Temperature Dependence of the Distribution of Organochlorine Compounds in the Mosses of the Andean Mountains

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Organochlorine compounds (OC), namely pentachlorobenzene, hexachlorobenzene, hexachlorocyclohexanes, polychlorobiphenyls (PCBs), and DDTs, have been studied in mosses distributed over three altitude gradients of the Andean mountains in Chile at 18°S (3200–4500 m above sea level), 37°S (345–1330 m), and 45°S (10–700 m). The observed concentrations range among the lowest values ever reported in remote sites, but they are still higher than those found in previously studied Antarctic areas. The log transformed OC concentrations show a significant linear dependence from reciprocal of temperature independently of the origin of the compounds, e.g. industrial, agricultural, or mixed. In the case of the more volatile OC these correlations involve variance percentages higher than 50%. This good agreement gives further ground to temperature as the driving factor for the retention of long-range transported OC in remote ecosystems, including those in the southern hemisphere such as the Andean mountains. In the context of the samples selected for study, the temperature dependences in the areas of similar latitude are related to altitude. Thus, all OC in the highest altitude gradient (18°S) and most compounds in the other two profiles (37°S and 45°S) exhibit higher concentrations with decreasing annual average temperature and thus increase with elevation above sea level. However, theoretical examination of the exponential equation relating OC concentrations to reciprocal of absolute temperatures shows that besides the temperature differences between highest and lowest elevation, the most relevant factor determining the OC concentration gradients is the lowest temperature value of each altitudinal series. That is, the point at highest elevation.

Introduction

Huge dilution capacity is traditionally attributed to environmental compartments. The effects of pollution episodes are therefore assumed to decrease with increasing distance from the contamination site. This intuitive extrapolation of the Fick's law may not be realistic in the case of the persistent organic pollutants.

The physicochemical properties of these compounds such as chemical stability, semivolatility, and organic matter affinity in combination with the planetary latitudinal temperature gradient generates a net transfer of pollutants from low-medium to high latitude regions avoiding the "dilution effects" that such long-range transfer should involve according to the traditional intuitive concepts. Significant concentration increases at higher latitude have been found for α-hexachlorocyclohexane (α-HCH), γ-HCH, hexachlorobenzene (HCB), and pentachloroanisol in tree bark (*1*) or HCHs in seawater (*2, 3*), far away from the sites where these compounds were produced or used. The latitudinal distribution of these compounds as a consequence of the temperature gradients has been described to respond to a "global distillation effect" (*3–5*).

However, temperature gradients are also defined in mountain regions. Again, the "global distillation" should involve transfer of these organochlorine compounds from low to high altitudes. That is, from sites close to pollutant sources to remote areas. Recent studies on fish and sediments from high mountain European lakes (*6, 7*), soils in Teide (Canary Islands (*8*), and snow in western Canada (*9*) have shown that this transfer effectively occurs. The sites at higher altitude are more polluted than those at lower elevation.

Nevertheless, the number of experimental studies describing these long-range transport effects is limited. More work is needed in order to define the extent of global distillation, e.g. compounds involved, distribution patterns, transport mechanisms, main physicochemical constants, and environmental variables of concern, etc. Thus, the environmental physicochemical properties determining their retention in the remote ecosystems are still to be clarified.

These aspects are even more significant when interhemispheric transport is considered. About 86% of total usage of polychlorobiphenyls (PCBs) occurred between 30°N and 60°N (*10*), but these compounds have been identified as far as Antarctica (*11, 12*). Unfortunately, the mechanisms of interhemispheric exchange are still not clear (*13*), but the temperature-dependent latitudinal redistribution of the "global distillation effect" should potentially involve interhemispheric exchange. In addition to these processes, the possible influence of local sources in the southern hemisphere, although potentially small, must also be considered. The scarcity of data from large regions of the southern hemisphere, namely a series of samples distributed along large temperature transects, constitutes a major difficulty for a better appraisal of the transfer mechanisms from northern to southern hemisphere.

To the best of our knowledge, only a few studies including the latitudinal distribution of organochlorine compounds (OC) in this hemisphere has been reported to date (*1, 14–16*). Now, the altitudinal–latitudinal distribution of these compounds in a series of mosses sampled in the catchments of lakes distributed in the Andean mountains at 18°S, 37°S,

