



Baseline

Polybrominated Diphenyl Ethers (PBDEs) in Concepción Bay, central Chile after the 2010 Tsunami



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ABSTRACT

PBDEs (10 congeners) were analyzed using GC–MS in superficial sediments and organisms of the Concepción Bay after the 2010 Tsunami. From all congeners analyzed PBDE-47, -99, -100 and -209 were the most frequently detected. Concentrations (ng g^{-1} d.w.) in sediments for Σ PBDE-47, -99, -100 were low (0.02–0.09). However, PBDE-209 showed significantly higher values $\sim 20 \text{ ng g}^{-1}$ d.w. This result were ~ 10 times lower than those reported in a previous study of the 2010 Tsunami. The high result might be influenced by the massive urban debris dragged by the 2010 Tsunami. In organisms, concentrations of PBDE-47, -99, -100 ($\sim 0.4 \text{ ng g}^{-1}$ d.w.) were higher than those found in sediments ($\sim 0.04 \text{ ng g}^{-1}$ d.w.). Differences in PBDE pattern were also observed between different levels of the trophic food chain (primary and secondary consumers). This is the first attempt to assess the current status of Concepción Bay after the 2010 Tsunami.

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Concepción Bay is a coastal 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 neighboring 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 several activities including maritime traffic, recreational activities (i.e., fishing and swimming), management areas for benthic resources, small economic entrepreneurs (artisanal fisheries) and others. However, Concepción 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, shipyards, industrial wastewater and anthropogenic activities. The bay hosts some of the most important ports of the region and the country (Talcahuano, Lirquén and Penco). The Andalién River flows at the head of the bay into the southeast sector contributing to untreated sewage from nearby towns and residual chemicals from agriculture and forestry in the Cordillera de la Costa (Rudolph et al., 2002).

Previous studies have reported high levels of Polycyclic Aromatic Hydrocarbons (PAHs) in sediments of the Concepción Bay (Rudolph et al., 2002). However, information of other toxic chemicals in the bay is scarce. In February 2010, the Biobío Region was hit by a high magnitude earthquake (8.8 moment magnitude scale) that triggered a tsunami that might have changed the marine ecosystem and environmental state (e.g. chemical composition of surface sediments) of Concepción Bay (Castilla et al., 2010).

Brominated organic compounds (BFRs) are flame retardants that have been used widely to prevent the spread of fire. BFRs are estimated to represent 39% of the global market flame retardants from 2000, and its use in the electronics industry, in particular, accounted for 35–40% of total flame retardants used (Wang et al., 2009). Polybrominated Diphenyl Ethers (PBDEs) are one type of BFR commonly used. As a result of its wide utilization, large amounts of these compounds have been released into the environment during its production and use. Commercial production of PBDEs began in the 1970s in Germany (ATSDR, 2004). PBDEs are not manufactured in Chile, but Chile imported them as commercial mixtures and used them for various intermediate and finished products, such as appliances, furniture, car seats, and a variety of electrical and electronic components.

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The main commercial mixtures used worldwide are the penta-, octa- and deca-PBDE. The “penta- product” contains mainly 4–6 Br congeners and has been most widely investigated because of the abundance and rapid accumulation in biological samples from remote areas (Ikonomou et al., 2002).

Due to their toxicity and persistence, the industrial production of some PBDEs (penta and octabromodiphenyl ethers formulations) is restricted under the Stockholm Convention (Stockholm Convention, 2011). Although penta- and octa-PBDEs have been banned in Europe and the United States since 2006, the fully brominated decabromodiphenyl ether (PBDE-209) is still used in parts of the world and its level in the environment is increasing in recent years.

In the past four years, only few studies had been conducted in Chile on emerging compounds such as PBDEs. For example, Montory et al. (2010) reported PBDE levels in wild chinook salmon (*Oncorhynchus tshawytscha*) in the Northern Patagonia and in farmed fish tissue (*Salmo Salar*) and most recently Barón et al. (2013a,b) reported levels of brominated flame retardants in central Chile. However, the PBDE literature in the Chilean environment is still very limited.

The main goal of this study is to determine PBDEs in sediments and organisms from Concepción Bay in central Chile after the 2010 Tsunami and contribute new and relevant environmental information for a highly urbanized and populated area. This investigation is part of an ongoing project in central Chile aimed at studying Persistent Organic Pollutants (POPs) and emerging compounds in sediments, water, organisms and air, in order to ascertain the chemical characterization of Concepción Bay.

Surface sediments (15 g) were taken at three stations in the Concepción Bay (Fig. 1) using Van Veen grab (0.3 m²). 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. Sediment samples were homogenized with anhydrous sodium sulfate, then spiked with ¹³C extraction standards and extracted using DCM in an automated Soxhlet extraction system (Büchi B-811). The extracts were reduced under stream of

nitrogen to 10 mL and split into 2 aliquots, similar to biotic samples. The POPs aliquot was cleaned-up on a glass column filled with 1 g AgNO₃ and 5 g 44% H₂SO₄ silica. The sample was loaded and eluted with 40 mL DCM:*n*-hexane mixture. The solvent was reduced in TurboVap II and transferred into a GC conical vial, recovery standards were added.

