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Are PBDEs In Marine Sediments At The Coast Of Baja California Mexico Increasing In Time? A Problem Revisited

J. Vinicio Macías-Zamora [1], Nancy Ramírez-Álvarez[1], Félix Augusto Hernández-Guzmán[1], Cristina Quezada-Hernández[1].

[1] Instituto de Investigaciones Oceanológicas, Universidad Autónoma de Baja California. Carretera Transpeninsular Ensenada-Tijuana No 3917, Fraccionamiento Playitas, Ensenada, B.C., México
vmacias@uabc.edu.mx; nancy.ramirez@uabc.edu.mx; augusto.hernandez@uabc.edu.mx; cristina.quezada@uabc.edu.mx

Abstract **-** We report here on the finding for PBDEs in coastal marine sediments in the south end of the Southern California Bight. We propose that there are two main contributors to the distribution of these chemicals in this part of the world for the surface distribution and composition of the PBDEs found. On the one hand, the presence of potential local sources such as wastewater treatment plants and on the other, the energy in the area provided mainly from the currents, the winds and waves for each area (North, Central, and South) and a third component due to the local topography. The range of concentrations for the sum of 14 PBDEs was; from undetected to a maximum of 9.74 ng/g dry weight. Generally, the largest concentrations coincided with samples collected in the deeper sites and located to the north. As previously found, the BDE-209 is predominant congener which indicates the trend given the discontinued commercial use of Penta-BDE and the Octa-BDE mixtures while maintaining still in use the Deca mixture. We also found an apparent increase in concentrations for the sum of these 14 PBDEs analysed as compared to that reported by us in 2013.

Keywords**:** PBDEs, marine sediments, Southern California Bight, emerging pollutants, BDE-209.

1. Introduction

The Southern California Bight (SCB) is an area located on the Coastal Pacific shared by Mexico and the USA. It is a region where the coast of California makes a turn and as a consequence, generates a very particular environment. The external border of the Bight in the ocean is the California Current (CC). This current is of around 4 cm/sec velocity (characterized by bringing cold nutrient rich water to the region [1]. This current, that travels from north to south during the year, extends to around Sebastian Vizcaino Bay in central Baja but mainly in summer is meet by a current from the south, with warm and salty water that becomes the Southern California Countercurrent [2], [3]. Also, a characteristic for the area are the frequent upwellings events that bring water from medium depths, again rich in nutrients, to surface water improving the productivity for the impacted zone. Additionally, another important feature is the presence of extended kelp forest along the rocky bottoms which also increase the productivity of the SCB given that they serve as forage and protection for many marine organisms. The net result of circulation for SCB is a Mediterranean type of weather with both mild summers and winters for the region.

The year around mild weather results in a large economy on both sides of the border with large human settlements (around 17 million people in the USA part of the Bight [4] and around 3 million on the Mexican side and in addition, a very large floating population visiting the area estimated as around 100 million visitors per year. Large wastewater treatment plants at both sides continuously discharge water with different levels of treatment. This along with some poor land vegetation and relatively large rain events (associated to El Niño events) produces run-offs with large amounts of garbage, plastic, bacterial pollution, and debris that end up in the coastal zone. Along with these materials, several other dangerous substances are discharged either accidentally or on purpose via wastewaters, such as PCBs, PAHs, PBDEs, PFAS, and other pollutants. Given that PBDEs have been found in large concentrations in the northern part of the Bight) [4], [5], the Mexican part of the Bight may be also importantly affected. PBDEs belong to a group of chemicals used as fire retardants that have been extensively applied to protect from rapid ignition on many materials including; plastic foam used in furniture, in computers, cables, and many other materials. They use to be sold in three commercial formulations; the so-called Penta, Octa, and Deca mixtures, where the first two were actual mixtures and the last being composed mostly of BDE-209.

