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Field-derived Henry's law constants for polychlorinated biphenyls in oceanic waters

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[1]   Accurate knowledge of Henry's law constants (K_{aw}) is very important for fate and transport studies of organic chemicals. Here field-derived K_{aw} values for polychlorinated biphenyl (PCB) congeners (PCBs 28, 49, 52, 118, 138, 149, and 153) were determined in the open Atlantic Ocean, at locations where air and seawater were assumed to be at equilibrium. Field-based K_{aw} values were derived from air and seawater samples simultaneously collected at these locations, and their relationship with temperature was determined. The average field-derived K_{aw} for PCBs 28, 49, 52, 118, and 138 was generally 2–3 times higher than laboratory-derived values reported in the literature. Possible causes of differences between the field and the laboratory data may be attributed to differences between pure water and seawater and the use of much higher persistent organic pollutant concentrations in laboratory studies compared to that of the remote ocean. Field-derived K_{aw} values for PCB 149 and PCB 153 were up to 10 times higher than literature values. The comparison of field- and laboratory-derived K_{aw} shows that their temperature dependence is not significantly different (95% confidence) from those reported in the literature.

1.   Introduction

[2]   Persistent organic pollutants (POPs) can undergo long-range atmospheric transport and can be deposited to open oceans. The open ocean and large water bodies are important reservoirs and sinks for the global cycling of POPs. Their capacity to store these chemicals is dependent on many factors in space and time, such as temperature, biomass, mixing depth, and the physical and chemical properties of the compound of interest [*Jurado et al.*, 2004b]. Atmospheric POPs can be incorporated into the base of the aquatic food chain (phytoplankton and bacteria), mediated by air-water exchange [*Dachs et al.*, 1999, 2002]. These processes have been studied previously in the Great Lakes region of North America, the Chesapeake Bay and other coastal areas of the mid-Atlantic region, and European seas [*Ashley and Baker*, 1999; *Dachs et al.*, 1997; *Hornbuckle et al.*, 1995; *Miller et al.*, 2001; *Nelson et al.*, 1998; *Totten et al.*, 2004]. These studies identify the importance of air-water exchange in understanding the environmental fate of POPs at local, regional, and global scales. Knowledge of whether surface ocean waters or lakes are in dynamic equilibrium with the atmosphere, or the net direction of flux (i.e., whether absorption or volatilization dominates), is therefore crucial for our understanding of the global cycling and fate of POPs. However, this is a highly complex issue to address.

[3]   There are large uncertainties in making such estimations [*Axelman et al.*, 2000; *Bruhn et al.*, 2003; *Wania et al.*, 2001]. Measurements of the physicochemical parameters, such as the Henry's law constant (K_{aw}), required to make such an assessment are subject to measurement difficulties and artifacts. Laboratory determinations of water solubility, the K_{aw}, and partition coefficients of compounds between environmental media are difficult to perform for compounds that are sparingly water soluble and have very low vapor pressures [*Li et al.*, 2003]. Different methodologies have been used, which can be a source of variability in the reported data including laboratory measurements and model predictions based on quantum mechanics solvation models [*Bamford et al.*, 2000, 2002; *Li et al.*, 2003; *Murphy et al.*, 1983, 1987; *Phillips et al.*, 2008; *ten Hulscher et al.*, 2006]. Laboratory determinations of K_{aw} values use pure water and therefore do not account for the influence of colloids, dissolved organic carbon (DOC), and salts present in natural waters. To give an example, reported values for the K_{aw} of PCB 28 and PCB 153 at 25°C range by factors of 2 and 3, respectively [*Bamford et al.*, 2000, 2002; *Burkhard et al.*, 1985; *Dunnivant et al.*, 1988; *Li et al.*, 2003; *ten Hulscher et al.*, 2006]. *Bruhn et al.* [2003] have discussed the significance of these uncertainties in the K_{aw} on air-water exchange

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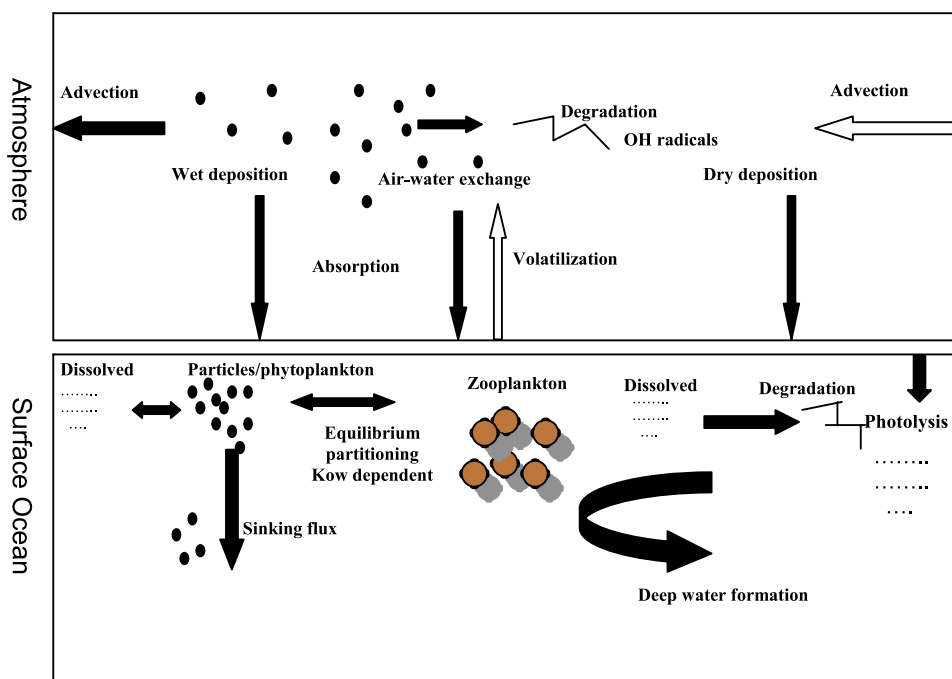[4]Department of Environmental Chemistry, IDAEA-CSIC, Barcelona, Spain.

