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Particle-Dissolved Phase Partition of Polychlorinated Biphenyls in High Altitude Alpine Lakes

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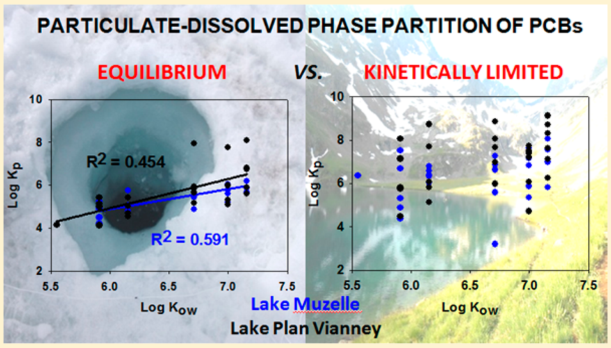
Supporting Information

ABSTRACT: We investigated whether polychlorinated biphenyls (PCBs) partitioning between the dissolved and particulate phases in two high altitude alpine lakes was determined by the quantity, size structure, or composition of suspended particles. Within- and between-lakes differences in water-particulate phase partition coefficient (K_p) were not related to total suspended matter, phytoplankton biomass, or taxonomic composition. Yet, a seasonal relationship between K_p and K_{ow} was detected for both lakes, revealing equilibrium of PCBs partition when lakes were ice covered. On the contrary, PCBs partitioning between particles and water appeared kinetically limited during the open water season. Partition is therefore mainly governed by thermodynamic laws during the ice-covered period, while none of the tested physical or biological parameters seemed to explain the distribution of these particle-reactive contaminants in the open water period. PCBs were always mainly associated with particulate matter, but partitioning within different particulate size-fractions varied between seasons and between years during open water periods. When ice cover is absent, PCBs were mainly adsorbed on microplankton, the largest phytoplanktonic size fraction, which is the least likely to get grazed by pelagic microconsumers.



INTRODUCTION

Resistance to breakdown and semi-volatility of polychlorinated biphenyls (PCBs) lead to contamination of numerous ecosystems even far from human activities such as alpine lakes.[1−4] Recent studies have focused on PCBs export to high altitude lakes and highlighted that snowpack was the primary source of annual inputs.[5,6] If most attention has been given so far to the dominant pathways by which PCBs are deposited in these remote ecosystems, the processes governing their fate (storage, export, or integration within the food webs) remain to be scaled.

The fate of organic chemicals in aquatic systems is controlled by their partition between particulate matter and water.[7] In rivers, several physical−chemical factors such as concentrations of total suspended matter, colloids, or particulate organic carbon affect particulate-dissolved phase partition of PCBs.[8−13] PCBs partition has further consequences on their exchange at the air−water interface that was considered as an important loss process of such chemicals in aquatic ecosystems.[14,15] Besides, previous studies have shown that phytoplankton biomass plays an important role in the fate of organic contaminants in lakes, both enhancing their exchanges across air−water interface[16,17] and their export to deep waters or sediments.[18,19] Furthermore, the size fraction on which PCBs are preferentially adsorbed shall determine their uptake by organisms, further transfer into food webs, and final contamination of fish resources.[20−24] If such processes are important in aquatic systems contaminated by local sources, it is unknown whether they contribute at the same scales on the fate of PCBs in high altitude lakes where inputs are lower. It is however crucial to better understand processes governing PCBs accumulation, volatilization, and sedimentation in these remote ecosystems since they are doomed to get even more contaminated in a near future because of revolatilization of previously deposited pollutants from contaminated surface reservoirs (soil, snow, ice surfaces, etc.).[25−27]

In high altitude lakes, PCBs partitioning in water appeared to be influenced in part by physical−chemical parameters such as water temperature and octanol−water coefficient (K_{ow}).[4,28,29] However, field evidence for the influence of biological

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Table 1. Seasonal Variations of Water Temperature and Concentrations in Total Suspended Matter (TSM), Total Organic Carbon (TOC), and Particulate Organic Carbon (POC) in 2012 and 2013 for Lake Muzelle and Lake Plan Vianney[a]

Sampling campaign	April 2012		June 2012		September 2012		February 2013		April 2013		July 2013	
Lake	Muzelle	Plan Vianney	Muzelle	Plan Vianney	Muzelle	Plan Vianney	Muzelle	Plan Vianney	Muzelle	Plan Vianney	Muzelle	Plan Vianney
Surface (4m depth)												
water temperature (°C)	4.0	4.1	6.2	5.7	7.9	7.7	3.7	4.2	3.7	3.3	6.4	8.5
TSM (mgDW L^{-1})	9.3	5.0	2.9	1.5	2.1	1.4	1.7	2.8	2.7	0.6	2.8	0.4
TOC (mgC L^{-1})	0.6	0.3	ND	4.9	1.0	1.3	2.6	0.9	2.6	1.0	0.7	0.9
POC (mgC L^{-1})	0.3	NQ	ND	0.4	0.3	0.3	0.2	0.2	0.2	0.2	0.2	0.2
Bottom (3m above max depth)												
water temperature (°C)	ND	ND	4.5	5.9	5.4	3.7	4.0	4.5	3.9	4.3	5.2	6.8
TSM (mgDW L^{-1})	ND	ND	2.1	1.6	4.0	0.9	1.2	1.1	2.5	0.4	1.7	0.4
TOC (mgC L^{-1})	ND	ND	ND	5.6	1.6	2.5	0.7	1.0	0.7	1.0	0.7	0.7
POC (mgC L^{-1})	ND	ND	ND	1.1	0.7	0.1	0.1	0.4	0.1	0.3	NQ	NQ