We have previously reported on the presence of Polybrominated diphenyl ethers (PBDEs) which is a group of manmade chemicals and of global distribution [6]. Because of their very wide environmental distribution, they are a concern. In particular for this part of the world where nearby in Southern California, some of the largest values have been reported. In

addition, we have previously reported also on a not very visible but constant transport mechanism through time. This mechanism of transport occurs all along the Mexico-USA International border. In particular, at the California-Baja California border, old furniture, curtains, old mattresses, old carpets, and other PBDEs containing materials are constantly crossing the border into Mexican territory. After some limited use, most of these materials end up in municipal landfills. From there, rain and wind will end up transporting these (and many other) chemicals into the marine environment. Once in the marine environment, frequently marine sediments are a final destination for PBDEs. Our concern is that from the marine environment, mollusks, fishes, and other marine life maybe impacted and that these and other marine products are consumed locally.

As a component of a monitoring program along the more developed part of the Baja Coast on the Pacific side, we set out the sampling of 2018 of the south end of the Southern California Bight. For this purpose, we have included the following available PBDE isomers: BDE-17, BDE-28, BDE-47, BDE-71/49, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-181, BDE-183, BDE-190, and BDE-209. In addition to these BDEs; BDE-33, 66, and 77 were only considered in the 2013 sampling, while BDE-85 was not considered.

This coastal region starts at the international border between California and Baja California and runs for about 100 km reaching Todos Santos Bay in the south, which is a portion of the complex Southern California Bight ecosystem. The samples of marine sediments were collected from on board the Catamaran Alguita. Sampling extended from about ten meters depth and samples were collected as much as near the 250 m mark. Along the coast, urban development of the largest three cities (Tijuana; in the north, with more than 2.5 million people, Ensenada; in the south with around 0.65 million people, and Rosarito with estimates of near 0.2 million people) are threatening the coastal environment. Three main routes of entry can be mentioned for these substances into the coast. First, and one of the most frequently indicated is the wastewater discharges of treated, poorly treated or even untreated wastewater. Second, the runoff after rain events, which as contrary to other countries, in this part of Mexico, it gets partially combined with wastewater. The third and less evaluated route is the atmosphere. Given the particular environment of the region, semiarid land with few plants' coverage, runoff appears to be an important route [3]. Most creeks and rivers are dry most of the year. The Tijuana River is the only river in this area, but it includes a dam that has diminished water discharges to the coast. Most of the time this river contains, after the dam, a flow of untreated wastewater discharged on the Mexican side then reaching the Tijuana River Estuary located on the US side. In addition, along the coast, from north to south we have five mayor wastewater treatment plants. All plants on the Mexican side are either in poor service conditions or their capacities are exceeded, thus discharging poorly treated wastewater into the coast. Circulation is complex, basically the California Current (CC) travels equatorward offshore and there is a weaker countercurrent system that brings warm water in a poleward direction with different intensities during the year [2]. In addition, the poleward current includes the California Undercurrent, the Davison Current and the Southern California Eddy [7], [8]. This is a complex system of currents eddies and countercurrent as well as upwellings in the region (Figure 1).

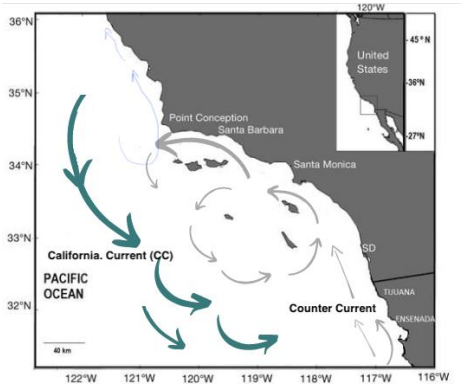

Fig. 1: Simplified diagram of some of the main currents along the California-Baja California Coast. This Southern California Bight diagram does not include subsurface currents, undercurrents, and upwellings.

2. Materials and Methods

The sampling design has consistently been based on a randomly stratified design using that used by the Southern California Bight projects. Surface sediment samples were collected with a Van Veen dredge. The collected samples were were kept cold until they arrived at the laboratory. Once in the laboratory, they were kept at -20 °C until analysis.

