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Passive-Sampler Derived Air Concentrations of Persistent Organic Pollutants on a North–South Transect in Chile

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Passive air samplers consisting of polyurethane foam (PUF) disks, were deployed in six locations in Chile along a north–south transect to investigate gas-phase concentrations of polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs). The study provides new information on air concentrations of these persistent organic pollutants (POPs) which is lacking in this region. It also provides insight into potential sources and long-range transport (LRT). The samplers were deployed for a 2-month period in five remote sites and one site in the city of Concepción. Mean concentrations (pg m^{-3}) for ΣPCB were 4.7 ± 2.7 at remote sites and 53 ± 13 in Concepción. PCB levels at remote sites were related to proximity to urban source regions and/or air back trajectories. With the exception of endosulfan I, mean concentrations (pg m^{-3}) of OCPs at background sites were consistently low: 5.4 ± 1.4 for $\alpha\text{-HCH}$, 7.0 ± 1.1 for $\gamma\text{-HCH}$, 2.5 ± 0.5 for TC, 2.5 ± 0.6 for CC, 1.9 ± 1.2 for dieldrin, and less than 3.5 for toxaphene. Endosulfan I showed a decreasing concentration gradient from 99 to 3.5 pg m^{-3} from the north to south of Chile. Concentrations of OCPs in the Concepción City were generally 10–20 times higher than at the background sites suggesting continued usage and/or re-emission from past use. For instance, at remote sites, the α/γ ratio (0.76) was typical of background air, while the ratio in Concepción (0.12) was consistent with fresh use of $\gamma\text{-HCH}$. Levels of ΣPBDEs were below the detection limit of 6 pg m^{-3} at all sites.

Introduction

Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), and polybrominated diphenyl ethers (PBDEs) are semivolatile organic compounds (SOCs) that are ubiquitous on the planet.

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PCBs and OCPs have been measured in remote polar regions in the Arctic (1–4) and Antarctic (5–9) and are believed to arrive in these regions via long-range atmospheric transport (LRT) from source regions; once deposited, they become highly accumulated in the food chain (10). In Antarctica, several researchers report OCPs and PCBs in the wildlife and air (1, 5–9) with South America implicated as a source of these pollutants (6, 9). PBDEs have been reported in the Arctic and exhibit exponential increasing trends in some biota (11). So far, no data for PBDEs exist for the Antarctic.

Although the production and use of PCBs and many OCPs have been prohibited in most industrialized countries, they continue to be detected in the atmosphere. This is believed to be the result of LRT from sources where these chemicals may still exist in high concentrations—for instance, contaminated soils in the case of OCPs and urban/industrial centers in the case of PCBs (12).

PCBs have been widely used in Chile as dielectric fluids over the past 50 years, and some still remain either in use or stored. Their use was banned in 1982, but more than 50% of transformers currently in-use contain PCBs. It has been estimated (13) that the cumulative use of PCBs in Chile is 900 tons, of which two-thirds are still in-use or stored. Only a single study reports air concentrations of PCBs in urban areas of Chile (14). No data are available for background/remotes areas in Chile.

OCPs were used in Chile for over 60 years prior to being banned in 1984 (15). Pesticides pollution was first reported in the Chilean environment in 1985, when DDT and lindane were detected in dolphins (16). Organochlorine pesticides were also detected in fish and invertebrates (17), in wildlife at pristine Chilean sites (18), and in lake sediment (19). OCPs that exist in the Chilean atmosphere likely arrive by advection (long range atmospheric transport) from source regions or are due to emissions from previously contaminated agricultural soils. In urban areas, it is likely that some use of selected OCPs continues for domestic pest control.

PBDEs are a class of brominated flame retardants (BFR) that are added to commercial and household products such as furniture foams, textiles, and electronic components such as TVs and computers (20). PBDEs are produced in several formulations. The “penta-product” containing mainly 4–6 Br congeners has been most widely investigated because of the occurrence and rapid accumulation in biological samples from remote regions (11).

Currently, the high volume sampler is the most widely used approach for sampling SOCs in air. This approach utilizes a pump that draws air through sampling media that trap SOCs. Because this approach requires costly sampling equipment and a source of electricity, it is not feasible for conducting spatial mapping studies of POPs at remote sites. Sparse air data in the Southern Hemisphere and Antarctic is partly attributed to the difficulties and high costs associated with conventional high volume air sampling. An alternative and more feasible approach that was employed here was to use passive air samplers (PASs) consisting of polyurethane foam (PUF) disks. PASs are chemical accumulators that rely on air currents to deliver chemical to the sampler. Thus, they do not require electricity. The uptake of SOCs by PASs has been characterized which allows air concentrations to be determined (21). PUF disk PASs are increasingly employed in investigations of persistent organic pollutants (POPs) (22–26).

In this study passive samplers were deployed at six sites along a north–south transect in Chile, South America,

TABLE 1. Location of Sampling Sites with Latitude/Longitude and Average Temperature (°C)^a

sampling site	latitude/longitude	altitude masl	location	temp ^b (°C)
Chungará Lake	18°13' S; 69°10' W	4320	remote area	4.8
Laja Lake	37°22' S; 71°21' W	1433	remote area	13.5
Concepción City	36°49' S; 73°02' W	10	urban area	16.6
Nahuelbuta NP	37°49' S; 72°57' W	1189	remote area	19.6
Huinay NR	42°22' S; 72°24' W	15	remote area	13.5
Fjord of Pta. Arenas	51°50' S; 72°40' W	10	remote area	10.8

^a Abbreviations: NP, National Park; NR, National Reserve; masl, meters above sea level. ^b Average temperature for the sampling period.

extending approximately 4200 km (from 18° S to 53° S). The aim of the study was to investigate air concentrations and patterns of PCBs, OCPs, and PBDEs at urban, remote lowland, and remote highland sites. Such information may also provide insight regarding sources of these chemicals in this region.

Theory of Passive Air Samplers

As the name suggests, passive air samplers (PASs) operate without the aid of a pump and consist of an accumulating/adsorbing medium that has a high retention capacity for the target analytes. The uptake of POPs by PUF disks and other materials has been described in an earlier study (21) and was shown to be air-side controlled and thus a function of the air-side mass transfer coefficient (MTC), k_A . This parameter is a weak function of temperature and strongly related to wind speed, with higher values at higher air velocities. However, windspeed dependence is minimal at very low wind speeds (27). During outdoor deployment of the PUF disk PAS, a low-wind environment is preserved by housing samplers in protective chambers. Such samplers therefore allow for integrative sampling in locations where active samplers would not be practical over long periods, due to lack of electricity supply in remote locations.

The maximum amount of chemical that may be taken up by the PUF disk is defined by its retention capacity or PUF-air partition coefficient, K_{PUF-A} . Previous work has shown that K_{PUF-A} is well correlated to K_{OA} which is known for many POPs as a function of temperature including PCBs (28–30) and OC pesticides (31). The complete uptake profile is described by

$$C_{PUF} = K_{PUF-A} C_A (1 - \exp - [(A_{PUF}) / (V_{PUF}) * (k_A / K_{PUF-A})] t) \quad (1)$$

where C_{PUF} and C_A are concentrations (mass cm^{-3}) of analyte in the PUF disk and air, respectively, A_{PUF} and V_{PUF} are the planar surface area (cm^2) and volume (cm^3) of the PUF disk, k_A is in cm d^{-1} , and t is the exposure time in days (21). Values for the various calibration parameters including the relationship between K_{PUF-A} and K_{OA} are presented elsewhere (21). Note that K_{PUF-A}' differs from K_{PUF-A} in ref 21 in that K_{PUF-A}' is dimensionless (i.e. $K_{PUF-A}' = K_{PUF-A} \times \text{density of PUF disk}$).

