



Survey of persistent organic pollutants (POPs) and polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of rural, urban and industrial areas of Concepción, Chile, using passive air samplers

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ABSTRACT

Passive air samplers (PAS) consisting of polyurethane foam (PUF) disks were used to assess air concentrations of polychlorinated biphenyl (PCBs), polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs) in rural, urban, and industrial sites in Concepción, Chile during a two-month deployment in the summer of 2007. Results for PCBs and PAHs showed a clear rural–urban–industrial gradient. PCB air concentrations ($\mu\text{g m}^{-3}$) ranged from ~30 to ~350 and were ~2 to 5 times higher at industrial sites compared to rural sites. For PAHs, air concentrations (ng m^{-3}) ranged from 26 to 230 and were 4 to 8 times higher at industrial sites. The PCB congener profile was dominated by high molecular weight PCBs at urban and industrial sites. The PAH profile was dominated by 3- and 4-ring PAHs accounting for more than 90% of the $\Sigma_{15}\text{PAH}$, and dominated by phenanthrene (~40%). Of the HCH isomers, only γ -HCH was detected with air concentrations ranging from 5 to 120 $\mu\text{g m}^{-3}$. While for DDT isomers, *p,p'*-DDE was the only compound detected, ranging from below detection limit (BDL) to 360 $\mu\text{g m}^{-3}$. Other OCPs (chlordanes, heptachlor and Dieldrin) showed low air concentrations ($\mu\text{g m}^{-3}$) on the order of ~1–3. Endosulfan, which is a newly listed persistent organic pollutant (POP) under the Stockholm Convention (SC) on POPs, ranged from 14 to 20 $\mu\text{g m}^{-3}$. Polybrominated diphenyl ethers (PBDEs) also newly listed under the SC, were relatively uniform across the transect with air concentrations ($\mu\text{g m}^{-3}$) in the range of ~5 to 10. This study represents one of the first efforts to characterize the POPs composition in ambient air for urban and industrial areas of Chile.

Keywords:

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1. 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 an initial group of twelve compounds – the “dirty dozen”. This list includes 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) (Stockholm Convention, 2011). Currently, a process exists under the Convention to nominate and review candidate POPs and add them to the Convention if it is determined that they satisfy the POPs criteria (Stockholm Convention, 2011). In May 2009, nine new POPs were added to the Convention and in 2010 the 22nd chemical, Endosulfan, was listed with several other compounds currently at the review stage (Stockholm Convention, 2011). Some of the newly listed POPs that are investigated under

this study include α - and γ - hexachlorocyclohexane (HCH), polybrominated diphenyl ethers (PBDEs, a class of flame retardant) and endosulfan (a current use pesticide). Article 16 of the Convention deals with evaluating its effectiveness in protecting human health and the environment. As part of the effectiveness evaluation process, a global monitoring plan (GMP) has been implemented that requires reporting of monitoring data on POPs in core media of air and human tissues so that temporal trends and regional/global transport can be evaluated.

Several countries in South America are Parties to the Convention; Chile signed the Stockholm Convention in May 2003 and ratified it in 2005. Reporting to the GMP is coordinated through the five UN regions and Chile contributes to the GRULAC (GRoUp of Latin American and Caribbean countries) region.

The transport and deposition of POPs has been investigated in remote areas of Chile for the past ten years. For instance, levels of PCBs and organochlorine pesticides have been detected in sediments of remote lakes (Barra et al., 2001; Barra et al., 2004; Borghini et al., 2005; Pozo et al., 2007) and in air samples at

background sites along a north–south transect (Pozo et al., 2004). Recently, Shunthirasingham et al. (2011) reported the spatial variability of atmospheric semivolatile organic compounds along altitudinal gradients in northern, central and southern regions of Chile. Some limited measurements in air have been reported at urban sites in Temuco and Santiago, for PAHs and PCBs (Mandalakis and Stephanou, 2002). However, information on POPs in air in Chile's urban regions is still scarce.

Urban areas tend to be centers of industrial activity where chemicals are emitted to the atmosphere, transported, and then deposited downwind in potentially sensitive environments such as lakes, rivers and oceans (coastal areas) (Totten et al., 2004). The Concepción area, located in the Bío Bío region, is surrounded by several urban (Chiguayante, San Pedro de la Paz and others) and industrial settlements (Talcahuano and Coronel city). The population in the Bío Bío Region was 1 861 600 inhabitants in the census year 2002 or about 12% of the national population. The region contains large industries including steel making and associated activities, within 15 km of Concepción, especially in the industrial area of Talcahuano. In response to concerns regarding the contamination of this area, local authorities took steps to restrict atmospheric emissions which led to significant reductions from industrial sources (CONAMA, 2007). The regional ministry of environment has implemented continuous atmospheric monitoring measurements in the Concepción area for PM₁₀, PM_{2.5}, SO₂, NO₂, CO, O₃. However, there is currently no atmospheric monitoring program to assess POPs in the region. This information is needed to assess spatial and temporal trends of POPs and to evaluate effectiveness of international and national control measures. One of the challenges of air sampling is partly due to the high cost of conventional high volume samplers (HVS) which also require a source of stable electricity. Alternative solutions to HVS are PUF (polyurethane foam) disk, passive air samplers, developed by Shoeib and Harner (2002). The simplicity and cost–effectiveness of this sampling approach has resulted in numerous spatial studies on POPs at local, regional, continental, and even global scales (Ockenden et al., 1998; Shoeib and Harner, 2002; Pozo et al., 2004; Jaward et al., 2004a; Jaward et al., 2004b; Harner et al., 2006a; Klanova et al., 2006; Harner et al., 2006b; Pozo et al., 2006; Klanova et al., 2008; Pozo et al., 2009; Klanova et al., 2009).

In this study, PUF disk samplers were deployed at six sites in the Concepción area, during the period January to March 2007. The main objectives of this study were: (i) to assess air concentrations of POPs and PAHs in the urban and industrial areas of Concepción and (ii) to characterize the composition of PCBs and PAHs. Principal component analysis (PCA) was carried out in order to identify spatial distributions and potential sources of POPs in the study area. In addition to providing new information on POPs in Chile, this study also demonstrates the feasibility of this passive sampling approach for investigating POPs in urban/industrial regions. This study represents the first phase of 1–year study conducted in 2008 to investigate POP levels in the largest Chilean cities of Santiago, Concepción, and Temuco.

