POPs in *Mytilus californianus* from coast and islands off Baja California, Mexico.

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Introduction

Legacy POPs are organochlorine compounds long prohibited from fabrication and distribution around the world. POPs linger for very long time in several compartments of ecosystems and tend to cause toxicity effects in exposed populations. These compounds have been well reported in the northern part of the Southern California Bight (SCB) and much less so in the southern part of the Bight. Among the largest concentrations worldwide for example for DDT in mussel tissue have been reported at the south of California, USA [1]. The Southern California Bight (SCB) is a shared water body between Mexico and the USA where some of these large concentrations for DDTs, and other pollutants have been reported. On the Mexican side, there is much less information on legacy POPs in mussels. There are some works on pesticides on mussels using relatively few POPs [2]. Mussels have been shown to represent an integrator over time of marine pollutants [3]. In this work, we have measured legacy POPs in *Mytilus californianus* in islands and coastal sites. The study area extends from the International Border between California, USA and Baja California, México to Punta Banda and Todos Santos Bay in Ensenada, Mexico. Additionally, we also included one site about 320 km at south from the International Border, located in an unpopulated area and with low anthropogenic impact. This is a coastal extension of about 100 km and represents the developed part of the Southern California Bight on the Mexican side (Figure 1). Given that these pollutants are legacy pollutants and have been prohibited for several decades on both countries, we hypothesize that there should be a relatively homogeneous distribution of the measure pollutants independently of the site where the samples are collected.

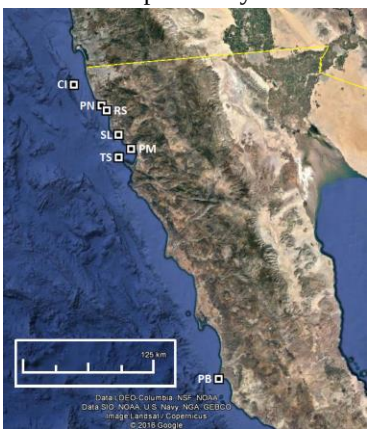

Figure 1. Sites where mussel samples were collected. CI= Coronado Islands, PN= Puerto Nuevo,RS= Rosarito, SL= Salsipuedes, PM= Punta Morro, TS=Todos Santos Island, and PB= Punta Baja.

Materials and methods

Mussels (*Mytilus californianus* Conrad, 1987) were collected from rocky intertidal locations along the Pacific coast of Baja California, and from two islands. At each site, mussels of commercial size (shell length: 6 to 10

cm) were collected from one to three intertidal mussel patches (60 mussels from each sampled patch) following the sampling protocol described by the Mussel Watch Program [4]. These were mixed and homogenized according to standard procedures. Briefly, three to five grams of homogenized mussels were Sohxlet extracted for 16 hours using HPLC grade dichloromethane (BHD. VWR, Inc.), following a modified method described by Macias-Zamora et al. (2014). Acid-activated copper wireballs were used to remove elemental sulfur interferences in the organochloride pesticides and PCBs analysis. Prior to Sohxlet extraction, the samples were spiked with a recovery surrogate mixture (TCMX, and PCB-209). Then, the extracts were cleaned-up using 1x30 cm glass column packed with 3% deactivated silica and alumina. The elution was performed using 15 mL hexane (F1), and successively with 40 mL hexane:DCM (70:30, v/v) and 20 ml hexane:DCM (60:40, v/v), being the last two eluates collected as one fraction (F2). Then, both fractions were rota-evaporated to 1 mL, and reduced to 0.5 mL in N_2 stream. Procedural blanks and standard reference materials (NIST SRM 2974a) were used for quality control evaluations in each analyzed set of samples.

Prior to GC analysis, a mixture of PCB-30 and PCB-205 were added to the vials as internal standard. The organochloride pesticides and PCBs were determined and quantified using a Hewlett Packard 6890 Plus GC equipped with an Electron Capture Detector (ECD). A 60 m DB-XLB column (0.32mm i.d. x 0.25 µm film) was used in the analysis; Helium was used as the carrier gas and set to 1.1 mL/min. The oven temperature was programed as follows: 80 °C for 1 min, 15 °C/min to 150 °C, 1 °C to 250 °C, and 5 °C to 300 °C for 25 min. Finally, the temperature of the injection port and the detector were 280 and 310 °C, respectively.

