A first look at PBDEs and other POPs in commercial harvest of *Mytilus* sp. and *Crassostrea gigas* from the Pacific coast of Mexico.

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Introduction: Concern about the presence of PBDEs and other persistent organic pollutants (POPs) in bivalves has grown in our geographical area, out of reports along the California Coast in the USA where PBDEs and frequently other POPs have shown large concentrations in some marine organisms including bivalves. PBDEs as well as other pollutants, in particular organochlorine pesticides are well know for their lipophylicity, resistance to degradation, tendency to bioaccumulation and biomagnifying along the trophic webs. Mussels in particular and bivalves in general are well known for being sessile organisms, their large capacity to filter water for feeding and breathing and also for their lack of metabolic ability to transform pollutants. On coastal waters of Mexico, we have previously determined the presence of PBDEs in marine sediments as well as on wild mussels (*Mytilus californianus*) [1]. However, wild mussels are mostly consumed only locally. On the contrary, most of the harvested bivalves (oysters and mussels) in this area are grown for exportation market.. This incipient market is mostly dedicated to the USA and China markets with about 1350 ton to the USA and about 81 ton to China per year for mussels only. The oyster harvested and measured was *Crassostrea gigas* and the mussel was *Mytilus galloprovincialis*. The purpose of this work was double, first was to investigate if harvested bivalves had similar concentration of PBDEs (and other POPs) than those collected in the wild, and second, if the concentration found may represent a danger for human consumption. We also wanted to find out if the PBDEs composition was similar or if the exposure is different to that of mussels in the wild. The other POPs analyzed included were PCBs, DDTs as well as other organochlorine compounds.

Materials and Methods: We received samples from seven separate commercial sites with >30 organisms per site. One of the mussel sites had two types of mussels; one that contained normal size mussels (6 to 12 cm long) and a group of mussels of very large size (>12 cm) that were treated as an extra site. Tissues from >30 organisms were collected and homogenized. Three samples were prepared for separate measurements from each sample site. For quality control during the experimental process, we used the SRM-1974c from marine mussel of the species *Mytilus edulis* from the National Institute of Standards & Technology (NIST). Within each set of samples, a fortified target and a process target were included, where the fortified target contains the 14 PBDEs to be measured in this work at a known concentration. Also control blanks were included and surrogate (FBDE-6001S) and internal standards (FBDE-4001S) were also used for QA/QC.

Quantification of 14 PBDEs was performed using an Agilent 7890A gas chromatograph coupled to an Agilent 5975C mass selective detector using a DB-XLB chromatographic column (15m, 0.18mm i.d., 0.07µm thick stationary phase). Helium was used as a carrier gas at a flow rate of 2.25 ml/min and methane was used as the reagent gas. The injection volume was 2µl sample in the splitless injection mode. The injection port temperature was 250 °C, the initial oven temperature was set to 80 °C for 0.5 minute, followed by two ramps, at 12 °C/min to 250 °C kept for 0.5 minute followed by 20 °C/min ramp up to 330 °C with standby time of 5 minutes. The detector was operated in negative chemical ionization (NCI) mode, with source temperature and quadrupole kept at 150 °C. Three ions were monitored for 14 PBDEs; m/z 79, 81and 161, while congener 209 was also monitored for m/z 486.4 and 490 ions. [2,3]

Quantification of all other OCs compounds was carried out with an Agilent 7010-triple quadrupole mass spectrometer. with two HP-5ms chromatographic columns (15m, 0.25mm i.d., 0.25µm thick stationary phase). Helium was used as a carrier gas at a constant flow rate of 1.1 ml/min, while that a constant flow of Helium (2.25 ml/min) and Nitrogen (1.5 ml/min) were used in the collision cell. The injection port temperature and the MS interface were kept at 280 °C, while that the initial oven temperature was set to 60 °C for 1 minute, followed by two ramps, at 40 °C/min to 120 °C, followed by 5 °C/min ramp up to 285 °C, for a total runtime of 35.5 minutes. A backflush post-run program at 310 °C for 5 minutes was used after each sample analysis. The ion source were used at 300 °C, while the temperature of both quadrupoles was set to 180 °CA dynamic multiple reaction monitoring (MRM) method was developed for the simultaneous determination of 27 legacy pollutants: Aldrin, a-BHC, b-BHC, d-BHC, g-BHC, cis-Chlordane, trans-Chlordane, 2,4'-DDD, 4,4'-DDD, 2,4'-DDE, 4,4'-DDE, 2,4'-DDT, 4,4'-DDT, Dieldrin, Endosulfan I, Endosulfan II, Endosulfan sulphate, Endrin, Endrin aldehyde, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, 4,4'-Methoxychlor, Mirex, cis-Nonachlor, trans-