2. Material and Methods

2.1. Study area

Concepción city is located in the Bío Bío region in central Chile. The most heavily populated areas are in the coastal region of the province of Concepción, especially in the conurbation known as The Great Concepción that includes 11 communes. Regional development in Bío Bío started in the early decades of the 20th century. This was followed by a surge of regional industrial activity in the 1940s with the creation of CORFO which played an important role in promoting the industrialization of the region, both directly through the creation of new industries such as the iron and steel factories “Huachipato” in San Vicente Bay and the Hydroelectric Plant “Abanico” (Bío Bío basin), and indirectly

through the support and promotion of industrialized fishing. The establishment of these enterprises in the region led to further growth of related industries such as iron–steel manufacturing, petrochemical, glass, power plants, fish meal plants, forest industries and cement. Thus, industrial centers that developed in the cities of Concepción, Talcahuano and Coronel resulted in a large proportion of the regional population concentrated in these cities. Nowadays, the main cities contributing to the industrial regional development in the vicinity of Concepción are: Talcahuano, Coronel and Concepción. Figure S1 in the Supporting Material (SM), is a schematic/map showing the locations of industrial settlements in the study area.

PUF disk samplers of the type used under the GAPS (Global Atmospheric Passive Sampling) Network (Pozo et al., 2006; Pozo et al., 2009) were prepared according to methods reported in Pozo et al. (2004; 2006; 2009) including the addition of depuration compounds (DCs) for assessing site–specific sampling rates. Six DCs were used in this study: 3 isotopically labeled PCBs – ¹³C (PCB–9, –15, and –32) – and three native PCBs that do not exist in ambient air (PCB–30, –107 and –198).

Details on extraction procedures have been reported elsewhere (Pozo et al., 2009). Briefly, prior to extraction PUF disk was spiked with a recovery standard (surrogate) consisting of ¹³C PCB–105 (99%, Cambridge Isotope Laboratory) and Phenanthrene–d₁₀ (99%, Supelco Analytical). PUF disk samples were extracted in a Soxhlet for 24 h using petroleum ether (300 ml) and extracts were concentrated by rotary evaporation followed by solvent reduction under a gentle stream of nitrogen to 0.5 mL and solvent exchanged to isoctane. Mirex (100 ng) was added as internal standard to correct for volume difference.

Samples and field blanks were analyzed for a range of target compounds that included 48 PCBs, 27 PBDEs, 19 OCPs and 15 PAHs. Target compounds were analyzed by gas chromatography–mass spectrometry (GC–MS). Detailed information about instrumental conditions and methods are presented in the SM.

2.2. Sampling sites

Six sampling sites were located in the Bío Bío region, in central Chile, with sampling taking place over two–month periods from January to March, 2007 (summer season) in different land–use categories in the area around Concepción (Figure 1). Sampling sites included one rural site (Penco=PE), one urban (Concepción downtown=CON), and four industrial sites (Coronel=COR; Masisa=MAS; Indura=IND; and Libertad=LIB). Detailed information about each site and information on sampling periods, temperature and derived sampling rates is provided in the SM (Tables S1 and S2). Photographs of each sampling site are also shown in Figure S2.

2.3. Quality assurance/Quality control (QA/QC)

The analytical procedures described above were checked for recoveries and reproducibility. Method recoveries for PCBs were assessed using the surrogate ¹³C PCB–105 (240 ng) that was added to all samples prior to extraction. For PAHs, method recoveries based on phenanthrene–d₁₀ (240 ng) have also been assessed (70% ± 10) (Estellano et al., 2012). Blank levels were assessed from the field blanks (n=2) and laboratory blanks (n=2 solvent blanks). The instrumental detection limits (IDL) were determined by assessing the injection amount that corresponded to a signal–to–noise value ≥ 3. Method detection limits (MDL) in air samples were defined as the average blank (by combining field and laboratory blanks, n=4) plus three standard deviations (SD). When target compounds were not detected in blanks, 1/2 of IDL value was substituted for the MDL. Peaks were only integrated when the signal to noise ratio was ≥ 3; otherwise, they were considered not detected. The MDL values for each target compound are reported in Table 1.

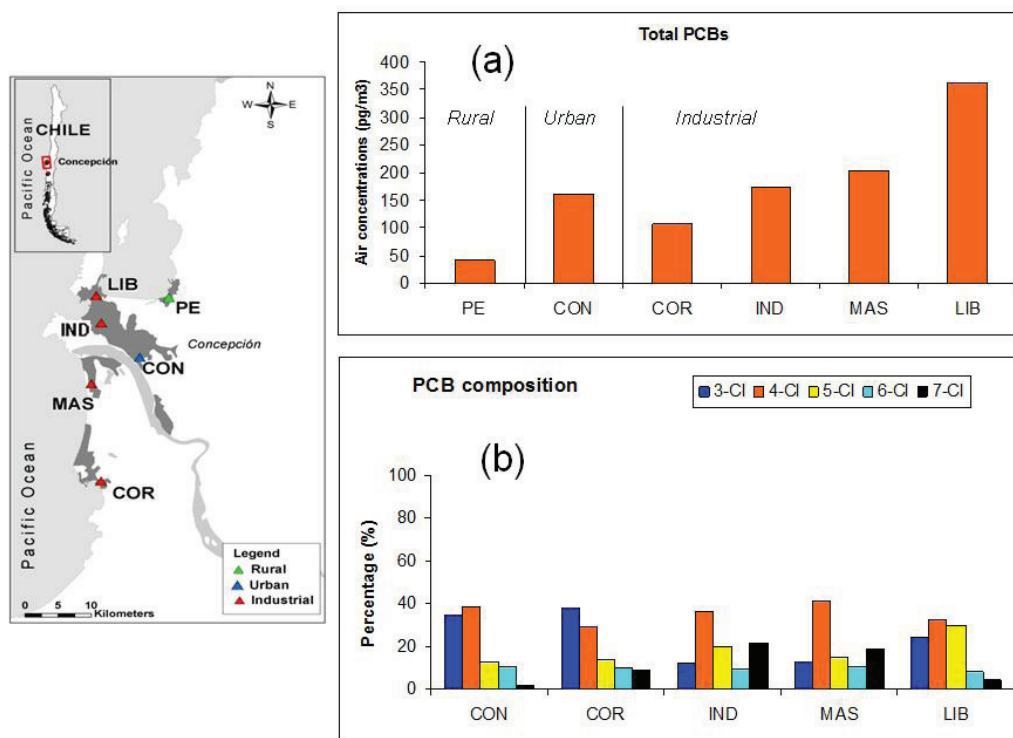


Figure 1. Air concentrations (pg m^{-3}) of total PCBs (a) and homologue composition across sampling sites in Concepción (b).