Figure 1. Conceptual diagrams of the important input and removal processes affecting surface ocean water and the atmosphere in an ice-free region.

estimation. They calculated fugacity ratios for PCBs between the atmosphere and the Baltic Sea but showed that uncertainties in the K_{aw} made derivation of the net direction of flux impossible.

[4] This study made use of data obtained from cruises in the South and North Atlantic Ocean. These data have been presented and described elsewhere [*Gioia et al.*, 2008a, 2008b]. The air and seawater concentration data from these studies are used to derive field-measured K_{aw} values. It is reasoned that gaseous and dissolved phase PCBs will be in equilibrium when the rate of air-water exchange is greater than the rate of other fluxes or removal processes from the atmosphere and the surface ocean. With response times to air-water exchange of a few weeks, if it is faster by about 10%, it would be enough to assure conditions close to equilibrium.

[5] Sampling locations conforming to these conditions for air-water equilibrium were identified by assessing whether air-water mass transfer coefficients (MTCs) were higher than those of various removal processes from the atmosphere and the water as shown in Figure 1. Finally, field-based K_{aw} values and their temperature dependency were derived from these locations, compared with published laboratory-derived measurements or relationships and the trends and the implications discussed. This study represents the attempt to derive field-derived K_{aw} values for PCBs as there are not any other published studies reporting the same approach to estimating the Henry's law constant.

2. Methods: The Theoretical Approach

2.1. Air and Seawater PCB Concentrations

[6] Air and seawater samples were collected on the R/V *Polarstern* during scientific cruises from Germany to the Arctic Ocean and from Germany to Cape Town, using pub-

lished and accepted procedures. Details of the air and water sampling and analytical procedures have been described elsewhere [*Gioia et al.*, 2008a, 2008b].

2.2. Introductory Comments on Air-Water Exchange and Removal Processes

[7] Field-derived K_{aw} should only be obtained if gas and dissolved phase PCBs are at equilibrium. This will occur only if diffusive air-water exchange is faster than all the other processes affecting the PCB concentrations in the gas phase or dissolved phase. In order to evaluate the occurrence of equilibrium conditions, a systematic approach to considering relevant processes in the lower atmosphere–upper ocean was followed.

[8] Figure 1 is a conceptual diagram of the processes known to influence the fate and transport of POPs in the open ocean. Airborne PCBs may be deposited to the surface ocean by air-water gas exchange or wet and dry deposition or may be degraded by OH radicals. Previous assessments for oceanic regions have shown that air-water gas exchange is a major depositional process for PCBs, and it is always faster than the other depositional processes [*Dachs et al.*, 2002; *Jurado et al.*, 2004a]. However, wet deposition can be important in rainy regions [*Jurado et al.*, 2005], and OH radical degradation can become faster than air-water exchange in tropical regions, where the air temperature and OH radical concentrations, and hence reaction rates can be relatively high.

[9] The aquatic carbon cycle, and specifically phytoplankton biomass, plays an important role in influencing the net air-water exchange by controlling the dissolved water concentration and consequently the fugacity gradient with the atmospheric gas phase. Air-water exchange and partitioning to or uptake by phytoplankton act as coupled processes in aquatic environments [*Dachs et al.*, 1999]. Once

PCBs are in the dissolved phase, they may sorb to particles, and organisms such as phytoplankton, and can be removed from the surface water and delivered to the deep ocean by sinking particles and by zooplankton vertical migration. If air-water exchange is not fast enough to reestablish equilibrium with the dissolved phase in the water, the system will not be at equilibrium. This depends on the trophic status of the ocean and chemical hydrophobicity. In high-productivity areas of the open ocean, the sinking fluxes of PCBs will be relatively high [Dachs et al., 2002], leading to efficient removal of PCBs from the surface oceans, especially for the more hydrophobic compounds. In more oligotrophic regions, where productivity is limited by nutrient availability, relatively few particles and low phytoplankton biomass will be generated. Here air and water will be closer to equilibrium conditions, and air-water exchange will be faster than sinking fluxes of PCBs. Previous assessments of these interactions were performed considering midterm (monthly) variations [Dachs et al., 2002], but since response times of water column concentrations are long in response to settling fluxes this approach can be generalized to the data set shown here. This is in contrast to short-term variability of surface POP concentrations driven by precipitation events [Jurado et al., 2005], which will need to be considered for each sampling period.

[10] Since the purpose here is to establish whether field data from different open ocean regions represent conditions of dynamic air-water equilibrium, each of the removal processes was considered individually, operating in a water column representative for the regions sampled during the two cruises discussed above. This was done by comparing the air-water MTCs with the MTCs of each of the removal processes from the atmosphere and the water column. Equations for the estimation of MTCs for all processes and discussion of their associated uncertainties can be found in the auxiliary material.[1] Areas of the ocean where the atmosphere and the surface water are assumed to be close to equilibrium were identified and used to determine field K_{aw} values.