It is also possible to interpret K_{PUF-A}' as the equivalent volume of air that contains the same mass of analyte as 1 unit volume of passive sampling medium under equilibrium conditions i.e., $K_{PUF-A}' = V_{AIR} / V_{PUF} = C_{PUF} / C_{AIR}$. Thus by analogy and replacing terms in eq 1, the equivalent air sample volume is

$$V_{AIR} = K_{PUF-A}' V_{PUF} (1 - \exp - [(A_{PUF}) / (V_{PUF}) * (k_A / K_{PUF-A})] t) \quad (2)$$

For chemicals with K_{OA} values larger than $10^{8.5}$, the sampling rate remains linear over the first 100 days at $\sim 3\text{--}4 \text{ m}^3 \text{ d}^{-1}$ and is mainly defined by the air-side MTC (24). For compounds of lower K_{OA} , the PUF disk becomes saturated

with respect to the air in less than 100 days. The time required for a chemical to reach saturation (or to attain its maximum equivalent air volume) is inversely proportional to K_{PUF-A} (or K_{OA}). Thus sample air volume can be estimated based on calibration results and using eq 2.

It is also possible to measure sample volumes directly by adding depuration compounds to the sampler prior to deployment (7). Depuration compounds can be isotopically labeled or unlabeled chemicals that exhibit negligible concentrations in air. Because uptake of SOCs is air-side controlled, the rate of uptake of chemical will be the same as the rate of loss. Equation 1 is a first-order rate expression having the form $\ln(C/C_0) = -k_E t$, where k_E is the loss rate constant (units of time^{-1}). From eq 1, k_E is equivalent to $1/\delta_{FILM} \times (k_A / K_{PUF-A})$. Thus, k_A can be calculated from the recovery of depuration compounds initially spiked into the PUF disk (i.e. C/C_0) using

$$k_A = \ln(C/C_0) \delta_{FILM} K_{PUF-A}' / t \quad (3)$$

The PUF disk air sampling rate, R in $\text{m}^3 \text{ d}^{-1}$, is equivalent to $10^6 A k_A$ (i.e. 10^6 is required to convert to m^3 since k_A has units of cm d^{-1}).

Materials and Methods

Sample Collection. Samples were taken at 6 sites in Chile along a $\sim 4200 \text{ km}$ north–south transect at 5 remote areas and 1 urban area (Figure 1). Chungará Lake, Laja Lake, Nahuelbuta National Park, Huinay National Reserve, and Fjord of Pta. Arenas are remote areas characterized by small communities of inhabitants. Concepción City is located close to the Bio Bio River and is one of the largest cities in Chile (second to Santiago). Details for the sampling locations are given in Table 1. In remote areas, passive samplers were mounted in open areas with unobstructed air flow. In Concepción samplers were deployed in the downtown area on a roof of a $\sim 5 \text{ m}$ tall building.

PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm^2 ; mass, 4.40 g; volume, 207 cm^3 ; density, 0.0213 g cm^{-3} ; PacWill Environmental, Stoney Creek, ON) were housed inside a stainless steel chamber (Figure 1). The chamber consisted of two stainless steel domes with external diameters of 30 and 20 cm. Air is allowed to flow over the sampling surface through a 2.5 cm gap between the two domes and through holes in the bottom surface of the lower dome. The PUF disk chamber protects the sampler from precipitation, UV sunlight, and particle deposition—although it is likely that fine particles are sampled. The chamber also reduces the dependence of sampling rate on wind speed resulting in a sample that is equally weighted with time over the integration period.

PUF disks were handled using solvent-rinsed tongs. Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation of the passive sampling media which was done using clean gloves. Sample installation and removal was performed outside to avoid the risk of contamination. Twelve air samples were collected over a 2-month

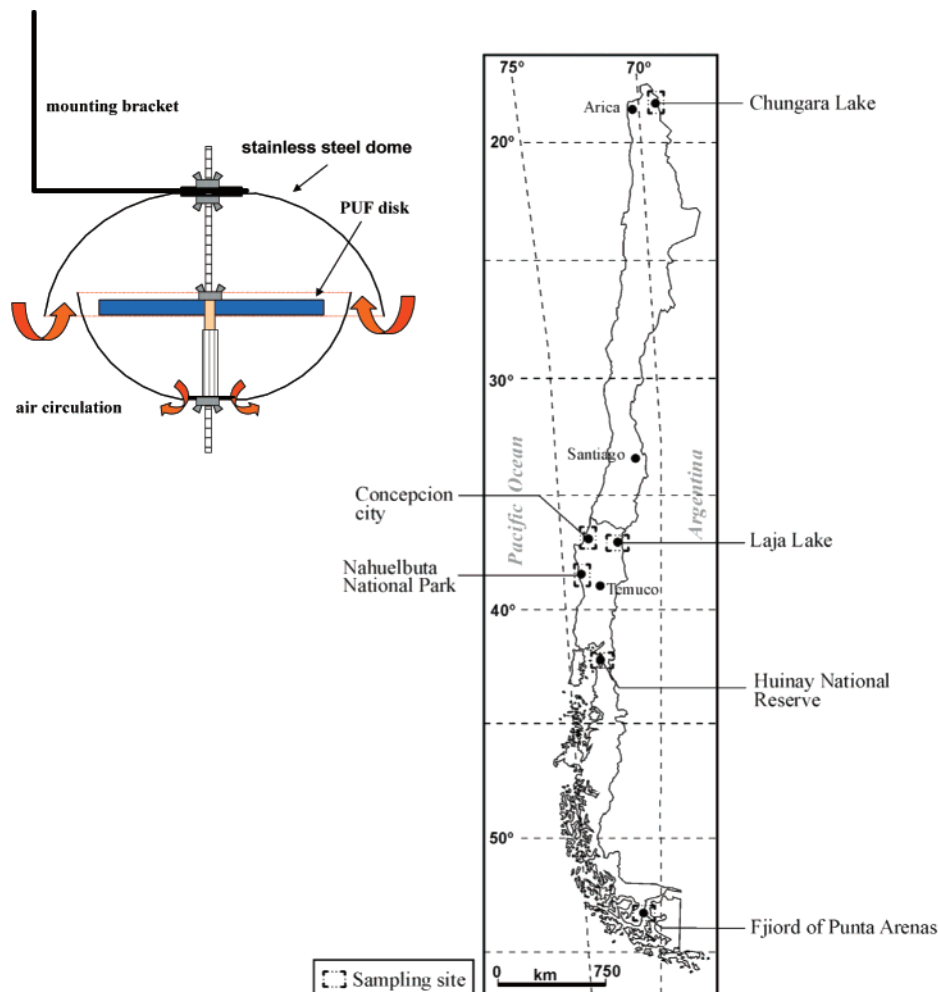


FIGURE 1. Location of passive air sampling sites in Chile and sampler schematic.

period from December 2002 to February 2003. Duplicate samples were deployed at each of the six sites. Three field blanks were taken at Huinay NR, the Fjord of Pta. Arenas, and Chungará Lake, where PUF disks were installed in the stainless steel domed chambers, then removed, and stored. Harvested PUF disks were stored cold (4 °C) and in the dark until extraction. Unfortunately, one of the blank jars was damaged during transportation, leaving 2 viable field blanks.

Sample Preparation. Prior to exposure PUF disks were precleaned at Meteorological Service of Canada (MSC) with water and then by Soxhlet extraction for 24 h using acetone and then for another 24 h using petroleum ether. PUF disks were dried in a desiccator and stored in glass jars with Teflon-lined lids.

Before sending them to the study site, PUF disks were fortified with depuration compounds: d_6 γ -HCH (262 ng), PCB 30 (64 ng), PCB 107 (9.6 ng), and PCB 198 (5.6 ng) for assessing sampling rate variability from site to site. The depuration compounds do not typically exist in air and cover a range of volatility (e.g., based on their K_{OA} values) (31).