2.4. Statistical analysis

Principal Component Analysis (PCA) is a multivariate statistical method and was performed using the XLSTAT program. In this analysis new variables are derived from linear combination of the original variables. The first axis explains the maximum amount of variation within the data set. Subsequent axes are derived with the added constraint that they are orthogonal to the previous derived axes. Spatial arrangement of compounds was analyzed to understand relationships among the compounds analyzed, which could provide insight to the potential sources. Prior to performing PCA analysis, the data were natural log transformed. Varimax rotation was used as the rotation method for PCA analysis (Kaiser, 1958). This rotation is aimed at maximizing the variances of the squared raw factor loadings across variables for each factor; this is equivalent to maximizing the variances in the columns of the matrix of the squared raw factor loadings.

3. Results and Discussion

3.1. QA/QC

Surrogate recoveries for ^{13}C PCB-105 ranged from 71% to 92%. This result coupled with previous external recovery checks for target compounds indicated that the analysis method was satisfactory and that recovery correction of the data was not needed. None of the target compounds were detected in field or method blank samples. Therefore, the MDL was set as 1/2 the instrumental detection limit (IDL) value (see Tables 1, 2, and 3).

3.2. Air concentration calculations

Air concentrations for the target chemicals were derived from the amount accumulated in the PUF disk (ng sampler^{-1}) divided for the effective air volume (V_{AIR} , m^3). For the estimation of V_{AIR} , the Equation (2) from Shoeib and Harner (2002) was used; this equation considers the full uptake profile—linear phase and the plateau phase. For the less volatile POPs having higher octanol-air partitioning coefficient (K_{OA}) values and hence higher PUF-air partition coefficient ($K_{\text{PUF-A}}$), the effective air volumes are

calculated based on specific R -values (i.e. sampling rates in $\text{m}^3 \text{d}^{-1}$) multiplied by the number of days (d) of exposure. The more volatile chemicals with lower K_{OA} values (e.g. HCB, HCHs, PAHs) may approach equilibrium (saturation with respect to air) during the sample deployment time ranging from 2 to 4 months. Approach to equilibrium for low K_{OA} chemicals results in reduced sample air volumes compared to higher K_{OA} chemicals (i.e. plateau phase of the uptake profile). For most compounds, the effective air volumes (V_{AIR} , m^3) were between ~ 200 to 260 for PCBs and ~ 60 to 300 for PAHs (see Tables 1 and 2). This is based on a specific sampling rate (R) (see the SM, Table S2) and a deployment time of ~ 60 days.

R -values are derived from the loss of deuration compounds (DCs) (Poza et al., 2004; Gouin et al., 2005). Average R values ($\text{m}^3 \text{d}^{-1}$) are presented in Table S2 (see the SM) and ranged from 3.3 to 4.0 (3.8 ± 0.3). The low variability in R -values between sites is consistent with results from previous studies (e.g. Poza et al., 2009). The resulting air concentrations for PCBs, OCPs, and PAHs are summarized in Tables 1, 2, 3 and are discussed below. V_{AIR} are given in Tables 2 and 3 for PCBs and PAHs, respectively.

An important consideration for the calculation of PAH concentrations is that the PUF disk medium mainly samples the gas-phase (which are mainly the lower molecular weight PAHs) and only about 10% of ambient particles (mainly higher molecular weight PAHs). This is due to the protective chamber (Klanova et al., 2008) around the PUF disk which limits the ability of particles to deposit on the PUF disk. Considering this, PAHs were estimated using the R -value for entirely gas-phase PAHs of $\sim 4 \text{ m}^3 \text{d}^{-1}$ while for PAHs that are entirely on particles (e.g 5 and 6-rings PAHs), an R -value of about $\sim 0.4 \text{ m}^3 \text{d}^{-1}$ was used (Klanova et al., 2008). We should emphasize that the particle-phase sampling rate of $0.4 \text{ m}^3 \text{d}^{-1}$ is a rough estimate based on results from only one study. The efficiency of particle-phase sampling for the PUF disk sampler is an area of ongoing study. Sampling efficiencies are likely to vary with particle type and meteorological conditions. The results for the high molecular weight, particle-phase PAHs should be therefore considered as semi-quantitative.

Table 1. Air concentrations (pg m^{-3}) of OCPs, PCBs, and PAHs (ng m^{-3}) at rural, urban, and industrial sites in Concepción

Location	Site Type	γ -HCH	TC	CC	TN	Chl ^a	Dieldrin	Endo I ^b	<i>p,p'</i> -DDE	Total ^c PCBs	Total ^d PAHs
PE	RU	40	1.2	<0.5	<0.5	1.2	20	14	<5	40	30
CON	UR	80	2.2	<0.5	<0.5	2.2	15	<1	30	160	40
COR	IN	120	<0.5	<0.5	<0.5	<2	7	16	6	100	50
IND	IN	5	<0.5	<0.5	<0.5	<2	<1.5	15	<5	150	210
MAS	IN	6	<0.5	<0.5	<0.5	<2	<1.5	15	<5	180	60
LIB	IN	20	1.1	1	1	3	6	20	<5	350	230
Average		50	1.5	-	-	2	9	14	9	160	100
SD		50	-	-	-	2	8	16	10	100	90
MDL		0.5	0.5	0.5	0.5		1.5	1	5		

Penco (PE); Concepción downtown (CON); Coronel (COR); Indura (IND); Masisa (MAS); Libertad (LIB)