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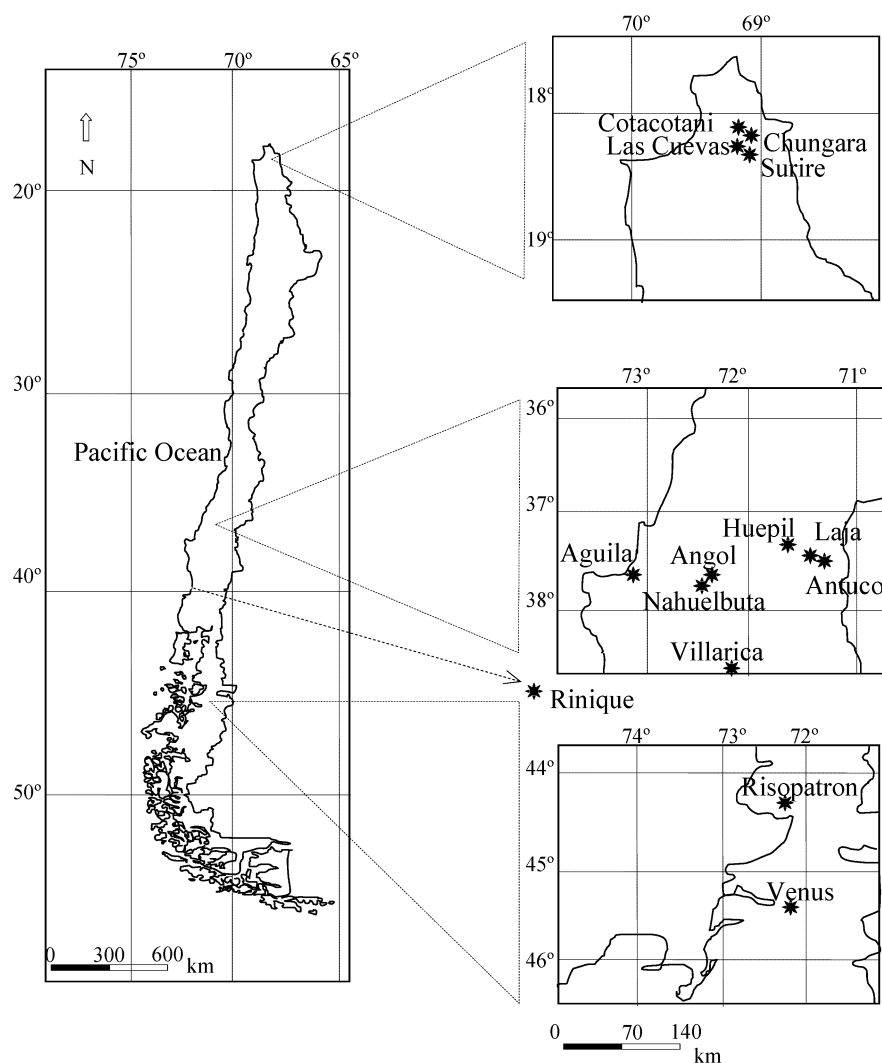∥ University of Concepcion.
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FIGURE 1. Sites selected for study.

TABLE 1. Sample Site Description and Concentrations of the Major Organochlorine Compounds in Mosses (ng·g^{-1} dw)

sampling sites	latitude	longitude	altitude (m asl)[a]	temp[b] (°C)	samples analyzed	PCBz	HCH	HCB	PCB	4,4'-DDE
Chungara	18°15'S	69°11'W	4500	−2.1	3	2.0	7.0	7.0	52	2.3
Cotacotani	18°11'S	69°14'W	4400	−1.5	1	2.4	11	6.8	67	2.0
Surire	18°49'S	69°40'W	4300	−1.4	1	1.3	7.3	5.5	38	0.95
Las Cuevas 2	18°22'S	69°37'W	3700	1.6	2	1.1	6.0	5.2	37	2.2
Las Cuevas 3	18°25'S	69°40'W	3200	3.8	1	0.81	3.2	1.9	20	1.5
Antuco 1	37°23'S	71°29'W	1335	2.3	1	0.45	2.4	1.6	26	2.6
Piedra del Aguila	37°47'S	73°20'W	1330	5.2	1	0.33	1.2	1.5	21	3.2
Antuco 2	37°23'S	71°29'W	1200	6.1	1	0.31	1.5	1.7	32	3.7
Villarica	39°17'S	72°13'W	1125	5.8	2	0.80	2.0	1.3	17	2.3
Nahuelbuta	37°50'S	72°59'W	770	8.6	1	0.54	2.4	1.8	26	2.7
Laja	37°19'S	71°37'W	700	9.1	2	0.27	1.8	0.78	20	1.6
Angol	37°48'S	72°44'W	500	10.2	2	0.26	3.4	2.5	25	3.6
Huepil	37°15'S	71°57'W	345	11.1	1	0.35	1.7	1.1	18	1.8
Riñihue	39°49'S	72°27'W	120	11.3	1	1.4	4.1	1.2	34	4.8
Venus	45°33'S	72°30'W	700	4.4	2	0.90	1.9	0.60	37	1.8
Risopatron	44°16'S	72°32'W	10	8.9	3	0.24	2.2	0.67	21	2.0

[a] Meters above sea level. [b] Annual average temperature.

and 45°S is considered (Figure 1). The sites selected for study are remote and far from any anthropogenic source. They are distributed between 10 and 4500 m above sea level (asl; Table 1). OC arriving to them were long-range transported through the atmosphere.

