WHAT ARE PBDEs IN COASTAL MARINE SEDIMENTS OFF BAJA CALIFORNIA TELLING US ABOUT THEIR SOURCE?

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Introduction

Commercial polybrominated diethyl ethers (PBDEs) are chemicals used as flame-retardants in different products that were originally sold or provided in three main presentation mixtures. These chemicals have the characteristics typical of POPs. The commercial mixtures used were penta-BDE mixture, octa-BDE mixture and deca-BDE mixture[1]. These three mixtures have apparently been extensively used in USA and Mexico, and given that the products in which these mixtures were used are also similar in both countries, then it is expected that we would find no differences in uses at both sides of the border. As it has been extensively explained, the source of these chemicals to the marine environment is the result of their use in electronic equipment and furniture, such as television, computers, sofas, mattresses and other foam based materials, which are imported into Mexico mostly from USA, either as new products or used ones. Many of these products eventually will end up in dumping municipal sites. It is also expected that because of very low precipitation regimes in the area, the main route for input into the marine environment would be the result of wastewater discharges more than run-off introduced in the study area. In addition, we are proposing that the distributions found in our study area (Figure 1) along the coast from the international border and all the way to Todos Santos Bay, about 100 km at south from the border is the result of two main factors; one, the closeness of the sampling sites to wastewater treatment plants and the effect of local circulation and to some extent, to the energy of currents and waves at the sampled sites. The coastal waters extending from Southern California from Point Conception and reaching as far south as Point Colonet in Baja California, Mexico, are waters that have a complex local circulation[2] which favors an important exchange (dissolved in water and attached to particles) of chemicals from both sides of the international border. We propose that the Coastal Surface Current (CSC) described by those authors is the main responsible for the type of sediment distribution that we have observed.

We must keep in mind that the deca-brominated congener, the BDE-209 may produce via de-bromination, other BDEs congeners[3, 4]. Consequently, it becomes important to determine the concentration of this particular congener.

As part of the Bight-2013 Mexican contribution, we collected samples in the Southern part of the Southern California Bight (SSCB). Sediment samples were collected using a Van-Veen grab sampler and surface sediments (top two centimeters) were collected to measure the following congeners; BDE-17, BDE-28, BDE-47, BDE-66, BDE-71/49, BDE-77, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-181, BDE-183, BDE-190, BDE-209.

The sampling area has approximately 100 km in length and extends as deep as 500 m isobath. The sampling area has been historically divided in three strata depending on population density: a northern, a central and a southern stratum, this year we included the estuary as a stratum. It has also been divided in three depth related strata; the inner-shelf, the medium shelf and the deep-shelf stratum. The objectives of the study were to determine if the concentrations in our coastal marine sediments are similar to those reported to the north of our study area but in Southern California Bight Coastal marine sediments. This was prompted by the statement that "the range of $\Sigma PBDE_{13}$ concentrations measured in the SCB… is on the high end of marine and estuarine concentrations reported in other North American regions"[5]. Other indications that we had to look at our environmental concentration were the reported concentration of PBDEs in mussels[6] and in marine mammals, both among the largest in the world.

Materials and methods

We have already reported the methods used for the analysis of PBDEs in marine sediments[7]. In brief the method is as follows; the sampling design has been based in a randomly stratified design[8, 9] as is customary for the Southern California Bight projects. Samples were collected using a Van Veen drag and the sediments were kept in cold until laboratory where they were maintained at -20 ^{o}C until analyzed. We sampled a total of 91 stations; 41 were obtained at the northern stratum, 19 at the central stratum, 19 in the southern stratum plus 12 additional stations located at the estuary within the southern stratum. All GC–MS experiments were performed using a gas chromatograph Agilent 7890A GC (Agilent Technologies, Santa Clara, CA, USA) coupled to a triple quadrupole mass spectrometer Agilent 7000 MS (Agilent Technologies) operated in EI mode. The GC system was also equipped with an autosampler Agilent model 7693A (Agilent Technologies), an air cooled multimode inlet (MMI) and a pneumatics control module (PCM). The column used for the separation of these compounds was the Agilent DB-XLB of 15 m long, 0.250 mm diameter and 0.10 µm film thickness. We used, with minor modifications the method proposed by Agilent[10] that consist of an injection of 2µL of sample in a pulsed splitless multimode inlet (MMI). We used a compressed air-cooled pulsed splitless injection to 88 ^{o}C during 0.2 min and then we used a ramp of 600 ^{o}C/min to 285 ^{o}C. Transfer line was kept at 300 ^{o}C and all other parameters were equal to those reported by them. Transfer line was kept at 300 ^{o}C and all other parameters were equal to those reported by them. In general, we also used the same table of precursor ion, and product ion as those suggested; however, we change the gain for most of the BDEs except for BDE-209. The oven temperature program was also the same as that suggested with the exception that we extended the final temperature for 4.0 min.

