Levels of Persistent Organic Pollutants (POPs) in the Industrial area of Las Higueras Talcahuano, in central Chile, using passive air sampler PUF Disk.

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Introduction

The Great Concepción (VIII Region) includes approximately 11 communes and is part of the Bio Bío region in central of Chile. 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. These 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 Concepcion, Talcahuano and Coronel resulted in a significant proportion of the regional population concentrated in these cities. Nowadays, the central cities contributing to the regional industrial development in the vicinity of Concepción area: Talcahuano, Coronel, and Concepción[1].

Persistent organic pollutants (POPs) are organic compounds that, to a varying degree, resist photolytic, biological and chemical degradation. They are characterized by low water solubility and high water solubility, leading to their bioaccumulation in fatty tissues. They are also semi-volatile, enabling them to move long distances in the atmosphere before deposition occurs[2]. These compounds enter into the environment by both natural processes and anthropogenic sources[3,4,5]. The Stockholm Convention (SC) (2001) on POPs, which is coordinated through the United Nations Environment Programme (UNEP), is intended to reduce or eliminate the use, discharge and emission of these compounds to improve the health of the environment and reduce the risk to humans and wildlife[6,7].

The main objective of this study was to assess air concentrations of POPs in the industrial areas of Las Higueras in Talcahuano city in Central Chile. PUF disk samplers were deployed at seven sites in the industrial area of Las Higueras in Talcahuano, during three months, to quantified POPs including polychlorinated biphenyls (PCBs) congeners and organochlorine pesticides (OCPs).

Materials and Methods

The passive air samplers consisting of the polyurethane foam disks (15 cm diameter, 1.5 cm thick, density 0.030 g cm^{-3}, type N 3038; Gumotex Breclav, Czech Republic) housed in the protective chambers were employed in this study. A theory of the passive air sampling using the similar devices were described elsewhere[1]. Surrogate recovery standards (PCB30 and PCB185 were used for PCBs and OCP analysis) were spiked on each sample before extraction. One laboratory blank and one reference material were analyzed with each set of ten samples. All samples

were extracted with dichloromethane in a Büchi System B-811 automatic extractor. After extraction, the sample volume was reduced under a gentle stream of nitrogen at ambient temperature. Fractionation was achieved on a silica gel column; a sulphuric acid modified silica gel column was used for PCB/OCP samples. PCB121 was used as the internal standards for PCB/OCP analyses, respectively. Samples were analyzed using a GC-MS/MS instrument (GC 7890 / MS-MS Triple Quadrupole 7000B (Agilent) with a 60m x 0.25mm x 0.25µm HT8 column (SGE Analytical Science, USA) in electron impact ionization and MS/MS mode for PCBs: PCB28, PCB52, PCB101, PCB118, PCB138, PCB153, PCB180, OCPs : α-hexachlorocyclohexane (HCH), β-HCH, γ-HCH, δ-HCH, ethylene (*p,p´*-DDE), 1,1-dichloro-2,2-bis (p-chlorophenyl) ethan (*p,p´*-DDD), 1,1,1-trichloro-2,2-bis (*p*-chlorophenyl) ethan (*p,p´*-DDT), *o,p´*-DDE, *o,p´*-DDD, *o,p´*-DDE, *o,p´*-DDT.

Quality Assurance/Quality Control

Recoveries were determined for all samples by spiking with the surrogate standards before extraction. Recoveries were 76-100%, and 71-98% for all samples, for PCBs/OCPs, respectively. Recovery factors were not applied to any data. Recovery of native analytes measured for the reference material varied from 88 to 103% for PCBs, from 75 to 98% for OCPs. The laboratory blanks were under the detection limits for all compounds. The field blanks consisted of the pre-extracted PUF disks and were taken at each sampling site. They were extracted and analyzed in the same way as the samples, and the levels in field blanks never exceeded 3% of the quantities detected in the samples for PCBs, 1% for OCPs, indicating minimal contamination during the transport, storage, and analysis[8].

Results

The showed the highest ΣPCB levels were detected in the Elqui 318 site (S2) (128 pg/m^3), followed by in Vallenar 334 sites (S5) (48 pg/m^3). Individual PCB congener patterns were different at all sampling sites; Elqui 318 (S2) presented a higher proportion of the lower molecular weight (PCB28, PCB52, and PCB101). The predominant PCBs congeners were PCB52 (~79%) followed by PCB101 (~51%) and finally PCB28 (47%) at Elqui 318 (S2). However, PCB28 (~37%) in Valllenar 334 (S5) was the most abundance PCB congener (See Fig 2). Pozo et al., 2012 reported. PCB air concentrations (pg/m^3) ranged from a 30 to a 350 and were a 2 to 5 times higher at industrial sites (Coronel=COR; Masisa=MAS; Indura= IND) and included Libertad=LIB, sampling site very near from Las Higueras[2]. The significant PCB contribution was from congeners PCB31, 28 (3-Cl), 149, and 153 (5-Cl, 6-Cl), respectively that accounted for 45% of total PCBs concentrations. Pozo et al., 2017 also reported the abundance of higher molecular weight PCBs (PCB153, 180) detected at industrial sites (in Concepción city)[9].