2.3. Net Air-Water Exchange Flux

[11] Gas exchange rates were calculated using a modified version of the Whitman two-film resistance model [Whitman, 1923]. The net air-water flux is given by

$$F_{net} = v_{aw}\left(C_w - \frac{C_a}{K'_{aw}}\right), \qquad (1)$$

where F_{net} is the flux (pg m^{-2} d^{-1}) and v_{aw} (m d^{-1}) is the air-water exchange MTC, estimated as reported in the auxiliary material. $C_w - (C_a/K'_{aw})$ describes the concentration gradient (pg m^{-3}). C_w (pg m^{-3}) is the dissolved phase concentration of the compound in water. C_a (pg m^{-3}) is the gas phase concentration of the compound in air, which is divided by the dimensionless Henry's law constant (K'_{aw}).

2.3.1. OH Radical Degradation in the Atmosphere Versus Air-Water Exchange

[12] Atmospheric degradation of PCBs (F_{deg}, pg m^{-2} s^{-1}) is dominated by reaction with OH radicals. By assuming

that PCBs are well mixed in the atmospheric boundary layer (ABL), this can be expressed as follows:

$$F_{deg} = hk_{OH}C_{OH}C_a, \qquad (2)$$

where h is the height of the ABL, k_{OH} (cm^3 molecule^{-1} s^{-1}) is the second-order degradation rate constant for air, C_{OH} (molecule cm^{-3}) is the concentration of OH radical, and C_a (ng m^{-3}) is the gas phase concentration of the compound in air. The height of the ABL in this case was taken to be an average value of 200 m. NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory (HY-SPLIT) model and the National Centers for Environmental Prediction–National Center for Atmospheric Research (NCEP-NCAR) global reanalysis data set were used to calculate atmospheric mixing height, which showed that the mixing layer depth was stable at 200–300 m. Degradation rate constants and activation energies were from Beyer et al. [2003] and Anderson and Hites [1996], and the temperature corrected as indicated was from Beyer et al. [2003]. The OH radical concentration was calculated using $C_{OH} = [0.5 + 4(T - 273.15)] \times 10^5$ [Beyer et al., 2003], where T is the temperature in kelvin. The 24 h C_{OH} averages of the first 0–200 m varied from 3.0×10^5 to 1.3×10^6 molecules cm^{-3} in the Arctic (65°N–85°N) during the summer season (June–August) and from 2.8×10^5 to 1.5×10^6 molecules cm^{-3} from 45°N to 30°S in October–November.

[13] Clearly, there will be greater atmospheric degradation of PCBs in warmer periods and regions. It will be of minor importance in the Arctic, where temperatures ranged between −2°C and 10°C during the sampling. Degradation due to reactions with OH radicals approached the rate of air-water exchange in some tropical locations. However, at several locations in the tropical South Atlantic the air-water exchange is found to be faster than degradation by OH radicals by a factor of 4–5 for the more volatile PCBs and by a factor of 20–30 for the less volatile PCB congeners.

2.3.2. Wet and Dry Deposition Versus Air-Water Exchange

[14] The contribution of wet deposition to the overall depositional fluxes can be important (contributing up to 35% of the total flux) in the Intertropical Convergence Zone (ITCZ), where convective precipitation rates are high [Jurado et al., 2005]. However, precipitation periods occurred in about 10% of the samples, mostly collected in the ITCZ. For approximately 60% of the samples in the Arctic, fog was dominant during sampling. Data from these two regions, where precipitation or fog events occurred during sampling, were therefore not suitable for derivation of the field K_{aw} values because of the high deposition rates of fog and because it may have biased air concentrations.

[15] Dry depositional fluxes for less volatile PCBs may be the dominant deposition mechanism at midlatitudes to high latitudes (±50°–±80°), where low temperatures and high wind speeds can enhance the relative importance of dry depositional fluxes for the less volatile PCB congeners [Jurado et al., 2005]. Low temperatures can increase the fraction of PCBs bound to aerosols (especially for the less volatile congeners). However, PCBs are found predominantly in the gas phase, and these samples were collected in remote ocean regions far from sources, where the total

suspended particle burden in the atmosphere is relatively low and particles are small in size.

2.3.3. Sinking Flux Versus Air-Water Exchange

[16] Vertical sinking of particle-associated POPs is a nonfugacity-driven process and is key to their removal from the photic zone to the deep ocean. *Dachs et al.* [2002] parameterized sinking fluxes in the Atlantic; they showed that the dissolved phase of hydrophobic PCBs can be depleted in the mixed surface layer. Air-water exchange will keep surface dissolved phase concentrations close to equilibrium with the atmospheric gas phase, except in areas with very high primary productivity (phytoplankton biomass approximately >1 mg L^{-1}) [*Dachs et al.*, 2002]. Total chlorophyll *a* concentration was obtained on board the vessel for the Atlantic cruise, while chlorophyll *a* in the Arctic was determined by using climatological 3 year means of chlorophyll *a* from the Sea-viewing Wide Field-of-view Sensor (SeaWiFS) satellite because of the lack of direct measurement on board. For the Atlantic cruise chlorophyll *a* concentration ranged from 0.05 to 0.26 mg m^{-3}, while at the Arctic locations it ranged from 0.30 to 1.1 mg m^{-3}.

