbon (DOC) (see SI page S2−5 for more information).

Back Trajectories and Origins of Air Masses. NOAA's HYSPLIT model was used to obtain air mass origins and atmospheric boundary layer heights (*17*). Back trajectories (BTs) were calculated for the beginning and end of each sampling episode in coordinated universal time (UTC) and traced back for 10 days with 6 h steps at 300 m above sea level. Samples were grouped together based on their air mass origin/surface wind patterns. The general indication of BTs for each group is shown in Figure 1 (see SI page S5 for more details).

Air−Water Fugacity Ratios (FR) and Exchange Flux Calculation. Air−water FR was calculated according to

$$\frac{f_{gas}}{f_{sw\_dis}} = \frac{C_{gas}}{C_{sw\_dis} \cdot K_{aw}(T, sal)} \quad (1)$$

where f_{gas} and f_{sw_dis} are the POPs' fugacities in air and seawater, C_{gas} and C_{sw_dis} are gaseous (pg m^{-3}) and dissolved (pg L^{-1}) concentrations of PCBs and HCB, and K_{aw} (T, sal) is the seawater temperature and salinity corrected internally consistent air−water partitioning coefficient (see SI page S6 for more details). Considering the uncertainties introduced by K_{aw} (*18*), only FRs > 3.1 were treated as net deposition and FR < 0.32 as net volatilization with 95% certainty. FRs in between 0.32 and 3.1 were deemed not significantly different from air−water equilibrium.

Air−water gas exchange fluxes ($F_{a/w}$, ng m^{-2} d^{-1}) were calculated using a modified version of the Deacon boundary layer model as described elsewhere (*6*). A positive $F_{a/w}$ value indicates a net flux from the water to the atmosphere:

$$F_{a/w} = v_{POP,a/w} \cdot \left(C_{sw\_dis} - \frac{C_{gas}}{K_{aw}(T, sal)} \right)$$
$$= v_{POP,a/w} \cdot (C_{sw\_dis} - C_{gas}^*) \quad (2)$$

TABLE 1. Summary of Results. Northern Hemisphere (NH), Southern Hemisphere (SH), Detection Limit (DL)

compound	air concentration (pg m^{-3})								water concentration (pg L^{-1})							
	>% DL		mean		minimum		maximum		>% DL		mean		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
CB28	100%	100%	34	6.8	17	0.7	69	22	71%	55%	1.0	1.1	0.6	0.3	1.5	2.5
CB52	91%	94%	11	3.3	1.1	0.5	24	12	71%	50%	1.7	1.6	0.5	0.2	3.2	8.4
CB101	100%	66%	3.2	2.3	1.2	0.3	6.2	19	86%	20%	2.0	2.2	0.9	0.3	4.0	6.3
CB118	73%	29%	1.8	2.1	1.1	0.3	2.5	7.2	100%	40%	0.7	0.6	0.2	0.2	1.5	2.5
CB138	45%	20%	1.5	2.5	1.1	0.3	2.0	7.8	86%	45%	0.9	0.5	0.2	0.02	1.6	2.2
CB153	91%	26%	1.6	3.7	0.9	0.4	2.7	19	71%	15%	1.7	1.2	1.2	0.4	2.8	2.4
CB180	9%	26%	0.2	0.6	0.2	0.1	0.2	2.6	0%	0%						
Σ_{ICES}PCBs			51	12	28	1.5	103	36			6.3	2.0	0.2	0.3	15	7.8
Σ_{15}PCBs			94	25	59	3.9	169	67			10	4.2	3.0	0.6	22	14
HCB	100%	89%	61	31	42	14	89	61	86%	60%	0.9	0.5	0.4	0.4	1.6	0.8

where $v_{POP,a/w}$ is the air−water gas exchange mass transfer coefficient (MTC) (see SI page S6 for more details).