The species of organisms analyzed correspond to primary consumers (including filtering): *Venus antiqua* (*n* = 10), *Aulacomya atra* (*n* = 10) and secondary consumers: *Odontesthes regia* (*n* = 4) and *Merluccius gayi* (*n* = 4). Before extraction, organism samples were spiked with ¹³C extraction standards and extracted in an ultrasonic bath for 15 min with 50 mL of DCM, three times. Final solvent extracts (150 mL) were pooled and the solvent was reduced under stream of nitrogen to a volume of 10 mL. The reduced organism extract was split into 2 aliquots, 1/10 for PAHs analysis, and 9/10 for PBDE analysis. Clean-up of the PBDE aliquot was performed on a modified silica column, 25 mm i. d. (3 g silica + 20 g 44% H₂SO₄ silica + 10 g 22% H₂SO₄ silica + 6 g silica + 10 g Na₂SO₄), the column was prewashed with 80 mL *n*-hexane, the sample was loaded and then eluted with 150 mL *n*-hexane. The solvent was reduced in TurboVap II and transferred into a GC conical vial, recovery standards were added. The total lipid content of the species studied was determined by weight difference and accounted for ~5 (±2) %.

Sediment and organism samples were analyzed for 10 PBDE congeners (BDE-28, -47, -66, -99, -100, -85, -154, -153, -183, -209). The PBDE analyses were 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 × 0.10 µm) (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. For BDE-209, the resolution MS was set to >5000. Injection was splitless 2 µl to 280 °C, with He as carrier gas at 1 ml min⁻¹. GC temperature program was 80 °C (1 min hold), then 20 °C min⁻¹ to 250 °C, followed by 1.5 °C min⁻¹ to 260 °C (2 min hold), and 25 °C min⁻¹ at 320 °C (4.5 min hold) (Lohmann et al., 2013).

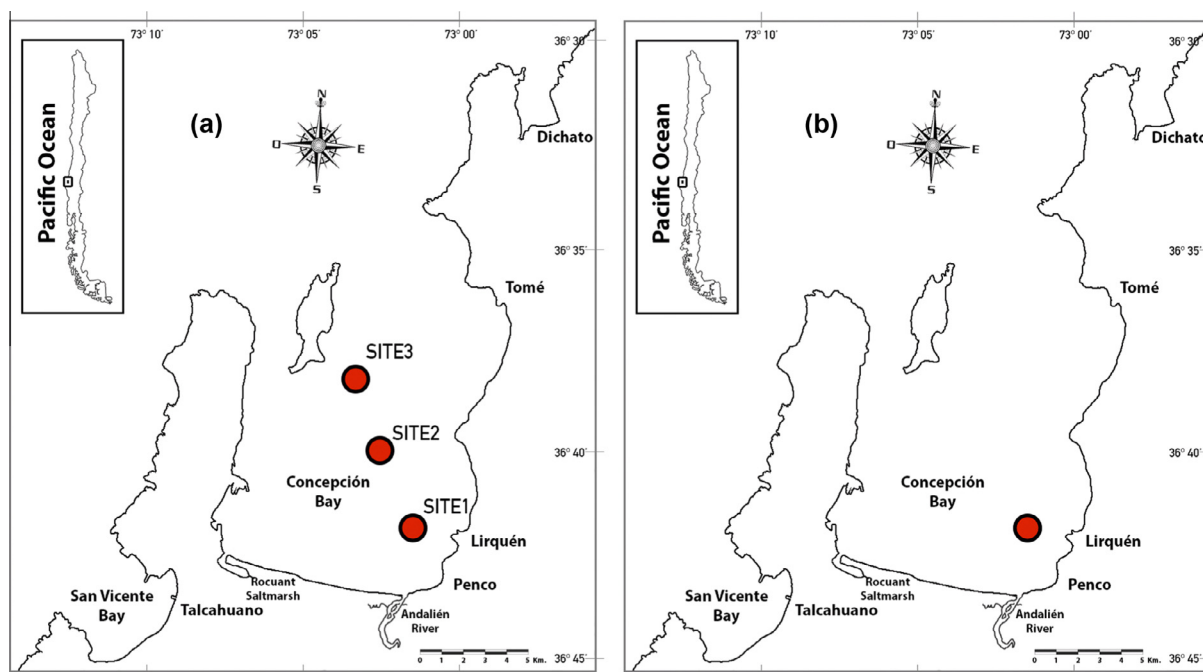


Fig. 1. Sampling locations for (a) sediments (*n* = 3 stations) and (b) organisms (*n* = 1 station) in Concepción Bay, during May 2013.