The method used for PBDE analysis is a modification of the method proposed by Murphy et al., [9]. Briefly, a 3-gram sample of dry sediment (0.5 g for the NIST 1944 standard reference material) was mixed with 1.5 g of diatomaceous earth and placed inside the cell of an Accelerated Solvent Extraction (ASE) equipment. The cell was packed sequentially as described below: First, a GF/F glass fiber filter without binder is placed inside, followed by 12 g of silica, 6 g of basic alumina (activated), a layer of white sand, followed by the mixture of sediment with previously homogenized diatomaceous earth.

The method used in the equipment consists of four static cycles of 5 minutes at 100 °C at a constant pressure of 1500 psi, with a turnover volume of 60% of the cell capacity, 180 seconds of purging. The extraction solvent used was pesticide grade dichloromethane. Elemental sulfur interferences were removed by adding balls of activated copper wire to each collecting flask. The extract obtained was concentrated by evaporation using the GENEVAC Rocket equipment to approximately a volume of 2 mL and its volume was reduced to about 1.0 mL, prior to the cleaning procedure. The cleaning procedure was carried out using the method proposed by Macias-Zamora et al., [6] with some modifications. Cleanup was performed by liquid chromatography on a 1 × 30 cm glass column packed bottom-up with 12 cm of silica (Sigma-Aldrich, 60-200 mesh, 150 Å, 3% deactivated) and 6 cm of alumina (Sigma-Aldrich, ~150 mesh, 58 Å, 3% deactivated). The elution sequence consisted of 10 mL hexane, 20 mL hexane/DCM (70:30, v/v), 25 mL (60:40, v/v), and 15 mL dichloromethane. The fraction obtained was concentrated with the GENEVAC Rocket equipment to approximately 2 mL and was subsequently reduced to 0.5 mL using a smooth flow of N_2 (g). Before gas chromatography (GC) analysis, the volumes were adjusted to 0.5 mL with hexane and the internal standard 4'-Fluoro-2,3',4,6-tetrabromodiphenyl ether, (FBDE-4001S, AccuStandard Inc., 500 ng/mL) was added.

All experimental GC-MS measurements were performed using an Agilent 7890A GC gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) coupled to an Agilent 7000 MS triple quadrupole mass spectrometer (Agilent Technologies) operated in electron impact (EI) mode. The GC system was also equipped with an Agilent model 7693A autosampler (Agilent Technologies), an air-cooled multimode inlet (MMI), and a pneumatic control module (PCM). The column used for the separation of these compounds was an Agilent DB-XLB (with a length of 15 m, a diameter of 0.180 mm and a film thickness of 0.08μm). The chromatographic method used was a modification to the one proposed by McGrath et al., [10], which consists of an injection of 2 μL of sample in splitless pulsed mode using the multimode injector (MMI). It should be noted that the injection port remained cooled by compressed air at 100 °C for 0.2 min and then suddenly increased with a ramp of 900 °C/min to 330 °C during the total time of the chromatographic run (15.09 min) Helium was used as carrier gas at a constant pressure of 33.814 psi with a flow rate of 1.8 mL/min (8.25 minutes), 100 mL/min to 4 mL/min. The injector temperature was kept at 280 °C and the detector at 300 °C. The MRM transition table used for data acquisition were those suggested by Kalachova et al., [11] modifying only the gain for most of the BDEs, except for BDE-209.

PBDEs were identified using an AccuStandard mixture of standards (14-PBDEs in the BDE-COC mixture). The calibration curve was prepared with the following concentration points 1, 10, 50, 250, and 500 ng/mL.

2.1. Results And Discussion

The surface sediment distribution for the sum concentrations of the 14 BDEs included in this study, are shown below in Figure 1. Both maps show consistency as to the areas where the largest concentrations are found. Similarly, their distribution may be explained by the same transport in the sea that we originally proposed [6].

