**Persistent Organic Pollutants (POPs) in Concepcion Bay, Chile Central**

Pozo K[1,2], Přibylová P[2], Kukucka P, Audy O[2], Klánová K[2], Rudolph A[1], Banguera Y[1], Ahumada R[1]

[1]*Facultad de Ciencias, Universidad Católica de la Santísima Concepción (Kpozo@ucsc.cl);* [2]*Recetox (Research center for toxic compounds in the environment), Masaryk University, Brno 62500, Czech Republic.*

## 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). Chile signed the Stockholm Convention in May 2003 and ratified it in 2005.

In Chile, pollution by chlorinated pesticides was first reported in the early '50. DDTs were banned in the country in the early 80's and in the case of hexachlorocyclohexane (HCHs), these compounds were used in Chile since 1950 as a commercial insecticide in two formulations i.e., technical HCH and lindane. Technical HCH is a mixture of several isomers including α-HCH and 60-70%, γ-HCH comprises 10-12% (the γ-HCH is the major component of lindane). Lindane was banned for agricultural use in Chile, in 1998, but continued to be used in pharmaceutical preparations for the treatment of head lice and scabies/mange in humans and animals. In December 2007, the Department of Health of Chile (Ministry of Health) prohibited the import, production, distribution, marketing and use of lindane for sanitary and domestic usage (Pozo et al., 2012).

Concepción Bay is a costal embayment located in the Biobío Region of central Chile. The environmental state of Concepción Bay has a vital role in the sustainability of the socio-economic development and health of the neighbouring population in the region. The Bay supports the adjacent coastal aquatic ecosystem, wild life and human food chain. For instance, Concepción Bay is used for maritime traffic, recreational activities (i.e., fishing and swimming), management areas for benthic resources, small economic entrepreneur activities (artisanal fisheries) *inter alia*. The Biobío Region was hit by a high magnitude earthquake (8.8 moment magnitude scale) in February 2010 that triggered a tsunami that might have changed the marine ecosystem (Castilla et al., 2010) and environmental state (e.g. chemical composition of surface sediments) of Concepción Bay (Pozo et al., 2015).

The main objective of this study is to determine levels and patterns of POPs in sediments from Concepción Bay in central Chile and contribute new and relevant environmental information for highly urbanized and populated areas. This investigation will also contribute in evaluating the effectiveness of international conventions such as the Stockholm Convention on POPs for the GRULAC Region (Group of Latin American Countries).

## Methodology

### Study area

Concepción Bay (36 ° 40'S, 73 ° 01'W), has a strong seasonality and high biological productivity of the water column due to wind-driven upwelling. Upwelling and the coastal zone intrusion of water with high content of nutrients contribute to the productivity of this system. The bay is surrounded by one of the most industrialized and urbanized areas of Chile (Ahumada et al., 1983). The sources of particulate organic matter within the Bay include biological productivity, fluvial input, authorized sanitary discharges, shipyard, industrial wastewater and anthropogenic activity. The Bay holds some of the most important ports of the region and the country (Talcahuano, Lirquén and Tome). The Andalién River flows at the head of the Bay into the southeast sector contributing with untreated sewage from nearby towns and residual chemicals from agriculture and forestry in the Cordillera de la Costa (Rudolph et al., 2002).

**Sampling**

Surface sediments (15 g) were taken at three stations in the Concepción Bay (Talcahuano) (Figure 1) using Van Veen grab (0.3 $m^2$). Samples were transported to the laboratory in pre cleaned glass jars, wet sieved (60 µm) and freeze dried at -50°C and 0.2 mbar for further chemical analysis. Sediments samples were homogenized with anhydrous sodium sulphate, then spiked with $^{13}C$ extraction standards and extracted using DCM in an automated Soxhlet extraction system (Büchi B-811). One laboratory blank and one reference material were analyzed with each set of ten samples. The solvent was reduced in TurboVap II and transferred into a GC conical vial; recovery standards were added. Results are expressed in ng/g dry weight (d.w.). 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. PCB-121 was used as the internal standards for PCB/OCP.

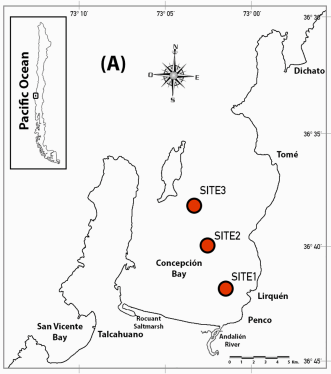


Figure 1. Sampling locations for sediments (n= 3 sites) in Concepción Bay, during May 2013. (Abbreviations for sediment stations: SITE1, SITE2, SITE3).