Plants play an important role in the global cycling of OC since they cover over 80% of the earth's land surface and have a high lipid content, and their surface area is larger than the ground area they cover (*17*). Mosses are particularly useful from this standpoint since they lack both cuticle and

internal transport mechanisms and depend on the atmosphere for delivery of nutrients. The analysis of HCB, HCHs, 4,4′-DDE, 4,4′-DDT, pentachlorobenzene (PCBz), and PCBs in the mosses around these lakes may provide a good appraisal of the main factors determining the accumulation of air transported OC in high altitude regions of the southern hemisphere.

Theoretical Section

The sampling sites considered in this study are distributed over large altitudinal and latitudinal gradients. In the absence of significant local pollution sources, temperature dependence is the primary factor to be evaluated for OC accumulation.

The temperature influence can be examined using the Boltzmann equation in the following form

$$C_X/C_A = A \cdot \exp(B/T) \qquad (1)$$

where C_X and C_A refer to the solid sample and air concentrations, respectively, T is temperature in K, and A and B are constants (18, 19). In the context of the present study, C_X refers to concentrations in mosses.

According to this equation, representation of the log-transformed ratios between OC concentrations in mosses and air OC concentrations and the reciprocal of the mean annual air temperatures in K should give rise to a linear expression.

The absence of atmospheric concentration data renders more difficult the application of eq 1. Previously reported atmospheric OC concentrations in remote high altitude sites have revealed rather constant values independently of air origin or location (20). Thus, eq 1 can be simplified by only considering OC concentrations in mosses and reciprocal of temperature. However, studies involving sites at different elevation showed that air OC concentrations at high altitude in the free troposphere were lower than near sea level by a factor of 2 (21, 22). These observations could be extrapolated to the present data set. However, in the absence of direct atmospheric measurements in the Andean region, corrections due to possible altitude differences of air OC concentrations have been avoided. Circumvention of possible concentration differences between the atmospheres at low and high elevation minimizes temperature influence since lower levels are currently found at higher altitude. However, it provides the most conservative option, and most solid results upon observation of temperature dependence.

On the other hand, re-elaboration of eq 1 for the calculation of the expected moss concentrations at various temperature intervals shows that an important parameter determining the concentration increments is the minimal mean annual air temperature represented by the data set (currently that corresponding to the sites of highest altitude and/or latitude)

$$\Delta C = A \cdot (\exp(B/T_{min} + \Delta T) - \exp(B/T_{min})) \qquad (2)$$

where ΔT and T_{min} are the temperature interval and the minimum temperature value represented by the data set, respectively, and ΔC is the expected concentration difference. As it will be shown later, in the present study these temperatures were calculated by averaging the annual averages of the mean monthly measurements.

Representation of the expected ΔC values as a consequence of the temperature changes shows that for a defined ΔT gradient lower ΔC should be observed at higher T_{min} (Figure 2). The differences are not linear and above T_{min} values of 2 °C strong ΔT are needed to obtain significant concentration differences. The theoretical values of Figure 2 have been calculated using the same A and B constants, $9 \cdot 10^{-18}$
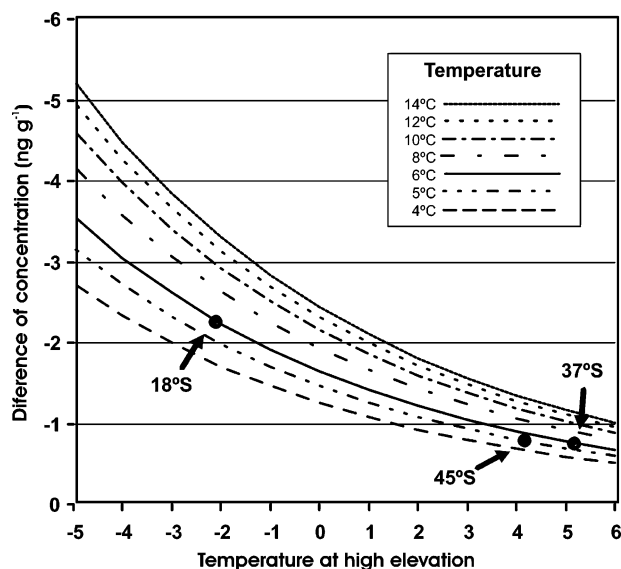
FIGURE 2. Expected concentration differences for minimal temperatures and temperature intervals as predicted from theoretical solid surface−air adsorption (equation 3). The plot predicts different concentration ranges for the same temperature intervals at different temperature minima. All plots were calculated for $A = 9 \cdot 10^{-18}$ and $B = 11000$ K^{-1}. Use of other constants will change the absolute values but not the relative differences. The points refer to the temperature intervals and T_{min} of the altitudinal data sets included in the study.

and 11000, respectively. That is, those currently observed after curve fitting the moss concentrations and reciprocal of temperature of the Andean data set to eq 1 (Table 2). The use of other concentration values will give rise to other concentration increments, but the relative differences will remain the same.