BDL: below detection limit; MDL: method detection limit; SD: standard deviation; UR: urban; RU: rural; IN: Industrial; Hexachlorocyclohexane (HCHs: α -HCH was BDL)

^a chlordanes (sum of trans-chlordane (TC), cis-chlordane (CC) and trans-nonachlor (TN))

^b Endosulfan I

^c Σ_{48} PCB= PCB-8, -15; -18, -17, -15, -16+32, -28, -33, -37; -52, -49, -44, -42, -74, -70, -66, -56+60; -95, -101, -99, -87, -110, -118, -114, -105, -123, -126, -128; -157, -149, -153, -137, -138, -156, -157; -187, -183, -185, -174, -177, -171, -180, -170; -199, -200, -203, -194, -205

^d Σ_{15} PAH= acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenz(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene

^e The MDLs in pg m^{-3} were calculated based on an average estimated air volume of 300 m^3

3.3. Legacy POPs

PCBs. Results for Σ_{48} PCB are summarized in Figure 1a and Table 1. Air concentrations (pg m^{-3}) of PCBs were detected at all sampling sites and ranged from ~40 to ~350 (Table 1). Highest PCB air concentrations (pg m^{-3}) were observed at the industrial site of LIB (350). PCBs were used intensively in Chile, principally in electrical equipment (e.g. transformers) PCB stocks have been estimated to be 700 tons with ~50 % still in use (CONAMA, 2004). Sources of PCBs in urban areas include off-gassing from PCB treated construction material and leakage from closed systems such as older electrical equipment (Breivik et al., 2007). In 2001, the Chilean ministry of environment (CONAMA) reported the VIII region, Central zone of Chile, as one of the major use and storage sites of PCBs in Chile (CONAMA, 2004).

These results are generally comparable or lower than PCB levels reported from other studies around the world at urban-industrial locations. For instance, Motelay-Massei et al. (2005) reported PCBs in air at concentrations (pg m^{-3}) of ~200 to ~800 in the urban area of Toronto, Canada. Klanova et al. (2009) also report PCB levels in, urban areas of Africa, with concentrations ranging from 500 pg m^{-3} to 1 ng m^{-3} . Pozo et al. (2009) reported PCB levels ranging from ~300 to 600 pg m^{-3} in other urban areas monitored under the global atmospheric passive sampling (GAPS) network. In selected other studies from around the world, Li et al. (2011) reported PCB air levels in the range $15\text{--}155 \text{ pg m}^{-3}$, at an industrial complex in northeast China; Mari et al. (2007) reported levels in passive samplers equivalent to $\sim 120\text{--}170 \text{ pg m}^{-3}$ at urban-industrial sites in Barcelona, Spain. Higher PCB air concentrations have been reported in some US cities – for instance in Cleveland ($1\,730 \pm 116 \text{ pg m}^{-3}$) and Chicago ($1\,130 \pm 58 \text{ pg m}^{-3}$) (Persoon et al., 2010).

Figure 1a shows air concentrations of Σ PCBs are increasing along a gradient from rural to industrial sites, by a factor of ~2 to 5. Air concentrations increased as follows: PE<COR<CON<IND<MAS<LIB). These results point to the contributing role of industrial areas in Concepción as potential emission sources of PCBs. Other studies in the northern hemisphere, have also investigated the role of urban areas as sources of PCBs (Motelay-Massei et al., 2005; Persoon et al., 2010). Harner et al. (2004) and Motelay-Massei et al. (2005) observed a clear increasing PCB concentration gradient (5 to 10 times increase) along a rural to urban transect in the area

of Toronto. Nevertheless, in this study, the role of the urban site (CON), as a source of PCBs was not indicated. This is likely due to the large number of contributing industrial sources of PCBs surrounding the area of Concepción.

The PCB profile at most of the sampling sites was dominated by 4-Cl homologue (30–80%) (Figure 1b). Two PCB homologue composition patterns were observed at the industrial sites, both showing an enrichment of higher chlorinated PCBs (Figure 1b). The first PCB pattern, detected at IND and MAS, was enriched in the 5-Cl to 7-Cl PCBs that contributed to more than 50% of the total PCBs composition. In the second pattern, observed at LIB (IN) and CON (UR), the PCB proportions followed the order 4-Cl > 3-Cl > 5-Cl. These patterns differ from PCB profiles detected in other industrial areas of the world. For instance, in China, Zhang et al. (2008) and Li et al. (2011) reported, 3-Cl, as the main PCB homologue group in industrial areas. In Europe, the dominance of middle chlorinated PCBs was reported by Jaward et al. (2004a). Persoon et al. (2010) reported differing PCB patterns for the US cities of Cleveland and Chicago, suggesting the influence of different source types. In this study, the dominance of the higher molecular weight PCBs may reflect the technical mixture used in this part of Chile and proximity of sampling sites to fresh emissions. Specific information about technical PCB mixtures used in Chile is not available.

The PCB pattern detected at COR (IN) was very different from all of the other sites and was dominated by the lower molecular weight 3-Cl, 4-Cl and 5-Cl congeners. This may be due to the proximity of COR (within 0.5 km) off the coast, and at ~50 (meters above sea level) (m a.s.l.). Despite its location in an industrial location, this site is likely to be subjected to the influence of clean air masses, from the southern trade winds off the Pacific Ocean. PCB air concentrations at the rural site PE, were quite low and only a few PCB congeners were detected (Table 2).

The PCB pattern in air can be used to elucidate potential emission sources. PCBs derived from fresh emission tend to resemble technical mixtures and are enriched in the higher homologue groups; whereas a PCB profile that is enriched in lower molecular weight congeners indicates the contribution from secondary sources (e.g. re-emission from soil, ocean) and a long-range transport/global background signature. In order to investigate potential PCB sources in the Concepción area, PCA was

performed (Figure 2a and 2b). The active variables were composed from the congener composition of PCBs at different sampling sites.

Based on the loading plot of the PCA for PCBs we observed differences in the congener pattern among all sites (Figure 2a). The first component and second component explained 50% and 40% of the total variance, respectively. The first component was mainly influenced by low to middle chlorinated PCBs while the second component was influenced by higher chlorinated PCBs. The PCA also groups the sampling sites according to similarity or differences in PCB composition. The sites MAS and IND are grouped together but differ substantially from the other sites, highlighting the large variability of the PCB mixture in air (and related sources) in the Concepción area.