Analysis. In preparation for extraction, PUF disk samples were spiked with a recovery standard consisting of ^{13}C PCB-105 (260 ng) (CIL, Andover, MA). PUFs were individually extracted by Soxhlet in petroleum ether for 24 h. Details of samples extraction and clean up are presented elsewhere (32). Mirex (100 ng) was added as internal standard to correct for volume difference.

Chemicals. Air sample extracts were quantified for 19 OCPs using a mixture of standards: α -, β -, γ -, δ -HCHs, aldrin, heptachlor, heptachlor epoxide, *cis*-chlordane, *trans*-chlo-

rdane, *trans*-nonachlor, endosulfan I, endosulfan II, endosulfan sulfate (SO_4), *o,p'*-DDE *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, obtained from Ultra Scientific (North Kingstown, RI, U.S.A. and U.S. Environmental Protection Agency, Research Triangle Park, NC) and toxaphene (Supelco Inc, USA). PCBs were quantified separately using a 48 component mixture (PCB-8, -18, -17, -15, -16+32, -28, -33, -52, -49, -44, -42, -37, -74, -70, -66, -95, -56+60, -101, -99, -87, -110, -123, -149, -118, -114, -153, -105, -137+138, -126, -187, -183, -128, -185, -174, -177, -171, -156, -157, -180, -200, -170, -203, -195, -205, and -206) (Ultra Scientific, North Kingstown, RI). Samples were also analyzed for 13 polybrominated diphenyl ethers (PBDE congeners 17, 28, 47, 66, 71, 85, 99, 100, 138, 153, 154, 183, and 190) obtained from Cambridge Isotope Laboratories (Andover, MA).

PCBs, OCPs, and PBDEs were analyzed by GC-MS on a Hewlett-Packard 6890 GC-5973 MSD. PCBs were determined in EI-SIM (electron impact-selected ion monitoring), and OCPs and PBDEs were determined in negative chemical ionization (NCI) in SIM mode with methane as reagent gas with a flow of 2.2 mL min⁻¹. GC conditions were the same for both methods as were described elsewhere (21). For PBDE analysis oven temperature was modified to 90 °C hold for 0.5 min, 15 °C min⁻¹ to 240 °C, then 20 °C min⁻¹ to 290 °C, hold for 5 min, and transfer line kept at 300 °C. Conditions for EI analysis of PCBs and information of target/qualifier ions measured are described elsewhere (21).

For NCI analysis of OCPs and PBDEs, the transfer line, ion source, and quadrupole temperatures were kept at 150 °C and 106 °C, respectively, and 250 °C and 106 °C for PBDE

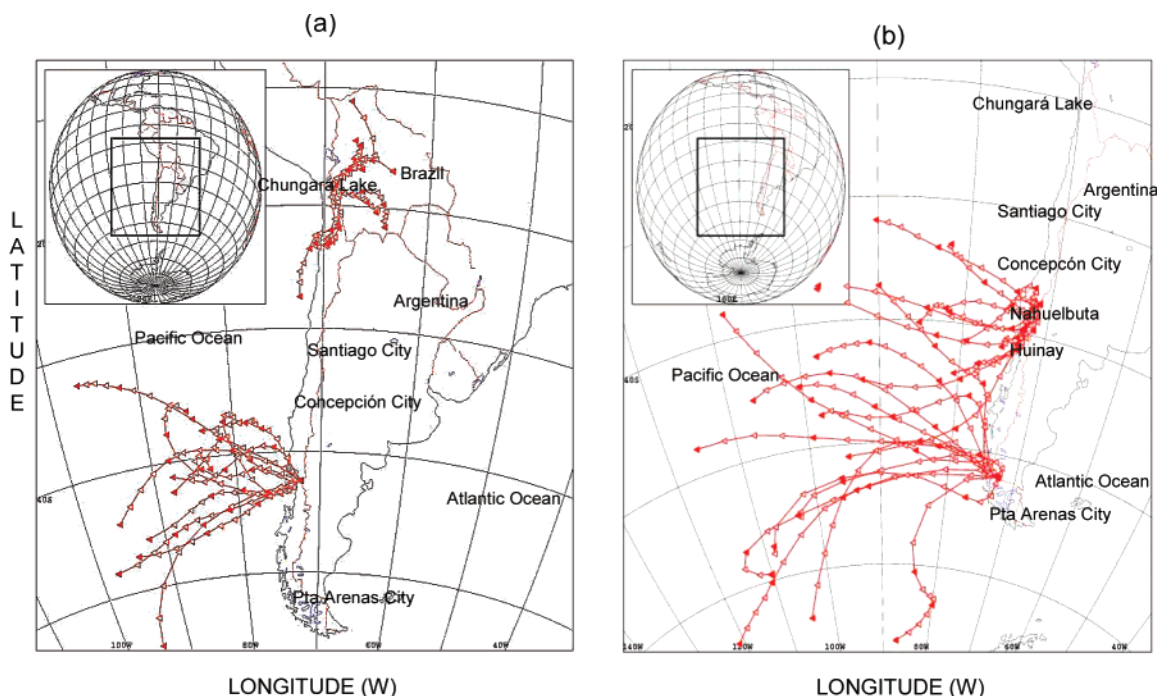


FIGURE 2. Three-day air parcel back trajectories at 10 m above ground level, calculated using the Canadian Meteorological Centre (CMC) Trajectory Model. Trajectories were calculated at various hours for every fifth day during the deployment period for (a) Chungará Lake and Huinay NR and (b) Laja Lake and the Fjord of Pta. Arenas.

TABLE 2. Retention Percentages for Depuration Compounds and Resulting Sampling Rates and Volumes Determined Using Eq 3^a

location	PCB 30 (%)	d ₆ -γ-HCH (%)	sampling rate ^b (R) (m ³ day ⁻¹)	sample vol (eq 3) (m ³)
Chungará Lake1	53	56	4.79	130
Chungará Lake2	52	59	4.41	120
Concepción City1	46	48	4.59	125
Concepción City2	40	42	5.44	148
Laja Lake1	18	24	8.98	244
Laja Lake2	16	23	9.33	253
Nahuelbuta NP1	39	50	4.86	132
Nahuelbuta NP2	46	59	3.78	103
Huinay NR1	47	57	2.29	62
Huinay NR2	49	52	2.65	72
Fjord of Pta. Arenas1	53	49	3.62	98
Fjord of Pta. Arenas2	62	54	2.59	70
mean ± SD	43 ± 14	48 ± 12	4.78 ± 2.3	130 ± 62

^a Abbreviations: vol, volume; SD, standard deviation; NP, National Park; NR, National Reserve. ^b The sampling rate is based on average values for PCB-30 and d₆-γ-HCH.

analysis. Details of target/qualifying ions are described elsewhere (26, 33). For toxaphene (M – Cl⁻) ions were monitored for the three main homologues (hepta to nona) – 343/345 (heptachlorobornanes), 379/381 (octachlorobornane), and 413/415 (nonachlorobornanes).

Surrogate recoveries were determined for all samples by spiking ¹³C PCB-105 prior to extraction. Analytical (method) recoveries of PCB were also determined by spiking two clean PUF disks with the working standard containing all the PCB congeners (1 ng of each PCB congener) and treating as real samples.

The risk of contamination due to sample storage and transport times of up to nearly 4 months was also investigated by collecting three field blanks of which two were viable (one was lost). Two solvent blanks (method blanks) were also performed. The instrumental detection limits (IDL) of the PCB congeners was variable for the different ions monitored: 0.025 pg for mass 222; 0.13 pg for mass 256; 0.19 pg for mass 292; 0.19 pg for mass 326; 0.29 pg for mass 360;

0.24 pg for mass 394; and 0.31 pg for mass 428. For OCPs IDL ranged from 0.01 to 0.48 pg. Peaks were reported only if the signal exceeded three times the baseline noise.