Materials and Methods

Materials. All solvents were for analysis of residues (Merck, Darmstadt, Germany). Their purity was checked by gas chromatography-electron capture detection (GC-ECD). No significant peaks should be detected for acceptance. Anhydrous sodium sulfate for analysis was also from Merck. Neutral aluminum oxide type 507C was from Fluka AG (Buchs, Switzerland). Cellulose extraction cartridges were from Whatman Ltd. (Maidstone, England). These three materials were cleaned by Soxhlet extraction with dichloromethane:methanol (2:1, v/v) during 24 h before use. The final purity was checked by ultrasonic extraction with n-hexane:dichloromethane (4:1; 3 × 20 mL), concentration to 50 μL, and analysis by GC-ECD. No interferences were detected. Sodium sulfate and aluminum oxide were activated overnight at 400 °C and 120 °C, respectively. Aluminum foil was rinsed with acetone and let dry at ambient temperature prior to use.

PCBz, HCB, α-HCH, δ-HCH, 4,4′-DDE, 4,4′-DDT, and the PCB congeners #18, 28, 30, 52, 70, 90, 101, 105, 110, 118, 123, 132, 138, 149, 153, 158, 160, 180, 194, 199, and 209 were from Cromlab (Barcelona, Catalonia, Spain). Standard mixtures in isooctane were prepared with these compounds for instrumental calibration. Surrogate solutions of PCB congeners #30 and #209 were prepared for recovery calculation. 1,2,3,4-Tetrachloronaphthalene (TCN) and octachloronaphthalene (OCN) were from Dr. Ehrenstorfer (Augsburg, Germany). These compounds were used for the preparation of surrogate solutions for assessment of instrument stability.

Sampling. Mosses were collected during July and August 1999 in the lake catchments. The moss genus selected for sampling, *Torula*, is widely distributed in circumpolar regions

TABLE 2. Concentration Ranges and Regression Coefficients for the Correlation of the Moss Concentrations of the Organochlorine Compounds (ng·g^{-1} dw) vs Temperature as Outlined in Eq 1^f

compound	all $\Delta T = 13.4$ °C (−2.1, 11.2); $n = 25$			ΔH^a	18°S $\Delta T = 5.9$ °C (−2.1, 3.8); $n = 8$			37°S $\Delta T = 5.8$ °C (5.3, 11.1); $n = 9$			45°S $\Delta T = 4.6$ °C (4.4, 8.9); $n = 5$		
	C_{min}, C_{max}	r^2	slope		C_{min}, C_{max}	r^2	slope	C_{min}, C_{max}	r^2	slope	C_{min}, C_{max}	r^2	slope
PCBz	0.12, 2.4	0.61^b	+11000	95	0.81, 2.4	0.84^b	(+)	0.12, 0.5	d	(+)	0.18, 1.2	0.76	(+)
a-HCH	0.29, 5.5	0.49^b	+11000	88	0.76, 5.5	0.53^c	(+)	0.36, 2.0	d	(+)	0.29, 1.3	d	(−)
HCB	0.41, 8.2	0.56^b	+11000	95	1.9, 8.2	0.69^b	(+)	0.75, 2.8	d	(+)	0.41, 0.9	d	(−)
γ-HCH	0.49, 5.2	0.22	+5200	43	2.4, 5.2	d	(+)	0.49, 2.4	d	(−)	0.54, 2.1	d	(−)
PCB-18	0.99, 9.6	0.55^b	+7800	65	3.2, 9.6	0.53^c	(+)	1.4, 3.2	d	(−)	1.0, 2.0	d	(−)
PCB-28/31	1.0, 6.4	d	(+)		1.2, 6.4	0.45	(+)	1.3, 3.6	0.40	(+)	2.1, 4.2	0.91^c	(+)
PCB-52	1.0, 7.8	0.56^b	+7200	60	3.4, 7.8	0.52^c	(+)	1.0, 3.6	0.56^c	(+)	1.4, 2.9	d	(+)
PCB-70	0.72, 4.6	0.25^c	+3800	32	1.2, 4.6	0.34	(+)	1.1, 3.7	d	(+)	0.72, 3.6	d	(+)
PCB-101/90	1.4, 7.8	0.45^b	+5900	49	2.4, 7.8	0.63^c	(+)	1.8, 6.4	d	(+)	1.4, 5.2	d	(+)
PCB-110	0.92, 5.9	0.31^c	+4700	39	1.9, 5.9	0.51^c	(+)	0.97, 3.7	d	(+)	0.99, 4.2	d	(+)
PCB-123/149	0.64, 5.3	0.35^c	+5900	49	1.8, 5.0	d	(+)	0.77, 5.3	d	(+)	1.4, 4.8	0.76	(+)
PCB-118	0.43, 4.4	0.29^c	+5200	43	1.2, 4.4	d	(+)	0.43, 2.5	d	(−)	0.53, 2.2	d	(+)
PCB-105/132	0.61, 5.7	0.43^c	+7200	60	0.61, 5.7	0.87^b	(+)	0.68, 1.9	d	(+)	0.84, 3.5	0.79^c	(+)
PCB-138	0.69, 9.7	0.27	+5900	50	0.87, 9.7	0.55^c	(+)	0.91, 2.7	d	(−)	0.76, 3.8	0.71	(+)
PCB-158/160	0.13, 2.2	d	(+)^e		0.19, 2.2	0.39	(+)	0.13, 0.9	d	(−)	0.29, 1.6	0.66	(+)
PCB-180	0.47, 3.2	d	(+)		0.63, 2.9	0.64^c	(+)	0.47, 1.4	d	(−)	0.57, 3.2	-	(+)
4,4′-DDE	0.95, 4.8	d	(−)		0.95, 2.7	d	(+)	1.0, 3.8	d	(+)	1.4, 2.6	-	(−)
4,4′-DDT	0.57, 2.4	d	(+)		0.83, 2.4	d	(+)	0.57, 2.1	d	(−)	0.89, 1.6	-	(+)

