

# Altitudinal and Seasonal Variations of Persistent Organic Pollutants in the Bolivian Andes Mountains

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Polyurethane foam disk passive air samplers were deployed over four periods of approximately 3 months along an altitudinal gradient (1820, 2600, 4650, and 5200 masl) on the east side of the Andean mountain range in Bolivia. The purpose of the study was to assess the gas-phase concentration and the altitudinal and seasonal trends of organochlorine pesticides and polychlorinated biphenyls (PCBs). Target compounds that were regularly detected included  $\alpha$ - and  $\gamma$ -hexachlorocyclohexane (HCH), endosulfans, and select PCB congeners. Endosulfans and HCH concentrations increased with altitude. Enrichment factors (concentration at the highest altitude divided by concentration at the lowest altitude) ranged from 10 to 20 for HCHs and 3 to 10 for endosulfans. Air parcel back trajectory analysis indicated that, in general, the high-altitude sites were exposed to a larger airshed and hence susceptible to long-range atmospheric transport from more distant regions. Seasonal differences were also observed with  $\Sigma$ HCH concentrations peaking during periods 2 and 3 (March–September 2005). Airsheds (derived from the analysis of back trajectories) for periods 2 and 3 were less oriented along the Andes range (mountain air) with greater input from coastal regions. Endosulfans peaked during periods 1 and 2 (February–June 2005) and also exhibited the highest air concentrations of the target compounds, reaching  $\sim 1500$  pg/m<sup>3</sup> at the two highest elevation sites. PCB air concentrations at all sites were generally typical of global background values ( $< 12$  pg/m<sup>3</sup>) and showed no increase with altitude. This is the first study to measure air concentrations of persistent organic pollutants (POPs) in Bolivia and one of only a few studies to investigate altitudinal gradients of POPs.

## Introduction

Persistent organic pollutants (POPs), such as organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), are stable in the environment, toxic, resistant to the photolytic, chemical, and biological degradation, and undergo long-range atmospheric transport (LRAT) (1). Consequently they remain in the environment and are available to bioaccumulate through the food chain, posing a risk to human and

ecosystem health (2–9). Concern has arisen during the past few decades about the presence of POPs in the environment. With vapor pressures between  $10^{-2}$  and  $10^{-5}$  Pa, POPs tend to cycle between the earth's surface and the atmosphere—evaporating at ambient temperature and condensing when temperatures cool (2, 3, 5). In the past decade, many studies have shown that POPs have a worldwide distribution. Their ability to transport through the atmosphere allows them to enter a variety of remote ecosystems, such as polar regions, high mountains, and open seas (6–11).

So far no studies have measured POPs concentrations in Bolivia (12). Bolivia is a country with a diverse climate and biology. It is divided into two main regions: in the east, the mainly forested low lands of the Amazon with an annual mean temperature of about 20 °C and annual precipitation up to 3000 mm, and to the west, the highlands (Andean Plateau) with peaks that rise up to 6000 masl, eternal snow, an annual mean temperature of less than 1 °C, and annual precipitation of about 500–1000 mm. This area contains diverse ecosystems (13) and is home to several big mammals such as the Andean bear, puma, lama, vicuna, and fox (13). The southwest of Bolivia is crossed by the Andean Mountain range, which is the second highest in the world (after the Himalayas) peaking at 6952 m (Aconcagua). In Bolivia, the Andes are split into the Oriental and Occidental ranges, and between these ranges lies the Bolivian (Andean) Plateau that covers an area of approximately 100000 km<sup>2</sup> where more than half of the Bolivian population resides. With an average altitude between 3600 and 4000 masl, it is the second highest plateau in the world (14). The climate of the plateau is variable with daily temperature extremes of up to 30 °C (13).

Very little is known about the use of OCPs and PCBs in Bolivia; however, studies in surrounding countries have identified potential continental sources through LRAT (12). Agricultural regions within Bolivia are also expected to be sources of some OCPs. The transport of POPs to Bolivia's alpine regions is of particular interest given its biological diversity as discussed above and potential threats posed by exposure to POPs. Other studies have shown that alpine regions may act as cold condensers and accumulate POPs from the atmosphere (15–17).

