OCCURRENCE OF PBDEs IN MARINE SEDIMENTS AT TODOS SANTOS BAY AND PUNTA BANDA ESTUARY

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Introduction

Polybrominated diphenyl ethers (PBDEs) constitute one family of manmade chemicals considered as of emerging concern. These compounds have become a problem due to their wide and ubiquitous environmental distribution. This family of flame-retardants is present in many modern life items including furniture, computers, rugs, and other household items. Close contact with humans is to be expected. In fact, it has been stated that the concentration in humans has been doubling each five years[1]. In addition, and because the coastal environment is frequently a final destination for many land based materials, it becomes important to understand how the coastal environment is being impacted. Additionally, it has been stated by others[2] that Southern California showed some of the largest concentration values for PBDEs for example; in *Mytilus sp*, in California Sea Lion and in Harbor seal tissues and even relatively large concentrations in marine sediments. As a consequence and given that the Southern California Bight (SCB) is a shared feature of the coast (extending from Point Conception, northwest of Los Angeles and as much as 190 km at south of the International Border) we are interested in understanding if our coastal environment has concentrations resembling those reported in the north of the SCB. We were also interested in studying if the composition of the PBDEs isomers is similar to that up north or if on the contrary, we have differences that may be the result of differences in the composition of PBDE isomers. In addition, to the best of our knowledge, this is the first report of PBDEs in marine environments in Mexican coastal waters. In this study, the following PBDEs were included: BDE-17, BDE-28, BDE-33, BDE-47, BDE-66, BDE-71, BDE-77, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-181, BDE-183, BDE-190, BDE-209.

Todos Santos Bay and its estuary are located about 100 km to the south from the border between Mexico-USA, within the southern part of the SCB (figure 1). Todos Santos Bay is a semi-protected shallow bay of around 180 km^2 with an average of about 30 m of depth[3,4].Todos Santos Island is located closer to the southern end of the Bay and the mouth at that end is approximately 6.3 km wide. The northwest mouth between the Island and Punta San Miguel has only about 11.5 km wide. It includes in this part, a deeper canyon with depths of as much as 400 m. The Bay is the base for the city of Ensenada, Baja California with an estimated population of about 580,000 persons in 2010. The main potential routes of PBDEs to the Bay, according to the findings of others[2] are the mouths of rivers and creeks transporting water through highly urbanized zones and not so much from wastewater discharges. The main expected source would be the Ensenada Creek that discharges intermittently (during rain season) into the bay but most importantly, into the port facilities. There are other three minor creeks that are also intermittent but that do not run through the city. There are in addition two wastewater discharges, one from the El Gallo wastewater treatment plant (WWTP) and the other from the El Naranjo WWTP. Both of these potential sources run though el Gallo creek (mostly dry) that runs into the bay just a few tens of meters south of the Port facilities. In a previous study, we had found that the grain size for sediment samples was generally coarser at the north (starting right at the international border) and a little less so at the center and south of this area, therefore this allow to correctly understand the possible movement and transport of these (and other) organic compounds in Todos Santos Bay[5].

Materials and methods

The method used for PBDEs analysis is a modification the proposed by Zeng and Vista[6]. Briefly, 40 g dried sediment samples were spiked with a surrogate (FBDE-4001S, AccuStandard) soxhlet extracted for 16 h with dichloromethane (J.T. Baker, HPLC grade). Elemental sulfur interferences were removed by adding activated copper wire balls to each collecting flask. The clean-up procedure was carried out using liquid chromatography in a 1x30 cm glass column packed from bottom to top with 12 cm high of silica (Sigma-Aldrich, 60-200 mesh, 150Å, 3% deactivated) and then 6 cm high of alumina (Sigma-Aldrich, ~150 mesh, 58Å, 3% deactivated). Elution sequence consisted of 15 ml with Hexane (F1) and 60 ml Hexane/DCM (40 ml: 70/30 y 20 ml: 60/40 v/v, in sequence-F2). The fraction F2 was concentrated by roto-evaporation to about 2 ml, and further reduced to

0.5 ml in a gentle N_2 stream. Prior to GC analysis, the volumes were adjusted to 0.5 ml with isooctane and was added the internal standard (FBDE-6001S, AccuStandard).
The sampling design has been based in a randomly stratified design as is customary for the Southern California Bight projects[7]. 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. 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 0.10µm film thickness. We used, with slight modifications the method proposed by Kalachova et al[8] that briefly consist of an injection of 2µL of sample in a pulsed splitless multimode inlet (MMI). We used a compressed air cooled injection to 100 ^{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. In general, we also used the same table of precursor ion, and product ion as those suggested. However, we did 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 5.5 min.