^{a} Enthalpies in kJ·mol^{-1}. ^{b} $p < 0.01$. ^{c} $p < 0.05$. ^{d} Values without statistical significance ($p > 0.1$). ^{e} (+) and (−) indicate positive and negative concentration increases with reciprocal of temperature, respectively. ^{f} The coefficients have been calculated over the whole data set and over sample subgroups of the same latitude (18°S, 37°S, 45°S).

and is one of the most common species for biomonitoring purposes (*23, 24*). Moss cushions were taken using stainless steel tools and disposable plastic gloves. They were wrapped up with prerinsed aluminum foil. Samples were transported with portable refrigerators containing ice (~4 °C) and stored frozen at −20 °C in the laboratory. Mosses were gently sorted to remove extraneous materials and soil particles, and only the green parts of the moss cushions were used for analysis. They were freeze-dried before analysis.

Sample Extraction and Clean Up. Samples were weighed into Whatman Soxhlet cellulose thimbles, spiked with PCB congeners #30 and #209, and extracted with hexane:dichloromethane (4:1) for 16 h. All extracts were first concentrated by rotary vacuum evaporation to 1 mL and fractionated by column chromatography using 3 g of neutral alumina. OC were obtained by elution with 8 mL of hexane:dichloromethane (9:1). The elution solvents were concentrated to 50 μL in isooctane after rotary vacuum and nitrogen stream evaporation.

Instrumental Analysis. The extracts were injected into a Hewlett-Packard 5890 Series II GC-ECD (Palo Alto, CA). A DB-5 fused silica capillary column (30 m length, 0.25 mm i.d, 0.25 μm film thickness) coated with 5% phenyl 95% methylylpolysiloxane was used for the analyses. The oven temperature program started at 90 °C (holding time 2 min), increased to 150 °C at 15 °C·min^{-1}, and finally to 280 °C at 4 °C·min^{-1} (holding time 10 min). Injector and detector temperatures were 270 °C and 310 °C, respectively. Helium was used as carrier gas (50 cm·s^{-1}). Injection was performed in splitless mode, keeping the split valve closed for 35 s. Nitrogen was used as makeup gas (60 mL·min^{-1}).

Compound identification was confirmed by GC coupled to mass spectrometry in the chemical ionization mode and negative ion recording (Fisons 8000 Series, Mass Selective Detector 800 Series; ThermoQuest, Manchester, UK). The gas chromatograph was equipped with a nonpolar fused silica capillary column HP-5-MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness). Helium was used as carrier gas (1.1 mL·min^{-1}). The oven temperature was programmed from 80 °C (1 min) to 120 °C at 15 °C·min^{-1} and then to 300° at 4 °C·min^{-1} with a final holding time of 10 min. The samples were injected in split/splitless mode (48 s) at 280 °C (hot needle technique) and data acquisition started after a solvent delay of 4 min. Ion source and transfer line temperatures were 150 and 280 °C, respectively. Ammonia was used as reagent gas. Ion source pressure (currently 1.6 Torr) was adjusted to maximize the perfluorotributylamine ions (*m/z* 312, 452, 633, and 671). Ion repeller was 1.5 V. Data were scanned from *m/z* 50 to 450 at 1 s per decade. Data were also acquired in selected ion monitoring mode with dwell time and span of 0.06 s and 0.10 amu, respectively.

Quantification. OC were identified by retention index comparison by reference to tetrachloronaphthalene (TCN) and octachloronaphthalene (OCN). In some cases, structural identification was confirmed by GC coupled to mass spectrometry in the negative ion chemical ionization mode (GC-MS-NICI). Solutions of TCN and OCN were added to the vials prior to injection. Calibration curves (detector response vs amount injected) were performed for each compound to be quantified. The range of linearity of the detector was evaluated from the curves generated by representation of detector signal/amount injected vs amount injected. All measurements were performed in the ranges of linearity found for each compound. In some cases, the samples were rediluted and reinjected for fitting within the linear range of the instrument. Quantification was performed by reference to TCN and OCN in order to correct for instrumental instabilities. The values were also corrected by recoveries of PCB-30 and PCB-209 (78±7% and 93±12%, respectively).

