A TEMPORAL TREND (1998-2008) COMPARISON STUDY OF POP AT THE SOUTH OF THE SOUTHERN CALIFORNIA BIGHT

Macías-Zamora JV[1]*, Ramírez-Álvarez N[1], Sánchez-Osorio JL[1]

[1] Instituto de Investigaciones Oceanológicos-UABC, Carretera Tijuana-Ensenada No. 3917, Fraccionamiento Playitas, Ensenada, CP 22860, Baja California, México. *vmacias@uabc.edu.mx

Introduction

Persistent Organic Pollutants includes a group of organo-chlorine (OCs) chemicals widely distributed in the environment. These substances were highly employed from 1960 till 1990 to control pest in agriculture, damage to agricultural harvest and to control malaria's vector. As it is known, most of marine pollutants come from land. Agricultural as well as urban uses of these chemicals represent the brunt of the original source to the ocean. Coastal environment such as that of the Southern California Bight (SCB), highly populated (about 20 million people) that extends from Point Conception in Southern California and ends south of Ensenada, Baja California, Mexico, is a large marine ecosystem with a large history of sediment pollution due to OCs (Dodder et al., 2011). Globally however, the temporal trend for OCs has been abundantly described as showing a strong declination trend after the 1980s. The decline has been based on the elimination and substitution of several of these substances. Since 1998, we have been carrying-out monitoring programs in the coastal region south of the international border of the SCB. We are attempting to provide a good database and provide a detailed record of the changes both, in a spatial as well as a temporal perspective. We have now completed the analysis of the 2008 sediments and wanted to compare temporal trends. It was expected that a clear downward trend in most if not all of OCs concentrations would be found. We summarize the results from 1998 and 2008 for PCBs and DDTs and provide with possible scenarios for these results.

Materials and methods

Sampling design for the whole SCB was based on a randomly stratified design (Stevens, 1997). Marine sediments were collected during 1998 and 2008 using similar procedures established in the operation manual (Schiff, et al., 2011) for 1998 and 2008. Briefly, from a randomly stratified sampling design site, the two top cm of sediments collected using a Van Veen drag of 0.1 m^2 capacity are collected in amber glass jars and kept frozen till analysis. A list of 41 PCBs congeners were selected in 1998 and those are the same ones used for a comparison to the 2008 samples. (Congeners by UPAC numbers: 18, 28, 52, 49, 74, 70, 101, 99, 87, 110, 151/82, 149, 118, 153/132,105, 138, 158, 187,183, 128, 177, 56,180, 170, 169, 194, 206). For OCs, the following were also measured and are compared to those measured in 2008. Organochlorine pesticides included were: α-HCH, γ-HCH, β-HCH, δ-HCH, Heptachlor, Aldrin, heptachlor epoxide, α-chlordane, γ-chlordane , Endosulfan I, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT, Endosulfan II, Dieldrin, Endrin, Endrin aldehyde, Endosulfan sulphate, Metoxichlor. The method used for OC analysis was that proposed by Zeng and Vista (1997), and it was also described by us previously (Macías-Zamora, et al; 2008). briefly; 40 g dried samples were spiked with surrogate standards and soxhlet extracted 12 hrs with DCM. Clean up by LC in a 1x30 cm column packed with silica and alumina (2:1) 3% deactivated. Elution: consisted of 15 ml with Hexane (F1) and 40 ml with 70/30 (v/v) Hexane/DCM (F2). F2 was reduced to 0.5 ml in a N_2 stream and spiked with internal standards. OCs were determined and quantified using a GC HP 6890 Plus, coupled with an electron capture detector (ECD). The GC was equipped with a 60 m DB-XLB column (0.32 mm i.d. x 0.25 μm film) and He as carrier gas.

These methodologies were all tested and inter-calibrated using unknown samples collected from the SCB. Confirmation was carried-out in a GC-MS equipped with the same column. The sampling sites for 1998 and 2008 are shown in Figure 1. It has been customary in some of the monitoring plans to keep a certain percentage of sites to be the same as before to make direct comparisons and also to include new random sites. The area has been divided in three strata; North, Central and South strata. Originally, the strata were considered on the basis of population considerations. The North stratum coincides with the city of Tijuana with near 1.5 million people. The South strata, in the Todos Santos Bay, near the city of Ensenada with a population of about 0.5 million people and the central stratum with much less significant population density.