The purpose of this study was to assess the atmospheric concentration of PCB and selected OCP compounds on an altitudinal gradient (1820–5200 masl) on the west side of the Occidental Andean mountain range. Polyurethane foam (PUF) disk passive air samplers were deployed at four sites over four sampling periods of approximately 3 months. This is the first atmospheric study of POPs in Bolivia and is a subproject of the Global Atmospheric Passive Sampling (GAPS) study, which was established for researching the spatial and temporal trends of POPs globally (18).

## Materials and Methods

**Sampler Preparation and Deployment.** Prior exposure PUF disks (14 cm diameter; 1.35 cm thick; surface area, 365 cm<sup>2</sup>; mass, 4.40 g; volume, 207 cm<sup>3</sup>; density, 0.0213 g cm<sup>3</sup>; Tisch Environmental, Village of Cleaves, Ohio), were precleaned (by washing with water and then Soxhlet extraction in acetone, 24 h, followed by petroleum ether, 24 h) and fortified with seven depuration compounds (DCs) (*d*<sub>6</sub>- $\gamma$ -hexachlorocyclohexane and PCB congeners 3, 9, 15, 30, 107, and 198) at the Hazardous Air Pollutants Laboratory, Thomson Laboratories, Environment Canada, in Toronto. DCs are added to determine the site-specific sampling rate as described previously (18, 19). Prior to and after sampler collection and during shipping, PUF disks were stored in

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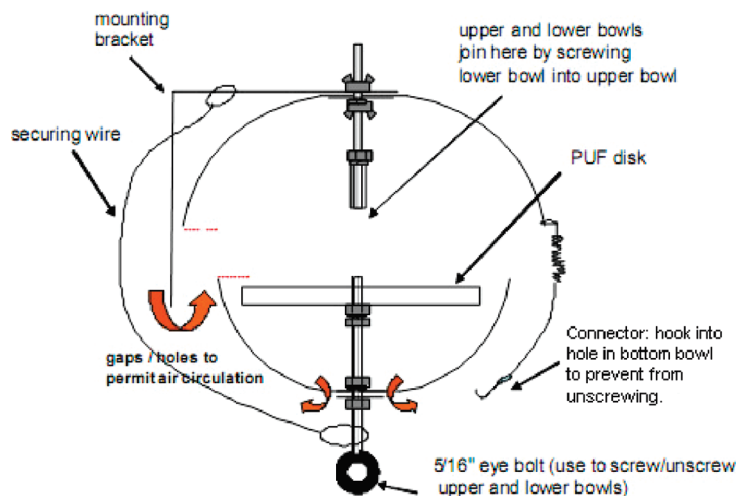


FIGURE 1. Schematic representation of the PUF disk sampler and photo of sampler deployed at Alto Hurnuni, 2600 masl.

TABLE 1. Information on Passive Sampling Sites

sampling site	latitude/longitude	altitude masl <sup>a</sup>	annual mean temp (°C)
Bajo Hurnuni	16°, 12' S/67°, 53' W	1820	17 <sup>b</sup>
Alto Hurnuni	16°, 11' S/67°, 53' W	2600	13 <sup>b</sup>
Base Huayna	16°, 17' S/68°, 07' W	4650	2 <sup>c</sup>
Campamento de Roca	16°, 16' S/68°, 08' W	5192	1 <sup>c</sup>

<sup>a</sup> masl = meters above sea level. <sup>b</sup> Source: Bach et al. 2003, Marcus Schawe 2001–2002 (personal communication). <sup>c</sup> Source: "réseau d'observation du Glacier Zongo, ORE et MEVIS-IRD-France", 2005.

solvent-cleaned, 1 L amber glass jars having Teflon-lined lids. PUF disks were handled using solvent-rinsed tongs. Sampling chambers were prewashed and solvent-rinsed with acetone prior to installation of the PUF disk, which was done using clean gloves. Passive air samplers were mounted in open areas with no obstruction of airflow. PUF disks were housed in stainless steel chambers (Figure 1) (19–21) that provided protection from direct precipitation, UV sunlight, and particle deposition and that also reduced the dependence of sampling rate on wind speed (19).