Quality Assurance. Procedural blanks were performed with each set of 8 samples. Briefly, detection and quantification limits were in the order of 10 pg·g^{-1}. The method was validated by replicate ($n = 4$) analysis of a reference sediment sample BCR 536 (Community Bureau of Reference, Brussels, Belgium). The results obtained were in agreement with the certified values (deviations lower than 15% were found). Reproducibility was lower than 10% for all compounds and 13% for 4,4′-DDE. Quantification and detection limits were calculated from real samples as 10 times the signal/noise ratio and were in the order of 10−40 pg.
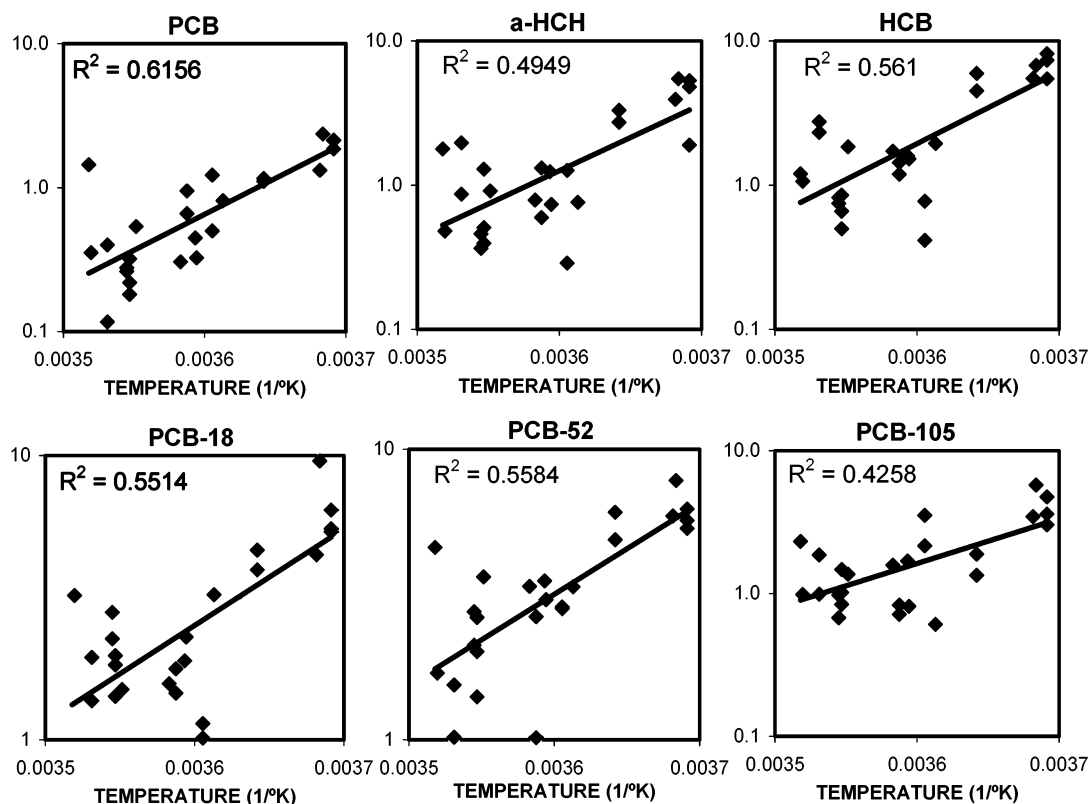
FIGURE 3. Correlation plots for the concentrations of organochlorine compounds in mosses (ng·g^{-1}) vs reciprocal of temperature (K).

Results and Discussion

Mean Annual Average Air Temperatures. The calculations of the mean annual average air temperatures involved two steps. First, a ground data set of monthly average measurements obtained from meteorological stations situated between 5 and 94 m (asl) were compiled for periods between 7 and 30 years. The stations included in this preliminary data set were Arica (18°28′S, 70°20′W, 15 years of compiled data), Antofagasta (23°42′S, 70°24′W, 22 y), Valparaiso (33°1′S, 71°38′W, 30 y), Valdivia (39°48′S, 73°14′W, 29 y), Ancud (41°47′S, 73°52′W, 30 y), Puerto Aisen (42°24′S, 72°42′W, 8 y), Cabo Raper (46°50′S, 75°38′W, 8 y), Los Evangelistas (52°23′S, 75°7′W, 16 y), and Punta Arenas (53°10′S, 70°54′W, 15 y). Two stations situated at higher altitude, Santiago (33°27′S, 70°42′W, 14 y, 520 m) and Potrerillos (26°30′S, 69°27′W, 7 y, 2850 m), were also included in this group. Sea level annual average temperatures were compiled from the data sets available from each station. The resulting annual values were averaged providing a latitudinal gradient.