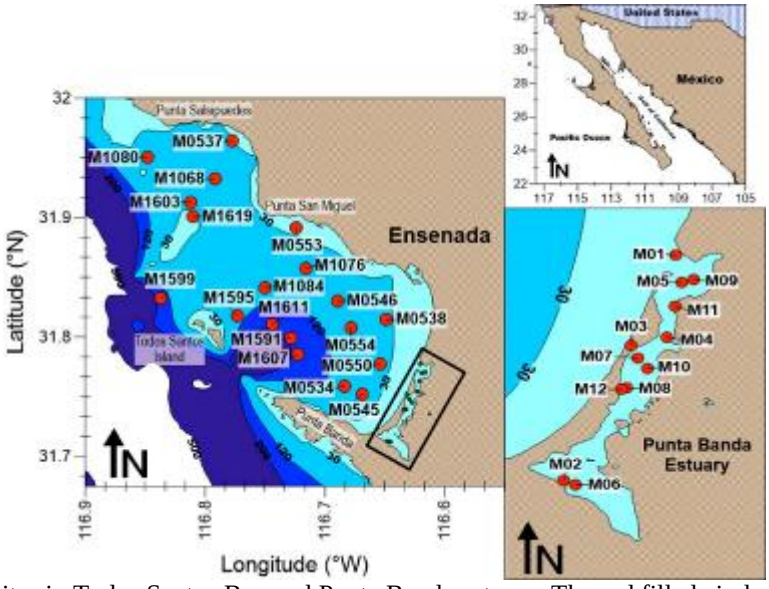

Figure 1. Sampling sites in Todos Santos Bay and Punta Banda estuary. The red filled circles indicate the geo-referenced sites where sediment samples were collected.

Results and discussion
Although we included 16 PBDEs, only thirteen of those were detected in at least one sampling station. The other three were not detected. Not surprisingly, we have found that the most frequently detected PBDEs are, in that order; BDE-209, BDE-47, BDE-99, BDE-100, BDE-71 and BDE-66 (figure 2).
It is clear from their extensive distribution overlaps that there were no statistically significant differences in concentration between the whole bay and the Punta Banda Estuary. These congeners are relatively consistent with those reported elsewhere[2,9]. This also suggests that the deca-BDE mixture source has been used in Ensenada city household products. It has been stated that the deca-BDE mixture was banned in Europe and that the US would stop its production in 2013[9]. The presence of the BDE-47 may suggest the use of the penta-BDE mixture.
In 28 out 31 stations, BDE-209 was predominant and it was only absent in three stations within the Punta Banda Estuary. In those sites within the estuary, the absence of BDE-209 resulted in that the three other most abundant congeners shared similar percentage abundance.

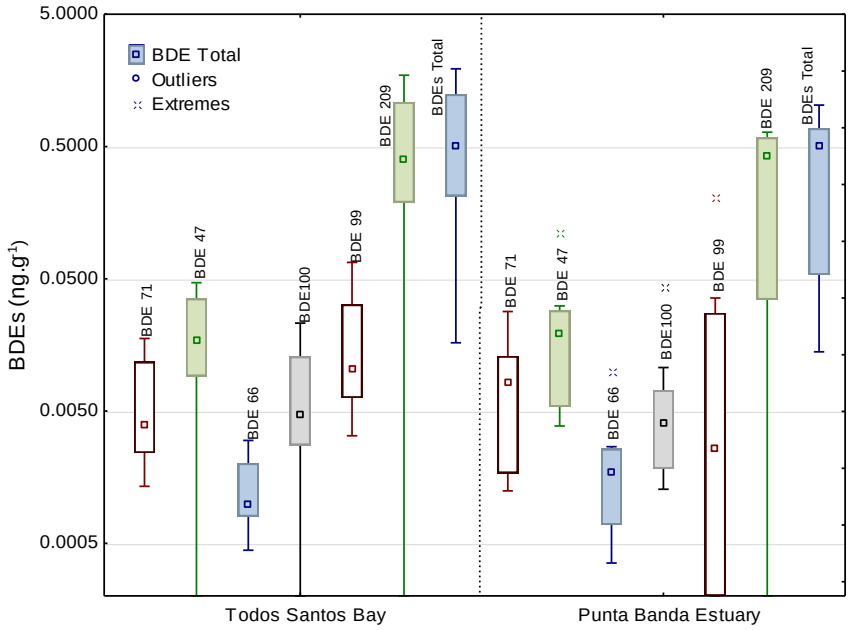

Figure 2. Relative abundances of the most frequently found PBDEs in sediment samples from Todos Santos Bay and Punta Banda Estuary.