Four samplers were deployed—one sampler per site (21)—for four periods of approximately three months duration over the period of February 2005 to January 2006 at four background sites in Bolivia (Table 1 and Figure S1 showing map and locations). The samplers were located along an altitudinal gradient (1820, 2600, 4650, and 5198 masl), with a southeast exposure. The risk of sample contamination during handling, transport, and storage (up to nearly 6 months) was investigated by collecting two field blanks at Bajo Hurnuni and Campamento de Roca by installing PUF disks into the chambers for 30 s and then removing and treating them as a sample. Two solvent blanks (method blanks) were also performed to assess contamination during

extraction and analysis (19). The period 1 sample from Base Huayna (4650 masl) was lost during transport.

**Extraction and Analysis.** For assessing the effectiveness of the extraction and cleanup procedures, the PUF disks were spiked with a method recovery standard consisting of <sup>13</sup>C-PCB-105 (260 ng), *d*<sub>6</sub>-α-hexachlorocyclohexane (220 ng), and *d*<sub>8</sub>-*p,p'*-DDT (240 ng) (CIL Andover, MA). Details of sample extraction and cleanup are presented elsewhere (18–22). Mirex (100 ng) was added as an internal standard to correct for volume differences.

All samples and field blanks were analyzed for 20 OCPs—α-, β-, γ-, and δ-hexachlorocyclohexane (HCH), aldrin, dieldrin, heptachlor, heptachlor epoxide, *cis*-chlordane (CC), *trans*-chlordane (TC), *trans*-nonachlor (TN), endosulfan (Endo) I, endosulfan II, endosulfan sulfate (SO<sub>4</sub>), *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT—using a mixture of standards obtained from Ultra Scientific (North Kingstown, RI, and U.S. Environmental Protection Agency, Research Triangle Park, NC). PCBs were quantified separately using a 48-component mixture (Ultra Scientific, North Kingstown, RI), and details were presented previously (19, 22).

PCBs and OCPs were analyzed on a Hewlett-Packard 6890 gas chromatograph—5973 mass spectrometer (GC-MS) using electron impact—selected ion monitoring (EI-SIM) for PCBs and negative chemical ionization (NCI) for OCPs in SIM mode with methane as the reagent gas with a flow of 2.2 mL/min. Details are provided elsewhere (19, 22) for GC conditions, EI analysis of PCBs, and NCI analysis of OCPs as well as for information regarding target/qualifier ions of target compounds.

## Results and Discussion

**Quality Assurance/Quality Control.** Method detection limits (MDL) in air samples were based on the GAPS study (18), and it was defined as the average of the field blanks (*n* = 30) plus three standard deviations (SDs) of the average. When target compounds were not detected in blanks, one-half of the instrumental detection limits (IDL) value was substituted for the MDL, and one-half of the MDL was used for calculating means for a particular chemical in cases of nondetected

peaks. All qualified data (i.e., exceeding the MDL) have been blank corrected. MDL values are given in Table 2.

Method recoveries for target PCBs and OCPs were generally >85% (18, 19). Surrogate recoveries were  $(94 \pm 15)$  % for  $^{13}\text{C}$ -PCB-105,  $(80 \pm 22)$  % for  $d_6$ - $\alpha$ -HCH, and  $(70 \pm 20)$  % for  $d_8$ - $p,p'$ -DDT, and they were used to confirm analytical integrity. The instrumental detection limits were determined by assessing the injection amount that corresponds to a signal-to-noise value of 3:1. For PCBs, IDL values ranged from 0.025 pg for dichlorobiphenyls to 0.31 pg for octachlorobiphenyls. For OCPs, IDLs ranged from 0.02 to 0.99 pg.

Solvent and field blanks levels were not detected for all the OCPs, with the exception of Endo I and TN in field blanks where levels were detectable but very low, 0.12 and 0.01 pg, respectively (Table S1).

**Air Parcel Back Trajectories.** To assess the potential influence of air mass movement from various source regions, 5-day air parcel back trajectories were calculated using the Canadian Meteorological Centre (CMC) trajectory model. Trajectories at 10 m above ground were produced once per day (12 noon) at each site resulting in a trajectory "spaghetti" plot for each site and for each sampling period. The 16 plots are summarized in Figure S2.