Results and Discussion

Gaseous and Dissolved PCB Concentrations. Table 1 and SI Table 2a and b summarize the results for air and seawater PCB concentrations. The sum of the 15 measured PCBs (Σ_{15}PCBs) in the air ranged from 59 to 169 pg m^{-3}, with 73−81% accounting for tri- (Cl$_3$Bs) and tetra- (Cl$_4$Bs) homologues in the NH and from 3.9 to 67 pg m^{-3} with 39 to 90% accounting for Cl$_3$Bs and Cl$_4$Bs in the SH. The Σ_{ICES}PCBs (PCB-28, 52, 101, 118, 138, 153, and 180) were 28−103 pg m^{-3} in the NH and 1.5−36 pg m^{-3} in the SH. Figure 1 shows the spatial distribution of Σ_{ICES}PCBs along the cruise track. In the NH, highest Σ_{ICES}PCB air concentrations ([Σ_{ICES}PCB]$_{gas}$) occurred at the beginning of the cruise when the air mass originated from the west coast of North America. The lowest [Σ_{ICES}PCB]$_{gas}$ found in the NH was comparable to the highest one in the SH. The samples taken furthest south displayed lowest concentrations of PCBs. BTs suggested these air masses originated from the Southern Ocean and had not been in contact with land for at least 10 days. In general, average NH air concentrations were about 4 times higher than the SH ones.

The range of atmospheric Σ_{ICES}PCBs reported is similar to measurements by Jaward et al. (4.5−120 pg m^{-3}) (14) and Gioia et al. (3.7−220 pg m^{-3}) (11) for the Atlantic and the Arctic Ocean (0.8−100 pg m^{-3}) (19).

[Σ_{15}PCBs]$_{sw\_dis}$ ranged from 3 to 23 pg L^{-1} in the NH and from 0.6 to 15 pg L^{-1} in the SH. Contrary to the air profiles, Cl$_3$Bs and Cl$_4$Bs contributed less to Σ_{15}PCBs measured in seawater (25−40% in the NH, 0−68% in the SH). In the NH, highest [Σ_{ICES}PCBs]$_{sw\_dis}$ (15 pg/L) occurred close to land and low concentrations at the equatorial upwelling (5 pg/L). In the SH, highest concentrations were observed between 10 and 20° S in the S equatorial current (8 pg/L), and lowest in the SPG (20− 40° S, 0.3 pg/L). In general, trends were similar between PCB concentrations in air and water: Highest near N America, low at the equator, higher south of the equator and lowest in the SPG.

In this study, [PCBs]$_{sw\_dis}$ were higher than recent findings in the Atlantic (Σ_{ICES}PCBs, 0.017−1.7 pg L^{-1}) and Arctic (<1 pg L^{-1}) (11, 19). First, this reflects that the Pacific and Atlantic are very different oceans. Sorption of dissolved PCBs to settling particles and subsequent burial in sediments is considered to be one of the most important processes for removing PCBs from water columns (8). The cruise track from Samoa to New Zealand covered one of most oligotrophic areas in the open ocean (Figure 1). Low sedimentation rates due to minimal biological activities could cause PCBs to accumulate in the water, which possibly explains the higher [PCBs]$_{sw\_dis}$ observed than in the South Atlantic. Also, very high PCBs concentrations were found in plastic garbage (27−980 ng/g) collected in the North Pacific Gyre (20). If the PCBs in these plastics were in equilibrium with the seawater, [PCBs]$_{sw\_dis}$ would be ∼100s pg L^{-1} (21).

Gaseous and Dissolved HCB Concentrations. Gaseous HCB concentrations (Figure 2, [HCB]$_{gas}$) in the NH ranged from 42 to 89 pg m^{-3}, slightly lower than concentrations in East Asia (53−157 pg m^{-3}) (22), North America (50−133 pg m^{-3}) (23), and global (∼ 50−150 pg m^{-3}) (24). Previously reported HCB concentrations in the Atlantic atmosphere averaged ∼50 pg m^{-3} (14, 25). These agreements suggest that HCB is fairly uniformly distributed across the Northern Hemisphere and has a long atmospheric residence time. Highest atmospheric HCB concentrations were found at the beginning of the cruise close to land. Even though there are no current commercial uses of HCB as an end product in North America, it exists as an intermediate product and byproduct in the production of a large number of chlorinated compounds and continues to volatilize from contaminated soils to the atmosphere (26). In the SH, the average atmospheric HCB concentration was 31 pg m^{-3}, roughly half that in the NH. The hemispheric difference indicates slow interhemispheric mixing and lower previous usage in the Southern Hemisphere. However, the hemispheric difference for HCB is smaller than that for PCBs suggesting HCB is faster approaching global equilibrium. The lowest atmospheric HCB concentration (14 pg m^{-3}) was found in the SPG, similar to South Atlantic concentrations (10−20 pg m^{-3}) (14).