[a] NQ: not quantifiable. ND: no data. DW: dry weight.

parameters such as phytoplankton biomass on the partition of PCBs in these lakes has not been previously investigated.

The main objectives of this work were (i) to depict PCBs partition between particulate and dissolved phase in high altitude lakes and (ii) to test which physical−chemical or biological processes regulate this phase partition. For this purpose, PCB concentrations in particulate and dissolved phases were measured in two high altitude lakes (Alps, France) in 2012 and 2013.

■ MATERIAL AND METHODS

Site Description. The study was carried out in two lakes located in the French North Alps (Isère) and situated 4.3 km apart. Lake Muzelle is located at 2115 m above sea level (asl), has a maximum depth of 18.2 m, and a surface area of 10 ha. The catchment area of Lake Muzelle is 466 ha. Corresponding values for Lake Plan Vianney are 2250 m asl, 12.2 m, and 5 ha. Lake Plan Vianney has a catchment area of 86 ha. Both lakes are oligotrophic (<5 μgP L^{-1}). Water temperature, concentrations of total suspended matter (TSM), total organic carbon (TOC), and particulate organic carbon (POC) were measured for each sampling campaign (Table 1). Our previous study[6] has shown that both lakes are subjected to similar PCB atmospheric inputs (115 ± 24 ng m^{-2} yr^{-1} in 2012), and the catchment area does not act as a source of PCBs.

Sampling Method. Six sampling campaigns were carried out in 2012 and 2013 (April, June, and September 2012 and February, April, and July 2013). The ice-cover period is referred to as April 2012, February 2013, and April 2013 (spring thaw occurs in June), and the ice-free period is referred to as June 2012, September 2012, and July 2013. At a single location (corresponding to maximum depth of the lake), surface (4 m below surface) and bottom (3 m above maximum depth) water was pumped into stainless steel barrels (approximately 60 L for each depth). Water samples were filtered *in situ* through two nylon filter cups connected in series (200 and 20 μm). The >200 μm size fraction was excluded from this study because PCBs analysis revealed concentrations below quantitation limit for all congeners. According to Sieburth,[30] the 20−200 μm size fraction contains the microplankton and is then further referenced as "microplankton fraction". In the laboratory, the 2.7−20 μm and 0.7−2.7 μm size fractions (respectively referenced nanoplankton and picoplankton fractions[30]) were collected using filtration on glass fiber filters of the corresponding nominal cutoff (GF/D and GF/F Whatman). TSM was quantified (mgDW L^{-1}) according to the standard method for the examination of natural waters as the mass retained after filtration of 1 L of bulk water. Total suspended matter (TSM) was made of particulate organic matter (quantified as POC) and of mineral particles. Indeed, as for most alpine lakes, the total suspended solids in the water column are made of living and senescent biomass, detrital particles from soil erosion of the catchment area, and snowpack during thaw. Then, each size fraction (referenced pico-, nano-, or microplankton fraction) contained mineral particles, planktonic biomass, and other organic suspended matter. Subsamples of bulk water were carried out to determine TOC by using a Shimadzu TOC-5000 analyzer. Dissolved organic carbon (DOC) was analyzed from water samples filtered through AP40 glass fiber filters (Millipore). The POC value is the difference between TOC and DOC. PCBs were quantified in each particulate phases. PCBs from the dissolved and colloidal fractions were obtained by adding methanol to the final filtrate (0.5% final concentration) and pumping at a flow-rate of 100 mL min^{-1} through Resprep-C18 Solid Phase Extraction disks (70 Å silica pore size, 47 mm diameter, Restek Corporation) previously cleaned using *n*-heptane and conditioned with methanol.

Phytoplankton Biomass and Composition. Subsamples were processed for identification and quantification of phytoplanktonic organisms. Nanophytoplankton (2.7−20 μm size class) and microphytoplankton (20−200 μm size class) were fixed with an alkaline solution of Lugol (1% v/v). Cells were counted and identified according to the Utermöhl method[31] using an inverted microscope. Biovolumes were estimated for each sample by measuring the linear dimension of cells and equating shapes to standard geometric forms. Carbon biomass was calculated using a conversion factor of 0.11 pg C μm^{-3} to 0.22 pg C μm^{-3} depending on phytoplankton classes.[32] Such methods are not adequate to address picoplankton taxonomic structure, explaining the absence of similar data for that size fraction.