Overall, trajectories for a given period seem fairly similar at the four sites. However, upon further inspection, the trajectories at the higher elevation sites have a greater reach and sometimes extend over agricultural regions (potential source regions of OCPs) (see Figure S3). Trajectories during periods 1 and 4 were almost entirely land-based at all sites and followed the Andean range whereas period 2 and 3 showed a departure from this behavior with greater inputs from coastal areas and the Pacific Ocean region. Given the large geographic scale of the air-sheds (geographic region that shares an air supply) that contributed to each sample, this technique is not capable of distinguishing the influence of local sources.

**Deriving Air Concentrations from Depuration Compounds Recoveries.** Losses of DCs from the deployed PUF disks were used to assess the site-specific air sampling rate. This, combined with the  $K_{OA}$  values for the target chemicals, was used to calculate the effective air volume and ultimately air concentration. Details for this calculation have been presented in earlier papers (18, 19). Previous calibration studies and field deployments where DCs were used have shown that the PUF disk sampling rate,  $R$ , is on the order of 3–4 m<sup>3</sup>/day (18, 19, 22). The mean value of  $R$  ( $n = 8$ ) for this study (periods 3 and 4 only) is  $2.7 \pm 1.1$  m<sup>3</sup>/day (Table S2) which compares well to the value of  $3.9 \pm 2$  m<sup>3</sup>/day derived for more than 50 sites operated under the GAPS study (18). The GAPS sampling range average value was used for calculating air concentrations during period 1 and period 2 where DC losses were insufficient to calculate site specific rates. Sampling rates for the four sites were uniform across sites during period 3, at about 2.4 to 2.5 m<sup>3</sup>/day, and more variable during period 4, ranging from 2 to 5 m<sup>3</sup>/day. Variability in sampling rates is attributed to site-specific meteorology, such as wind speed, that may have an effect on the sampling rate (23).

**Air Concentrations for Target POPs.** Table 2 reports air concentrations for several OCPs and  $\Sigma$ -PCBs during four deployment periods, from February 2005 to January 2006. Results for HCHs, endosulfans, and PCBs, which were all detected consistently at most sites, are considered in detail with respect to seasonal and altitudinal differences. The remaining OCPs that were screened had very low concentrations and/or were BDL in most samples. These are considered briefly here.

Chlordane concentrations were low at all sites and typically near or BDL. This is consistent with global background concentrations of chlordanes (18) and with mea-

surements at alpine sites in Chile in 2003 (19) where the concentration of individual chlordane isomers was between 1 and 4 pg/m<sup>3</sup>.

Heptachlor (hept) and heptachlor epoxide (hepx) were BDL in most samples—consistent with previous results from alpine sites in Chile (19). Heptachlor is an insecticide that was used primarily against soil insects and termites but also against cotton insects, grasshoppers, and malaria-carrying mosquitoes. Heptachlor is metabolized in soils, plants, and animals to heptachlor epoxide, which is more stable in air and biological systems and is carcinogenic (12). Three cases of elevated hepx concentrations were observed—at Base Huayna during period 2 and 4 (276 and 54 pg/m<sup>3</sup>) and at the highest elevation site, Campo Roca, during period 2 (250 pg/m<sup>3</sup>) (Table 2).

DDT isomers were also BDL most of the time. In two cases, the dominant isomer in technical DDT,  $p,p'$ -DDT (technical DDT is a mixture of about 85%  $p,p'$ -DDT and 15%  $o,p'$ -DDT), was detected at the lowest elevation site, Bajo Hurnuni, at concentrations of 99 pg/m<sup>3</sup> (period 3) and 119 pg/m<sup>3</sup> (period 4) (Table 2). DDT use in South America began during the 1940s primarily to control insects that are vectors for diseases such as malaria, dengue fever, and typhus. Following this, it was widely used in agriculture. DDT continues to have limited use in the control of vector diseases in South America (12).

Back trajectory analysis (Figure S2) was not helpful in explaining the intermittent detection of these three target classes/compounds.