Table 2 shows a list of the more dominant Σ_{13} PCB congeners detected in air samples. This PCB list accounts for ~60% of the total PCB congeners analyzed (i.e. 48 congeners) in this study. Selected PCBs were detected at most of the sampling sites with the exception of PE where only low molecular weight PCBs were determined (i.e. PCB-16+32, -28, -31 and -49). The major PCB contribution was from congeners PCB-31, -28, -149, and -153 that accounted for 45% of total PCBs concentrations.

OCPs. Organochlorine pesticides have been used in Chile since the 1950s, mainly in agriculture. It is estimated that approximately 15% of Chileans work in the agricultural sector which accounts for 10% of the national wealth. Of the 19 OCPs targeted in this study, only seven were routinely detected i.e., α - and γ -HCH, endosulfan, chlordanes, dieldrin, heptachlor, *p,p'*-DDE. OCPs that were not detected included: aldrin, β -HCH, δ -HCH, endosulfan II, endosulfan sulphate, *o,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD and *o,p'*-DDT.

Hexachlorocyclohexane (HCH) was used in Chile since the early 1950s as a commercial insecticide in two formulations – technical HCH and lindane. Technical HCH includes multiple isomers and is dominated by α -HCH (~80%) and γ -HCH (~15%). Air concentrations (pg m^{-3}) of α -HCH were below detection limit (<BDL) at all the sampling sites (Table 1).

γ -HCH is the main component of lindane. Lindane was banned for agricultural uses in Chile in 1998 but was still used in public health and pharmaceutical preparations for the treatment of the pediculosis and scabies/mange in humans and animals. In December 2007, the Chilean Department of Health (MINSAL) prohibited the import, production, distribution, commercialization and use of the lindane for sanitary and domestic uses (PAN, 2008). Air concentrations (pg m^{-3}) of γ -HCH were detected at all sampling sites, peaking at COR (120) followed by CON (82) and PE (44). Lowest γ -HCH air concentrations were detected in the industrial areas, ranging from (5 to 20) pg m^{-3} . Overall, measurements in this study for γ -HCH are consistent with values reported by Pozo et al. (2004) (44 pg m^{-3}), in Concepción but considerably higher than those found by Shunthirasingham et al. (2011) (~2 pg m^{-3}) in the same study area. These differences may be associated to

contributions from nearby agricultural activities during the sampling periods.

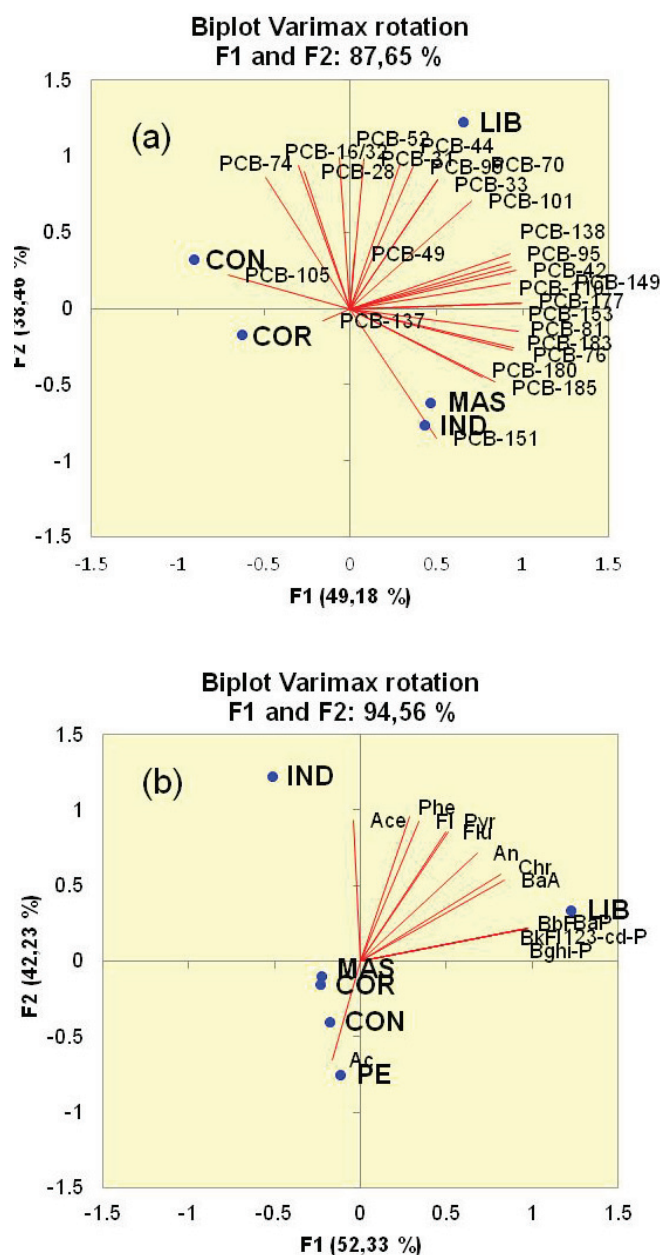


Figure 2. Score plot for principal component analysis (PCA) applied to air measurements across sampling sites in Concepción. (a) PCA analysis of PCBs congeners ($n=26$ compounds) and (b) PCA analysis of PAHs ($n=15$) in Concepción.

Table 2. Air concentrations (pg m^{-3}) of selected dominant PCBs congeners at each sampling site, method detection limit (MDL), and air volumes (V_{AIR})

Location	Type	PCB-31	-28	-52	-49	-44	-95	-101	-110	-149	-153	-137	-138	-180
PE	RU	10	10	<0.5	8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.8	<0.8	<0.8	<0.8
CON	UR	20	10	8	20	8	2	5	2	5	3	6	5	2
COR	IN	10	10	5	3	7	3	5	3	3	5	5	4	7
IND	IN	10	6	3	6	6	8	6	10	10	20	5	10	10
MAS	IN	10	7	3	9	7	10	8	6	20	20	6	10	9
LIB	IN	20	20	10	9	20	30	30	20	30	30	5	20	7
MDL		0.4	0.4	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.8	0.8	0.8	0.8
Air vol. (m^3)		210	210	230	230	250	250	250	250	250	250	250	250	250

Abbreviations: MDL: method detection limit (pg m^{-3}), an average air volume of 240 m^3 was used to calculate MDL.