2.3.4. Active Vertical Fluxes of Zooplankton Versus Air-Water Exchange

[17] Vertical migration of zooplankton plays a significant role in the biological pump by contributing to carbon export from the surface to the deep waters. Removal of PCBs from the surface water could occur by active and passive vertical fluxes of zooplankton. Active vertical fluxes are due to diel and seasonal migration of zooplankton to the surface water. Zooplankton can undertake diel vertical migrations up to several hundreds of meters [*Bougis*, 1974]. They are generally at the surface during the night and in deeper waters during the day. The percentage of the total mesozooplankton biomass (copepod dominated) constituted by diel vertical migrators is generally 10%–40% [*Longhurst et al.*, 1990; *Steinberg et al.*, 2000; *Turner*, 2002; *Zhang and Dam*, 1997]. *Steinberg et al.* [2000] reported averaged organic carbon (OC) fluxes of 26 mg m^{-2} d^{-1} in the Sargasso Sea for an integrated water column of 150 m depth. Therefore, the amount of PCBs removed from the surface because of zooplankton migration would strongly depend on OC fluxes. However, in order to be compared with air-water diffusional fluxes, only the zooplankton-driven flux from the mixed layer depth (MLD) should be considered, which must be a small fraction of the total since zooplankton will feed on phytoplankton, the maximum of which is usually below the thermocline.

[18] The vertical migration of zooplankton can reach a maximum of 10–20 m water depth, where most of the plankton is [*Steinberg et al.*, 2000; *Turner*, 2002], and hence have little interaction with the surface mixed layer. The MLD during the two scientific cruises ranged from 5 to 40 m, and hence, vertical fluxes of zooplankton are considered to have little influence on the removal of PCBs from the surface waters.

2.3.5. Variability in the Wind Speed, Chlorophyll, Water Temperature, and Salinity

[19] An average wind speed measured at the time of sample collection is not the wind speed responsible for the observed concentration gradient. However, the difference between the average wind speed and the actual wind speed responsible for the concentration gradient is minimized when

there is little variability in the wind speed. The wind speed ranged from 2.6 to 11 m s^{-1} in the Arctic and from 0.6 to 11 m s^{-1} in the tropic region, but variability was much lower within samples. *Gioia et al.* [2008b] reported that PCB concentrations in air and water were constant in this region. As for the Arctic region, we found the same situation confirmed by *Gioia et al.* [2008a], that PCB concentration in air and water did not vary much between samples in the region used to derive the field K_{aw} with a small variability in wind speeds. Another way to look at this variability is to assess the common variability in oceanic wind speeds, as reported elsewhere [*Dachs et al.*, 2002; *Simó and Dachs*, 2002]. It is possible to use satellite-borne estimations of wind speed and the knowledge of the climatology of wind speeds to estimate the error associated with using an average wind speed for estimating the air-water mass transfer coefficients. This is possible because wind speeds follow a Weibull distribution. Using the appropriate mathematical models, *Simó and Dachs* [2002] concluded that the error associated with estimating the mass transfer coefficients (thus the flux) was of 30% on average. The error can only be higher than this in regions with extreme variability in wind speeds, which is not the case in the tropical and Arctic regions.

[20] The water samples were taken when the ship was moving; thus, they are integrated samples. However, the sampling stations chosen to derive the Henry's law constants are those in oligotrophic regions, thus those with low and constant chlorophyll concentrations. The variability of salinity and temperature was even lower. Salinity varied from 33 to 35 parts per thousand in both regions. The difference in salinity between oceanic regions is lower than 10%, thus introducing a negligible error in K_{aw} estimates. The measured temperature values in the tropics and the Arctic were always with a variability lower than 2°C and, for half of the sites, lower than 1°C (Table 1). Therefore, the error or uncertainty introduced by these variations on K_{aw} measurements is minimal.

2.3.6. Formation of Deep Oceanic Water

[21] The global thermohaline circulation can transport surface waters to the deep ocean, removing PCBs in the process [*Lohmann et al.*, 2006]. This is very important in the Norwegian Sea in the winter months. However, it does not affect the samples considered here, which were collected in the Arctic summer.

3. Results and Discussion

3.1. Selection of Sampling Locations With Equilibrated Gas and Dissolved Phase PCBs

[22] Samples taken from 8 locations out of a total of 24 on the cruises satisfied the conditions considered in section 2 to result in air gas phase–surface ocean dissolved phase equilibrium. At the remaining 16 locations there was at least one process that was estimated to be faster than air-water exchange (e.g., OH radical degradation or wet deposition). The MTCs of the air-water exchange for the selected eight locations are compared to the MTCs for the removal processes in Table 1. Four of the eight sites were in the tropical southern Atlantic, and four were in the Greenland Sea. All were remote, far from potential land PCB sources. Details of these samples and the concentrations measured in air and water are given in Table S1 in the auxiliary material.