Result and Discussion

Quality Assurance/Quality Control. Surrogate recoveries for ¹³C PCB-105 ranged from 68.7 to 94.3% (mean 83.6% ± 7.7%). Recoveries of PCBs were further assessed for PCBs by spiking PUF disks (n=2) with the calibration solution and treating as samples. Average recoveries for all PCBs were satisfactory (75% ± 4.0%), and no recovery correction was applied to the samples. Method recoveries were assessed previously in the same laboratory for OCPs (32) and PBDEs (33) and found to be good.

Blank levels were assessed from the two field blanks and two laboratory blanks. All blanks levels were below the detection limit for OCPs except for γ-HCH, TC, and endosulfan I which were also low and ranged from 0.4% to 3%

of the sample amounts. Results for *p,p'*-DDE and endosulfan SO₄ were either excluded or flagged because of high blanks that were ~40% of the sample amounts. For PCBs, field blanks had quantifiable levels of di- (PCB-8), penta- (PCB-101, PCB-123), and hepta- (PCB-170) congeners. Solvent (method) blank values for individual PCB congeners were low and not detectable for most higher molecular weight PCBs.

Method detection limits (MDL) in air samples were defined as the average blank (*n*=4) plus three standard deviations (SD). When target compounds were not detected in blanks, 2/3 of the instrumental detection limit was used as the MDL. All qualified data (i.e. exceeding the MDL) has been blank corrected.

Sample Volumes Derived from Depuration Compounds.

To calculate air concentrations, sample volumes were derived based on the fraction of depuration compounds (PCB-30 and d₆-γ-HCH) retained by the PUF disk (Table 2) using eq 3. Calculations are based on PCB-30 and d₆-γ-HCH. Based on their *K*_{OA} values, these compounds are expected to experience ~50% depletion over the sampling period (21). A retention percentage of ~50% is desirable for this calculation to minimize errors with the estimate—i.e., enough chemical is depleted that it is distinguishable from analytical variability, yet recoveries are not so low that a small error in their value would result in a large error for the calculation. For high molecular weight compounds such as PCB-107 and PCB-198, the time to 50% loss is on the order of years and hence 100% recovery is expected. Results for PCB-30 and d₆-γ-HCH were corrected based on factors that would give 100% recovery for PCB-198. Prior to this correction, the mean recovery of PCB-198 (*n*=12) was 79% ± 13% which agrees well with the method recovery for PCBs of 75% ± 4% presented previously.

Mean recoveries for depuration compounds PCB-30 and d₆-γ-HCH (corrected for 100% recovery of PCB-198) were 43% ± 14% and 48% ± 12%, respectively. This yielded sampling rates (eq 3) of 4.8 ± 2.3 m³ day⁻¹ and sample volumes of 130 ± 62 m³. The sampling rates are consistent with previous calibration results (21) which indicates that the sampling chambers were largely effective at dampening the wind effect on uptake rate. One exception was the site at Laja Lake where sampling rates for the duplicate samplers were consistent and about two times higher than the average for all sites (Table 2). This may be partly attributed to the inability of the sampling chamber to completely dampen the high winds that were characteristic of this site.

Air Mass Back Trajectory Analysis. To examine the influence of air mass movement from source regions, 3-day air parcel back trajectories were performed for each sampling location using the Canadian Meteorological Centre (CMC) Trajectory Model. Trajectories were calculated at 10 m above the ground at 00:00 h for every 5th day of the integration period.

Two air flow pattern types were identified. The northeast (NE) air flow in Chungará Lake passing over Brazil's Amazonas, Uruguay, Bolivia, and Perú (Figure 2a) and the West air flow for all the other sites where back trajectories spent more than 90% of the time over the Pacific Ocean (Figure 2b). Chungará Lake is the most northernly and highest altitude site and experienced variable air trajectories which were mostly over land during their 3-day history. Punta Arenas, the most southernly site, received southernly inputs with some trajectories originating from Antarctica during the sampling period.

PCB Concentrations. Table 3 compares PCB air concentrations for the six sites in this study to results from other studies in remote, background, and urban (Chile) areas. The 48 PCB congeners investigated here typically represent 48–74% of ΣPCB reported in other studies (7, 14, 34–37).

TABLE 3. Comparison of Passive Sampler Derived Air Concentrations for ΣPCB (pg m⁻³) in This Study (Chile) to Other Studies in Remote, Background, and Urban Locations

location	Northern Hemisphere	
	mean PCB	reference
Remote		
Bering sea 1989	12	(1) ^a
North Pacific 1989	24	(1) ^a
North Atlantic Ocean	26	(1) ^a
Alert	28.3	(2) ^b
Tagish	18.4	(2) ^b
Dunai	30.2	(2) ^b
Background		
Eagle Harbor	90	(53) ^c
Sleeping Bear Dunes	160	(53) ^c
Point Petre	170	(53) ^c
North Pacific 1989–1990	24	(1)
North Atlantic Ocean	26	(1)
Gulf of Mexico	16	(38) ^d
Southern Hemisphere		
Remote/Background		
Admirantly Bay-Antarctic	37.4	(9) ^e
Chungará Lake	2.6–2.7	this study
Laja Lake	6.5–11.4	this study
Nahuelbuta NP	3.4–4.9	this study
Huinay NR	4.2–7.2	this study
Fjords of Punta Arenas	1.9–2.5	this study
Urban (Chile)		
Concepción City	53	this study
Temuco City	672–1790	(14) ^f
Santiago City	1760–2750	(14) ^f

^a Sum of congeners present in mixture of kenachlor. ^b Sum of PCB 4/10, 6, 7, 8/5, 16/32, 17, 18, 19, 22, 24/27, 25, 26, 28, 31, 33, 40, 41/71, 42, 44, 45, 46, 47, 48, 49, 52, 56/60, 64, 66, 70/76, 74, 82, 83, 84/89, 85, 87, 91, 95, 97, 99, 101, 105, 110, 114, 118, 128, 130/176, 131, 132, 134, 136, 137, 138, 141, 144/135, 146, 149, 151, 153, 156, 158, 170, 171, 172/197, 174, 175, 177, 178/129, 179, 180, 183, 185, 187, 189, 191, 193, 194, 195, 196/203, 198, 199, 200, 201/157, 205, 206, 207, and 209. ^c Sum of PCB 18, 44, 52, and 101. ^d Data not available. ^e Sum of PCB 18, 44, 52, 101, 118, 128, 138, 153, 180, and 187. ^f Sum of PCB 8+5, 12+13, 18, 17, 16+32, 31+28, 33+20, 22+52, 49, 47+48+75, 44, 41+64, 74, 70, 66, 95, 101+90, 99, 136, 110, 123, 149, 118, 153, 132, 105, 138+164+163, 158+160, 174, 180, 199, 170+190, and 194.

PAS-derived PCB air concentrations in remote/background Chilean sites ranged from 2 to 11 pg m⁻³. This is consistent with other data from remote regions around the world (12–30 pg m⁻³) and with values reported over the Southern Pacific Ocean (1) and Gulf of Mexico (38) (Table 3). Somewhat higher concentrations are reported in background regions (90–360 pg m⁻³) of the Northern Hemisphere (Table 3). Here we differentiate “background” sites as possibly impacted by advection from regional sources, whereas “remote” sites are considerable distances from any known sources. Often, there is not a clear distinction, and a site may be considered remote/background. Higher levels of PCBs in the Northern Hemisphere are attributed to the influence of PCB emissions from various point sources as well as diffuse sources which are contained primarily in the Northern temperate zone (12).

PCB concentrations were detected at all passive sampling sites (Table 3 and Figure 3). As expected, Concepción City had the highest average ΣPCB concentrations (53 pg m⁻³), followed by Laja Lake (8.9 pg m⁻³) and Huinay NR (5.7 pg m⁻³). The lowest concentrations were detected at Nahuelbuta NP (4.1 pg m⁻³), Fjord of Pta. Arenas (2.2 pg m⁻³), and Chungará Lake (2.7 pg m⁻³).