Water HCB concentrations were in the range of 0.4−1.6 pg L^{-1} (average 0.9 pg L^{-1}) in the NH, which were lower than those reported 1−2 decades ago (5.1−19 pg L^{-1}) (27, 28). A more recent study in North Atlantic and Arctic Oceans suggested a strong negative correlation between water HCB concentrations and the reciprocal of water temperature, with 1−2 pg L^{-1} at water temperatures of 9−11 °C and increasing to 4−10 pg L^{-1} between −1 and −3 °C (25). The low concentration found in the NH could likely be explained by the high water temperature (SI Table 1). HCB concentrations in the SH seawater (0.4−0.8 pg L^{-1}) were slightly lower than those in the NH, and were comparable to those in the South Atlantic (1.9−3.3 pg L^{-1}) (29). Due to its lower octanol−water partitioning coefficient (K_{ow}), HCB is not expected to be affected by organic carbon settling fluxes, which is one of the factors explaining why we observed a difference between the Pacific and Atlantic Oceans for PCBs but not HCB.

Air−Water Gas Exchange of PCBs and HCB. *Fugacity Ratios.* A total of 23 paired air−water samples were used to assess the equilibrium status of PCBs and HCB between air and water and the direction of air−water gas exchange. The FR for PCBs ranged from 0.02 to 9.05. Only two samples indicated net deposition (FR > 3.1, SI Table 3). One was observed for PCB-44 at the beginning of the cruise
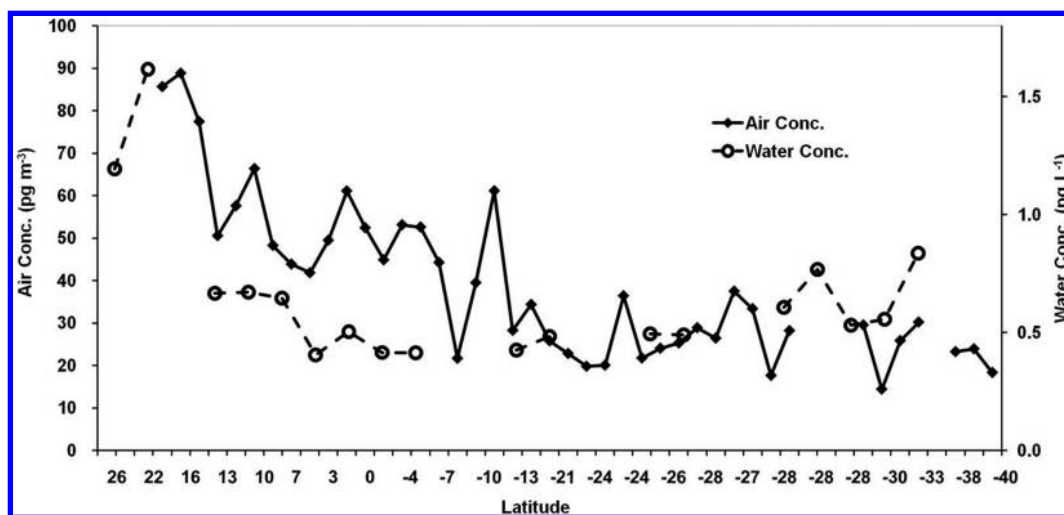
FIGURE 2. HCB concentrations in air (pg/m³) and water (pg/L). Positive latitudes: Northern Hemisphere. Negative latitudes: Southern Hemisphere.

close to North America with a high gas phase concentration. The other one was for PCB-138 close to the end of the cruise with very low water concentrations resulting in large air to water fugacity gradient and a low sea surface temperature (SST) favoring deposition. Most other FR observed for di-, tri-, and tetra-PCBs in the SH were significantly smaller than 0.32 (SI Table 3) suggesting PCBs were volatilizing from the water. It was the PCB air−water concentration gradient which determined the direction of gas exchange not temperature, as water temperatures were in a narrow range of 25−30 °C. This study represents the first comprehensive study of the air−water gas exchange of PCBs in the North Pacific since the late 1980s/early 1990s (*16*) and (to our best knowledge) the first to cover the South Pacific. Net deposition of PCBs was reported in previous work in the Pacific and other oceans (*16, 19*). However, Iwata et al (*16*) suggested PCBs volatilized from tropical waters and condensed into colder places such as Bering Sea.