Phytoplankton dry weight was determined from cell biovolumes using the equation:[33]

$$W_C = 0.47 \times \nu^{0.99} \tag{1}$$

where W_c is the cell dry weight (pg), and ν the cell biovolume (μm^3).

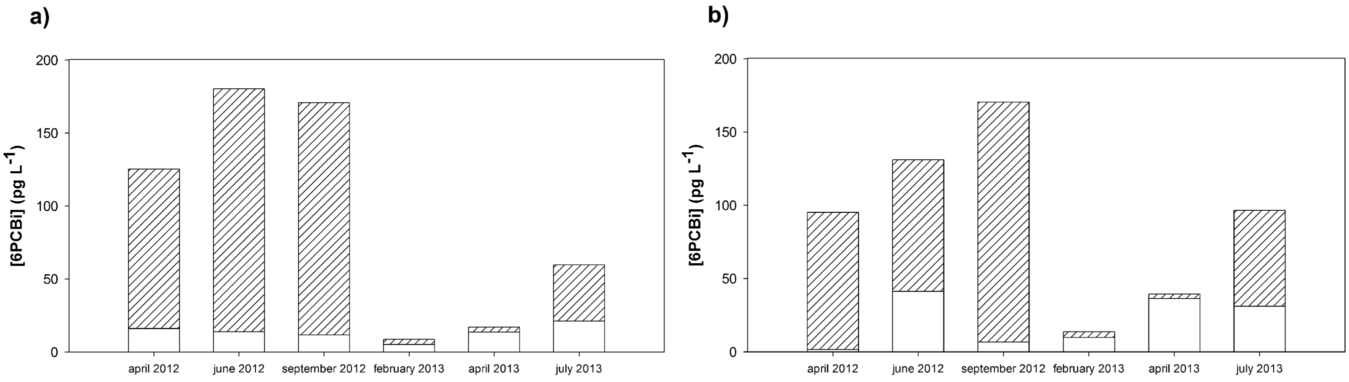

Figure 1. Mean PCBs concentration (sum of the six indicators) associated with particulate matter (hatched bar) and in dissolved phase (white bar) for (a) Lake Muzelle and (b) Lake Plan Vianney.

PCBs Extraction and Quantification. Sample treatment and analytical methods have been described elsewhere[6] in detail, and as such, only summaries are provided herein. Prior to extraction, samples were spiked with a known amount of isotope-labeled standard (PCB 116-d5) to correct for extraction efficiency and instrumental variability. SPE disks were eluted with 15 mL of *n*-heptane pumped at 2 mL min^{-1}. PCBs in particulate phases were extracted by Accelerated Solvent Extraction (ASE 200, Dionex) with a mixture of dichloromethane and acetone (1/1, v/v). After purification on an activated silica column, each extract was concentrated and resuspended in 100 μL of *n*-heptane for analysis. The PCBs were analyzed with a Clarus 500 Gas Chromatograph coupled with a MS 560 Mass Selective detector (PerkinElmer) using splitless injection on a Optima 5 Accent column (Macherey-Nagel). Selected-ion monitoring (SIM) was used for the quantification of six nondioxin-like PCBs (congeners 28, 52, 101, 138, 153, and 180), and the calibration curves were established with pure standards and the PCB116-d5 internal standard (checked every fifth sample at six levels of concentration between 2.5 and 100 pg μL^{-1}). Quality assurance efforts were performed by field and laboratory blanks (blank values are reported in the Supporting Information, Table S1). The analytes present in the appropriate blanks were subtracted from those in the sample extracts. Analytical recoveries were evaluated using the PCB 116-d5 standard. The average recoveries (mean ± standard deviation) were 56 ± 8% and 51 ± 6% for dissolved phase and particulate phase, respectively. The reported values were corrected for blanks and recoveries. The method detection limit (MDL) and method quantitation limit (MQL) were derived from the field blanks and quantified as 6 and 10 times their standard deviation, respectively. MDLs ranged from 0.02 to 0.1 pg L^{-1} of lake water; MQLs were 0.03−0.2 pg L^{-1} of lake water. In accordance with previous papers,[34,35] the reproducibility of the method was assessed as a ± standard deviation of PCB 116-d5 concentrations obtained from all analyzed samples, thus leading to a precision of ±21% for dissolved fractions (22 samples) and ±18% for particulate matter (66 samples).

Partitioning. Partitioning of PCBs between the dissolved (<0.7 μm) and particulate phase (from 0.7 to 200 μm, i.e., from picoplankton to microplankton) was determined by calculating the water−particle phase partition coefficient (K_p) as

$$K_p = \frac{C_p/\text{TSM}}{C_d} \quad (2)$$

where C_p is the particulate PCBs concentration (i.e., sum of PCBs concentration associated with the particles of the different size fractions; pg L^{-1}), TSM is the total suspended matter concentration (i.e., sum of particles of size >200 μm, 20−200 μm, 2−20 μm, and 0.7−2 μm; kgDW L^{-1}), and C_d is the dissolved PCBs concentration (pg L^{-1}).