Table 1. Range of Values for All Seven PCB Congeners Showing Wind Speed, Temperature, and Comparison of the Mass Transfer Coefficients for Air-Water Exchange and for the Removal Processes for the Eight Locations Where the Field-Based Air-Water Partition Coefficients Were Derived

	Locations							
	1	2	3	4	5	6	7	8
Wind speed (m s^{-1})	2.1–5.1	0.6–3.5	0.3–2.1	6.8–11	6.3–11	5.2–11	2.6–9.3	4.2–7.4
Temperature (°C)	5.7–7.3	4.6–6.5	2.4–3.6	2.4–2.9	24–26	23–24	19	18–19
Air-water exchange MTCs (cm d^{-1})	42–48	16–18	17–19	150–174	164–184	167–185	140–155	111–122
OH radical degradation MTCs (cm d^{-1})	0.56–10	0.62–13	0.55–10	0.53–11	4.7–64	4.6–64	4.1–55	3.6–46
Sinking fluxes MTCs (cm d^{-1})	0.12–1	0.12–1	0.12–1	0.12–1	0.2–1.5	0.2–1.5	0.2–1.5	0.20–1.5

3.2. Derivation of Field-Based K_{aw} Values Under Dynamic Equilibrium Conditions

[23] Seven congeners (PCBs 28, 52, 49, 118, 138, 149, and 153) were detected in air and water at most of the eight locations. Field-based K_{aw} values were obtained from

$$K'_{aw} = \frac{C_a}{C_w}. \qquad (3)$$

[24] The dissolved phase concentration was corrected for DOC as reported elsewhere [*Burkhard*, 2000; *Totten et al.*, 2001]. A constant DOC concentration of 1 mg L^{-1} [*Dachs et al.*, 2005] was assumed for the entire Atlantic Ocean. The DOC concentration is quite constant in the open ocean compared to the coastal areas [*Dachs et al.*, 2005]. Furthermore, the DOC concentration averaged 0.5 ± 0.2 mg L^{-1} in the open Atlantic Ocean. Therefore, assuming a 1 mg L^{-1} DOC concentration is considered the upper estimate and therefore the worse case scenario of the DOC in the open ocean. In addition, the DOC correction is more important for the heavier PCBs, but at these DOC concentrations the dissolved phase concentrations of the hexabiphenyls is only reduced by 10%. Assuming that the uncertainty in the measured "dissolved" (not DOC-corrected) water concentration and the air concentrations are each about 20%, the uncertainty in the K_{aw} is 28%. In any case, the uncertainty of measured dissolved concentrations associated with DOC cannot explain the differences in K_{aw} values. The fractions of PCBs sorbed to the colloidal phase predicted by the model described by *Totten et al.* [2001] are 2%, 4%, 6%, and 10% for the tribiphenyls, tetrabiphenyls, pentabiphenyls, and hexabiphenyls, respectively.

[25] K'_{aw} can be compared with K_{aw} values from the literature by conversion to Pa m^3 mol^{-1} using

$$K_{aw} = K'_{aw}RT, \qquad (4)$$

where R is the universal gas constant (8.314 m^3 Pa mol^{-1} K^{-1}) and T (K) is the water temperature recorded for every sample.

[26] The field-derived ln K_{aw} was plotted against $1/T$ and compared with literature values reported by *Bamford et al.* [2000] and *Li et al.* [2003] in Figure 2. The temperature range used to derive the field-based K_{aw} is 2.7°C–26°C. Field-based K_{aw} values at 25°C were derived by using the relationship with temperature obtained by plotting ln K_{aw} versus $1/T$. The temperature dependence will be discussed in section 3.6. Table 2 shows the K_{aw} values derived from this

study for 25°C and compared with those reported in the literature at the same ambient temperature, including studies by *Burkhard et al.* [1985], *Dunnivant et al.* [1988], *Murphy et al.* [1987], and *ten Hulscher et al.* [2006]. Uncertainty in calculated field-derived K_{aw} results from propagation of random measurement errors of gas phase and dissolved phase concentration and correction of the dissolved phase concentration for DOC. To assess the relative magnitude of random errors in the instantaneous K_{aw} calculations, a propagation of error analysis was performed. The standard deviations associated with C_a and C_w measurements were 10% and 20% on the basis of replicate samples, repeated sample injections for measurement precision, and the relative standard deviations of surrogate recoveries. The error for the DOC correction of the dissolved phase was estimated to be 10%. The error of the estimation of the field-derived K_{aw} was calculated to be 24%. The literature K_{aw} values [*Burkhard et al.*, 1985; *Dunnivant et al.*, 1988; *Murphy et al.*, 1987; *Li et al.*, 2003; *ten Hulscher et al.*, 2006] were corrected for real-time salinity data from the ship and the Setschenow constant (K_s) of 0.3 L mol^{-1} [*Schwarzenbach et al.*, 2003], as shown in the auxiliary material. The presence of dissolved salts or minerals generally leads to a moderate decrease in the solubility of hydrophobic organic solutes due to the "salting-out effect." Constants can be found in the literature, and they generally range from 0.1 to 0.4 L mol^{-1}. In the case of PCBs (dichlorobiphenyls to hexachlorobiphenyls), K_s ranges from 0.3 to 0.4 L mol^{-1} [*Schwarzenbach et al.*, 2003].