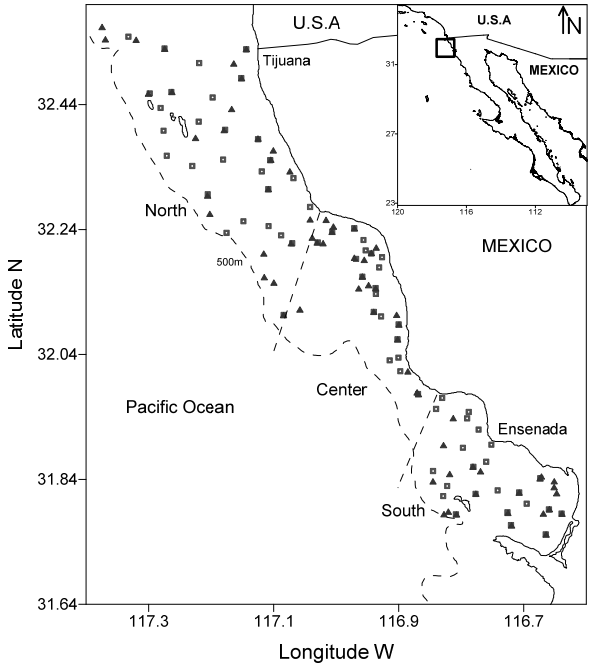

Figure 1. Sampling sites of the 1998 and 2008 monitoring campaigns for the southern end of the SCB. Squares represent sites sampled in 1998 and triangles represent sites sampled in 2008. The discontinuous line represents the 500m-depth isobath. The two broken lines perpendicular to the coast separate the three strata.

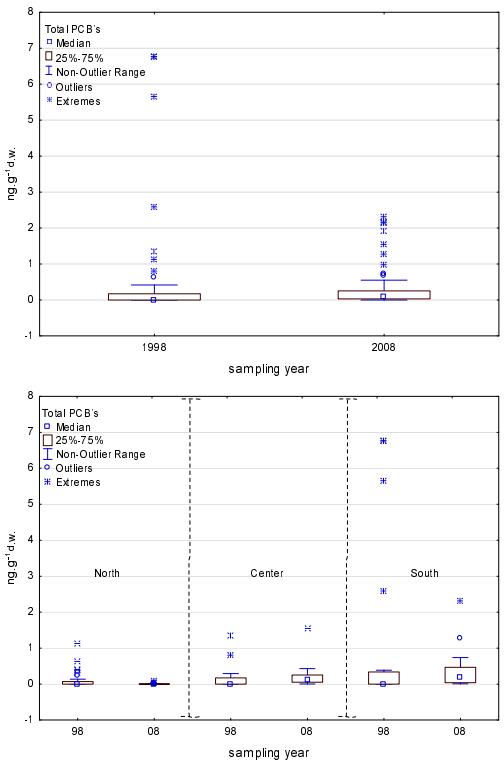

Figure 2a. Whole area comparison between the sum of PCBs congeners measured in 1988 and in 2008. Figure 2b lower figure shows a comparison based on the three strata originally proposed for the area.

Results and discussion

A summarized description of the comparative results for the two main groups of chemicals i.e., for the sum of PCBs, total pesticides and the sum of DDTs is presented in the two following figures in a box and whisker arrangement.

Although the medians and general distributions are not significantly different from one another, the largest maximum values were found in the southern stratum. In addition, it is also clear that the largest values (extremes) were found in 1998 in the South stratum, but the values of PCBs were more homogeneous and apparently higher in 2008.

For the OCs pesticides, we show the Figures 3a and 3b below. Again, there appears to be no significant differences between 1998 and 2008 neither for p,p-DDTs which is the main OC found nor for the rest of OC chemicals measured. However, relatively higher concentrations were found in the Center zone, in the 1998 sampling. This also shows that this is the area where there is a greater relative decrease of chlorinated pesticides

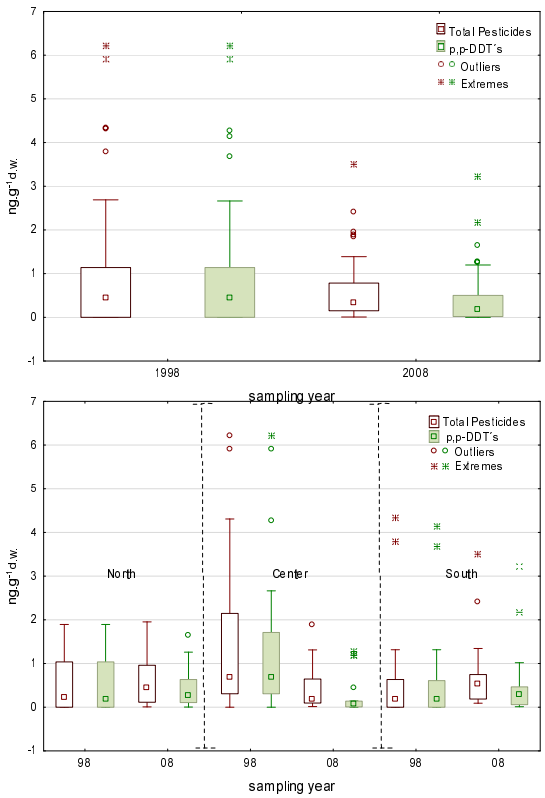

Figure 3. a) Box and whiskers comparison between the sum of p,p DDTs and b) the sum of all OCs including p,p-DDTs. It is clear that the largest values correspond to the central stratum.