Nonachlor, Oxychlordane. The PCBs congeners analyzed included 34 compounds: 17, 18, 44, 49, 52, 70, 74, 82, 87, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 156, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 199, 206, y 208. We used as surrogate TCMX and PCB-209, and as internal standard PCBs-30 and PCB-205, for both families of compounds.

Results and discussion: The lipid content of the mussels ranged from as low as 0.28 % to as much as about 1%. For oyster the lipid content varied from 1.45% to 2.26%. For PBDEs, the first surprising result was that for these samples, the BDE-209 congener was the most abundant and prevalent compound at all sites and for both organisms. The other three congeners of importance were BDE-99 second in importance at four commercial sites and BDE-47 second at three of the sites. The fourth most abundant congener was BDE-190. These congeners, in particular BDE-47, BDE-99 are frequently found in this organisms as the predominant congeners The range in concentration for the Σ_{14}PBDEs went from 7.8 to 9.8 for Mytilus sp and from 9.4 to 12.5 for Oysters, both ranges in ng/g w.w. This range in concentration for PBDEs is not to be disregarded. When compared to wild mussels, BDE-209 although present, was not the most predominant congener for wild mussels, which may suggest that the materials used during harvest operations for mussels and oyster, may probably introduce extra BDE-209 content and put this compound in proximity to harvested organisms.

With respect to the legacy pollutants, we observed that for organochlorine pesticides, about 40% of the total load of these compounds corresponds to methoxychlor, followed by about a 15% of endrin and about 10% of p-p'-DDE (Figure 2). The range in concentrations for DDTs was from 0.52 to 0.70 ng/g for mussels and 0.40 to 0. 92 ng/g for oysters.