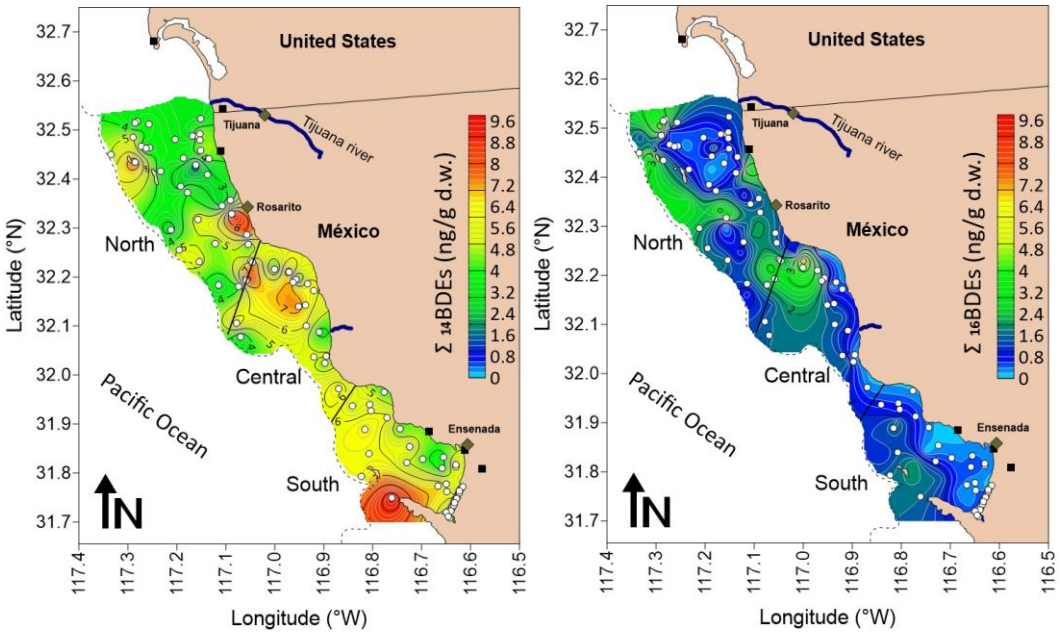

Fig. 2: Sampling sites along the coast of Baja California. The white unfilled circles indicate the geo-referenced sites of sediment collection. The map on the left represents the results for the $\sum_{14}$ PBDEs of 2018. The map on the right represents the $\sum_{16}$ PBDEs measured in 2013 shown in our previous paper and modified for the same concentration scale. Black squares on the land represent the sites for the main wastewater treatment plants. The broken line indicates the 200m depth isobath

The abbreviated form of the results obtained for the $\sum_{14}$ PBDEs of 2018 are shown in the box and whiskers diagram shown below as Figure 3. This new concentration increase results are easily visualized when set-up at the same scale