The main conclusion that can be drawn from this data set is that after 10 years, few changes are clearly observed in the concentration of most of these substances. This is in itself surprising because the elapsed time is not minor but in addition, the year of 1998 was an “el niño year” with an unusual amount of rain. The only apparent change is that the maximum values visible in Figures 2a and 3a, are less intense or smaller when detected during the second sampling in the year 2008. In addition, there are at least two more general conclusions to be drawn from these figures. The first conclusion is that the largest PCB values were found in the south stratum, that is, in the

Todos Santos Bay. This conclusion maybe a result of a more restricted ocean circulation and less energy in a semi protected area. We originally predicted that the largest PCB concentrations would be found near the largest population center at the northern stratum, which, in addition, also has the largest wastewater discharges to the coast. One possible explanation for this is again, a more open and energetic environment at north, which reflects in larger percent sand concentration (as seen in Table 1 below), than the sediment at Todos Santos Bay. In addition the PCBs, we found that the abundance of the larger heavier molecular weight (> #77) are the most abundant in the region except for a very small number of stations were this was not the case. This same behavior is the equal for both the 1998 survey as well as the 2008. It suggests that the PCBs are residues of a not very resent release into the ocean or, that these PCBs have traveled long before settling down in the sediment. Both conditions would result in loss of the lighter PCBs.

A second conclusion is that the largest DDTs, and in general OC pesticide concentrations were found in the central stratum, again not associated to the largest population centers. The most logical explanation for this finding is that the permanent "La Mission" creek located in the central stratum is bringing in pesticide residues from inland valleys where agriculture takes place. The creek actually runs through the Ojos Negros, and Guadalupe Valleys, two of the most intensive agricultural sites in this part of the region. Moreover, the coastal area in the central stratum is characterized by a topography that includes a small canyon where a depositional environment is developed. This characteristic is reflected in a larger percentage of smaller grain size sediments than at any of the other two strata. We would like to stress the fact that most important constituents of the OCs pesticides measured in this area are those of DDTs family of compounds.

It would appear, that one may argue that such a small change suggest that there is still an equilibrium between the inputs of OCs and the mechanisms that decompose them plus the physical outputs.

A more detailed analysis of both PCBs and DDTs composition will be provided at a latter date in a longer format.

Table 1. Finer size distribution for the three strata of the study area. Larger percentages of finer grain sizes indicate depositional environments.

Zone	**Fine grain size**							
	1998				**2008**			
	Median±DS							
	<4 mm	<16 mm	<40 mm	<63 mm	<4 mm	<16 mm	<40 mm	<63 mm
North	**2.9**±2.6	**8.1**±2.4	**12.6**±14.2	**16.2**±22.7	**2.7**±9.0	**13.1**±31.5	**19.4**±39.1	**10.8**±32.6
Center	**3.8**±2.3	**11.0**±2.5	**27.3**±17.3	**45.2**±22.8	**2.4**±1.5	**14.1**±10.0	**37.4**±26.6	**53.3**±33.1
South	**4.7**±2.6	**15.5**±8.0	**31.4**±16.0	**39.0**±24.8	**1.7**±7.7	**11.5**±23.3	**24.3**±32.9	**24.8**±31.3

Acknowledgements

We would like to acknowledge the partial funding of CEC and also to CONACyT for the partial funding of the 1998 campaign with contract # 084005. In addition, we also would like to thank UABC for the use of their facilities to conduct this work.

References

1.- Dodder, N.G., Lauenstein, G.G., Ramirez, J., Ritter, K.J., Maruya K.A., Schiff, K.C., 2011. Distribution and sources of polybrominated diphenyl ethers in the Southern California Bight, 261-270 in: Southern California Coastal Water Research Project 2011 Annual Report.

2. Macías-Zamora JV, Ramírez-Álvarez N, Sánchez-Osorio, JL. (2008); *Organohalogen Cmpd*. 74: 299-303

3. Schiff K, Richard G, Ritter K, Tiefenthaler L, Dodder N, Lao W, and Maruya K. (2011). Southern California Bight 2008 Regional Monitoring Program: III. Sediment Chemistry. Southern California Coastal Water Research Project, Costa Mesa, CA.

4. Stevens DL. (1997). *Environmetrics* 8: 167-195.

5. Zeng, E.Y. and Vista, C.L.1997. *Environ Toxicol and Chem.* 16: 179-18