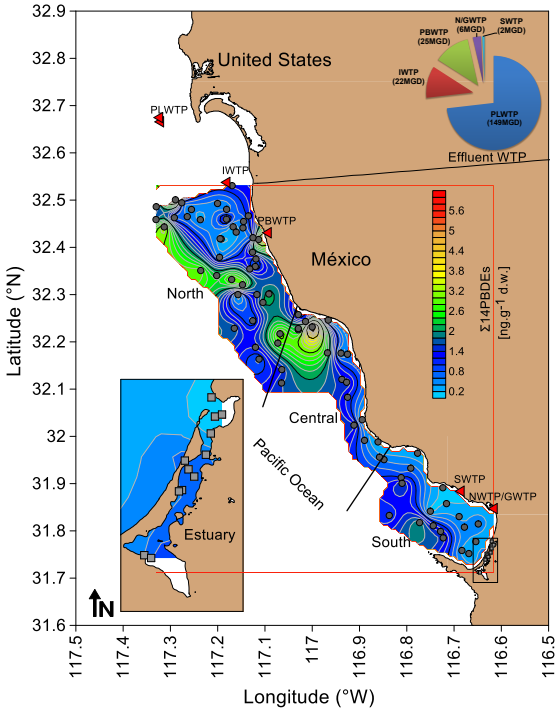

Figure 1. Sediment sampling sites and surface distributions for ΣPBDEs in the coastal region of Baja California, Mexico. Main wastewater treatment plants locations are shown as red triangles. In the inset we show as a pie, the proportional volume discharges in average (million gallons per day-MGD) for the most important wastewater plants.

Results and discussion:

PBDEs concentrations in marine sediments were detected at 91 of the 91 sampling sites making them widely distributed in SSCB sediments. From the 16 PBDE studied, the total concentration was dominated by BDE-209 at 78% of the total (Figure 2), followed by BDE-99 at 4 %, BDE-47 at 3.9 %, BDE-49/71 at 2.5%, BDE-154 at

2.1%,BDE-153 at 1.6%, BDE-100 at 1.6%, the BDE-17, 66,183,28 each at 1.0%. However BDE-190 which was found in only 16 out of 91 samples and BDE-138 (found in 27 out of 91 samples) were detected at near detection level and represented <<1.0 %. In the particular cases of BDE-77 and BDE-181 these two congeners were not detected at any of the sampled sites.

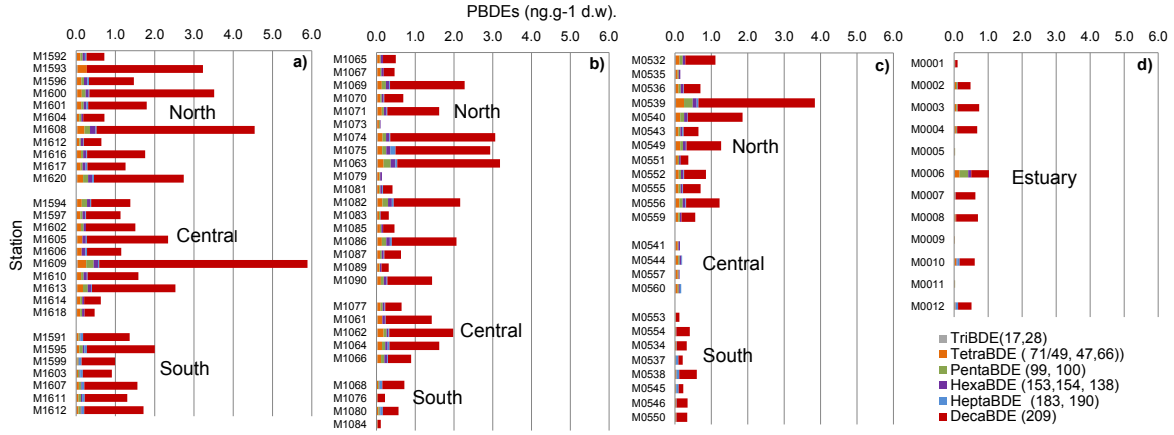

Figure 2. Depth related concentrations of PBDEs in surface sediments at the inner, mid and outer shelf in the north, central and south stratum. The predominance of BDE-209 is clear. a) Outer shelf, b) Mid shelf, c) Inner shelf and d) Estuary

From Figure 2 above, one can deduce that the two most frequently used mixture at or near these sites were in first place the deca-mixture, which consist mainly of BDE-209 with only a minor contribution from other PBDEs. The second mixture used appears to be the penta-mixture (composed mainly by the tetra, penta and hexa BDE), although we did not include all the congeners of the octa-BDE mixture (see also Figure 3).