**Hexachlorocyclohexanes ( $\alpha$ - and  $\gamma$ -HCH).** HCH was used as a commercial insecticide in two formulations: (i) technical HCH, which includes multiple stereoisomers and is dominated by  $\alpha$ -HCH (~80%) and  $\gamma$ -HCH (10–15%), and (ii) lindane, which consists almost entirely of the  $\gamma$ -isomer (20, 21). Air concentration (pg/m<sup>3</sup>) ranged from BDL (0.1) to 19 (arithmetic mean, AM = 6.9 and geometric mean, GM = 3.4) for  $\alpha$ -HCH, and it ranged from BDL (0.3) to 49 (AM = 15 and GM = 9) for  $\gamma$ -HCH (Table 2, Figure 2). These agree well with results from alpine sites in Chile (9.8–49 pg/m<sup>3</sup>) (19) and with the data reported for coastal areas of Brazil, Uruguay, and Argentina (3.9–32.5 pg/m<sup>3</sup>) (24).

The relative abundance of the two isomers is often expressed by the  $\alpha/\gamma$  ratio. The  $\alpha/\gamma$ -HCH ratio in the technical mixture is around 4–7 (24–26). In this study the  $\alpha/\gamma$ -HCH ratio ranged from 0.06 to 1.19, with an average of  $0.66 \pm 0.4$ , reflecting the more recent use of lindane. Similar values were reported for Signy Island in Antarctica ( $\alpha/\gamma = 0.4$ –0.8) (24), Chile ( $\alpha/\gamma = 0.12$ –0.99) (19), and along the coastlines of Brazil, Uruguay, and Argentina ( $\alpha/\gamma = 0.3$ –3.3) (24).

A gradient in air concentrations was observed for both  $\alpha$ - and  $\gamma$ -HCH, with highest concentrations at the higher altitude sites (Figure 2). The enrichment factor (EF, ratio of compound concentration at highest altitude versus lowest altitude) was as high as 10–20 for  $\alpha$ -HCH during periods 2 and 3—the only periods where  $\alpha$ -HCH was detected at the two highest elevation sites. Similar EF values were observed for  $\gamma$ -HCH and were consistent across all seasons. Similar enrichment of  $\alpha$ - and  $\gamma$ -HCH at high altitude sites were reported for the Rocky Mountains (15, 27) and the central Himalayas (28).

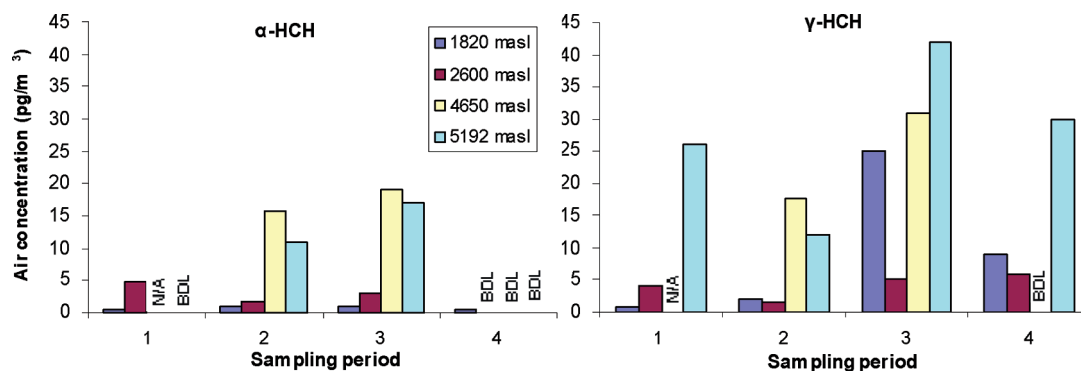
Some seasonal differences in air concentrations were observed for the  $\alpha$ - and  $\gamma$ -HCH isomers. Although  $\alpha$ -HCH concentrations remained low (<5 pg/m<sup>3</sup>) at the two low altitude sites across all seasons, higher concentrations were detected during periods 2 and 3 at the two high altitude sites. For  $\gamma$ -HCH, air concentrations were low during period 1 and increased during period 2 to 4. Back trajectories (Figure S2) show that periods 2 and 3 are characterized by greater proportion of air arriving from coastal areas in Chile/Pacific Ocean with less of a contribution from regional Andean mountain air. Coastal sources associated with agriculture