Samples were analyzed using a GC-MS instrument (GC 7890/MS-MS Triple Quadrupole 7000B (Agilent) SGE Analytical Science fused silica column HT-8 (8% Ph) in electron impact ionisation and MS/MS mode for PCBs: PCB 28, PCB 52, PCB 101, PCB 118, PCB-153, PCB-138, PCB-180, OCPs: α-hexachlorocyclohexane (HCH), β-HCH, γ-HCH, δ-HCH, 1,1-dichloro-2,2-bis (p-chlorophenyl) 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, hexachlorobenzene (HCB), and pentachlorobenzene (PeCB).
Sediment samples were analyzed for 10 PBDE congeners (BDE-28, -47, -66, -99, -100, -85, -154, -153, -183, -209). The PBDE analyses were also performed by gas chromatography - mass spectrometry (GC-MS) on a 7890A GC instrument (Agilent, USA) equipped with a RTX-1614 column (15 m × 0.25 mm x 0.10 m) (Restek, USA) coupled to an AutoSpec Premier MS (Waters, Micromass, UK). The mass spectrometer (MS) was operated in EI + mode in the resolution of> 10 000. The resolution MS was set to > 5000 for BDE-209. Injection was splitless 2 µl to 280 °C, with He as carrier gas at 1 ml/min. GC temperature program was 80 °C (1 min hold), then 20°C/min to 250 °C, followed by 1.5 °C/min to 260 °C (2 min hold), and 25 °C/min at 320 °C (4.5 min hold).

**Quality Assurance/Quality Control**

Recoveries were determined for all samples by spiking with surrogate standards prior to extraction. Recoveries were 76-100 % for PCBs/OCPs. Recovery factors were not applied to any of the data. Recovery of native analytes measured for the reference material varied from 88 to 103 % for PCBs, and from 75 to 98 % for OCPs. The laboratory blanks were under the detection limits for all compounds.

**Results and discussion**

**Clorinathed pesticides concentrations**

The results showed that the levels of chlorinated pesticides are generally low, in sediments, of Conception Bay after the 2010 tsunami in central Chile. In particular, HCH and DDTs compounds were> 1 ng/g d.w. Levels of *pp'*-DDE (ng/g d.w.) ranged from ~0.1 to 2 and for *pp'*-DDT fluctuated between ~0.1 to 1.

In the environment the *pp'*-DDT becomes *p p'*-DDE. Often, the relative abundance of DDT/DDE isomers is used to distinguish the different types of contributions: i) recent use (i.e., DDT/DDE> 1) and ii) past use (i.e., DDT/DDE <1). In Concepción Bay, the DDT/DDE ratio was ~0.5 suggesting old use of DDTs. Levels of DDT in the Chilean environment is very scarce; however, if we compare our results with those reported in other studies around the world we found that DDT levels in this coastal environment are very low.

Hexachlorociclohexano (HCH: α- y γ-) has been banned in Chile since 1980 (Pozo et al., 2012). Concentrations of ΣHCHs, in sediments were low and ranged from 0.2 a 0.6 ng/g d.w. From all HCHs isomers studied, γ-HCH was the most abundant and represented more than 60% in all samples analyzed.
HCB (Hexaclorobencene) is a fungicide and started to be used for seed treatment in 1945. It was intensively used in Chile. HCB is also a byproduct of the manufacture of other industrial chemicals, including organic solvents. It is one of the most persistent environmental pollutants because of its chemical stability and resistance to degradation. HCB has not been manufactured, or marketed in the country; its environmental levels are presumably derived from industrial activities. Possible sources of HCB are: 1) by-products of the manufacture of certain chlorinated solvents; 2) fluxing agent used in the manufacture of aluminium; and 3) pesticides containing HCB as impurity (for example pentachlorophenol (PCP). In Chile, PCP has been intensively used, during the 80s, to protect exotic plants and as paddy field herbicide in the Bíobío basin. In this study levels of HCB were very low and only detected at site 2 (middle bay station) .

These low levels of OCPs in Concepción Bay might be influenced by three main factors: firstly due to the prohibition of this chemicals in the country that started 30 years ago, and therefore reflect the effectiveness of national and international regulations positively; secondly because since the beginning of 2000 there was a reduction in the industrial activities within the bay, and lastly, because the 2010 Tsunami might have removed the superficial sediments and therefore changed the chemical composition of its sediments. However, more research is still need to complete this investigation.