For several reasons we think that the described volatilization of PCBs over the Pacific is accurate: (i) Ceased production and usage of PCBs as well as degradation have led to lower environmental concentrations. Large water bodies could function as buffers, accumulating PCBs during periods of high emissions, whereas the atmosphere responds more quickly to decreasing emissions, resulting in low air−water FR. Volatilization of PCBs has already been reported over lakes (*10, 12*) estuaries, bays (*30*), and seas (*16, 18, 31*) due to high dissolved concentrations and relatively low gas phase concentrations (SI Table 4). (ii) The downward loss of PCBs through sinking of particulate organic matter is extremely low in the South Pacific, which is one of the most oligotrophic ocean regions. This has likely caused an increase in [PCBs]$_{sw\_dis}$ to a point where the fugacity gradient switched from net uptake by the ocean to net release. Thus, the low FR in the South Pacific coupled with high water temperatures could make the South Pacific a secondary source of PCBs. The cruise track enabled sample collection from the open Pacific, whereas most Atlantic cruises were close to the continents (*11*). (iii) There is evidence for several dioxins (L. Nizetto, personal communication) and PAHs (*32*) volatilizing from the Atlantic. Modeling results also indicated that the world oceans returned DDT to the atmosphere (*13*). (iv) There is no indication that the R/V *Revelle* was contaminated by PCBs, as evidenced by low atmospheric concentrations and the fact that seawater PCBs were collected in a sealed apparatus. (v) The observed diel cycle in the atmosphere (see below) supports a scenario where PCBs were supplied from the surface seawater.

The FR of HCB were in the range of 0.67−2.89. They decreased from slightly favoring deposition in the NH to be at/near equilibrium in the SH (SI Table 3). Concurrent measurements of air and water samples in the Atlantic also suggested that HCB was closest to equilibrium between air and water and cold condensation effect was significant on [HCB]$_{sw\_dis}$ (*25*). Although the FR varied seasonally, HCB was also close to equilibrium in the Canadian Arctic Archipelago (*33*). However, an early study on Lake Baikal indicated HCB was undergoing volatilization in cold water (3.5 °C) (*34*).

Air−Water Gas Exchange Fluxes ($F_{a/w}$, ng m^{-2} d^{-1}). are a significant component of POPs mass balances (*35*). To precisely determine $F_{a/w}$ is difficult due to uncertainties of the air−water gas exchange mass transfer coefficient (MTC, $v_{a/w}$). The MTC not only highly depends on instantaneous wind speed, but also on surface conditions (i.e., sea surface microlayer), water currents, and wind history (*6, 35*).

Instantaneous ΣPCB fluxes were from water to air ranging from ∼0.5 to ∼30 ng m^{-2} d^{-1} except for one sample showing net deposition of −0.4 ng m^{-2} d^{-1} at the beginning of the cruise (Figure 3). Di- (PCB-8) and tri-PCBs (PCB-18) dominated the ΣPCB fluxes (>80% at most sites; SI Table 3). These congeners were also most frequently detected in the dissolved phase (SI Table 2b). This finding was slightly different from observations in the midlatitude Great Lakes with tri- and tetra- PCBs being the dominant congeners (*36*) (SI Table 4), which is probably because lighter weight PCBs could be transported further to the remote Pacific, whereas heavier ones would deposit closer to emission sources. In this study, congeners with four or more chlorines were closer to air−water partitioning equilibrium. The magnitude of ΣPCB fluxes are determined by both wind speed and air−water concentration gradient ($C_{sw\_dis} - C_{gas}*$) (eq 2). ΣPCB fluxes were mostly driven by ($C_{sw\_dis} - C_{gas}*$) (Figure 3). For example, air samples nos. 15 (2.2°S, 159.3° W) and 17 (5.6°S, 163.2° W) had wind speeds of 10.2 and 6.7 m s^{-1}, respectively. Yet ($C_{sw\_dis} - C_{gas}*$) were 1.5 and 24.2 pg L^{-1} resulting in the ΣPCB fluxes of 3.9 and 30.4 ng m^{-2} d^{-1}. Our results show for the first time the volatilization of PCBs in the open ocean, representing a removal mechanism for PCBs from the tropical South Pacific and a net secondary source of PCBs to the overlying atmosphere.