Second, vertical temperature profiles between surface and 500 mb (approximately 5000 m asl) were obtained using TIROS and NOAA databases. Compilation of the available monthly averages for the standard levels of atmospheric pressure (1978−1988) allowed the calculation of monthly vertical thermal gradients which resulted into the following annual gradient estimates: 0.0046 °C·m^{-1}, 0.006 °C·m^{-1}, and 0.0062 °C·m^{-1} at 18°S 70°W, 38°S 70°W, and 46°S 70°W, respectively. Combination of the ground level temperature data with these vertical gradients afforded the estimation of the annual average temperature at each sampling site (Table 1). These temperature estimates agree with local descriptions of the climatic conditions in the Andean mountains.

Organochlorine Compounds in Mosses. Total PCB concentrations range between 17 and 67 ng·g^{-1} (Table 1). These values are in the same order as those reported for the moss *Hylocomium splendens* in Norway, e.g. 6.7−52 ng·g^{-1} (*25*). The Andean concentrations of total DDTs, HCH, and

HCB range between 1.6 and 7.2, 0.9−7.9, and 0.6−7 ng·g^{-1}, respectively (Table 1). The DDTs and HCH values are lower than those generally reported in remote sites (*26*), and the HCB concentrations are similar to those found in remote regions (*26*). In any case, the Andean moss values are higher than those found in previously studied Antarctic sites, <5−16, 0.2−1, 0.6−2.8, and 0.3−0.8 ng·g^{-1} for PCB, DDTs, HCHs, and HCB, respectively (*27, 28*).

Temperature Dependence. The whole data set ($n = 25$) encompasses annual average temperatures between −2.1 °C and 11 °C ($\Delta T = 13.2$ °C). Calculation of the correlation coefficients for eq 1 shows significant values (mostly p < 0.01) in nearly all compounds except PCB-158/160, PCB-180, 4,4′-DDE, and 4,4′-DDT. The temperature-correlated concentration changes encompass about 1 order of magnitude (Figure 3) which is not far away from the total concentration ranges observed in these samples (Table 2). The highest correlation coefficients are found among most of the more volatile compounds, e.g. PCBz, α-HCH, HCB, γ-HCH, and PCB congeners #18 and 52 (subcooled liquid vapor pressure > $10^{-2.5}$ Pa ((*29*) Table 2) among which r^2 coefficients equal or higher than 0.5 are observed (involving that more than 50% concentration variability is essentially related to temperature). The compounds not exhibiting significant temperature correlations in the mosses are the less volatile, including two of the more chlorinated PCB congeners (#158/160 and 180), 4,4′-DDE and 4,4′-DDT (subcooled liquid vapor pressure < $10^{-2.5}$ Pa (*29*)). With the only exception of 4,4′-DDE, these compounds also exhibit higher concentrations at lower temperature values (Table 2).

Altitude Dependence. Representation of the database in groups of the same latitude allows the evaluation of the significance of altitude in the observed temperature dependence. Accordingly, the samples have been grouped in three subsets, 18°S, 37°S, and 45°S, and the linear dependences between log-transformed concentrations and reciprocal of

temperature have been examined in each of them independently.

The samples collected at 18°S (Chungara, Cotacotani, Surire, and Las Cuevas 2 and 3; Table 1) involve an altitude range between 3200 and 4500 m asl (Δ1300 m) which represents annual average temperatures between −2.1 °C and 3.8 °C (Δ5.9 °C). The correlation coefficients of log(concentration) vs reciprocal temperature are again significant ($p < 0.05$ or 0.01; Table 2). The smaller number of samples requires much higher correlation coefficients for statistical significance which in practice renders more difficult the observation of the linear correlations for all compounds. In any case, thirteen out of eighteen compounds exhibit significant correlations, and all show higher concentrations at lower temperature values. That is, at higher altitude of the sampling site.

The subset at 37°S (Antuco 1 and 2, Piedra del Aguila, Villarica, Nahuelbuta, Laja, Angol, and Huepil; Table 1) encompass sites between 345 and 1330 m (Δ955 m) involving annual average temperatures between 5.3 °C and 11.1 °C (Δ5.8 °C). In this case, statistically significant temperature dependence is only observed for two PCB congeners #28/31 and #52 (Table 2). However, most of the compounds examined exhibit higher concentrations at lower temperature, e.g. higher altitude.

The five samples at 45°S were only distributed between two sites Venus and Risopatron (Table 1). They are situated at 700 and 10 m asl, respectively (Δ690 m), corresponding to annual average temperatures of 4.4 °C and 8.9 °C (Δ4.6 °C). These samples also exhibit statistically significant temperature dependence for the differences in concentration of some compounds, e.g. PCBz and PCB congeners #28/31, 123/149, 153, 105/132, 138, and 158/160. As in the previous cases, even most compounds not showing statistically significant correlation coefficients are found in higher concentrations at lower annual average temperatures (higher altitude).