Air concentrations of PCBs in Concepción City are substantially lower than reported previously for other Chilean cities. Mandalakis et al. (14) reported PCB levels in air particulate samples of 1420 ± 436 pg m⁻³ in Temuco City

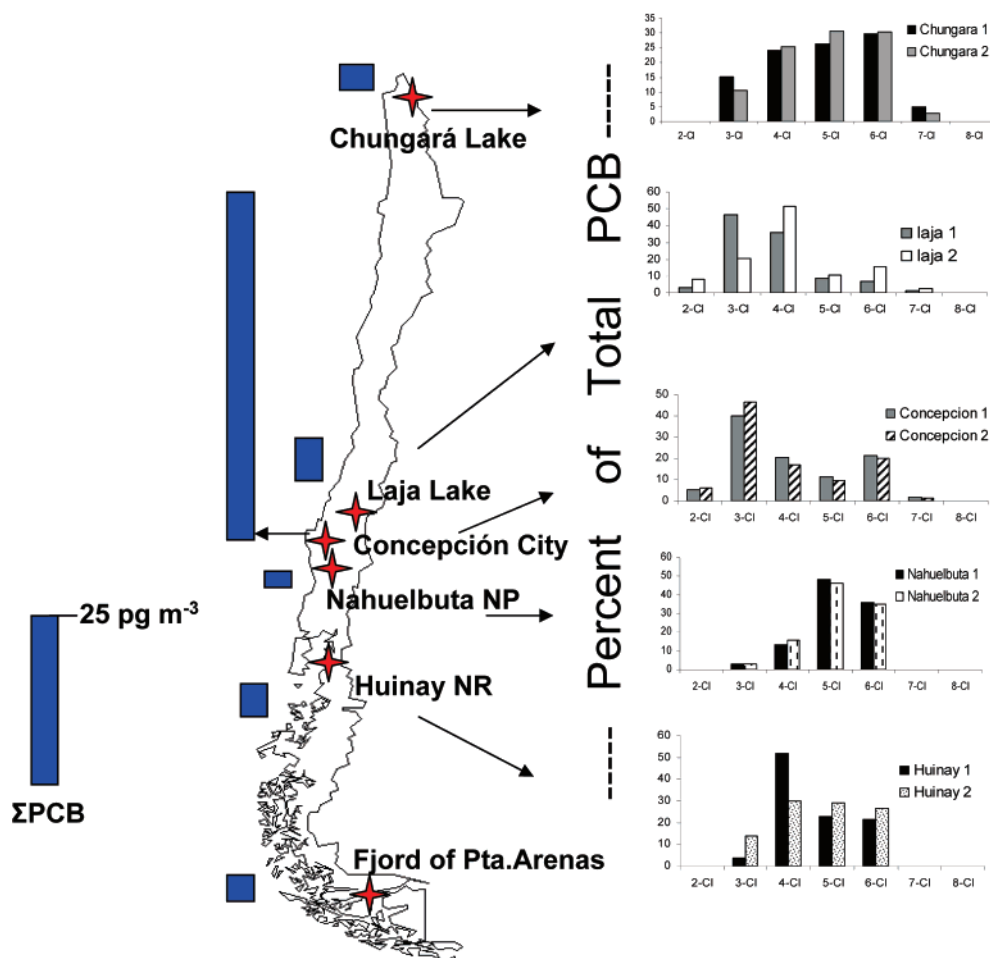


FIGURE 3. (a) Σ PCB concentrations (pg m^{-3}) and (b) homologue composition for duplicate PUF disk samples collected at each site. Fjord of Pta. Arenas was excluded because a large number of congeners were nondetectable.

and $2320 \pm 462 \text{ pg m}^{-3}$ in Santiago City (Table 3). Lower values in Concepción may be related to its proximity to the coast ($\sim 10 \text{ km}$) and the influence (dilution effect) of clean air masses from the Pacific Ocean (Figure 2) during the sampling period.

The Fjord of Pta. Arenas and Chungará Lake which are the most remote sites (furthest from any urban/industrial activity) exhibited the lowest PCB concentrations of approximately 3 pg m^{-3} . Air parcel back trajectories for the Fjord of Pta. Arenas (Figure 2) show that it represents the continental or oceanic background level of Σ PCB in the Southern Hemisphere.

Previous studies (39, 40) found increasing Σ PCB in mussels from north (Arica (18° S)) to south Chile (Punta Arenas City (56° S)). A similar gradient was not observed for atmospheric PCBs in this study, but it should be noted that sampling locations in this study were mainly inland and hence differ from the coastal sites sampled during the mussel studies. Comparing PCBs in air to concentrations in mussels may also not be appropriate. PCB uptake and accumulation by mussels is complex and related to water concentrations of PCBs, water temperature, and other ecosystem parameters.

PCB Homologue Composition. Figure 3 shows the homologue composition for duplicate PUF disk samples collected at each site. Results are also listed in Table 4 for the dominant congeners observed in the air samples. The profiles for Fjord of Pta. Arenas are not given because a large number of congeners were nondetectable at this site.

Agreement between the duplicate samplers was satisfactory with a mean difference of $60\% \pm 35\%$ ($n=6$, Figure 3).

This variability is not much larger than what one might expect for conventional high volume air samplers and is largely attributed to analytical variability. An additional source of uncertainty for the PAS, however, is the estimation of the effective air volume using depuration compounds (Table 2).

Of the three highland/mountain sites, Chungará Lake and Nahuelbuta NP have similar homologue profiles that show an enrichment of the higher molecular weight congeners (4-Cl, 5-Cl, and 6-Cl). This pattern is not typical of background sites that are usually dominated by lower molecular weight PCBs (2, 7, 9, 41). Reasons for this are unknown. The third highland/mountain site, Laja Lake, has higher PCB levels and a different homologue profile which is dominated by lower molecular PCBs (3-Cl, 4-Cl). This profile is similar to that observed at Concepción and may indicate a contribution from this urban area which may act as a regional source. The lower chlorinated profiles observed at Laja Lake and Concepción also reflect the profiles reported from other Chilean cities—i.e., Santiago and Temuco (14, 42) (Table 4).

OCPs Concentrations. Table 5 shows the PAS-derived concentrations of OCPs at the sampling sites. Figure 4 summarizes trends for three classes of OCPs along the Chilean transect—namely, the dominant isomers of the hexachlorocyclohexanes (HCHs), chlordanes (CHL), and endosulfans (Endo).

Several OCPs that were targeted were not detected in any of the samples; these include the following: aldrin, β -HCH, δ -HCH, and toxaphene which are reported as less than the MDL. Results for p,p' -DDE and endosulfan SO_4 are not reported because of high blank values (Table 5).

TABLE 4. Concentrations (pg m⁻³) of Selected Dominant PCB Congeners in Chilean Air^a

locations	-28	-52	-49	-101	-99	-149	-153	-180	ΣPCB ^b
This Study									
Chungará Lake	0.07	0.33	0.08	0.24	0.15	0.19	0.20	0.10	2.0
Concepción City	3.19	4.57	1.64	2.83	0.72	1.07	1.18	0.41	53.0
Laja Lake	0.85	1.93	0.33	0.30	<0.19	0.18	0.18	0.08	26.0
Nahuelbuta NP	0.15	0.38	0.07	0.35	0.17	0.28	0.35	<0.24	19.4
Huinay NR	<0.13	0.96	0.70	0.41	0.22	0.27	0.31	<0.24	7.0
Fjord of Pta. Arenas	0.75	<0.19	<0.19	0.89	<0.19	1.11	1.12	<0.24	3.1
Other Studies in Chile^c									
Temuco City	194	33	19	22	4	29	63	36	1412
Santiago City	264	28	41	17	10	36	44	46	2325

^a Abbreviations: NP, National Park; NR, National Reserve. ^b ΣPCB = 2-Cl: PCB-8, -15; 3-Cl: PCB-18, -17, -16+32, -28, -31, -33, -37; 4-Cl: PCB-52, -49, -44, -42, -74, -70, -66, -56+60, -81, -77; 5-Cl: PCB-95, -101, -99, -87, -110, -123, -118, -114, -105, -126, 6-Cl: PCB-151, -149-153, -137+138, -128, -156, -157, 7-Cl: PCB-187, -183, -185, -174, -177, -171, -180, -170, 8-Cl: PCB-200, -203, -195, -205, and 9-Cl: PCB-206. ^c Mean concentrations during the summer period (14).