The water−particle phase partition coefficient K_p was also calculated by using the total phytoplankton biomass instead of TSM. The statistical analysis of the relation between the K_p values and the other parameters led to the same conclusions (data not shown).

Statistical Analysis. Pearson's product moment correlation coefficient (R^2), simple linear regression, analysis of covariance (ANCOVA), Student's test (*t* test), and Fisher's exact test were carried out using R2.15.2 statistical software (R Development Core Team, 2012). Variables that were not normally distributed as detected by Fisher's test were log10-transformed.

■ RESULTS AND DISCUSSION

PCBs Concentration. The concentration of PCBs in particulate and dissolved phases measured at each depth (surface and bottom) for Lake Muzelle and Lake Plan Vianney are listed in the Supporting Information (Tables S2 and S3). Total PCBs concentration in water, i.e., sum of concentrations associated with particulate and dissolved phases, did not significantly vary between both depths for each sampling campaign (*t* test, Supporting Information, Table S4) except in September 2012, when higher PCB concentrations were recorded in surface samples (e.g., 207 ± 37 pg L^{-1} in bulk (particulate + dissolved) surface water vs 127 ± 23 pg L^{-1} in bulk water collected near the bottom for Lake Plan Vianney). At this period, the air−water exchange flux (2.5 ± 2 mg yr^{-1}) occurred through deposition[6] and enhanced PCBs content in the surface water. According to Dueri et al.,[36] PCBs were not transferred to deep water because of the thermal stratification of the water column (*data not shown*). Thus, PCBs concentration in surface water increased. The mean annual PCBs bulk concentration (particulate + dissolved) was not significantly different between Lake Muzelle and Lake Plan Vianney for a same year (Figure 1; in 2012:159 ± 29 pg L^{-1} and 134 ± 24 pg L^{-1}; *t* test $T = 1.25$, *p*-value = 0.22; in 2013:28 ± 14 pg L^{-1} and 42 ± 21 pg L^{-1}; $T = -1.48$, *p*-value =0.15) and was consistent with recently reported values in remote lakes.[4] PCB concentrations differed between years, mainly because of different PCBs input through snowmelt, i.e., 71 ± 8 ng m^{-2} yr^{-1} in 2012 vs 42 ± 5 ng m^{-2} yr^{-1} in 2013.[6] Though

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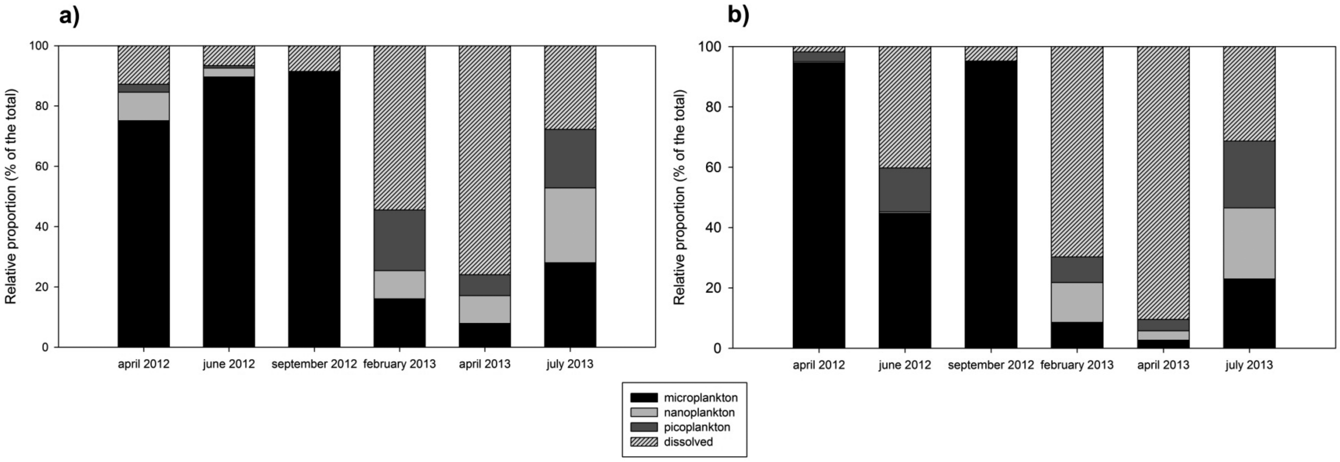

Figure 2. Mean PCBs partitioning (average of samples collected at 4 m depth and 3 m above max depth) between dissolved phase, micro-, nano-, and picoplankton for (a) Lake Muzelle and (b) Lake Plan Vianney.

PCB concentrations were higher in 2012 than in 2013 for both lakes, their seasonal variation was reproducible over years. PCBs concentrations were lower when lakes were ice covered (April 2012, February and April 2013) than in ice-free cover periods (June and September 2012, July 2013). PCBs concentration probably increased during the spring as a consequence of PCBs input by snowmelt (40% of annual input to the lake[6]). As described in detail in our previous paper,[6] the phytoplankton biological pump could be responsible for these seasonal patterns. In ice-covered periods, the frozen surface of the lake and the snowpack on top of the ice limited light admission and prevented any phytoplankton production. A high settlement of senescent planktonic biomass therefore induced a higher PCBs flux to the sediments.