Chlordane (sum of *cis*- and *trans*- isomers and *trans*-nonachlor) is a persistent and bioaccumulative chlorinated cyclodiene. The technical grade chlordane is not a single chemical, but is a mixture of isomers and many related chemicals, of which about 10 are major components, including: *trans*-chlordane, *cis*-chlordane, chlordene, heptachlor, and *trans*-nonachlor. Chlordane was used as a pesticide on agricultural crops, lawns, and gardens including vegetables, small grains, maize, other oilseeds, potatoes, sugarcane, sugar beets, fruits, nuts, cotton and jute. In the late 1970s and at the beginning of the 1980s many countries, including Chile, severely restricted or banned its use. Air concentrations of chlordane (pg m^{-3}) were low, in the range of BDL to ~ 3 , and were dominated by TC which is in a similar range as previous measurements in the Concepción area reported by Pozo et al. (2004) ($1 - 4 \text{ pg m}^{-3}$) and by Shunthirasingham et al. (2011) (BDL – $\sim 5 \text{ pg m}^{-3}$).

Heptachlor (Hept) is an insecticide that was used primarily to control soil insects and termites. It was also used to combat cotton insects, grasshoppers, and malaria-carrying mosquitoes. Hept is metabolized in soils, in plants and animals to heptachlor epoxide (Heptx), which is more stable in air and in biological systems and is also carcinogenic (UNEP, 2002). Air concentrations (pg m^{-3}) of Hept and Heptx were detected only at CON (6 and 3, respectively).

Dieldrin is one of the most persistent OCPs and is the principal metabolite of Aldrin, another widely used OCP. Dieldrin is generally applied to soil as a termiticide and is used mainly for corn and citrus trees (Aigner et al., 1998). Air concentrations (pg m^{-3}) of Dieldrin ranged from BDL to ~ 20 . The highest concentrations were detected at PE (20), CON (15) and COR (7). These data agree well with a previous study in Chile where Dieldrin levels were elevated in Concepción (25 pg m^{-3}) and very low or BDL at background regions in Chile (Pozo et al., 2004).

DDTs. The use of DDT 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 in several countries. The World Health Organization (WHO) continues to recommend the use of DDT for use in public health for disease vector control. However, countries are required to notify the WHO Secretariat of the production/use, or the intention to use DDT (Stockholm Convention, 2011). In the environment, *p,p'*-DDT (the dominant component of DDT) is converted to *p,p'*-DDE. Often, the relative abundance of parent to metabolite is used to distinguish fresh inputs (i.e. DDT/DDE > 1) from an aged signature (i.e. DDT/DDE < 1). Air concentrations of DDT were below detection at all sites, however air concentration (pg m^{-3}) of *p,p'*-DDE were detected only at two sites COR (6) and CON (30) (Table 1). These results are higher than those reported recently by Shunthirasingham et al. (2011) at Concepción, where

DDT-related compounds were not detected. The DDT/DDE ratio observed across the various study sites suggests that inputs to air are not associated with fresh applications of DDT but rather to older, secondary sources such as soil-air exchange.

PAHs. Polycyclic aromatic hydrocarbons with 3–5 benzene rings are ubiquitous in the environment and typically derived from natural and anthropogenic combustion sources. Table 3 provides a summary of total and individual PAHs at the Concepción sites. Air concentrations (ng m^{-3}) of Σ_{15} PAH ranged from 26 (PE) to 225 (LIB) (Table 1). Levels of PAHs in air were higher than those measured in other studies in Chile, levels of PAHs in air were higher than those measured in other urban sites in Chile. Shunthirasingham et al. (2011) reported concentrations of 0.3 to $1\ 300 \text{ pg m}^{-3}$ for four-ring PAHs with the higher levels in air samples deployed in urban areas and close to roads. Nevertheless, our results are similar to other rural and urban areas in Europe and in Africa. Jaward et al. (2004b) reported PAH levels in the range of 0.5 to 60 ng m^{-3} and Klanova et al. (2009) found concentrations in the range of 80– 150 ng m^{-3} . The relatively high PAH levels detected at industrial sites (IND and LIB) are likely associated with industrial emissions in the area. For instance, the site IND is influenced by a petrochemical industrial complex where $18\ 000 \text{ m}^3 \text{ day}^{-1}$ of crude oil is processed. LIB is within $\sim 300 \text{ m}$ of a steel manufacturing plant that produces $1\ 250\ 000 \text{ tons y}^{-1}$ of steel.

Air concentrations of PAHs showed a strong gradient with industrial>urban>rural sites (LIB>IND>MAS>COR>CON>PE), with ~ 4 to 8 times higher concentrations at industrial sites (Figure 3a). The PAH profile was dominated by 3- and 4-ring PAHs accounting for more than 90% of the Σ_{15} PAH (Figure 3b). The most dominant PAHs were phenanthrene ($\sim 40\%$), followed by fluoranthene (20%) and pyrene (17%), which are primarily in the gas-phase (Odabasi et al., 2006) (Figure 4a). As discussed previously, the PUF disk sampler is less efficient at sampling particle-bound compounds. Although we attempt to account for this using the particle-phase sampling rate estimated by Klanova et al. (2008) we acknowledge the greater uncertainty associated with the air concentrations derived for the mainly particle-bound PAHs (e.g. BaP).

The profile for PAHs observed in this study is similar to results reported in other Chilean cities reported by Shunthirasingham et al. (2011) showing predominance of 4-ring PAHs; and also in agreement with other studies in the urban area of Manila, Philippines with observed contributions of $68 \pm 5\%$ for 3-ring and $30 \pm 4\%$ for 4-ring PAHs (Santiago and Cayetano, 2007), and in Tuscany Region, Italy with $76 \pm 6\%$ for 3-ring and $24 \pm 6\%$ 4-ring PAHs (Estellano et al., 2012). In the case of the higher molecular weight PAHs (BbF, BkF, BaP, I123cd-P, and Bghi-P), these were only detected at the industrial site of LIB (Figure 4b) and made up a small percentage ($\sim 3\%$) of the total PAH composition.