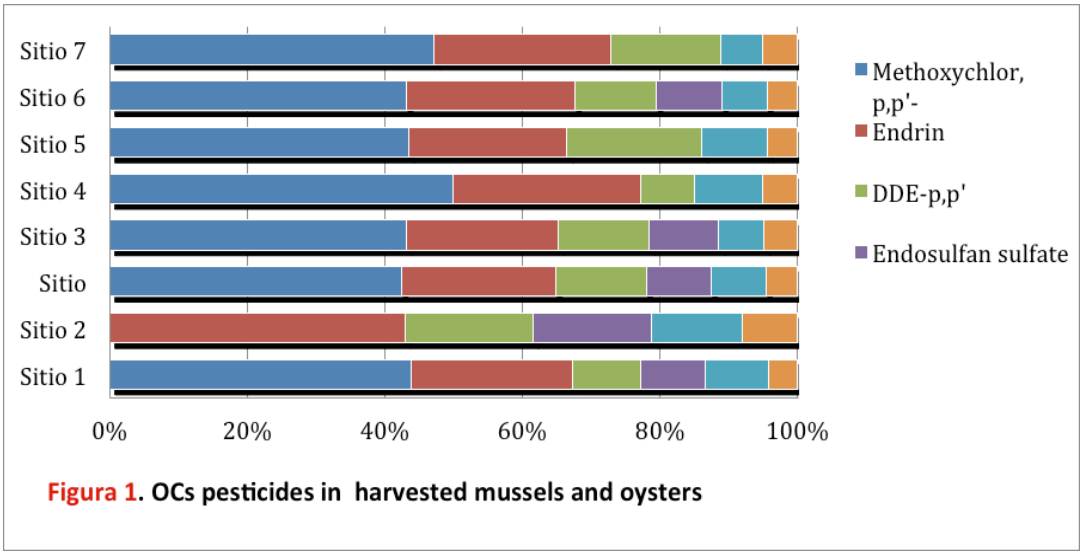

Figura 1. OCs pesticides in harvested mussels and oysters

Within the DDT family of compounds, we found that the proportion of DDT to DDE was of approximately in a proportion of three to seven as can be seen in Figure 3. The larger relative abundance of the degradation product of DDT suggests that this is not a condition resulting from recent application of DDTs but rather from historical use.

With respect to the DDT and other OCs pesticides concentrations found, the concentrations are relatively low as can be seen in a reduced version for all OCs in Table 1 below:

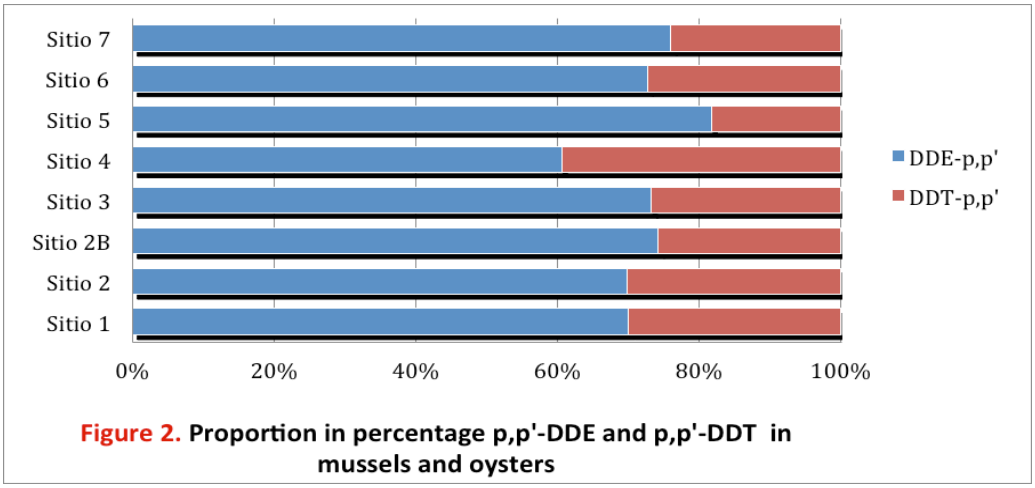

Figure 2. Proportion in percentage p,p'-DDE and p,p'-DDT in mussels and oysters

In fact, the proportion for the ratio of pp-DDE to pp-DDT is of about 0.4, which is somewhere about the ratio previously reported by us in marine sediments[4].

	Oyster			Mussels				
	Site 1	Site 2	Site 3	Site 2	Site 2B	Site 3	Site 6	Site 7
COMPOUND (ng/g) Methoxychlor	1.56	1.53	1.67		1.60	1.66	1.57	1.58
Endrin	0.84	0.84	0.89	0.85	0.84	0.85	0.89	0.86
p,p'-DDE	0.35	0.24	0.75	0.37	0.49	0.51	0.43	0.53
Endosulfan sulfate	0.33			0.34	0.35	0.39	0.35	
Hexachlorobenzene	0.33	0.30	0.37	0.26	0.30	0.25	0.24	0.20
p,p' -DDT	0.15	0.16	0.17	0.16	0.17	0.19	0.16	0.17
Sum DDTs	0.51	0.40	0.92	0.52	0.66	0.69	0.59	0.70
Total Pesticides	3.85	3.19	4.15	2.27	4.06	4.19	3.76	3.47
% LIPIDOS	**2.26**	**1.45**	**1.58**	**1.03**	**1.03**	0.63	0.28	0.32

A detailed analysis of these families of compounds including PCBs will be ready for the presentation

Acknowledgements:
We would like to acknowledge the University of Baja California for the use of their laboratories to do the work. Funding was obtained from soft money service contracts # 11169.

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