Diurnal Variations in Gaseous Concentrations and Interpretation. Paired air−water samples were taken from 6 a.m. to 6 p.m. as daytime samples, whereas nighttime samples were taken from 6 p.m. to 6 a.m. local time. No diel patterns were observed from San Diego to Samoa. Four pairs of diel air−water samples were obtained in the second part
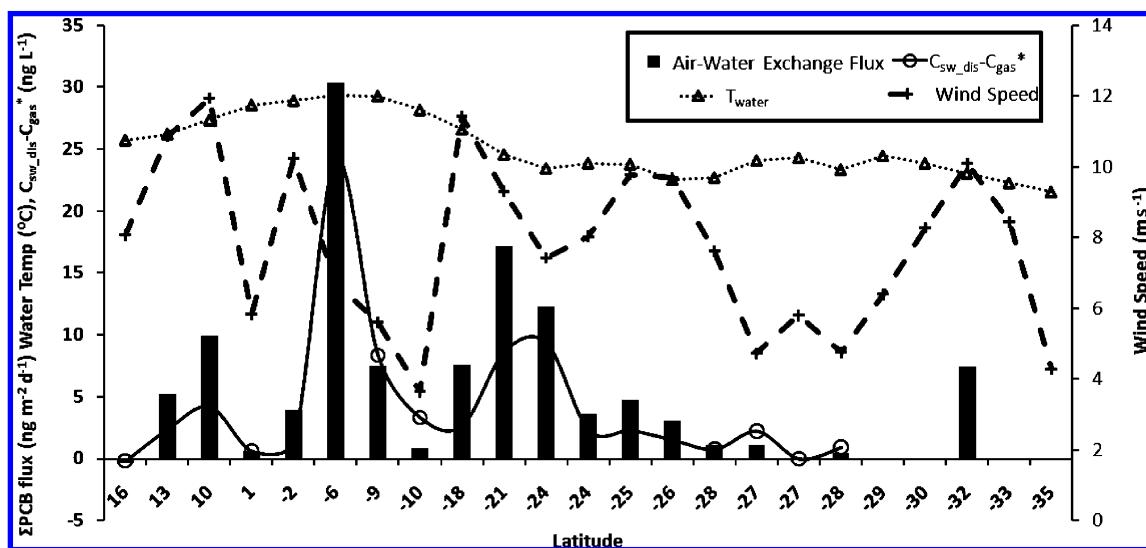
FIGURE 3. Net air–water gas exchange fluxes of PCBs (volatilization–deposition, ng m^{-2} d^{-1}) and concentration gradients (C_{SW_dis}–C_{gas}*, ng L^{-1}) of total PCBs along the sampling transect with wind speed (m s^{-1}) and water temperature (°C). Only fluxes with fugacity ratios >3.1 or <0.32 are displayed.
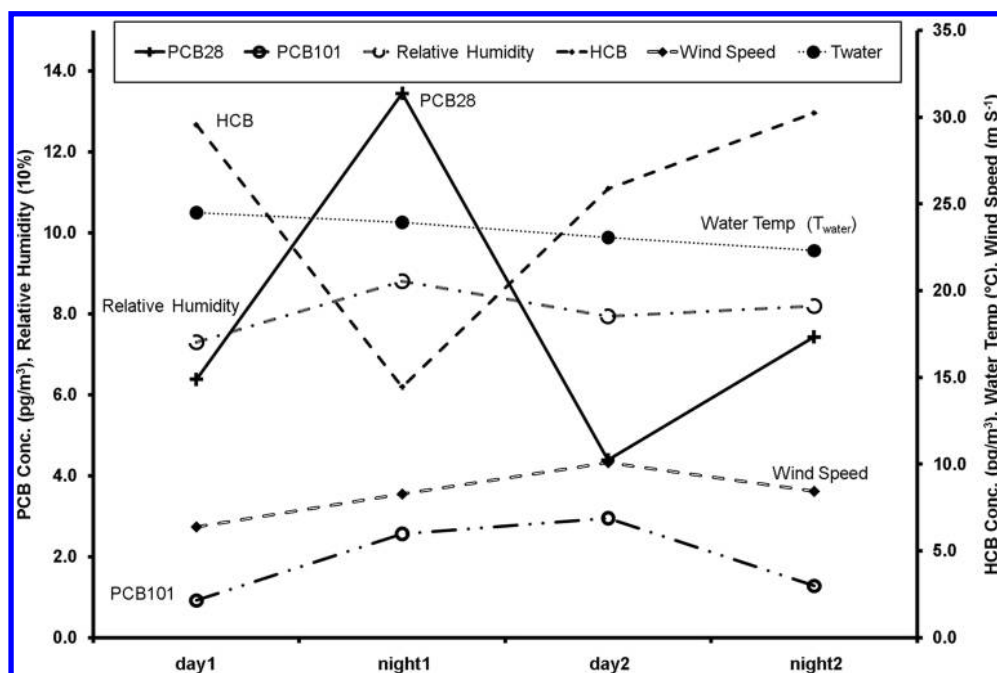