Particulate-Dissolved Phase Partition of PCBs. PCBs were mainly associated with particulate matter for all seasons in 2012 (Figure 1; 90 ± 2% and 88 ± 8% of the bulk PCBs concentration, i.e., particulate + dissolved, respectively, for Lake Muzelle and Lake Plan Vianney) and during open waters in 2013 (65 ± 7% in Lake Muzelle and 68 ± 7% in Lake Plan Vianney). During the 2013 ice-covered period (February and April), on the contrary, dissolved PCBs concentration was higher than the concentration of particles bound PCBs (31 ± 11% and 19 ± 11% of the bulk concentration, respectively, for Lake Muzelle and Lake Plan Vianney). The global partitioning of PCBs could change between years because of a modified congeners distribution, according to the respective hydrophobicity of each molecule. However, the PCB distribution (% of the total PCBs concentration for each congener) was similar between April 2012 and April 2013 for Lake Muzelle and Lake Plan Vianney, both in the particulate and dissolved phases (see Supporting Information, Tables S2 and S3, for details). Therefore, differences in PCBs partitioning between years could be only a consequence of the lower content of total suspended matter in 2013 (e.g., 9.3 mgDW L^{-1} in April 2012 vs 2.6 mgDW L^{-1} in April 2013 for Lake Muzelle) and the lower PCBs concentration in bulk water in 2013 (e.g., 125 ± 23 pg L^{-1} in April 2012 vs 17 ± 3 pg L^{-1} in April 2013 for Lake Muzelle), responsible for changes in the interaction between PCB congeners and suspended solids. Moreover, higher PCBs content in the dissolved phase in 2013 promoted PCBs volatilization as compared to 2012, especially in Lake Muzelle[6] where larger changes of PCBs partition between particulate and dissolved phase were recorded. Particulate matter accounted for 84 ± 7% of bulk PCBs concentration during open lake water (i.e., June and September 2012, July 2013) that was consistent with previous study conducted at comparable depths (6.5 and 14 m depth) and sampling period (September) in the European altitude lake Ladove Pleso.[37] Thus, particulate matter appears as an important reservoir of PCBs that could determine their fate in lakes. For instance, at higher concentrations of particles, especially when made up of phytoplankton biomass, PCBs settling flux could be enhanced,[38] therefore limiting the exposure of the pelagic food web to PCBs as observed in Lake Maggiore.[39]

PCBs partition between the different particulate phases (i.e., of the pico-, nano-, and microplankton fraction) and the dissolved phase (Supporting Information, Tables S2 and S3) did not differ between sampling depths for a same campaign (Fisher's exact test, Supporting Information, Table S4). Therefore, results were pooled. Even when PCBs were mainly bound to particles (for the whole year 2012 and for 2013 open water period), the size-fraction to which they were associated differed. In 2012, the microplankton fraction contained 72 ± 4% of the bulk water PCBs in Lake Muzelle and 84 ± 4% in Lake Plan Vianney. In contrast, right after the 2013 thaw, PCBs were rather uniformly distributed among fractions as shown in Figure 2. Observed differences of PCBs partition between 2012 and 2013 for both lakes could arise from differences in organic matter quantity (i.e., concentrations of organic particles or dissolved organic carbon) or quality (i.e., relative proportion of phytoplankton), which values are presented in Table S6 of the Supporting Information. In Lake Plan Vianney, PCBs partition among size fractions was not affected by the above-mentioned parameters (e.g., relative proportion of PCBs associated with the particles of the microplankton fraction (20–200 μm), Supporting Information, Table S7). Laboratory experiments or field surveys[40−43] reported that dissolved organic matter (DOM) or colloids content of the <0.7 μm fraction might account for these differences. In contrast, the concentration of particles of the microplankton fraction in Lake Muzelle was higher in 2012 than 2013 (1.49 ± 0.54 and 0.24 ± 0.07 mgDW L^{-1}, respectively) and could explained such partition differences between years. Altogether, observed within-lake differences in the PCBs partition highlighted the role of organic matter

