AIR CONCENTRATIONS OF PERSISTENT ORGANIC POLLUTANTS (POPS) IN URBAN AND INDUSTRIAL AREAS OF CENTRAL CHILE, USING PASSIVE AIR SAMPLERS

Pozo Karla[1], Harner Tom[2], Rudolph Anny[3], Oyola German[4], Mariottini Michela[1], Volpi Valerio[1], Perra Guido[1], Ahumada-Rudolph Ramon[3], Medina Paulina[3], Mabilia Rosanna[5] and Focardi Silvano[1].

[1]Department of Environmental Science, University of Siena, Via Mattioli 4, 53100, Siena Italy.
[2]Atmospheric Science & Technology Directorate, Environment Canada 4905 Dufferin Street, Toronto, Ontario, Canada M3H 5T4
[3]Facultad de Ciencias, Universidad Católica Santísima Concepción, Alonso de Ribera 2850, P.C. 407 01 29 Concepción,
[4] Comisión Nacional del Medio Ambiente (CONAMA), Región del Biobío, Licoyán 145, Concepción, Chile
[5]National Research Council - Institute for Atmospheric Pollution Via Salaria Km. 29.300, CP 10 - 00016 Roma, Italy.

Introduction

Persistent Organic Pollutants (POPs) are chemicals that persist in the environment, bioaccumulate through the food web, and exhibit toxic effects that may threaten the health of the environment. International efforts have been implemented to reduce levels and emissions of POPs in the environment. The Stockholm Convention created in 2001 identified a initial group of twelve compounds the "dirty dozen", including several organochlorine pesticides (OCPs) (Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Hexachlorobenzene, Mirex, Toxaphene, and dichlorodiphenyltrichloroethane (DDT)), polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-***p***-dioxins and –furans (PCDD/Fs)(1). Chile ratified the Stockholm Convention in 2005.
Contamination of the Chilean environment by POPs has been reported since the 1950s, however, information on primary and secondary sources of POPs is scarce and fragmented (1-7). Consequently, in 2002, the Chilean Environmental Commission (CONAMA) carried out a national PCBs and PCDD/Fs survey to identify their sources (2). Some limited measurements in air have been reported by Mandalakis and Stephanou, 2002 (8), for PAH and PCBs in Temuco and Santiago. Pozo et al., reported concentrations of PCB, OCPs and PBDEs, a class of brominated flame retardants (BFR), in a north-south transect of Chile (9). However, there is currently no atmospheric monitoring program to assess POPs in Chile, which is needed to assess spatial and temporal trends of POPs and to evaluate effectiveness of international control measures. The lack of such information is partly due to the high cost of conventional high volume samplers (HVS) which also require a source of stable electricity. An alternative solution to HVS are PUF (polyurethane foam) disk passive air samplers which have been developed and calibrated by Shoeib and Harner (10). The simplicity and cost-effectiveness of this sampling approach has resulted in numerous spatial studies on POPs at local, regional, and continental scales (9-13). In this study, PUF disk samplers were deployed at 6 sites in central Chile, during summer season, from January to March 2007 to 1) measure level of POPs in urban and industrial areas of Central Chile, 2) compare levels of POPs with others urban/industrial areas and 3) to contribute to the knowledge of POPs levels in air in the South America region.

Material and methods

PUF disk samplers of the type used under the GAPS (Global Atmospheric Passive Sampling) Network (13) were deployed at 6 sites over the three month period to assess POPs in different land-use categories in the area around Concepcion. PUF disk were prepared as described in Pozo et al. (4,13) including the addition of depuration compounds for assessing site-specific sampling rates. Samples and field blanks were deployed during the summer season (January to March 2007) (Figure 1) and analyzed for a range of target compounds that included 19 OCPs: α-, β-, γ-, δ-HCHs, aldrin, heptachlor, heptachlor epoxide, ***cis***-chlordane, ***trans***-chlordane, ***trans***-nonachlor, endosulfan I, endosulfan II, endosulfan sulphate, ***o,p'***-DDE ***p,p'***-DDE, ***o,p'***-DDD, ***p,p'***-DDD, ***o,p'***-DDT, ***p,p'***-DDT (Ultra Scientific, North Kingstown, RI, USA) and PCBs (48 congeners) (Supelco INC, USA).