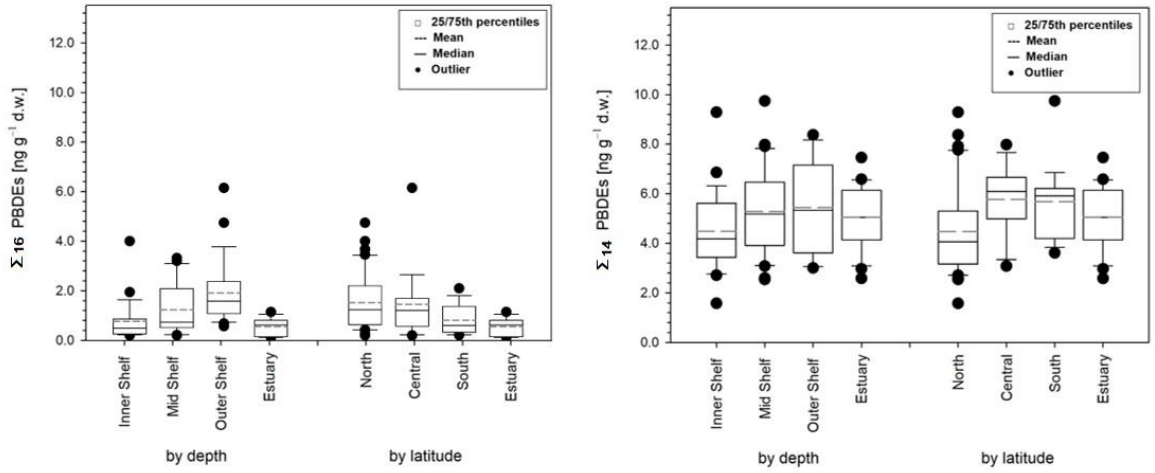

Figure 3. Box and Whiskers diagram for the $\mathbf{\Sigma}_{16}$ PBDEs in 2013 and for the $\mathbf{\Sigma}_{14}$ PBDEs in 2018 sampling. Data is presented in both forms of stratified sampling designs, by depth strata and by Latitude. Inner shelf (5-30 m), Mid shelf (30-120 m) Outer shelf (120-200 m)

Clearly, the overlap on concentrations shown above, either by depth or by latitude indicates that there are no statistically statistically significant differences in concentrations between strata. Small trends such as a slightly lower mean/median concentration in the northern strata may be due to a more open marine shelf with larger impact of waves, currents and tides. tides. Similarly, the small trend to increase in the mean and median concentration from the inner to the outer shell suggest that the depositional environment for PBDEs is favored in deeper parts with lower energy and consequently a generally smaller sediment grain size.

The two maps in Figure 2 set at the same scale strongly suggest that there was an increase in concentration for these substances in the period after 2013. This may be due to the occurrence of an "El Niño" event during 2015/2016 of large importance [12]. This event could be the source of run-off transporting large amounts of sedimentary materials to the coast including these as well as other pollutants from land via runoff. The increase in concentration has been estimated to be as much as more than 4 times the previous reported values. We estimated in 2013 a total of 47.2 kg of these compounds for the sampled area. For the 2018 samples, the concentration estimates a total of about 202.2 kg. Calculating the amounts in a km^2 base, this translates to 0.04 kg/km^2 for 2013 and goes up to 0.15 kg/km^2 in 2018. This data is summarized in Table 1.

As in 2013, the concentration was dominated by BDE-209. However, the other congeners had a greater contribution and the order kept was different from that found in the 2013 sampling (BDE-209>BDE-99>BDE-47>BDE-49/71) [5]. The 2018 order was: BDE-209, BDE-154, BDE-153, BDE-183, BDE-100, BDE-138, BDE-47, BDE-99, BDE-49/71, BDE-181, BDE-85, BDE-17, and BDE-28. The order found in 2018 may suggest the reductive debromination of BDE-209 into less brominated compounds in sediments as explained by others [13], [14], instead of the already banned presence of commercial Octa and Penta mixtures.

Table 1: Total mass inventory of the sum of BDEs found in the Bight campaigns 2013 and 2018.

Sampling year	kg BDEs	Total Area (km^2)	BDEs (kg/km^2)
2013	47.15	1293	0.036
2018	202.2	1326	0.152

Even though the concentration of BDEs in recent marine sediments along this coastal area, the values are still as much as one or even two orders of magnitude below those reported for Southern California coast [3] where they reported as much as 569 ng/g and as much as 150 ng/g in San Diego Bay. The increasing concentration trend we observed is however worrisome.

3. Conclusion

In a period of five years of following two sampling event (2013-2018) at the southern end of the Southern California Bight, we have noticed a significant increase in the concentration of PBDEs on surface coastal sediments. This increase we suspect may be associated to an El Niño event recorder during 2015/2016 that, given the semiarid coastal zone, translates in large soil and garbage being introduced with the runoff. Rain water also gets mixed with wastewater increasing the discharged volumes and simultaneously, decreasing the residence time of municipal wastewater at the treatment facilities and also decreasing the quality of the discharges. This strongly suggest the need for the local treatment plants to either divert the runoff as a separated water volume or augment the capacity of these facilities to be able to process the excess volumes during larger than normal rains, or both. Finally, it is expected that this increase in BDEs will continue in the near future and it will probably be particularly accelerated after strong rainy years usually associated to El Niño type events.

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