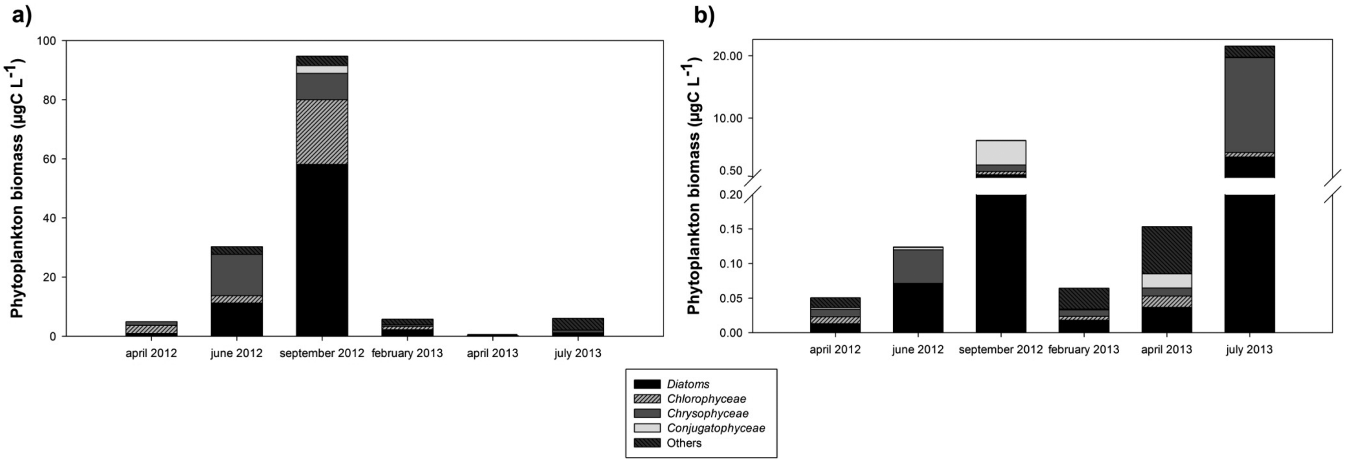

Figure 3. Biomass of different phytoplankton groups (μgC L^{-1}, average surface and bottom) for (a) Lake Muzelle and (b) Lake Plan Vianney (ordinate axis in graph b is broken from 0.2 to 0.5 μgC L^{-1} with a post-break interval of 10.0 μgC L^{-1}).

quantity as a driving factor for the fate of PCBs in high altitude lakes.

Factors Affecting PCBs Partitioning. Several parameters including water temperature, K_{ow}, TSM, and POC can affect phase partitioning of PCBs and consequently their fate in aquatic ecosystems.[4,14,15,44,45] We evaluated the respective influence of phytoplankton biomass and taxonomic composition, in addition to previous parameters, on particulate-dissolved phase partition of PCBs. The observed water−particle phase partition coefficient (log K_p) were comparable to previous values reported for lake or sea waters[28,44] (3.2 to 9.1 vs 4.6 to 7.9).

Particulate Matter. TSM and POC values are given in Table 1. POC is the quantitation of phytoplankton, detrital organic particles, and heterotrophic organisms. As phytoplankton biomass is low in these rather unproductive lakes, POC value is mainly explained by the water content of detrital organic particles, especially right after thaw probably because of the accumulation of particles in the snowpack. For both studied lakes, K_p was not correlated with TSM and POC. Thus, PCBs partitioning in Lake Muzelle and Lake Plan Vianney is not governed by the "particle concentration effect" (PCE) (i.e., higher particles concentration involving lower PCBs concentration in the particulate phase) in contrast to what had been observed in other studies.[4,44,46,47] Precise cause of PCE classically admitted in literature referred mainly to the existence of a third colloidal phase, which acts as an additional sorbent.[40−43] According to the model proposed by Baker et al.,[40] amounts of DOC in Lake Muzelle and Lake Plan Vianney (1.1 ± 0.8 and 0.9 ± 0.6 mg C L^{-1}, respectively) and TSM (4.9 ± 3.8 and 2.5 ± 2.2 mg L^{-1}, respectively) suggest that PCBs binding to colloids only account for about 15% of bulk (particulate + dissolved) PCBs concentration. Besides, PCB concentrations were close to MQL values that might cause the lack of relationship between K_p and TSM or POC. Yet, a study conducted on European high altitude Lake Redo[28] had similar conclusions regarding the K_p−TSM relationship (R^2 = 0.02), although PCB concentrations were above MQL values. As the statistical analysis led to the same conclusions when using a K_p value calculated with the phytoplankton biomass concentration instead of TSM, we hypothesized that the relation between K_p and POC was mainly influenced by the quality of organic matter (detrital versus algal) rather than by the quantity of particles.

Phytoplankton. Phytoplankton biomass (Supporting Information, Table S8) measured in Lake Muzelle (0.15−157 μgC L^{-1}) and Lake Plan Vianney (0.05−6 μgC L^{-1}) were comparable to those obtained in other high altitude lakes.[48,49] The abundances were typical for low productivity lakes.[50] Phytoplankton biomass and species showed large seasonal variations (Figure 3) with maximum biomasses (157 and 6 μgC L^{-1}, respectively for Lake Muzelle and Lake Plan Vianney) occurring in late summer/early autumn (i.e., September 2012), consistent to other European altitude lakes.[49,51] In Lake Muzelle, algal communities were dominated by diatoms (51% of the total biomass), while *Conjugatophyceae* were the most abundant (61% of the total biomass) in Lake Plan Vianney. These differences in algal species could affect the transfer of PCBs from primary producers to consumers (i.e., zooplankton) and therefore their accumulation into the fish compartment within food web. As mentioned above, when lakes were ice covered, the development of primary producers was limited. Accordingly, phytoplankton biomasses were low (0.15−5.7 and 0.05−0.15 μgC L^{-1}, respectively, for Lake Muzelle and Lake Plan Vianney) with no specific dominance.