Table 3. Air concentrations (ng m^{-3}) of PAHs at each sampling site, method detection limit (MDL) and air volumes (V_{Air})

Location	Type	Ac	Ace	Fl	Phe	An	Flu	Pyr	BaA	Chr	BbF	BkF	BaP	I123-cd-P	Bghi-P	Total Σ PAHs
PE	RU	2	1	1	10	1	5	6	1	1	<0.7	<1.0	<1.0	<1.0	<1.0	30
CON	UR	5	1	3	20	2	6	7	1	1	<0.7	<1.0	<1.0	<1.0	<1.0	40
COR	IN	6	1	3	20	2	8	8	1	1	<0.7	<1.0	<1.0	<1.0	<1.0	50
MAS	IN	6	1	3	20	2	10	10	1	1	<0.7	<1.0	<1.0	<1.0	<1.0	60
IND	IN	6	5	20	100	5	40	30	2	2	<0.7	<1.0	<1.0	<1.0	<1.0	210
LIB	IN	9	2	20	70	10	50	40	7	7	4	3	2	2	2	230
MDL		0.9	0.5	0.9	0.9	1.0	1.8	1.0	0.2	0.2	0.7	1.0	1.0	1.0	1.0	
Air vol (m^3)		60	70	140	200	200	250	250	270	270	270	270	270	270	270	

Abbreviations: Acenaphthylene (Ac), Acenaphthene (Ace), Fluorene (Fl), Phenanthene (Phe), Anthracene (An), Fluoranthene (Flu), Pyrene (Pyr), Benzo(a)anthracene (BaA), Chrysene (Chr), Benzo(a)pyrene (BaP), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Benzo(g,h,i)perylene (Bghi-P), Indeno(1,2,3-cd)pyrene (I123-cd-P).

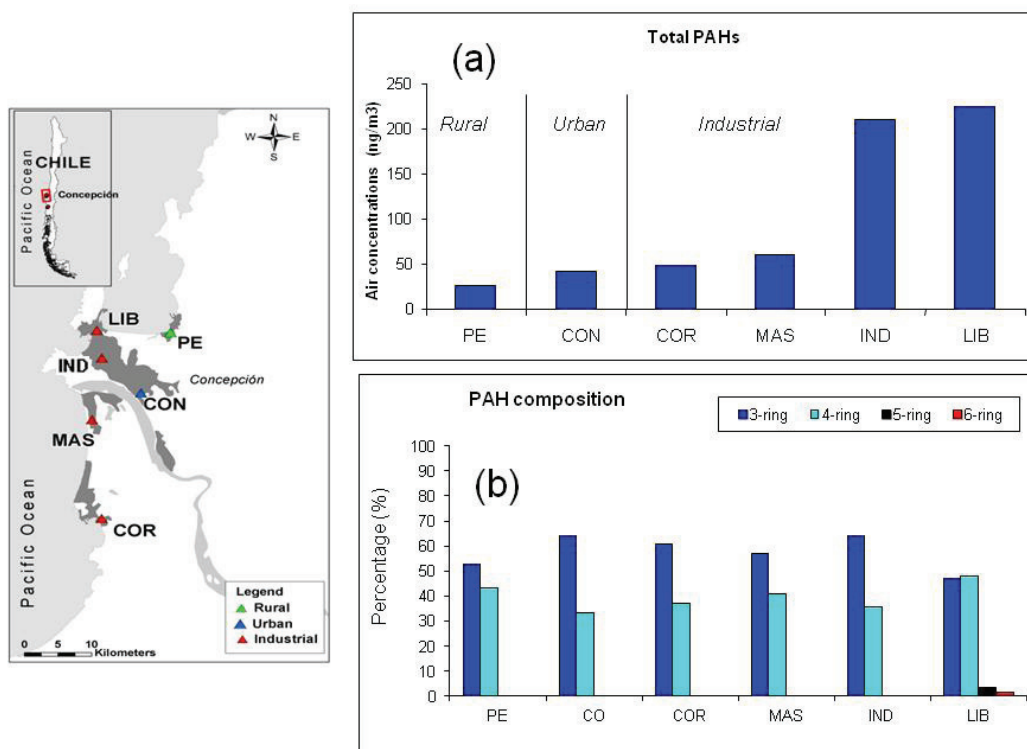


Figure 3. Air concentrations (ng m⁻³) of total PAHs (a) and PAH homologue composition across sampling sites in Concepción (b).