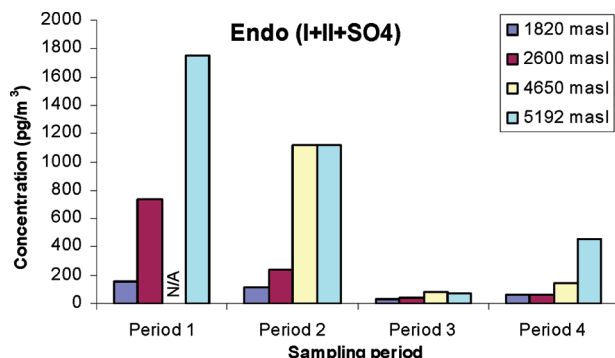
**TABLE 2. Air Concentration (pg/m<sup>3</sup>) of Select OCPs and Sum of 48 PCB Congeners at Four Locations along an Altitudinal Gradient in the Bolivian Andes Mountains during Four Sampling Periods in 2005<sup>a</sup>**

location (masl)	period <sup>b</sup>	mean temp (°C)	α-HCH	γ-HCH	Σ-HCH	hept	hepx	TC	CC	TN	Σ-chl	Endo I	Endo II	Endo SO <sub>4</sub>	Σ-Endo	p,p'-DDT	Σ-PCBs
Bajo Hurnuni 1820	1	17.3	0.54	0.82	1.4	BDL	BDL	0.18	BDL	BDL	0.18	149	3.7	5.4	158	BDL	5
Alto Hurnuni 2600	1	13.4	4.9	4.12	9	BDL	BDL	0.46	0.4	0.36	1.8	658	38	40	736	BDL	12
Base Huayna 4650	1	2.5 <sup>c</sup>	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Campo Roca 5200	1	2 <sup>c</sup>	BDL	26	26	BDL	BDL	BDL	BDL	BDL	BDL	1584	86	81	1751	BDL	BDL
Bajo Hurnuni 1820	2	17	1.1	2	3.1	0.5	BDL	0.2	0.4	0.1	0.7	105	3.6	8.2	117	BDL	7
Alto Hurnuni 2600	2	13	1.7	1.5	3.2	BDL	BDL	0.1	0.3	0.1	0.6	213	9.6	13	236	BDL	1
Base Huayna 4650	2	2 <sup>c</sup>	15.8	17.6	33.4	BDL	276	1.6	BDL	BDL	1.6	1055	41	27	1123	BDL	N/A
Campo Roca 5200	2	1.5 <sup>c</sup>	11	12.1	23.1	BDL	250	0.7	2.4	0.7	3.8	1078	21	18	1117	BDL	BDL
Bajo Hurnuni 1820	3	15.5	1	25	26	BDL	1	BDL	BDL	BDL	BDL	13	8	8	29	99	12
Alto Hurnuni 2600	3	11.5	3	5	8	BDL	BDL	BDL	BDL	BDL	BDL	20	13	6	39	BDL	9
Base Huayna 4650	3	1.3 <sup>c</sup>	19	31	50	BDL	BDL	BDL	BDL	BDL	BDL	75	6	4	85	BDL	BDL
Campo Roca 5200	3	-0.23 <sup>c</sup>	17	42	59	BDL	BDL	BDL	BDL	BDL	BDL	65	BDL	3	68	BDL	BDL
Bajo Hurnuni 1820	4	18	0.6	9	9.6	BDL	BDL	0.1	0.1	0.1	0.3	59	2.1	1.3	62.4	119	5
Alto Hurnuni 2600	4	14	BDL	6	6	BDL	BDL	0.2	BDL	BDL	0.2	57	6.9	2.5	66	BDL	5
Base Huayna 4650	4	2.2 <sup>c</sup>	BDL	BDL	BDL	BDL	54	BDL	BDL	BDL	BDL	143	BDL	BDL	143	BDL	BDL
Campo Roca 5200	4	1.5 <sup>c</sup>	BDL	30	30	BDL	BDL	BDL	BDL	BDL	BDL	453	BDL	BDL	453	BDL	BDL
MDL			0.1	0.3		0.1	0.1	0.1	0.4	0.2		0.7	0.8	0.5		0.5	0.12

<sup>a</sup> masl = meters above sea level; N/A = not available; BDL = below detection limit; MDL = method detection limit. Note: A value like 0 or BDL can be substituted for the respective method detection limit (MDL) value. <sup>b</sup> Period 1 (February–March 2005), period 2 (March–June 2005), period 3 (June–September 2005), and period 4 (September 2005–January 2006). <sup>c</sup> Source: “réseau d’observation du Glacier Zongo, ORE et MEVI-IRD-France”, 2005.