No relationship was found between log K_p and phytoplankton biomass (expressed in μgC L^{-1} or μgDW L^{-1}) for any of the lakes (Supporting Information, Table S9). Species-specific differences in accumulation of PCBs by phytoplankton have been reported in the literature.[52] Numerous contributing parameters have been suggested such as cell size[53] (i.e., surface area), surface type[54] (e.g., gelatinous), or algal growth.[55−57] However, no correlations were found between the taxonomic composition of phytoplankton and K_p (Supporting Information, Table S10) in accordance with a recent study conducted on the open Baltic Sea.[58] Thus, phytoplankton biomass and composition cannot explain the phase partition of PCBs in the two lakes we studied.

Temperature. Previous studies conducted on altitude lakes or seawater[28,44] detected a consistent negative relationship between K_p and water temperature for different PCB congeners, but no such relationships emerged from our study, except for the most chlorinated PCB (#180). Analysis of correlation between particulate phase concentration and water temperature (Supporting Information, Table S11)

Table 2. Parameters of Linear Regression between log K_p vs log K_{ow} for Lake Muzelle and Lake Plan Vianney (surface and bottom water were considered)

Sampling campaigns	Lake	N	R^2	p-value	Slope	Intercept
All sampling campaigns	Muzelle	52	0.136	0.007[a]	0.732	1.149
	Plan Vianney	52	0.206	7.0×10^{-4}[a]	1.219	−1.663
Ice-covered periods	Muzelle	23	0.591	1.8×10^{-5}[a]	0.935	−0.725
	Plan Vianney	25	0.454	2.2×10^{-4}[a]	1.368	−3.281
Open water periods	Muzelle	29	0.097	0.099	0.641	2.164
	Plan Vianney	27	0.129	0.065	0.938	0.817

[a] Significant correlation (p-value < 0.05), N = number of PCBs concentration data used.

revealed a significant inverse relationship for this congener (p-value = 0.045 for Lake Muzelle and p-value = 0.006 for Lake Plan Vianney). Higher water temperature involved lower concentration of particles-bound #180, maybe related to an exothermic particles' sorption. Regression coefficients indicated that water temperature could explain 37% and 42% of the variability of K_p, respectively, for Lake Muzelle and Lake Plan Vianney, suggesting a seasonal dependence of K_p for PCB 180.

Octanol–Water Coefficient. The log K_p and log K_{ow} relationships in Lake Muzelle and Lake Plan Vianney are presented in Table 2. A combination of all sampling campaigns data highlighted a positive dependence of these two parameters for both lakes, consistent with previous observations.[40,44,59,60] The linear regression slopes were statistically analogous (ANCOVA, p-value = 1.5×10^{-5}) for the two studied lakes. The correlation between K_p and K_{ow} was also examined for each sampling campaign and is presented in Table S12 of the Supporting Information. A significant correlation was observed for April 2012, February 2013, and April 2013. Data were then sorted into two categories (ice-covered period for April 2012, February 2013, and April 2013 data, and open water period for June 2012, September 2012, and July 2013 data; Figure 4) to test for a seasonal trend in the log K_p–log K_{ow} dependence. The positive relationship between K_p and K_{ow} was only significant when the lakes were ice covered (Table 2). In this case, the dependence was similar between both lakes (ANCOVA, p-value = 2.5×10^{-7}), highlighting that PCBs partition between particulate and dissolved phases was partially controlled by the hydrophobicity, as observed in adsorption studies.[61−64] During open water period, PCBs partition was in a thermodynamic nonequilibrium state. Particle associated PCBs are supposed to be non-negligible in snowpack. During the thaw, the high input of these particulate PCBs to the lake water could then deviate the partitioning from equilibrium. However, we have not determined whether PCBs were dissolved or associated with particles in snowmelt water right after thaw (in June 2012 or in July 2013). Thus, the way by which PCBs were transferred into the water column remained undisclosed. However, when the snow and ice cover was fully melted, a peak of phytoplankton biomass, resulting from higher light exposition that promoted phytoplankton growth, was observed in both lakes (Figure 3). The weak relationship between K_p and K_{ow} could then be due to this substantial temporal variability in particulate organic matter content. Historically, PCBs uptake by phytoplankton was considered as a fast equilibrium process (from few minutes or hours),[65−67] but this got challenged by more recent results,[55−57,68] highlighting that the time required to approach equilibrium is much longer (several days or weeks) and that equilibrium was, most of the time, not even reached. Authors suggested that under intense phytoplankton growth, partitioning of PCBs between the algae and the dissolved phase occurred at much longer time scales than algal growth and that therefore nonequilibrium was observed. Further reasons for disequilibrium were a co-excretion of PCBs with algal exudates or PCBs binding to these exudates during algae blooms.[69−71] The relative proportion of exudates in DOC was not determined. However, no significant difference of DOC concentration was observed between ice-covered and open water periods in Lake Muzelle (t test, T = 1.55, p-value = 0.220) and Lake Plan Vianney (t test, T = −1.31, p-value = 0.261) for year 2013, suggesting no increase of exudation during intense algal growth. Other possible explanations include insufficient phytoplankton biomass and DOC values in high altitude lakes (ranging from 8.8×10^2 to 6.43×10^5 cells L^{-1} and from 0.5 to 2.5 mgC L^{-1}, respectively) compared to batch cultures[69−71] (ranging from 2.8×10^8 to 2.14×10^{10} cells L^{-1} and from 6 to 14 mgC L^{-1}, respectively) in which the algal exudates effect could be quantified. Then, the lack of relationship between K_p and K_{ow} might result from a slower rate of PCBs uptake by phytoplankton than algal growth rates. These data challenge the results of a recent study[58] that suggested a situation of equilibrium of PCBs partitioning to phytoplankton. Thus, kinetics model describing particulate-dissolved phase partition of PCBs should include phytoplankton growth to accurately predict the repartition—and therefore aquatic behavior—of these persistent particle-reactive contaminants (i.e., export to sediments, volatilization to the air or transfer into food web). Moreover, the food web structure of the aquatic ecosystem should also be evaluated because the fate of phytoplankton might also greatly affect the fate of PCBs in freshwaters.