From all ∑HCHs the most abundant compound was γ-HCH with a maximum concentration of 183 pg/m^3 in Mejillones 1069. The prevalence of γ-HCH across these sites may indicate inputs of lindane use[9].

For ∑DDTs, the highest concentration was detected at Vallenar 334 (S5) (344 pg/m^3), followed at Elqui 318 (S2) (28 pg/m^3). The DDTs composition was dominated by *p,p´*-DDT (98%) at most sampling sites, in Mejillones 1069 (S1), and (60%) in Elqui 240 (S7). DDTs were detected with a prevalence of *p,p´* -DDE accounting for ~50% of the total DDTs[9].

In this study, it is important to mention that the steel company Huachipato SA is located at ~1 km of the sites of study. However, the levels reported are lower than others studies. Pozo et al., 2010 reported (247 pg/m^3 and 931 pg/m^3 of *p,p´*-DDE and *p,p´*-DDT respectively in Indian agricultural Regions[10].
Harner et al., reported air concentrations of α-HCH were in the range of <1 pg/m^3 to as high as 150 pg/m^3 in Little Fox Lake, Canada[11]. In another study, in India, using PUF disk samplers DDTs were detected with relatively high concentrations in air of *p,p´*-DDE and *p,p´*-DDT (247 and 931, respectively)[7] and in Bahia Blanca, Argentina[12], *p,p´*-DDE (the only isomer of DDT that was detected) was from below detection limit (BDL) to 20 pg/m^3.

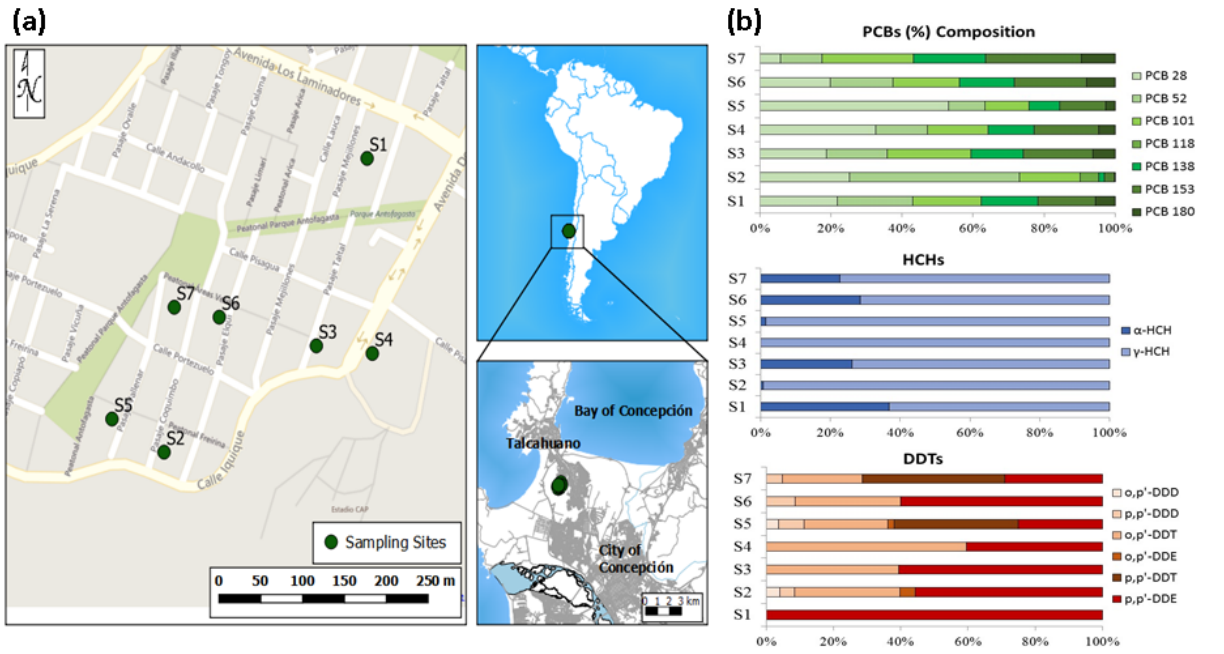

Figure 1. (a) Location of sampling sites in central Chile. S1: Mejillones1069, S2: Elqui 318, S3: Tal tal 219; S4: Desiderio García 240 S5: Vallenar 334; S6: Elqui 240; S7: Coquimbo 252. (b) Composition percentage of PCBs, HCHs, and DDTs in the different sites of study from Las Higueras Talcahuano.

Conclusions

Employing passive air samplers are an economical and simple way to drive chemical characterization studies which could help future efforts to implemented regulation at the regional level in central Chile. This study showed the significant variability in the concentrations in air of the targeted compounds which was associated with emission sources (e.g., predominant industrial activities) and also the geographic and meteorological influences in the study area.

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