As shown in the theoretical section and Figure 2, an exponential dependence of concentrations with reciprocal of temperature (equation 1) involves that the expected concentration gradients depend both on the temperature gradients and the minimum value of the distribution of temperatures represented by the samples (equation 2). Thus, an increase of 5.9 °C between −2.1 °C and 9.1 °C (samples at latitude 18°S) involves a concentration decrease of about 2.2 ng·g^{-1} (Figure 2). In contrast, the temperature increases of 5.8 °C (5.3 °C and 11 °C) at 37°S and 4.6 °C (4.4 °C and 8.9 °C) at 45°S involve concentration differences of 0.72 ng·g^{-1} and 0.70 ng·g^{-1}, respectively (Figure 2). Obviously, smaller concentration differences are a priori more difficult to detect within sample variability. Thus, the data set at 18°S is the one of expected higher temperature dependent concentration changes. This altitude gradient is effectively the one exhibiting the highest number of compounds with statistically significant correlation with reciprocal of temperature.

In any case, the temperature differences between the samples of these three subsets are due to the lake altitude since all of them are distributed at nearly the same latitude (18°11′S−18°49′S, 37°15′S−37°50′S, 44°16′S−45°36′S, respectively). The observed concentration differences reflect therefore the temperature gradient of the altitude, the highest samples (those situated further away from the low altitude sites where humans currently live) being those most polluted.

The higher concentrations of these OC at a higher altitude are consistent with the results of previous studies on mountain sites from other areas (6−9). The data on the European mountain lakes (6, 7) and Teide mountain (8) are those more directly comparable with the present set of Andean lakes at 18°S since they encompass similar air average annual air temperatures, −1.45 °C−8.7 °C, 4.9 °C−20°C, and

−2.1°C−3.8°C, respectively. The Teide and the Andean mountain data exhibit a close agreement since the concentrations of nearly all OC increase with altitude. Only the compounds of present or recent use in agricultural applications (HCHs and DDTs, respectively) did not show altitude dependence in Teide.

In contrast, the results from the European lakes only show altitudinal dependence for the OC compounds with volatilities lower than 10$^{-2.5}$ Pa. The difference between Andean and European lakes cannot be attributed to the temperatures represented by the samples included in both studies. However, the European lake study only includes samples obtained within the lakes (fish and sediments), whereas the Andean series essentially encompass mosses that are in direct contact with air. Studies on snow OC concentrations in a series of European high mountain lakes show significant correlation with altitude for compounds with volatilities higher than 10$^{-2.5}$ Pa (30). The closer parallelism between European snow and Andean mosses is probably due to direct air exchange in these two types of samples.

Enthalpies. The correlations between moss concentrations and the reciprocal of temperature afford the calculation of air−moss exchange pseudoenthalpies

$$\Delta H = S \cdot R \cdot \ln(10) \qquad (3)$$

where S is the slope of the regression line and R is the gas constant as 8.314 J·K^{-1}·mol^{-1}.

Most enthalpy values range between 40 and 95 kJ·mol^{-1} (Table 2). These field constants are close to the enthalpies of phase change between octanol and air calculated in laboratory experiments, 66−93 kJ·mol^{-1} (31). However, comparison of both types of values must be done with caution. The field series correspond to sites from which a constant annual average air temperature is assumed, whereas the octanol−air values were obtained from laboratory systems in which temperatures are fixed by experimental design. Furthermore, deviations from linearity of some field data may also have significant influence on the overall slope values. Last but not least, possible introduction of corrections for different air concentrations at different altitudes (see discussion in the theoretical section) would also influence the final enthalpy values. The comparison between both data sets is therefore only done on a tentative basis.

Despite the above indicated good agreement between experimental and theoretical constant ranges, the decreasing enthalpy values at decreasing compound volatility is in contradiction with the constants reported in laboratory experiments (air−octanol phase change enthalpies increase as the volatility of the compounds decrease (31)). This difference between low and high volatility OC in the air−moss enthalpies (Table 2) is consistent with the lower concentration ranges observed in the former (less than 1 order of magnitude) than the latter (more than 1 order of magnitude). This observation points to moss difficulties for the incorporation of the less volatile OC due to hindering effects, metabolic processes, or other aspects. Thus, our results suggest that in the context of the temperature forcing of OC accumulation in the Andean mountains, mosses are less able to incorporate efficiently the more chlorinated congeners and therefore provide smoothed temperature-dependent trends for these compounds.

In any case, the statistically significant dependence of OC concentrations with reciprocal of temperature irrespectively of compound origin, e.g. industrial, agricultural, and the good agreement between air−moss phase change enthalpies and experimental octanol−air phase change constants strongly supports that temperature is the ultimate accumulation factor determining the altitudinal concentra-

tion gradient in the moss samples from the Andean mountains.

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