**FIGURE 2.** Air concentration (pg/m<sup>3</sup>) for α- and γ-HCH over four sampling periods along an altitudinal gradient in the Andes Mountains in 2005. BDL = below detection limit; N/A = not available; masl = meters above sea level; Sampling periods: period 1 (February–March 2005), period 2 (March–June 2005), period 3 (June–September 2005), and period 4 (September 2005–January 2006).



**FIGURE 3.** Air concentrations (pg/m<sup>3</sup>) for Σ-endosulfans (I + II + SO<sub>4</sub>) over four sampling periods along an altitudinal gradient in the Andes mountains in 2005. N/A = not available; masl = meters above sea level. Sampling periods: period 1 (February–March 2005), period 2 (March–June 2005), period 3 (June–September 2005), and period 4 (September 2005–January 2006).

and/or ocean-air transfer of HCHs may explain the higher concentrations during these periods. This pattern is magnified for the higher elevation sites that show an even larger region of influence through long-range transport. Some of this seasonal difference may also be attributed to the higher precipitation during periods 1 and 2 which may scavenge HCHs from the atmosphere reducing their concentration in the gas phase.

**Endosulfans (Endo I, II, and SO<sub>4</sub>).** Endosulfan is a modern OCP that is used globally. It comprises two isomers (Endo I and II, having a I/II ratio of about 2.3 in the technical mixture) that breakdown in the environment to produce endosulfan sulfate (SO<sub>4</sub>). Endosulfan is used on a wide range of crops and also for the control of disease vectors (29). Air concentration (pg/m<sup>3</sup>) of Σ-Endo (I + II + SO<sub>4</sub>) showed the highest levels of all the OCPs investigated, in the range of 28 to 1751 (AM = 412 and GM = 187) (Table 2, Figure 3). The Endo I/II ratio was typically much higher than 2.3. An increase in this ratio occurs because Endo II is less stable in air and also converts to Endo I after it is applied (30). This suggests that endosulfan concentrations, in particular those with highest I/II ratios, are not associated with fresh applications but rather an older source that is likely transported into the region. This is also confirmed by the presence of endosulfan SO<sub>4</sub> in almost all samples.

Air concentrations (pg/m<sup>3</sup>) for Endo I, the dominant congener, at this background location (AM = 382; GM = 159) are consistent with previous measurements at regional background sites and global alpine sites, reported under the GAPS study for January–March 2005: for instance (AM values, pg/m<sup>3</sup>), 280 at Sede Arauca (Colombia); 266 in Chungará

lake (North of Chile, boarder with Bolivia), and 129 at Whistler mountain on the west coast of Canada (18).

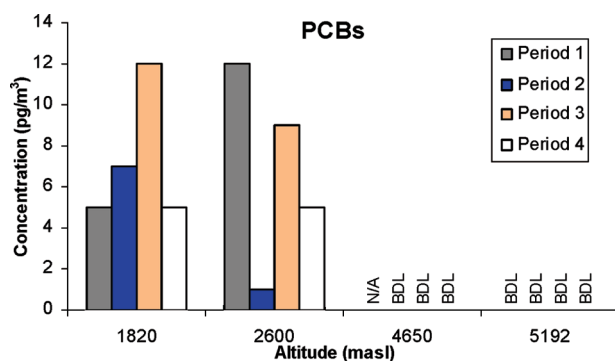
A strong altitudinal gradient was observed for Σ-Endo with EFs that ranged from about 3–10. These were highest during period 1, 2, and 3. Similar to the HCHs, the enrichment of endosulfan at the higher altitudes agrees with previous studies in the Rocky mountains and Himalayas (15, 27, 28). As discussed previously for HCHs, period 2 back trajectories show the greatest region of influence—especially from potential coastal source regions. Further, the airsheds for the two highest elevation sites are larger than the low lying sites (Figure S2).