TABLE 5. Air Concentrations (pg m⁻³) of OCPs at Passive Sampling Locations in Chile^{a,f}

compounds	MDL	Chungará Lake	Laja Lake	Concepción City	Nahuelbuta NP	Huinay NR	Fjord of Pta. Arenas	Antarctic Region	Canadian Arctic
α-HCH	<0.001	6.0	3.5	5.4	5.5	7.3	4.6	4.0; ^c 2.8; ^d 0.3–12 ^e	55; ^b 12–21 ^e
γ-HCH	1.16	6.1	6.3	44	6.6	8.8	7.4	3.8; ^c 22; ^d 0.7–45 ^e	12; ^b 2.9–15 ^e
ΣHCH		12	9.8	49	12	16	12		
α/γ		0.99	0.55	0.12	0.83	0.83	0.61	0.1–3 ^e	1.3–7.2 ^e
TC	0.94	1.9	2.3	26	2.3	3.3	2.6	0.82; ^c 0.90 ^d	0.64 ^b
CC	<0.001	2.1	2.0	6.6	2.3	3.4	2.6	0.96; ^c 0.2 ^d	1.32 ^b
TN	<0.001	1.2	1.4	2.6	1.5	2.1	1.6	0.10 ^d	1.14 ^b
ΣCHL		5.2	5.7	35	6.1	8.8	6.8		3.1 ^b
TC/CC		0.92	1.15	3.9	1.0	0.98	1.0		
HEPT	<0.001	BDL	3.24	50	BDL	BDL	BDL		0.04 ^b
HEPTX	<0.001	BDL	0.35	105	BDL	BDL	BDL	0.54 ^c	1.4 ^b
endosulfan I	<0.29	99	61	3.5	7.3	5.1	8.3		6.6 ^b
endosulfan II	<0.29	1.6	1.8	0.46	2.3	3.1	2.6		
Σendosulfan		101	63	4.0	9.6	8.2	11		
dieldrin	<0.24	2.2	3.8	25	0.98	1.2	1.4		1.3 ^b
pp'-DDE	1.70	NA	NA	NA	NA	NA	NA	0.40 ^d	0.62 ^b
op'; pp'-DDD	<0.13	NA	NA	NA	NA	NA	NA	0.07–0.10 ^d	
op'; pp'-DDT	<0.13	ND	ND	ND	ND	ND	ND	0.20–0.28 ^d	
ΣDDT									
toxaphene	<3.5	BDL	BDL	BDL	BDL	BDL	BDL		

^a BDL replaced by MDL. ^b Annual average 1994 calculated from ref 3. ^c Mean values. 1990 from Southern Ocean and Antarctica (5). ^d Mean values from December 1994–April 1995 (6). ^e Concentrations of HCHs in air from Arctic and Antarctic (8). ^f Abbreviations: BDL, below detection limit; MDL, method detection limit; NA, blank problem; ND, not detectable; NR, National Reserve; HCH, hexachlorocyclohexane; HEPT, heptachlor; HEPTX, heptachlor epoxide; TC, *trans*-chlordane; CC, *cis*-chlordane; TN, *trans*-nonachlor.

Hexachlorocyclohexanes (α- and γ-HCH). Air concentrations of α-HCH were consistent at all of the sampling sites, ranging from 3 to 7 pg m⁻³ (Table 5). This compared well with previous measurements in Antarctica, 3.8 pg m⁻³ (5); Terra Nova Bay, 5.9 pg m⁻³ (43); Southern Ocean, 3.1 pg m⁻³ (44); and Signy Island-Antarctica, 3.5 pg m⁻³ (6). It is interesting to note that levels of α-HCH reported from the Arctic are about 20 times greater (3) and reflect the much greater cumulative use of technical HCH in the Northern Hemisphere (45).

With the exception of Concepción City, levels of γ-HCH were consistent across sampling sites and ranged from 6 to 9 pg m⁻³. The ratio of α-/γ-HCH was also consistent (0.8 ± 0.2) and similar to results obtained from the Signy Island, Antarctica, where α-/γ- was 0.4–0.8 during a clean air period (6). In Concepción, the air concentration of γ-HCH was almost four times greater (44 pg m⁻³) with a much lower α/γ ratio of 0.1. These findings possibly reflecting continued local use and/or re-emission of lindane that was previously used for agricultural purposes throughout this central valley. Previous studies have also reported high levels of γ-HCH in fish and birds in Central Chile (16, 46, 47). Lindane was banned in Chile in 1998 for agricultural purposes; however,

this does not preclude its potential continued and unwarranted use in the region.

Heptachlor and Heptachlor Epoxide. Heptachlor (Hept) and its epoxide degradation product (HeptX) were detected at only two sites—Concepción City and Laja Lake—and were the most abundant pesticides in Concepción with concentrations of 50 and 105 pg m⁻³, respectively. With the exception of Laja lake, levels of Hept and HeptX in remote Chilean areas were lower than results from the Arctic where concentrations fluctuated from 0.05 to 0.07 pg m⁻³ and 0.92–1.47 pg m⁻³, respectively (3).

Chlordanes. Chlordanes (*trans*-, *cis*-, and *trans-nonachlor*) were detected at all sites with consistent concentrations in the range of 5–9 pg m⁻³ for the sum of the isomers (ΣCHL) (Table 5, Figure 4). Mean concentrations on an individual basis (excluding Concepción) were as follows: 2.5 ± 0.52 pg m⁻³ for TC, 2.5 ± 0.55 pg m⁻³ for CC, and 1.6 ± 0.34 pg m⁻³ for TN. These values are similar to reported concentrations at other remote sites (Table 5). Levels at Concepción were ~10 times higher for TC (26 pg m⁻³) and ~3 times higher for CC (6.6 pg m⁻³), indicating a potential source of chlordane in this area.

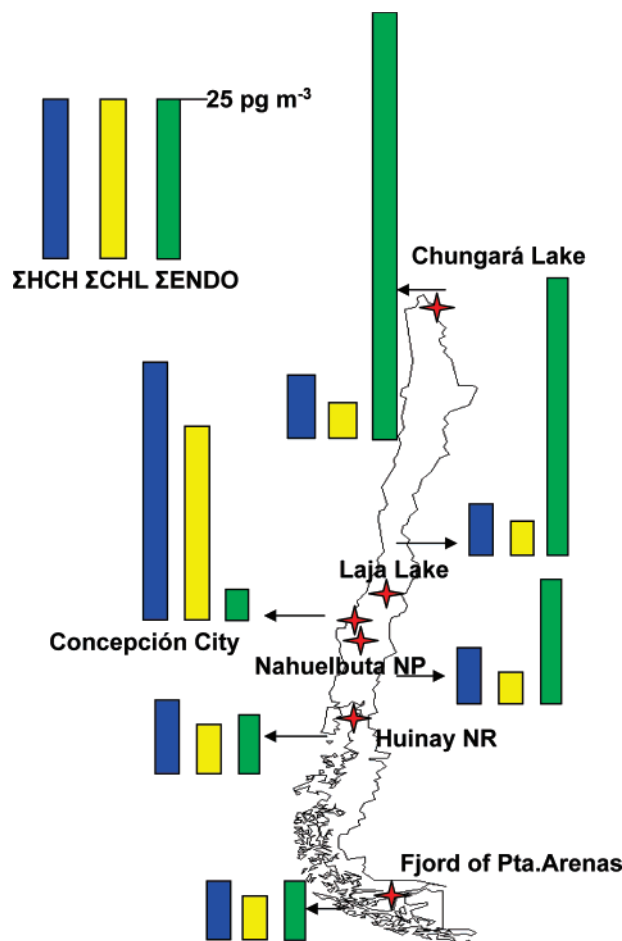


FIGURE 4. Passive sampler derived air concentrations for selected groups of organochlorine pesticides in pg m^{-3} . $\Sigma\text{HCH} = \alpha\text{-HCH} + \gamma\text{-HCH}$; $\Sigma\text{CHL} = \text{TC} + \text{CC} + \text{TN}$; $\Sigma\text{ENDO} = \text{EndoI} + \text{EndoII}$ (see Table 5).