PUF disks were individually extracted by Soxhlet for 24h using petroleum ether. Details of sample extraction, clean up and recovery tests are presented elsewhere (9). 15 PAH were also targeted (obtained from Supelco INC, USA) .

Analysis of PUF disk extracts was by gas chromatography-mass spectrometry (GC-MS) on a Hewlett-Packard 6890 GC-5973 MS. PCBs were monitored using electron impact-selected ion monitoring (EI-SIM) and OCPs were determined in negative chemical ionization (NCI) mode. Conditions for EI and NCI analysis and selection of target/qualifier ions are described elsewhere (9). 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 was the MDL.

Sampling sites: Sampling sites were located in six different zones of the Metropolitan Area of Concepción, VIII Region in Chile as shown in Figure 1 and range from suburban (site 1), urban (site 2) to industrial (sites 3-6). Details for each site are provided in the caption for Figure 1.

Results and discussion:

Field blanks were below detection for all compounds so no blank correction was required. Air concentrations for target compounds were derived by dividing the amount of chemical collected on the PUF disks by the product of the deployment period and specific sampling rate at each site. Site specific sampling rates were calculated based on recoveries of depuration compounds. Details of this calculation have been previously described (9). The mean sampling rate for all sites was 3.8 ± 0.9 m^3/day which agrees well with previous studies using these samplers (9, 13). The resulting air concentrations for PCBs, OCP and PAHs are summarized in Table 1.

PCBs were intensively used in Chile, principally in electrical equipment (i.e. transformers) and PCB stocks have been estimated to be 700 tons with ~46% still in use (CONAMA, 2001). PCB air concentrations were elevated the four industrial sites with concentrations (pg/m^3) ranging from 96 to 352. Moderate PCB levels were also observed at the urban site (70 pg/m^3) and were below detection at the suburban site (Figure 2a). These findings are generally consistent with results for similar site categories under the GAPS Network (13). Nevertheless, higher PCBs levels have been reported in other Chilean cities. Mandalakis and Stephanou, reported mean air concentrations of 1420 ± 436 pg/m^3 in Temuco and 2320 ± 462 in Santiago (8). Figure 2 shows the PCB profiles at the various sites and shows enrichment of the higher molecular weight congeners near the suspected source sites in the industrial areas.

OCPs have been used in Chile since the 1950s, mainly for agricultural activities. Agriculture is the main occupation of about 15 % of the population, accounting for 10% of the national wealth and produces less than half of the domestic needs. Of the 19 OCPs targeted in this study, only five were routinely detected. Aldrin, α-HCH, δ-HCHs, endosulfan II, endosulfan sulphate, *o,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD and *o,p'*-DDT were not detected in any sample.

Of the OCPs that were detected, results for γ-HCH are most noteworthy showing elevated concentrations at sites 1, 2 and 3 – possibly reflecting contributions from nearby agricultural activity. Lindane (comprising mainly γ-HCH) is still used in Chile (4). Concentrations of OCPs are generally in agreement with a previous passive sampling campaign in 2002 at Concepción city (9), with the exception of chlordanes which are much lower in the current study.

PAH with 3-5 benzene rings are ubiquitous in the environment and typically derived from natural and anthropogenic combustion sources. No emission measurements of PAHs have been conducted in Chile. Air concentrations (ng/m^3) of PAHs at the six sites ranged from 14 to 350, with the lowest value reported at the suburban site, as expected. The lower molecular weight PAHs, (fluorene to chrysene) accounted for 90% of the total PAH composition, respectively (Figure 2). Dominant PAHs were fluorene, anthracene, phenanthrene, fluoranthene and pyrene. These concentrations are consistent with PUF disk-derived air concentrations from the GAPS Network at other urban/industrial sites around the world.