Highest air concentrations for endosulfans occurred during periods 1 and 2, particularly at the two high elevation sites (~1600 pg/m<sup>3</sup> during period 2). This period coincides with higher agricultural activity during this time of the year (31). For instance, a very high Endo I air concentration of 14600 pg/m<sup>3</sup> was observed at an agricultural site at Bahía Blanca (Argentina) for the period January–March 2005, as reported under the GAPS study (18), demonstrating the potential inputs from agricultural regions in South America. Pozo et al. (19) saw a strong north–south gradient in air concentrations of Σ-endosulfans (pg/m<sup>3</sup>) at background and alpine sites in Chile during 2003 (19). Concentrations ranged from approximately 100 at Chungará lake (near Bolivia) to ~10 at the southernmost sites. This was attributed to a greater contribution of land-based (potential agriculture) inputs at Chungará lake whereas the southernmost sites received background air masses mainly from the Pacific Ocean.

**Polychlorinated Biphenyls (PCBs).** PCBs have been used throughout developed areas in the region, principally in electrical equipment (i.e., transformers). Detailed inventory information in the region is incomplete but there are some country estimates. For instance, in Brazil it is estimated that 250000–300000 tonnes for Askarel (PCB-contaminated oil) was used which implies a stock of 130000 tonnes of PCBs. In Chile, PCB stocks have been estimated to be on the order of about 700 tonnes, 46% of which are still in use, and in Peru it is estimated that ~1000 tonnes of PCBs were used. Obsolete electrical equipment and used oil constitute relevant secondary sources of PCBs. An important effort to export PCB-containing material for destruction has been initiated in the region (12).

Of the 48 PCBs that were targeted, most were below detection in samples. PCB congeners that were frequently detected included the following: 3-Cl (PCB –16/32, –17, –28, –31, and –33); 4-Cl (PCB –44, –49, –52, –56 + 60, –70, –74, and –76); 5-Cl (PCB –87, –95, –101, –118, and –123); 6-Cl (PCB –149 and –153).

Air concentration of Σ-PCBs ranged from BDL (0.12) to 12 pg/m<sup>3</sup>. These levels agree well with measurements in the range of 2–11 pg/m<sup>3</sup> from background and alpine sites in



**FIGURE 4.** Air concentrations (pg/m<sup>3</sup>) for Σ-PCBs over four sampling periods along an altitudinal gradient in the Andes mountains in 2005. BDL = below detection limit; N/A = not available. Sampling periods: period 1 (February–March 2005), period 2 (March–June 2005), period 3 (June–September 2005), and period 4 (September 2005–January 2006).

Chile (19) and from concentrations reported at background sites under the GAPS study (18). Unlike the HCH and endosulfans that increased with altitude, PCBs air concentrations tended to be BDL at higher altitudes (Figure 4). This suggests that long-range atmospheric transport is currently not a dominant source of PCBs in this alpine environment. A decrease in PCB air concentrations with altitude was also reported by Jaward et al. (2005) in the Italian Mountains (11).

In summary, this study reports the first measurements of OCPs and PCBs in Bolivia. Results from time-integrated passive air samplers deployed along an altitudinal gradient indicate that some OCPs—namely α-HCH, γ-HCH, and endosulfans—have higher concentrations at higher altitude. This information, coupled with air parcel back trajectories, highlights the importance of the potential inputs from distant sources through long-range atmospheric transport for these chemicals. PCB levels were less variable and generally low at all sites. This study demonstrates the feasibility of using PUF disks as time-integrated passive samplers, especially at background and alpine locations where electricity an infrastructure is not available for collecting pumped air samples. For future, similar studies, it is recommended that shorter integration periods are used (perhaps monthly) to better resolve seasonal differences and potential inputs using back trajectory analysis.

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## Supporting Information Available

Table S1 shows the field blanks and solvent blanks. Table S2 lists the precipitation, sampling rate, and deployment time. Figure S1 is a topographical map of Bolivia showing the locations of sampling sites. Figure S2 is a “spaghetti plot” of the sampling points. Figure S3 is a map showing land-use regions in South America. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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