3.3. Comparison Between K_{aw} at the Eight Selected Locations and the Other Locations

[27] As explained in section 3.1, only eight locations conformed to the set criteria for the derivation of the field-based K_{aw}. However, in this section, the K_{aw} values derived from the eight locations are compared to values derived using the data from elsewhere on the transect (see Table S2 and Figure S1 in the auxiliary material). K_{aw} values for the eight selected sites are similar or slightly lower than those for the remaining sites, where at least one removal process was predicted to be faster than air-water exchange. However, when temperature dependence regressions were obtained using all 24 data pairs, large variability arose, leading to poor regressions. This occurred most in the high-productivity areas for the high molecular weight congeners, consistent with expectations about nonequilibrium conditions in these regions. In general, this suggests that the site selection criteria have been adequate and cautious in identifying the sites where air and water could be close to equilibrium.
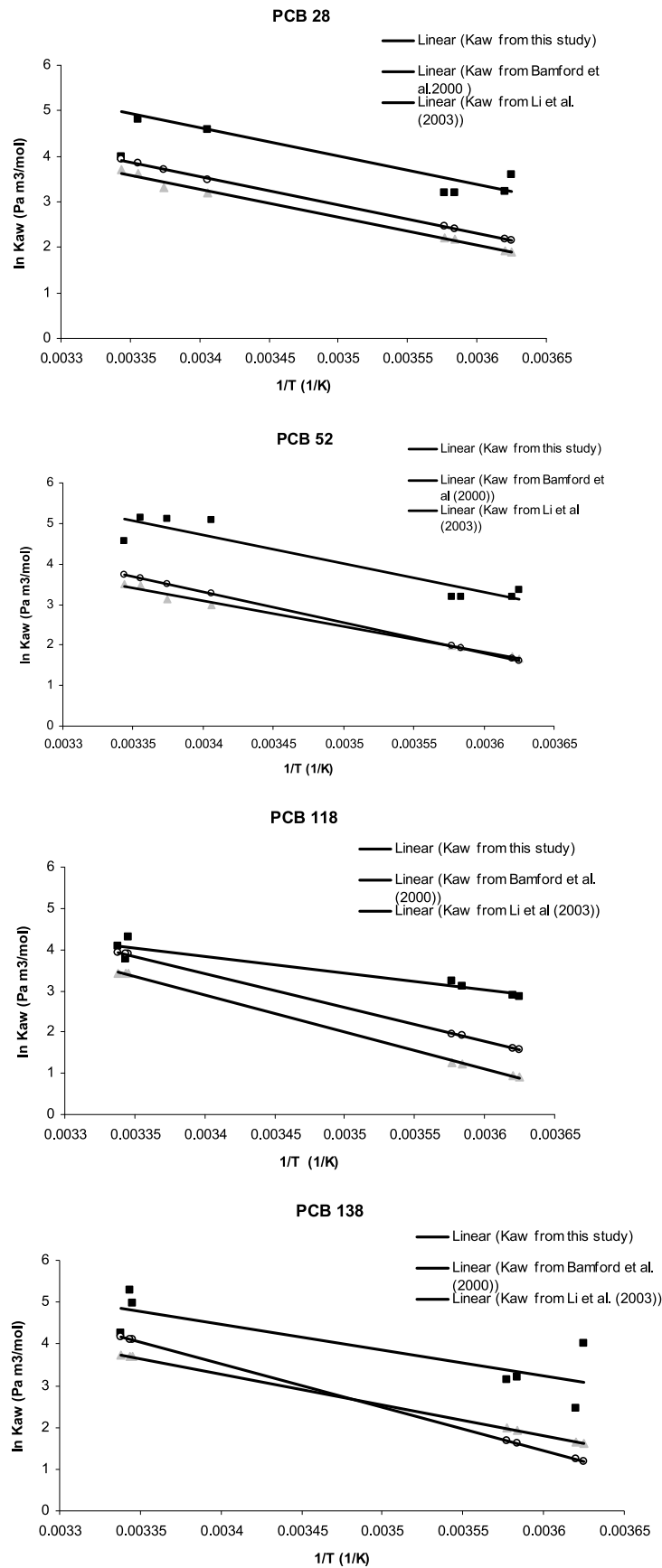
PCB 28

PCB 52

PCB 118

PCB 138

Figure 2. Plots of ln K_{aw} versus $1/T$ for four different congeners. Black squares are data from this study. Grey triangles are data from *Li et al.* [2003]. Open circles are data from *Bamford et al.* [2000].

Table 2. Field-Derived Air-Water Partition Coefficient and the Uncertainty Resulting From the Propagation of Errors on the K_{aw} for Seven PCB Congeners Compared to the Henry's Law Constant From the Literature

	Henry's Law Constants at 25°C (Pa m³ mol⁻¹)					
Compound	*Bamford et al.* [2000]	*ten Hulscher et al.* [2006]	*Murphy et al.* [1987]	*Burkhard et al.* [1985]	*Dunnivant et al.* [1988]	This Study
PCB 28	58	65	43	37	47	87 ± 37
PCB 49	49	57	na	na	na	179 ± 75
PCB 52	45	56	35	83	43	108 ± 45
PCB 118	55	20	67	15	21	84 ± 35
PCB 138	67	22	80	17	21	77 ± 32
PCB 149	82	37	na	na	na	125 ± 53
PCB 153	80	25	58	28	27	202 ± 84