In summary, the results from this study contributes new information on POPs levels at a regional scale in Chile, covering a variety of land-use types. It demonstrates the utility and cost-effectiveness of PUF disk samplers as a reconnaissance tool for screening POPs in air.

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Table 1. Air concentrations (pg/m^3) of OCPs, PCBs and PAHs at urban and industrial sites from Biobio region, central Chile.

Location	γ-hch	Chlordanes[a]	Endosulfans[b]	Dieldrin	HEPT	HEPTX	*pp'*DDE	Total [c] PCBs	Tot [d] PAHs
Site 1	44	1.2	14	19	BDL	BDL	BDL	BDL	14
Site 2	82	2.5	6	15	5.8	2.5	26	70	70
Site 3	121	0.6	14	7	BDL	BDL	6	96	133
Site 4	5	BDL	18	BDL	BDL	BDL	BDL	179	29
Site 5	6	BDL	15	BDL	BDL	BDL	BDL	146	51
Site 6	21	2.7	21	6	BDL	BDL	4	352	349
MDL[e]	0.5	0.8	0.6	1.2	0.2	0.2	1.3	0.35	0.5
Average	47	1	15	8	1	1	7	141	108
SD	47	1	5	7	2	1	10	121	125

BDL: below detection limit; MDL: method detection limit; SD: standar deviation; Hexachlorocyclohexane (HCHs: α-HCH was BDL), HEPT, heptachlor; HEPX, heptachlor epoxide [a]chlordanes (sum of trans-chlordane, cis-chlordane and trans-nonachlor), [b]ΣEndosulfans (sum of Endo I, Endo II and Endosulfan Sulfate). [c] $\sum_{48}$PCB= 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**.** [d]Σ_{15}PAH= acenaphthylene, acenaphtene, fluorene, phenanthrene, antracene, fluoranthrene, pyrene, benz(a)antracene, chrysene, benzo(b)fluoranthene, benzo(a)pyrene, dibenz(a,h)antracene, benzo(g,h,i)pyrene, indeno(1,2,3-cd)pyrene. [e]The MDLs in pg/m^3 were calculated based on an average estimated air volume of 360 m^3/day.

Figure 1. Sampling site at urban and industrial locations in the Biobio region, central Chile.

Site 1 is a suburban site near the beach in Penco, a small city in near Concepción Bay, with minor industrial activities. Site 2 is an urban site in downtown Concepción City. The site is directly impacted by transit, about 300 vehicles per day. Site 3 (Coronel city), is located 30 km south of Concepción City on the coastline, with a population of ~90.000. This site is influenced by two main industrial activities: 1) fishery (fish meal plants and conserveries) and 2) power generation (coal based). Site 4, is located approx 10 km south of Concepción City. The surrounding industry at this site produces approx 100 000 m^3/year melamine board and 300 000 m^3/year of MDF (medium density fiberboard) and PB (particle board) fiberboard. Several nearby sawmills produce sawed dry wood (~13 000 m^3 per year). Site 5, is located in Hualpen next to Talcahuano city. This site is influenced by a petrochemical industrial complex which its crude oil process is of 18 000 m^3/day. Site 6 (Libertad station), is located at Libertad neighborhood in Talcahuano City, near San Vicente Bay. This site is within ~300 m of a steel integrated company which produces 1 250 000 tons/yr of steel.

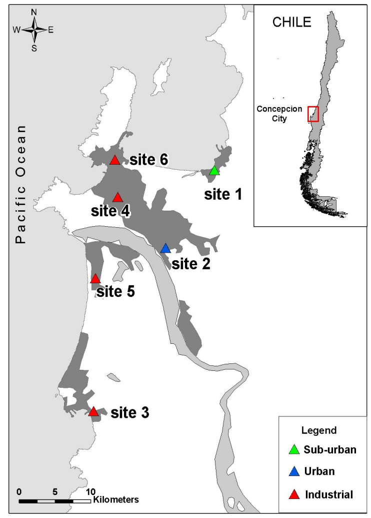

Figure 2. Total air concentrations (pg/m^3) and composition of PCBs (left panel) and PAHs (right panel) during January to March 2007 in the Biobio region, central Chile.