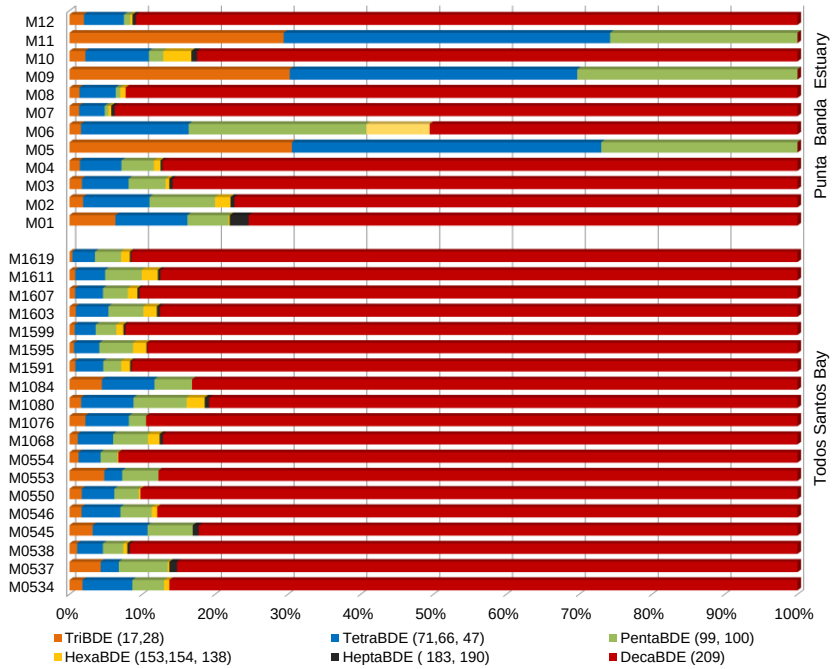

Figure 3. Sampling sites in Todos Santos Bay and Punta Banda estuary. The color scheme used for the different congeners is explained in the x axis.

One aspect that we found interesting was the correlation found between the sum of the total concentration for 13 BDEs and the fraction <63 µm grain sediment size (r^2=0.69). The same correlation is mostly due to the correlation between the BDE-209 and grain size distribution. It is clear that grain size determines, at least partially, the abundance of PBDEs in the samples. Additionally we found that, contrary to other findings in southern California, our maxima concentrations were not found in river mouths but were found associated to deeper water where less energy is available and the particles settle down.

As a result of grain size controlling the distribution of PBDEs, we can observe that their presence is most abundant in those sites where a depositional environment exist such as that of the deeper parts of the bay near the canyon as can be observed in Figure 4. It can also be observed that at the mouth of the estuary, where the water exchange is more violent between Todos Santos Bay and Punta Banda Estuary, the concentrations are very low. On the contrary, the largest concentrations found in the estuary are occurring in the sites furthest away from the mouth and were the water is more stagnant.

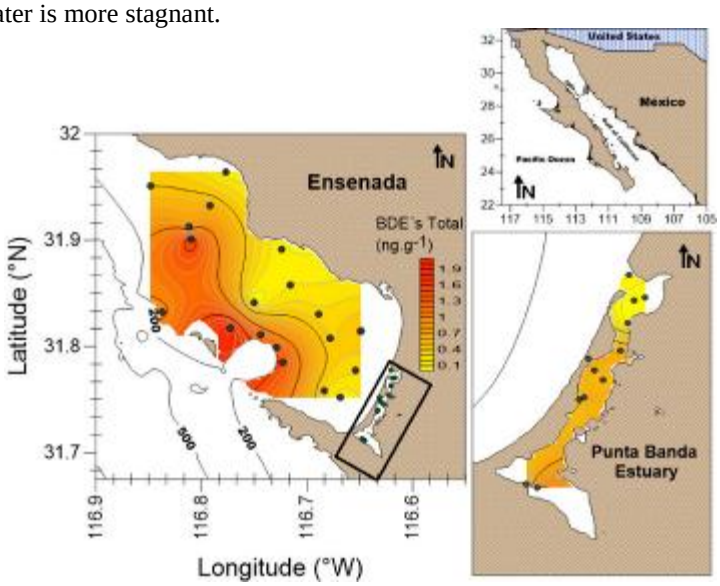

Figure 4. Surface sediment distribution for the sum of BDEs in the bay and estuary. The same color scale is used for both water bodies.

Concentration levels were small with a median for the sum of the 13 BDEs measured of only 0.50 ng g^{-1} for Todos Santos Bay and 0.51 ng g^{-1} for Punta Banda Estuary. The maximum value for this sum of thirteen measured PBDEs was of only 1.93 ng g^{-1}. These values are small when compared to others reported elsewhere[1,2]. If we calculate a back of the envelope number for the amount of PBDEs in Todos Santos Bay, using an extended area of 419 km^2 as the total area for the Bay, and using the formula provided by others[2], the total mass calculated for the top 2 cm of marine sediments is about 628 g. Similarly, there are only about 20.4 g of PBDEs in the upper 2 cm of Punta Banda Estuary.

Acknowledgements
We would like to acknowledge the help of the Algalita catamaran and his Captain Charles Moore for his help during the collection of the marine sediment samples. We also would like to thank the University Autonomous of Baja California for partially financing this work with the internal project from 17th call contract #629. Finally, we would like to thank CONACyT project # 173721 for financing the equipment to perform these measurements.

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