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AIR PASSIVE SAMPLING OF PERSISTENT ORGANIC POLLUTANTS IN THE SOUTHERN PATAGONIA, CHILE: BAKER RIVER BASIN

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Introduction
Contamination with POPs in the Chilean Patagonia has been reported previously by our group in different environmental media. The typical explanation for the patterns found is based in transport from distant sources since locally there are no direct sources (besides small urban centres) of POPs into the system. In this paper we describe a two year study on POPs in air in a very remote basin in southern Chile, the Baker basin. We deployed XAD 2 samplers along a gradient throughout the river basin for the monitoring of POPs in air including legacy POPs, brominated flame retardants and currently used pesticides (trifluraline, chlorotalonil). Air is an excellent media for long range transport of persistent chemicals, when measured in remote/background areas may serve as an additional evidence of distant source transport. In Chile, air pollution by POPs have been documented since 90's, mainly in urban settings[1], but also in rural and even remote areas [2,3]. As a global problem, pollution by POPs in remote areas is an indicator of how wide the pollution problem is and a way forward to regulate chemicals on an international basis. The Chilean Patagonia is seen as a freshwater reserve and conserved area away from direct anthropogenic impacts, however even their remoteness is not away for receiving inputs from long distance areas or from the increasing local anthropogenic activity developed in the last 25 years in the area.

Materials and methods
The figure 1 shows the study area selected for this study.

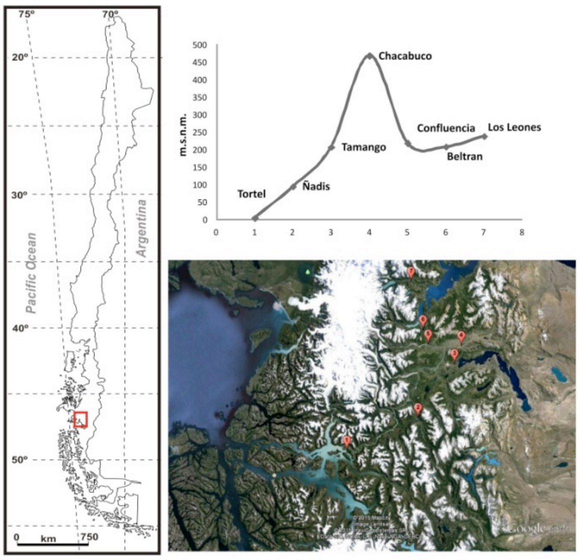

Figure 1. Study area and deployment sites for XAD2 samplers

Analytical Methods
Sampler design. The present network employs a stainless steel mesh cylinder filled with XAD-2 (styrene/ divinylbenzene - co-polymer resin) which is housed by a protective stainless steel chamber [4]
Extraction and analysis. Before extraction, surrogate standards (PCB103 and PCB198) were added to each of the samples. POPs adsorbed in the XAD-2 were Soxhlet extracted with hexane : dichloromethane (1:1 v/v) for

12 hr. The sample extract was concentrated down using a BÜCHI Syncore® Polyvap R-24 system parallel evaporator. The extracts were then injected in a GC/MS system to analyze PBDEs. PBDEs were identified and quantified using a Perkin Elmer Clarus 680 SQ-8T gas chromatograph equipped with a mass spectrometer (GC/MS) fitted with an ELITE 5MS capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness fused with silica). The data acquisition was done in SIFI mode (Selected Ion and Full Ion Scanning). Compound identification was based on individual mass spectra and GC retention times in comparison to literature, library data, and authentic standards. PCBs congeners and currently used pesticides were quantified using a GC Perkin Elmer Clarus 500 gas chromatograph equipped with a ^{63}Ni electron capture detector (ECD) and an Elite 5MS capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness fused with silica). The analytes were quantified using the internal standard and individual calibration curves. The identification of each analyte was confirmed by re-injecting the extracts under the same chromatographic conditions but using an Elite 17 column (30 m x 0.25 mm i.d. x 0.25 µm film thickness fused with silica). Whenever required/possible, the extracts were also re-injected in a GC/MS Perkin Elmer Clarus 680 SQ-8T fitted with an ELITE 5MS capillary column (30 m x 0.25 mm i.d. x 0.25 µm film thickness fused with silica).