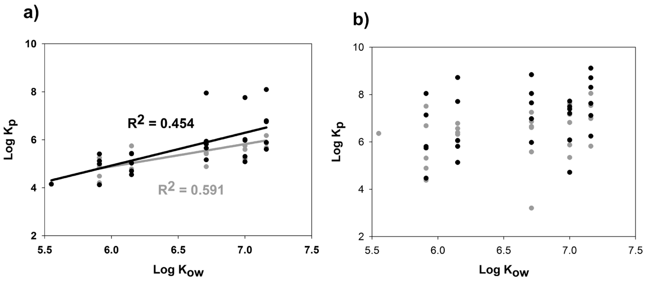

Figure 4. Log K_p vs log K_{ow} in Lake Muzelle (gray) and Lake Plan Vianney (black) when lakes were (a) ice covered and (b) ice free. Surface and bottom water were considered.

In summary, the parameters affecting the partition of PCBs in the water of two high altitude lakes differ between ice-covered and ice-free periods. When the lakes were ice covered, from November to May, the water column was isolated from the atmosphere, preventing large modification of the parameters governing PCBs partitioning (water temperature, PCB and POC inputs). The particulate-dissolved phase partition coefficient is then related to the octanol−water partition coefficient of the PCBs, reflecting a thermodynamic equilibrium between the water and the particles. When lakes were ice free, the lack of relationship between K_p and K_{ow} highlights a kinetically limited partition of PCBs between dissolved and particulate phases. In that case, a high algal growth rate due to efficient photosynthesis and a slower uptake rate of PCBs by phytoplankton might explain this disequilibrium. However, no correlation was found between K_p and other biogeochemical parameters (e.g., TSM, phytoplankton biomass). Allogenic perturbations, such as wind or precipitation, generating large variations of water temperature or TSM concentration on weekly or even daily scales, or a huge particles-bound PCB input during snowpack melting could also explain the absence of partition equilibrium. Therefore, a "high frequency" monitoring survey (every 2 weeks sampling) from May to July (i.e., before, during and after spring thaw) as well as during the phytoplankton growth phase (from August to October) could disentangle the two hypotheses and accurately evaluate factors governing the aquatic fate of PCB in high altitude lakes during ice-free period.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Blank values for PCB analyses; PCB congeners concentration range associated with dissolved phase, micro-, nano-, and picoplankton fractions in water near the surface and the bottom of Lake Muzelle and Lake Plan Vianney; results of Student's test testing the difference of PCBs concentration in particulate matter and dissolved phase between both depths for Lake Muzelle and Lake Plan Vianney; results of Fisher's exact test testing the difference of PCBs repartition between particulate phases and dissolved phase among sampled depths for a same campaign; seasonal variations of 20−200 μm particles concentration, dissolved organic carbon, and microphytoplankton biomass for Lake Muzelle and Lake Plan Vianney; relationship between organic matter quantity or quality and the relative proportion of PCBs associated with microplankton for Lake Muzelle and Lake Plan Vianney; average biomasses of dominant phytoplankton taxa and total phytoplankton biomass for Lake Muzelle and Lake Plan Vianney; linear regression of log K_p vs total phytoplankton biomass for Lake Muzelle and Lake Plan Vianney; linear regression of log K_p vs dominant phytoplankton species biomass for Lake Muzelle and Lake Plan Vianney; linear regressions of particulate phase concentration vs mean water temperature for Lake Muzelle and Lake Plan Vianney; and linear regressions of log K_p vs log K_{ow} for Lake Muzelle and Lake Plan Vianney for each sampling campaign. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01274.

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Notes

The authors declare no competing financial interest.

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