Pesticides analysis were HCH (α β γ and δ), HCB, Heptachlor, Heptachlor epoxide, α-chlordane, γ-chlordane, Endosulfan I, Endosulfan II, Endosulfan sulfate, p,p′-DDTs, as well as o,p DDTs, Aldrin, Dieldrin, Endrin, Endrin aldehyde, Oxichlordane trans and cis nonachlor, metoxychlor and mirex. In addition, 51 most frequently found PCBs (18, 17, 31, 28, 33, 52, 49, 44, 37, 74, 70, 66, 101, 99, 119, 87, 110, 81, 82, 151, 77, 149, 123, 118, 114, 153/132/168, 105, 138, 158, 187, 183, 126, 128, 167, 177, 171/201, 156, 157, 180, 191, 170, 199, 169, 208, 189, 195, 194, 206) were also measured.

Results and discussion

We found the presence of OCs in all samples used in this work. In general, pesticides had larger concentrations than PCBs. Pesticides were found in the following order; Endosulfan II> α-HCH> p,p'-DDE= o,p'-DDD. We can also say that 20 out of 27 compounds were found in the different samples collected. With respect to pesticides, one of the most important results is the fact that the most polluted samples for mussel tissue were those collected at Coronado Islands. These small Islands are located near the International border at north (Figures 1 and 2). In Fact, these samples had as much as four times the amount of pesticides found at any other location. This same unusually higher concentration was observed for PBDEs at the same island (in preparation).

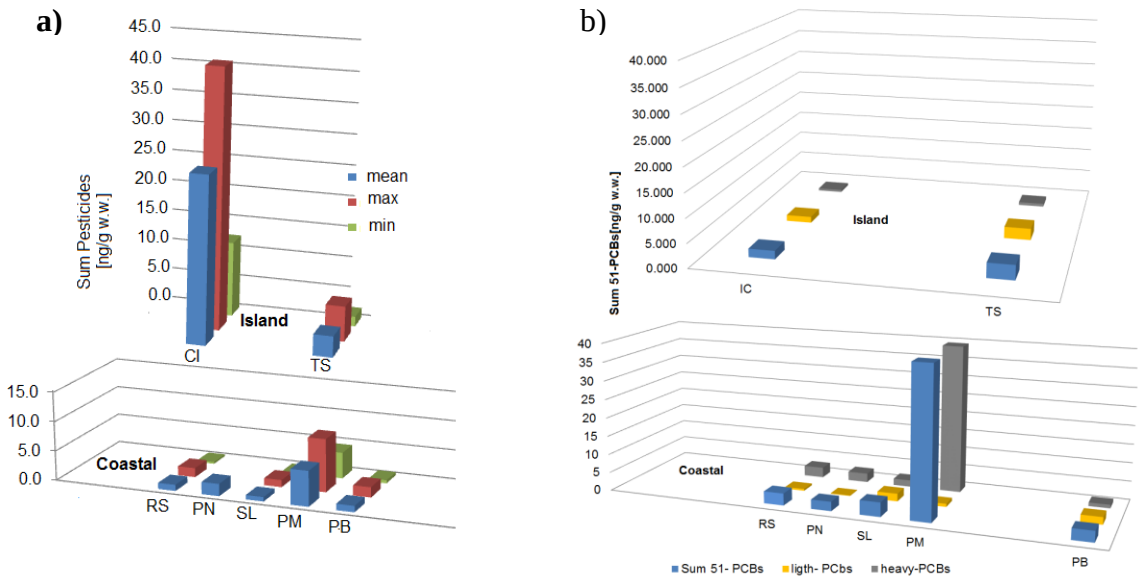

Figure 2. Mean concentration for the sum of pesticides (a) and sum of PCBs (b) in ng/g w.w. Comparison from at the islands and coastal zones in the southern part of the southern California Bight.
The names for the sites are mentioned in Figure 1.

With respect to PCBs, maximum concentrations were not found at the Coronado Islands. Concentrations for PCBs were more homogeneous than those for pesticides (Figure 3) except for Punta Morro site (PM).
These results suggest that there is bioconcentrations by mussels as values in marine sediments [5] for the region are below those of the CI reported here. Contrary to our main hypothesis, there was no homogeneous distribution of pesticides in the region. In fact, there is at least one of the sites (CI) that showed the largest concentration for the area sampled. However, PCBs did not show largest values at the same site, the largest sum for PCBs was located within Todos Santos Bay (PM). We can only speculate that the rather restricted circulation at that site may favors accumulation for these compounds and in addition there maybe an important local source. We must add that most PCBs found were those with relatively large molecular weight. It is worth mentioning that at the time of collection, most organisms contained around 4% lipids. Only at two sites (RS and PN) their lipid content was around 7%. This may suggest that most organisms had lost part of their pollutants load through spawning. This was very unusual because we observed water temperatures about 19 to 20 o C in November-December probably associated to the presence of the so-called BLOB.

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