3.4. Field-Based Versus Laboratory-Based K_{aw} Values

[28] The average field-derived K_{aw} values for PCBs 28, 49, 52, 118, and 138 are 2–3 times higher than those reported in the literature (Table 2) but are not statistically different (*t* test was performed at the 95% confidence level) from the higher estimates of *Bamford et al.* [2000], *Burkhard et al.* [1985], and *ten Hulscher et al.* [2006] for 3 Cl to 5 Cl congeners (with the exception of PCB 49, which is statistically different from those reported in the literature). Field-derived K_{aw} values for PCB 149 and PCB 153 were up to 10 times higher than literature values, but there is high uncertainty in these values because of their hydrophobicity. Hydrophobic compounds associate more with organic matter, and thus, their dynamics are more complicated in the water column. Even though we now know quite a lot about the organic carbon cycle and its role in POP cycling, any error in the quantification of the carbon will be larger for the more hydrophobic PCBs. Indeed, the regression between ln K_{aw} of PCBs 149 and 153 versus $1/T$ was not statistically significant for these two PCB congeners ($p = 0.14$ and $p = 0.37$, respectively; see Table 3). There is no clear trend of the field-based K_{aw} values decreasing with increasing chlorination of the compound at a fixed temperature (see Table 2). K_{aw} values for PCB 49 and PCB 52 are higher than those reported for PCB 118 and PCB 138. This is not in agreement with studies by *Burkhard et al.* [1985], *Dunnivant et al.* [1988], *Li et al.* [2003], and *ten Hulscher et al.* [2006], who reported K_{aw} values for the heavier congeners that were consistently lower than lighter congeners. Differences in the absolute value between the field-derived and laboratory-measured values may be due to artifacts introduced in the laboratory studies. Alternatively, there may be unknown processes operating in the field that deplete the apparent surface water concentrations or enhance the apparent gas phase concentrations relative to those used in laboratory determinations. It is appropriate to discuss these possible factors.

3.5. Possible Causes of Differences Between the Field and Laboratory Calculations

3.5.1. Differences Between Natural Waters and Experimental Conditions

[29] Laboratory experimental determinations of K_{aw} for PCBs are performed with pure water, while natural waters contain DOC, colloids, suspended particles, and salts. These constituents can modify the partitioning of hydrophobic compounds into the dissolved phase and, in turn, the K_{aw}. However, there is little systematic understanding of the role of these factors. Concerning sea salt, little is known about its influence on the water solubility and Henry's law constant values of PCBs. A salting-out constant of 0.3 L mol⁻¹ [*Schwarzenbach et al.*, 2003] was applied here to "correct" the literature values of all the congeners. Average K_s values are taken from different studies; therefore, the ranges indicated for these values show that, in general, there could be uncertainties up to ±20% in the reported K_s values [*Schwarzenbach et al.*, 2003].

[30] The salting-out constant may also be temperature-dependent. *Kucklick et al.* [1991] found that K_{aw} values determined at 35°C and 45°C in seawater were significantly higher ($p < 0.05$) than in distilled water for α- and γ-hexachlorocyclohexanes (HCHs) but not at lower temperatures. However, it seems difficult to conceive that the influence of sea salt alone can explain the higher values for field-derived K_{aw}. The salting-out correction only increases the K_{aw} values by 25%–30% considering a range of K_s of 0.3–0.4 L mol⁻¹.

[31] The role(s) of DOC in influencing the dissolved phase is also unclear. The dissolved phase was corrected for

Table 3. Field-Derived ΔH_H of the Regression Between ln K_{aw} and $1/T$ Compared With the ΔH_H of *Li et al.* [2003] and *Bamford et al.* [2002]

	$\Delta H_H \pm 1$ Standard Error (kJ mol⁻¹)			
Compound	*Li et al.* [2003]	*Bamford et al.* [2002]	This Study	R^2 for This Study
PCB 28	54 ± 0.5	52 ± 0.6	39 ± 9	0.76 ($p = 0.004$)
PCB 49	64 ± 2	64 ± 2	117 ± 26	0.84 ($p = 0.01$)
PCB 52	60 ± 0.1	62 ± 0.1	54 ± 9	0.85 ($p = <0.001$)
PCB 118	69 ± 0.2	69 ± 0.2	34 ± 5	0.91($p < 0.001$)
PCB 138	61 ± 0.1	87 ± 0.2	51 ± 15	0.70 ($p = 0.02$)
PCB 149	70 ± 0.4	70 ± 0.4	61 ± 59	0.34 ($p = 0.14$)
PCB 153	60 ± 1.3	71 ± 2.5	25 ± 27	0.08 ($p = 0.37$)

a typical DOC value of 1 mg L^{-1} [*Dachs et al.*, 2005], but DOC is a complex mixture of thousands of organic chemicals with a wide range of physical-chemical properties. Indeed, it may be different in different parts of the ocean. Traditionally, it has been considered that DOC has some sorbing capacity [*Burkhard*, 2000] and therefore could reduce the loading of purely dissolved chemicals. This would actually induce higher apparent solubilities and lower K_{aw} values. These issues are complex and could not be quantified here.

[32] It is always assumed that partitioning is a linear phenomenon, that is, the K_{aw} value is independent of the chemical concentrations. This is only true in the case of ideal solutions, and PCBs in seawater may certainly exhibit a nonideal behavior. Oceanic concentrations of PCBs are more than 1 million times lower than those used in laboratory experiments [*Bamford et al.*, 2000; *Murphy et al.*, 1987; *ten Hulscher et al.*, 2006], and therefore a small nonlinearity in partitioning could lead to the factor of 2–3 differences observed here between field-derived K_{aw} and laboratory determination of K_{aw} values. The air-water partitioning constant for nonideal solutions will be lower than at infinite dilution [*Smith et al.*, 2004]. It should also be noted that Henry's law will apply to the solute in a limited concentration range in which it is in a sufficiently diluted form. The range of concentrations in which it applies becomes narrower the more the system diverges from nonideal behavior [*Sangster*, 2003]. *Koga* [1995] concluded that at the most dilute point measured for *t*-butyl alcohol, $x_{tba} = 0.000068$ ($m_{tba} = 0.0038$ mol kg^{-1}), the solution is not yet dilute enough for Henry's law to be obeyed. Because of the low oceanic concentrations, the ocean water–PCB system is closer to an ideal solution than the laboratory solutions to determine the Henry's law constant. *Paschke and Schüürmann* [2000] proved that the concentration dependence of the octanol-water partition coefficients (K_{ow}) of HCH isomers seems to be an important source of scattering of data from the literature for which the underlying concentration levels are not reported. The occurrence and significance of nonideal solutions in environmental systems will need to receive more research attention in the future since it could not only influence laboratory determination of Henry's law constants but also other physical-chemical properties.