Technical chlordane has a TC/CC value of 1.56 (48). In light of the fact that TC degrades more quickly than CC in the environment, the ratio of TC/CC near to or less than 1 is indicative of aged chlordane, while values closer to 1.56 are indicative of fresh use and/or other sources of TC. At all sites except Concepción the TC/CC is near 1 (Table 5) indicating that what is measured in the air is likely due to past use. This is consistent with results from the Southern Ocean and Antarctica (5) where TC/CC = 0.85. The high levels of chlordanes, especially TC in Concepción (TC/CC = 4), is likely related to use of heptachlor which is also elevated in Concepción (Table 5). Technical heptachlor is contaminated with chlordane isomers, especially TC (49). Interestingly, of all the remote sites, Laja Lake has an elevated TC/CC ratio of 1.15 suggesting a probable influence of similar sources from Concepción City.

Dieldrin. As was previously observed for $\gamma\text{-HCH}$ and chlordanes, dieldrin also exhibits elevated concentrations in Concepción (25 pg m^{-3}) possibly due to current/past use in the central agricultural valley. The result for Concepción is similar to data from Belize City, 34 pg m^{-3} (50), and in Senga Bay, Africa, 80 pg m^{-3} (51). At remote/background sites in Chile, dieldrin concentrations were low with values of $1\text{--}4 \text{ pg m}^{-3}$ along the transect. This is similar to values reported for the Canadian Arctic, 1.3 pg m^{-3} (3).

Endosulfans. Endosulfan I is a currently used OCP that is globally distributed. For instance, air concentrations of $1\text{--}61 \text{ pg m}^{-3}$ are reported in Senga Bay, Africa (51), and in Southern Ontario, Canada, where endosulfan is still used, levels of 825

pg m^{-3} have been reported in an agricultural region (26). Levels of endosulfan in the Canadian Arctic have increased slightly over the period 1993–1999 with an average of 4.2 pg m^{-3} (4).

Of all of the chemicals investigated in this study, Endosulfan I shows the most interesting latitudinal transect with highest concentrations at Chungará Lake (99 pg m^{-3}) and Laja Lake (61 pg m^{-3}) and lower concentrations ($0.5\text{--}3.0 \text{ pg m}^{-3}$) at more southerly sites (Table 5, Figure 4). Air back trajectories (Figure 2) suggest that regions to the north are possible sources of endosulfan. In other areas of South America endosulfan is one of the only chlorinated pesticides allowed for agricultural use, and it has been imported since the early 1970s in considerable amounts. Imports of endosulfan to Argentina from 1992 to 1994 amounted to 641 tonnes from which 92–96% is the active ingredient (52), while Uruguay imported for the period 1973–2001 approximately 204 tonnes (52). Recent available data show that Brazil produced 1.6 and imported 3.4 tonnes of endosulfan in 2000 (52). In Chile, endosulfan continues to be used; however, fresh inputs could be related to the intensive use of insecticides, namely Decisdan and Thionex in which the principal active component is endosulfan. Concentrations of endosulfan II were much lower and consistent across all sites (Table 5).

DDTs. Due to interferences and reduced instrument sensitivity, results for DDT isomers are not reported. Values are reported for each isomers as less than the MDL ($<\text{MDL}$): DDE (<1.70); DDD and DDT (<0.13) (Table 5).

PBDEs. In all cases, PBDE levels were below detection limits. Results are therefore reported for each congener as $<\text{MDL}$ (pg m^{-3}): <0.69 for PBDE-17, <0.81 for PBDE-28, <1.10 for PBDE-47, <0.21 for PBDE-66, <0.77 for PBDE-100, <0.94 for PBDE-99, <0.42 for PBDE-85, <0.41 for PBDE-154, <0.44 for PBDE-153, and <0.25 for PBDE-190. Consequently, ΣPBDE is less than 6 pg m^{-3} at all sites.

Implications. The results from this study demonstrate the practical application of PASSs to investigate spatial trends of POPs over a large latitudinal scale. The measurements obtained here represent a first step in obtaining air data from remote and background areas in Chile. However, to better understand the link between sources and receptors and to develop and validate models of chemical fate, a more extensive air sampling network is required that would include other surrounding countries on the continent, particularly Bolivia, Brazil, Perú, Uruguay, and Argentina which have historically been the largest consumers of pesticides.

Acknowledgments

Thanks to the Chilean Army (FACH) for help with sampling at Chungará Lake. Thanks also to CONAF (National Forestry Corporation) for the permission to deploy and provide facilities to the researchers in the National Parks of Chile. Thanks to Dr. Cristian Mella from the NOVA Austral S.A. Aquaculture Centre and Dr. Humberto Campos from University of Tarapaca-Chile, for their help deploying PASSs in Chile, and to FONDECYT (Chile) Grant 1010640 for supporting the field work.

Literature Cited

- Iwata, H.; Tanabe, S.; Sakai, N.; Tatsukawa, R. *Environ. Sci. Technol.* **1993**, *27*, 1080–1098.
- Stern, G. A.; Halsall, C. J.; Barrie, L. A.; Muir, D. C. G.; Fellin, P.; Rosenberg, B.; Rovinsky, F. Y.; Kononov, E. Y.; Pastuhov, B. *Environ. Sci. Technol.* **1997**, *31*, 3619–3628.
- Halsall, C. J.; Bailey, R.; Stern, G. A.; Barrie, L. A.; Fellin, P.; Muir, D. C. G.; Rosenberg, B.; Rovinsky, F. Y.; Kononov, E. Y.; Pastukhov, B. *Environ. Pollution* **1998**, *102*, 51–62.
- Hung, H.; Halsall, C. J.; Blanchard, P.; Li, H. H.; Fellin, P.; Stern, G.; Rosenberg, B. *Environ. Sci. Technol.* **2002**, *36*, 862–868.