Although the presence of PBDEs has been attributed by others to mouths of rivers as the main source[11] and others have explained the important role of wastewater discharges[12], given our special circumstances of scarce rain events and in particular given the surface concentration found in our area (see Figure 1) we conclude that the main source to our sites is provided via wastewater discharges from treatment plants located in our study area. The PBDEs concentration has also been frequently associated to urban development; this would also explain the clear north to south gradient in median concentration shown in Figure 3. It is very likely that the circulation resulting from the CSC is transporting particles carrying the PBDEs as well as other pollutants near the isobaths of the 500 m. The accumulation spot located at the north of the central stratum has been a frequent feature of other pollutants and it has been attributed to an effect of local topography. It is the largest concentration site determined for the area but is only the 5.9 ng/g dry weight. An the north stratum, the main signal found and shown in Figure 1, is most probably attributable to the large discharge of particles from the Point Loma Wastewater Treatment Plant. The presence of the discharge from Punta Banderas Wastewater Treatment Plant can be observed near the coast with concentrations near 4 ng/g dry weight. At any rate, the comparison between sediments reported for the Southern California Bight from below the detection limit to 560 ng/g dry weight is two orders of magnitude larger than those found here that extend from 0.02 to 5.9 (median 0.71) ng/g d.w. This range in concentration is similar to that reported by Voorspoels et al., for a more reduced number of congener at the Belgian North Sea ranging from below LOQ to 24 ng/g.[13] Finally, these numbers measured at each strata translates in an estimated average concentration of about 36 kg of PBDEs for the north, about 22 kg for the central and about 10 kg for the south stratum. The small estuary in Todos Santos Bay contributes with just 0.2 kg; all of these were calculated considering the top 2 cm of sediment collected for each sample.

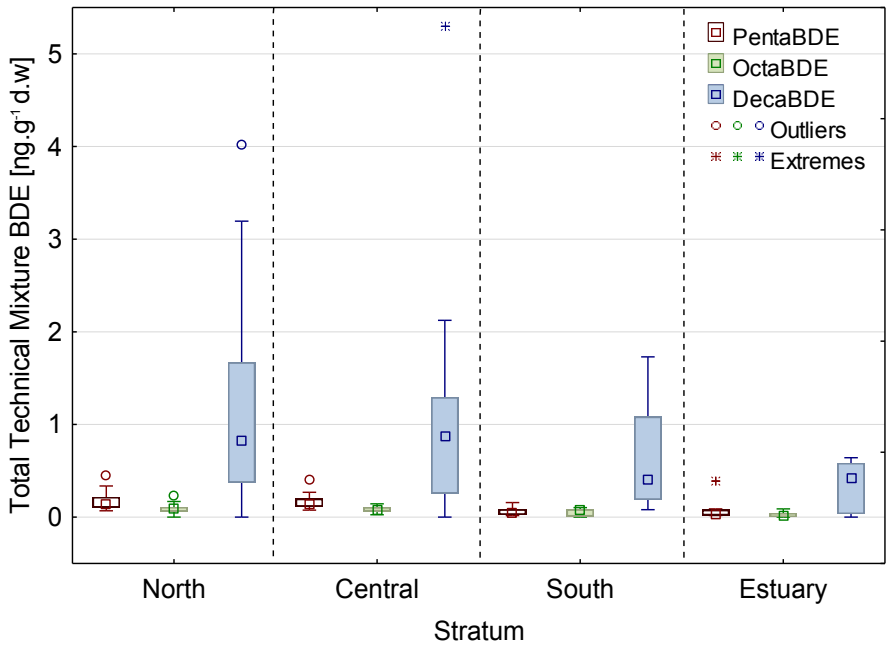

Figure 3. Total PBDEs mixtures at the different stratum. The blue Deca-BDE is the largest signal detected in the study area. A North to South gradient is observed.

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