3.5.2. Other Possible Influences That Could Affect K_{aw}

[33] Another possible influence is the surface microlayer. The K_{aw} values derived here assume that the measured subsurface water concentration is evenly distributed through the top meters of the water column. However, PCBs may be enriched in the surface millimeter, where a microlayer of organic matter accumulates [*García-Flor et al.*, 2005]. This is in the most intimate contact or exchange with the atmosphere. The enrichment of PCBs in the surface microlayer is influenced by organic matter [*García-Flor et al.*, 2005]. If PCB accumulation in the sea surface microlayer is an equilibrium partitioning process to the microlayer organic carbon, then it simply means that all three phases (air, water, and organic matter) would be in equilibrium with no influence on the field-derived K_{aw}. Conversely, if there is an unknown process that enhances the truly dissolved concentrations in the surface microlayer and the gas phase only sees the surface microlayer, then higher "field K_{aw}" values would be obtained.

However, the surface microlayer is not so important in oligotrophic waters. Further understanding of the role of the microlayer in the fate and partitioning of POPs in the "skin" of the oceans is needed. Knowledge of POP cycling in oceans is still incomplete, and therefore it cannot be disregarded that an unknown or unquantified process could drive the air-water system out of equilibrium, inducing higher apparent K_{aw} values.

3.6. Temperature Dependence of the Field-Derived Henry's Law Constants

[34] The regressions between the ln K_{aw} and $1/T$ are reported and compared to those of *Bamford et al.* [2002] and *Li et al.* [2003] in Figure 2. Correlations between ln K_{aw} versus $1/T$ are statistically significant ($p < 0.05$) for five of the congeners considered here (PCBs 28, 49, 52, 118, and 138) ($R^2 \geq 0.70$). Equations of these relationships are reported in Table S3 of the auxiliary material. Regressions are not statistically significant ($p < 0.1$) for the two remaining congeners (PCBs 149 and 153).

[35] Table 3 compares the enthalpies of air-water exchange (ΔH_H in kJ mol^{-1}) from *Li et al.* [2003] and *Bamford et al.* [2002] with those derived from the temperature dependence regressions of this study. Because of the small number of sites, the uncertainty in ΔH_H is high, and thus, statistically, the ΔH_H values estimated from this study are not statistically different than those reported by *Bamford et al.* [2002] and *Li et al.* [2003]. Indeed, previously published values fall within the mean ±3 times the standard deviation, except for PCB 118. PCB 49 displays a higher enthalpy value than those reported by *Bamford et al.* [2002] and *Li et al.* [2003], but it is still not significantly higher. Overall, the comparison of field- and laboratory-derived K_{aw} shows that their temperature dependence is not statistically different than those reported before, and because of the high standard error of ours it is not possible to state that the measurements support the *Bamford et al.* [2002] or the *Li et al.* [2003] estimations.

4. Conclusions

[36] There are large uncertainties associated with the estimation of the laboratory-based K_{aw} values. This manuscript adds to our knowledge of the equilibrium partitioning of PCBs between air and water, as well as estimation of K_{aw} values. These differ from literature K_{aw} values derived from laboratory studies. Field-derived air-water partition values are a factor of 2–3 higher than those reported previously from standard measurement procedures made in the laboratory using pure water and much higher POP concentrations. It is interesting to speculate that if the field-derived K_{aw} values were used, there would be important implications about the POPs cycling and modeling. This study highlights that significance of nonideal solutions in environmental systems will need to receive more research attention in the future. If there are systematic errors in the laboratory-derived K_{aw} values, this has important implications for modeling studies where flux and equilibrium statuses of the global system are estimated. The field-derived values are higher than the laboratory ones. This means that in those studies reporting a net absorption, this will be lower by a factor of 2–4 depending on the PCB congeners or will result in a net volatilization or situation closer to equilibrium con-

ditions instead of absorption. Conversely, in those studies reporting net volatilization, these fluxes will be higher by a factor of 2–4. If the Henry's law constant for PCBs is 2–4 times higher that those reported in the literature, then these compounds will tend to favor the gas phase and volatilize to the atmosphere faster than compounds with lower values. This also means that the idea of the ocean as a reservoir or sink could be different because it may act more as a source to the atmosphere, enhancing net volatilization of PCBs if the K_{aw} values are 2–4 times higher. Conversely, models that predict the oceanic sink from atmospheric concentrations of POPs will also lead to higher values by a factor of 2–3.

[37] In a climate change scenario, with rising temperature and ice cover decreasing at the poles, net volatilization, as well as air-water gas exchange, will be enhanced. Future research should focus on continuing to simultaneously measure air and water in different regions of the remote ocean, implementing sampling approaches and resolution as well as estimation of the air-water exchange fluxes by using different methods. More K_{aw} field-derived data on different classes of compounds are also needed for comparison, and implications on current knowledge of regional and global cycling of POPs should be assessed.

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