- (5) Bidleman, T. F.; Walla, M. D.; Roura, R.; Carr, E.; Schmidt, S. *Mar. Pollut. Bull.* **1993**, *26*, 258–262.
- (6) Kallenborn, R.; Oehme, M.; Wynn-Williams, D. D.; Schlabach, M.; Harris, J. *Sci. Total Environ.* **1998**, *220*, 167–180.
- (7) Ockenden, W.; Lohmann, R.; Shears, J. R.; Jones, K. C. *Environ. Sci. Pollut. Res.* **2001**, *8* (3), 189–194.
- (8) Lakaschus, S.; Weber, K.; Wania, F.; Bruhn, R.; Schrems, O. *Environ. Sci. Technol.* **2002**, *36*, 138–145.
- (9) Montone, R. C.; Taniguchi, S.; Weber, R. R. *Sci. Tot. Environ.* **2003**, *308*, 167–173.
- (10) UNEP 2003. *Regionally Based Assessment of Persistent Toxic Substances*; Global Report; UNEP-Chemicals: Geneva, Switzerland, 2003; p 220.
- (11) Ikonomou, M. G.; Rayne, S.; Addison, R. F. *Environ. Sci. Technol.* **2002**, *36*, 1886–1892.
- (12) Breivik, K.; Sweetman, A.; Pacyna, J.; Jones, K. J. *Sci. Total Environ.* **2002**, *290*, 199–224.
- (13) Comisión Nacional del Medio Ambiente (CONAMA). PCBs en Chile: DIAGNOSTICO Nacional de Contaminantes Organicos Persistentes (COPs), 2001, Documento de trabajo N°2.
- (14) Mandalakis, M.; Stephanou, E. *Environ. Toxicol. Chem.* **2002**, *Vol 21*, (11), 2270–2275.
- (15) Servicio Agrícola y Ganadero de Chile (SAG). Legislación de plaguicidas de uso agrícola en el país 1980, Decreto de ley N°3557.
- (16) Pantoja, S.; Pastene, L.; Becerra, J.; Silva, M.; Gallardo, V. A. *Mar. Pollut. Bull.* **1985**, *16*, 255.
- (17) Fuentealba, M. *Bol. Soc. Biol. Concepción* **1997**, *68*, 39–46.
- (18) Bonert, C.; Estrada, R. Sociedad Chilena de Ciencias Marinas, 18th Congreso de Ciencias Marinas, 1998; p 72.
- (19) Barra, R.; Pozo, K.; Urrutia, R.; Sisternas, M.; Pacheco, P.; Focardi, S. *Bol. Soc. Chilena Quím.* **2001**, *46*, 149–159.
- (20) IPCS. *Environmental Health Criteria* 192; World Health Organization: Geneva, Switzerland, 1997.
- (21) Shoeib, M.; Harner, T. *Environ. Sci. Technol.* **2002**, *36*, 4142–4151.
- (22) Harner, T.; Shoeib, M. *J. Chem. Eng. Data* **2002**, *47*, 228–232.
- (23) Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. *Environ. Sci. Technol.* **2004**, *38*, 34–41.
- (24) Jaward, F. M.; Farrar, N. J.; Harner, T.; Sweetman, A. J.; Jones, K. C. *Environ. Tox. Chem.* **2004**, *23*, 1355–1364.
- (25) Shen, L.; Wania, F.; Lei, Y. D.; Teixeira, C.; Muir, D. C. G.; Bidleman, T. F. *Environ. Sci. Technol.* **2004**, *38*, 965–975.
- (26) Harner, T.; Shoeib, M.; Diamond, M.; Stern, G.; Rosenberg, B. *Environ. Sci. Technol.* Accepted for publication.
- (27) Bertoni, G.; Tappa, R.; Allegrini, I. The internal consistency of the 'analyst' diffusive sampler – a long-term field test. *Chromatographia* **2001**, *653*–657.
- (28) Harner, T.; Mackay, D. *Environ. Sci. Technol.* **1995**, *29*, 1599–1606.
- (29) Harner, T.; Bidleman, T. F. *J. Chem. Eng. Data* **1996**, *41*, 895–899.
- (30) Kömp, P.; McLachlan, M. S. *Environ. Tox. Chem.* **1997**, *16*, 2433–2437.
- (31) Shoeib, M.; Harner, T. *Environ. Tox. Chem.* **2002**, *21*, 984–990.
- (32) Meijer, S.; Shoeib, M.; Jantunen, L. M. M.; Jones, K. C.; Harner, T. *Environ. Sci. Technol.* **2002**, *37*, 1292–1299.
- (33) Shoeib, M.; Harner, T.; Ikonomou, M.; Kannan, K. *Environ. Sci. Technol.* **2004**, *38*, 1313–1320.
- (34) Panshin, S. Y.; Hites, R. A. *Environ. Sci. Technol.* **1994**, *28*, 251–257.
- (35) Halsall, C. L.; Lee, R. G. M.; Coleman, P. J.; Burnett, V.; Harding-Jones, P.; Jones, K. C. *Environ. Sci. Technol.* **1995**, *29*, 2368–2376.
- (36) Manchester-Neesvig, A.; Andren, W. *Environ. Sci. Technol.* **1989**, *23*, 1138–1148.
- (37) Currado, G. M.; Harrad, S. *Environ. Sci. Technol.* **2000**, *34*, 78–82.
- (38) Giam, C. S.; Atlas, E.; Chan, H.; Neff, G. S. Phthalate esters, PCB and DDT residues in the Gulf of Mexico atmosphere. *Atmos. Environ.* **1980**, *14*, 65–69.
- (39) Sericano, J. L.; Wade, T. L.; Jackson, T. J.; Brooks, J. M.; Trip, B. W.; Farrington, J. W.; Mee, L. D.; Readmann, J. W.; Villeneuve, J. P.; Goldberg, E. D. *Mar. Poll. Bull.* **1995**, *31*, 214.
- (40) Barra, R.; Quiroz, R.; Mendoza, G.; Urrutia, R.; Pozo, K.; Focardi, S. *Organohalogen Compd.* **2002**, *58*, 481–484.
- (41) Patton, G. V.; Walla, M.; Bidleman, T.; Barrie, L. J. *J. Geophys. Res.* **1991**, *96/D6*, 867–877.
- (42) Richert, P.; Parra, R.; Calseron, K.; Romero, R.; Luque de Castro, M. D. Abstract of Papers, 24th Jornadas Chilenas de Químicas, Temuco, Chile, 2002, 28–30.
- (43) Oehme, M.; Haugen, J.-E.; Kallenborn, R.; Schlabach, M. *Organohalogen Compd.* **1994**, *20*, 523–528.
- (44) Weber, R. R.; Montone, R. C. In *Long-Range Transport of pesticides*; Kurtz D. A., Ed.; Lewis Publishers ed.; United States, 1990; Chapter 13, p 185.
- (45) Li, Y.-F.; Scholtz, M. T.; Van Heyst, B. J. J. *J. Geophys. Res.* **2000**, *105*, 6621–6632.
- (46) Ober, A.; Valdivia, M.; Santa Maria, I. *Bull. Environ. Contam. Toxicol.* **1987**, *38*, 528–533.
- (47) Focardi, S.; Fossi, C.; Leonzio, C.; Corsolini, S.; Parra, O. *Environ. Monit. Assess.* **1996**, *43*, 73–92.
- (48) Bidleman, T.; Jantunen, L.; Helm, P.; Brorstrom-Lunden, E.; Juntto, S. *Environ. Sci. Technol.* **2002**, *36*, 539–544.
- (49) World Health Organization. *Environmental Health Criteria 38: Heptachlor*; Geneva, Switzerland, 1984; pp 6–20.
- (50) Alegria, H. A.; Bidleman, T. F.; Shaw, T. J. *Environ. Sci. Technol.* **2000**, *34*, 1953–1958.
- (51) Karlsson, H.; Muir, D. C. G.; Teixeira, C. F.; Burniston, D. A.; Strachan, W. M. J.; Hecky, R. E.; Mwita, J.; Bootsma, H. A.; Grift, N. P.; Kidd, K. A.; Rosenberg, B. *Environ. Sci. Technol.* **2000**, *34*, 4490–4495.
- (52) UNEP, 2002 Regionally Based assessment of Persistent Toxic Substances, Eastern and Western South America Regional Report, 2002, 90 pp.
- (53) Hoff, R. M.; Strachan, W. M. J.; Sweet, C. W.; Chan, C. H.; Shackleton, M.; Bidleman, T. F.; Brice, K. A.; Burniston, D. A.; Cussion, S.; Gatz, D. F.; Harlin, K.; Schroeder, W. H. *J. Atmos. Environ.* **1996**, *30*, 3505–3527.

Received for review June 21, 2004. Revised manuscript received August 25, 2004. Accepted August 30, 2004.

ES0490651