**PCB concentrations and patterns**

The family of PCBs is composed of 209 congeners. In this study seven only PCBs (PCBs indicators) were studied. PCBs have been widely used as dielectric fluids in Chile (Pozo et al., 2014). The results obtained in this study showed low concentrations of PCBs (<10 ng/g d.w.) as well as a decreasing gradient of PCBs concentrations: SITE1> SITE2> SITE3 (Table 1). These values are similar than those detected in other areas of the country i.e., in the Chilean fjords (<8 ng/g d.w.) (Montory et al., 2008) and mountain lakes (<5 ng/g d.w.) (Pozo et al., 2007). The PCB congener composition was dominated by higher chlorinated PCB which accounted for ~70-80 % of total PCB concentrations (Figure 2). Individual PCBs abundance was characterized by: PCB-153>-138>-101>-180 (Figure 2).

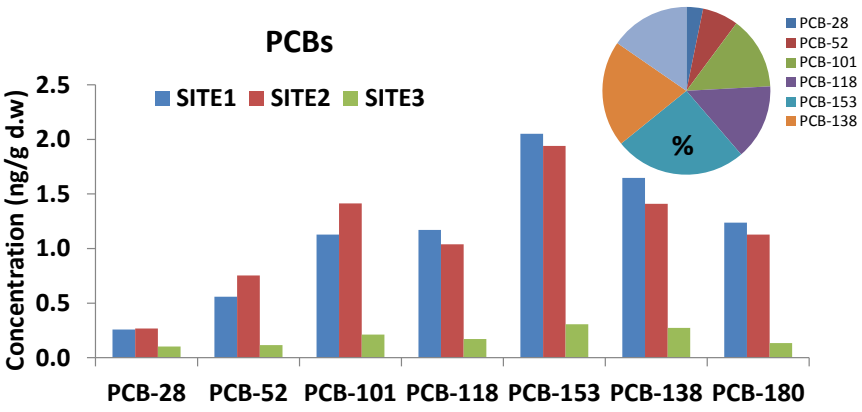


Figure 2. Concentrations and distribution of PCB congeners in sediments of Concepción Bay during 2013.

**PBDE concentrations and patterns**

Results showed from the 10 PBDE congeners analyzed, congeners BDE-47, -99, -100 (low brominated congeners) and PBDE-209 (high brominated PBDE) were the four most frequently detected congeners in all samples analyzed. The concentrations of ΣPBDE-47, -99, -100 in sediments were low (~1 ng/g d.w.) and decreasing from head to mouth on the inner Bay (in ng/g d.w. SITE1 [0.09] > SITE2 [0.05] > SITE3 [0.02]). However, PBDE-209 showed the highest concentration of ~20 ng/g d.w. with a similar pattern decreasing from head to mouth on the inner Bay (in ng/g d.w. SITE1 [21] > SITE2 [5] > SITE3 [2]) (Figure 2). These concentration values are higher than those reported in intertidal sediments of Bohai Bay in China (10-650 pg/g d.w.) (Zhao et al., 2010) and than those values reported by Baron et al. (2013) for PBDE-209 (~2 ng/g d.w.), before the 2010 Tsunami, showing a decreasing factor 10 times lower for BDE-209 (in the same study area). However, our results were similar to those detected in marine sediments in Shanghai (China) (50 ng/g d.w.) and the North Sea (Belgium) (30 ng/g d.w.). The prevalence of PBDE-209 might be influenced by the massive urban debris (material from destroyed houses, cars, and electronics) dragged by the 2010 Tsunami event, which has contributed with a new source of chemicals into the coastal ecosystem of the bay.

**Conclusions**

Levels of chlorinated pesticides and PCBs and OCPs detected in sediments were low in Concepción Bay. γ-HCH was the most abundant OCPs detected, however, this compound was banned in Chile in 2007. There is a prevalence of PBDE-209, which was influenced by massive urban debris during the 2010 Tsunami. These values may be influenced by two main factors: firstly, a reduction in industrial activities at the beginning of 2000 and secondly, due to the effect of the tsunami of 2010 in central Chile that might have removed the superficial sediments of the Bay. This study is one of the few research projects in the country that contributes with new information of POPs in coastal environments of Chile. Further research is still needed to understand the contamination status of Concepción Bay.

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