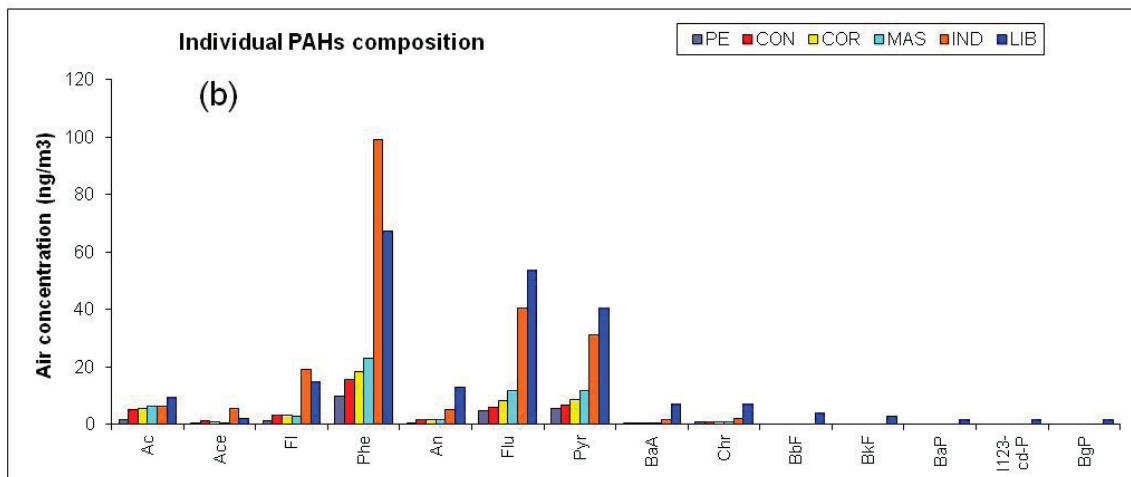
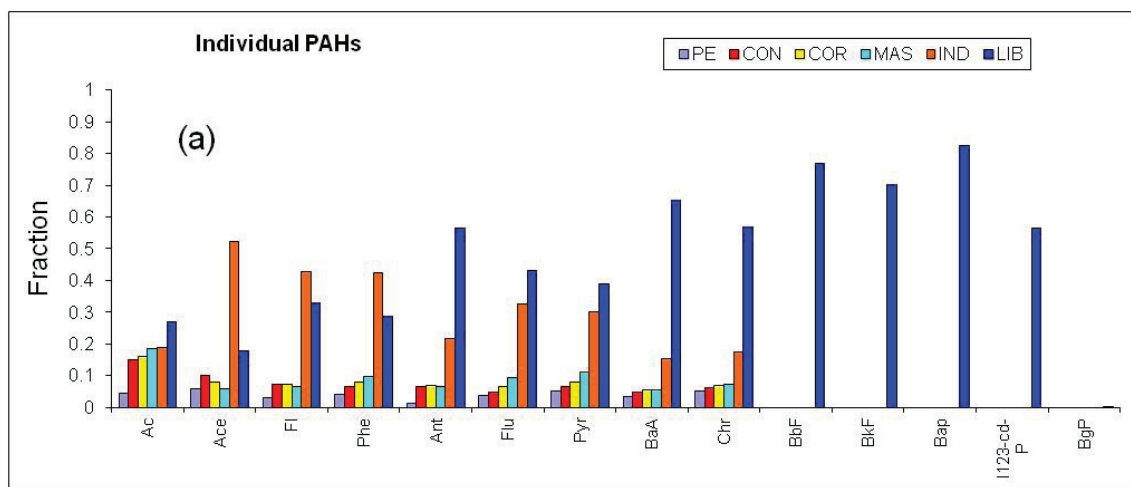


Figure 4. Fraction of individual PAHs (a) and air concentrations (ng m⁻³) (b) and at different sites in Concepción.

Figure 2b shows the results of PCA analysis for PAHs. The PCA first and second component explained 52% and 42% of the total variance, respectively. The PAH pattern was similar between most sites suggesting influences from similar source types. However, one industrial site (LIB) showed a different PAH pattern. The 2D plot varimax rotation was able to provide a better relationship between sampling sites and pollutants, with the two factors explaining 95% of the total variance. The LIB site was grouped separately in the 2D plot which might indicate the influence from specific point sources, as described earlier.

3.4. New POPs

Endosulfan. Endosulfan is a current use pesticide that is used globally and recently listed on the Stockholm Convention on POPs (Stockholm Convention, 2011). Endosulfans are used on a wide variety of crops and also for the control of disease vectors (Li and Macdonald, 2005). Endosulfan consists of two isomers, I and II, in the ratio of about 7:3 (in the technical mixture) that breakdown in the environment to produce endosulfan sulfate (SO_4) and endosulfan diol, both of which have structures similar to the parent compound and are also of toxicological concern.

Air concentrations (pg m^{-3}) of Endosulfan I ranged from <1 to 20 (13 ± 7). Endosulfan II and endosulfan sulfate were not detected in any of the samples. These results are similar to those reported by Poza et al. (2004) at background sites in Chile where endosulfan concentrations in air ranged from 3.5 to 99 pg m^{-3} .

PBDEs. Polybrominated diphenyl ethers are flame retardants that are a concern due to their POP-like characteristics and widespread distribution. Penta- and Octa-technical formulations of PBDEs were recently added to the Stockholm Convention on POPs (Stockholm Convention, 2011). Air concentrations for PBDEs were below detection limits at all sampling sites. Results are reported for each congener as <MDL (pg m^{-3}): <0.3 for PBDE-15, <0.3 for PBDE-17, <0.9 for PBDE-28, <0.9 for PBDE-47, <0.8 for PBDE-49, <0.9 for PBDE-66, <0.8 for PBDE-71, <1.6 for PBDE-100, <1.1 for PBDE-99, <1.1 for PBDE-85, <0.41. Consequently, Σ_{12} PBDE is less than 11 pg m^{-3} and Σ_3 (PBDE-47, -99, -100) PBDE is less than 4 pg m^{-3} at all sites. Although the results for PBDEs are limited because of detection issues they do provide an upper bound for the air concentrations i.e. we know that levels in air are below these values. These results also highlight some of the challenges in using the PUF disk samplers to measure low-to-trace concentrations of PBDEs in air because of the relatively high MDL values typically observed for PBDEs that are due to their presence in blanks samples (Koblikova et al., 2012) and associated with laboratory contamination. Improved laboratory protocols are required for PBDEs and other commercial POPs that are present in indoor and lab environments, to ensure low blank levels in PUF disk samples.

4. Implications

This study represents one of the first efforts to characterize the composition of POPs and PAHs in ambient air of urban and industrial areas of the Bío Bío region. The results show the important role of industrial settlements as sources of PCBs and PAHs. Levels of organochlorine pesticides were relatively low at most of the sampling sites with exception of γ -HCH at COR site. PCBs and PAHs were dominated by the lower molecular weight homologues/compounds at most of the sites, however, at the industrial sites (LIB and IND) some variable patterns were observed with increased contribution of higher molecular weight compounds. Although we estimated air concentrations for higher molecular weight PAHs using the particle-phase sampling rate obtained from previous field experiments, further investigations are needed to test the influence of different aerosol types on the particle-phase sampling rate. The results of this work inform efforts within Chile and the GRULAC region under the Global

Monitoring Plan of the Stockholm Convention on POPs to assess air concentrations of POPs and the effectiveness of control measures.

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Supporting Material Available

Description of instrumental methods and conditions of GC-MS analysis, Description and geographical location of sampling sites (Table S1), Deployment periods, total days, average temperature and specific sampling rates (Table S2), Schematic figure showing the locations of industrial settlements in the study area (Figure S1), Photos of the sampling sites in Concepción (Figure S2). This information is available free of charge via the Internet at <http://www.atmospolres.com>.

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