Derivation of passive air sampling rates. The analysis yields sequestered amounts (pg), which can be converted to volumetric air concentrations (pg m^{-3}) by dividing by the product of deployment period (365 days for example) and sampling rate R (m^3 day^{-1}). The levels of HCB sequestered in PAS were uniformly distributed across Chile and then we used such values for deriving the sampling rate in this study. Compound-specific Rs for pesticides and PCBs at different sampling sites in this study were then derived by multiplying the sampler specific R for HCB with an average compound-specific factor, which was calculated using the R values from three calibration studies [4,5,6]. These Rs account for the fact that different pesticides and PCB have different uptake rates.

Air mass back trajectory analysis. The analysis of back trajectories of air masses was conducted by using the HYSPLIT Model[7] on the highest altitude site (Chacabuco), which indicateshe main wind direction coming from the south and southwest.

Results and discussion:
The information on levels in pg m^{-3} is shown in the table 1. In this study, the highest concentrations were observed for PCBs (already forbidden back in the 80's in Chile) and one currently used pesticide (trifluralin). Concentration for the other chemicals analyzed ranged within the same order of magnitude seen for other remote areas in Chile [2,3].

Table 1. Concentration (pg m^{-3}) of the targeted chemicals in this study

Locations	Date	∑PCBs	∑PBDEs	Chlrotalonil	Trifluralin
Tortel	2010-2011	3.4	0.99	n.d.	9.31
	2011-2012	5.1	1.85	1.74	8.33
Ñadis	2011-2012	**14.0**	2.94	2.58	**18.03**
Tamango	2010-2011	7.6	n.d.	2.03	4.45
Chacabuco	2010-2011	5.3	0.51	1.27	2.88
	2011-2012	3.7	2.85	1.29	2.98
Bertran	2010-2011	10.3	1.70	1.36	5.35
Los Leones	2011-2012	7.3	2.75	1.94	7.71
	2010-2011	7.5	1.57	1.24	9.27

From 39 PCB congeners analyzed 20% gave positive results above the quantification limits. PCBs profiles showed a pattern dominated by volatile congeners similar to the data reported by Shunthirasingham et al [2] in the Cisnes river basin, located northern of our current study area. The differences seen from different sampling years are not significant to show any temporal trends of PCBs between Cisnes and Baker Rivers(figure 2a).

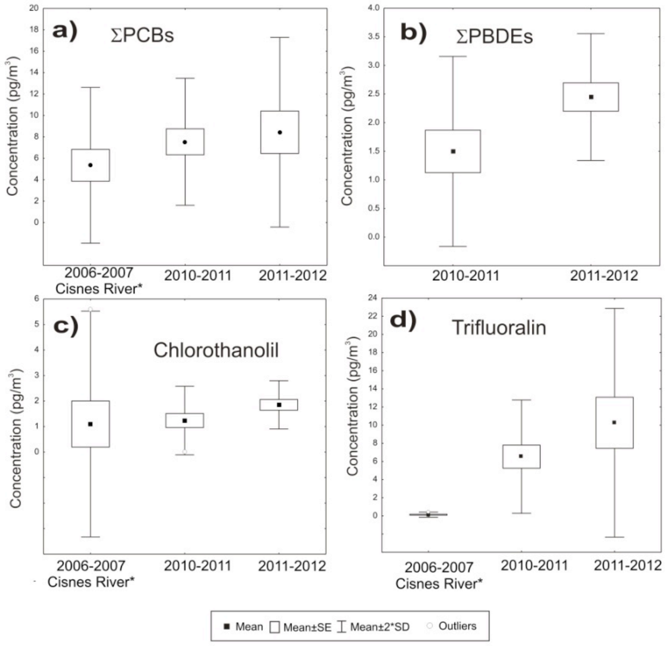

Figure 2. PCBs, PBDEs and currently used pesticide levels in air passive samplers for Baker and Cisnes River [2]

Brominated flame retardants were recently included as POPs in the Stockholm convention. In our study only congeners BDE 77 and 99 (BDE 47 was not analyzed) were observed in levels similar to those found in other remote areas[3]. We observe a small increase in the average values for ΣPBDEs (Figure 2b), which is in agreement with previous data on lake sediments where the arrival of PBDEs was recorded back at the beginning of 90's [8].
Currently used pesticides (Figure 2c and d) showed contrasting trends. While Chlorotalonil showed similar average levels over time, trifluralin seems to slightly increased its levels, although the variability is too high to assure any conclusion. Importantly, the chlorotalonil pesticide is continuously used for the nursery of a forest company located in a valley near the study area.

Acknowledgements
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