FIGURE 4. Short-term variations in gaseous PCB and HCB concentrations over the South Pacific Gyre with relative humidity (10%), water temperature (°C), and wind speed (m s^{-1}).

of the cruise, with daytime samples representing 3:30 a.m. to 5 p.m. and nighttime samples from 5 p.m. to 3:30 a.m. (SI Table 1). These samples were collected in the SPG (air sample no. 118–121); differences between air and seawater temperatures were less than 2 °C. A pattern of high nighttime [PCB]$_{gas}$ and low daytime [PCB]$_{gas}$ were captured in these samples (Figure 4). This is the first time such a pattern was observed in the open ocean. Previous findings in the open Atlantic were exactly the opposite (11, 14). Our results clearly show the low molecular weight PCBs displaying such cycle (e.g., PCB-28 in Figure 4). The night/day concentration ratios for the di- and tri-PCBs ranged from 1.6 to 2.1. Heavier PCB congeners (such as PCB-101) and HCB did not display a higher nighttime/lower daytime cycling pattern (Figure 4).

There are numerous factors that vary diurnally and could have potentially caused the observed pattern. However, we think we can rule out temperature, relative humidity, and other meteorological parameters as governing factors as they

would affect all POPs similarly, and are thus unable to explain the differences between HCB and lower chlorinated PCBs (Figure 4) (see more discussions in SI p S8).

Mass Balance Model. For a better understanding of the PCB cycling in the SPG, a mass balance model was used to discern what was driving the temporal changes in PCB concentrations in the atmosphere: diffusive air–water exchange, atmospheric chemistry, or both?

Volatilization from surface seawater to air was considered as the only input/source term of PCBs, with gaseous deposition and OH-radical depletion reaction as the loss terms (see SI page S7 for more details). Modeling results suggested atmospheric depletion reactions and deposition were similarly important loss processes. For low molecular weight PCBs, the removal of PCBs in the air was fast and large enough to modify the air–water concentration gradients and thereby cause volatilization of small PCBs from water to air. Heavy PCBs and HCB are less sensitive to OH radical

attack, thus it was air−water exchange that played a more important role in controlling their atmospheric concentration profiles. These results were also consistent with observations that only the lighter PCBs had distinguishable diurnal patterns in their gaseous concentrations, whereas heavier ones and HCB did not. In conclusion, the gaseous PCBs concentrations in SPG were driven by the interactions of removal by OH-radical depletion and supply by volatilization from surface seawater, rather than atmospheric chemistry alone.

Implications for Future Studies on POPs Cycling. This study reports, for the first time, that PCBs could volatilize from the oligotrophic open ocean during declining land-based emissions. Still unclear is whether the net volatilization was caused by swift changes in atmospheric patterns or is part of a longer-term trend for all oceans. Most previous Atlantic work has followed cruise tracts relatively close to the coast. Our work implies that the interior of the ocean could potentially behave very differently. Future work should focus on the underestimated and underexplored longitudinal (i.e., productivity) gradients in the oceans, thereby also avoiding the interference from land-based emissions. Simultaneously taken air−water samples are necessary to assess the directions and fluxes of diffusive air−water gas exchange, which is a key process in the cycling of POPs. Several studies speculate that biological activities could affect the air−water gas exchange equilibrium of POPs (8, 19, 25). Air−water samples taken simultaneously during phytoplankton blooms may help to verify this speculation.

Second, different day-night variation patterns in POPs' gaseous concentrations do exist over the oceans, although the exact patterns and forming reasons are still unclear. As suggested by the mass balance model, both the air−water exchange and OH radical depletion reaction contribute to the observed pattern and they both vary with time. Even though the temperature over the water surface varies much less than over land, air−water mass transfer coefficients still vary with wind speed. Plus, hydroxyl radical concentrations vary periodically. Thus, variations in gaseous concentrations over the open ocean are unlikely to be as regular as observed on land (37). If at all possible, it is suggested to increase the atmospheric sampling frequency from twice to four times a day under unknown oceanographic and meteorological conditions, to aid in revealing the cycling pattern and determining the effect of hydroxyl radical reaction on POPs gaseous concentrations through a mass balance model.

Supporting Information Available
Additional information on Material and Methods, tables with sampling details, POPs' concentrations, air−water exchange fluxes and comparisons, as well as selected internally consistent physicochemical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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