OLD POPs IN 98 AND 08 IN COASTAL SEDIMENTS OF THE SOUTHERN END OF THE SOUTHERN CALIFORNIA BIGHT

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Introduction.

The Persistent Organic Pollutants (POPs) are frequently divided in the old or legacy POPs and the new or emerging pollutants. In general terms, temporal trends for old POPs indicate that due to slow degradation and because of different decomposing pathways, they are disappearing from coast, soils and air. In fact we have seen reported time and again how this is already happening in many parts of the world[1]. For the past several 10 years we have participated in a bi-national monitoring effort, which we joined for the first time in 1998. We have tried to register if this general trend is also occurring in this particular coastal region. In particular, the question that we would like to respond is if we are really getting rid of old POPs in our coastal systems. Consecutive sampling programs of coastal sediments at the Southern end of the Southern California Bight have been developed. The first sampling was carried out in 1998 a second in 2003 and a third monitoring sampling event was carried out in 2008. As it has been published previously[2], the Southern California Bight (SCB) is a bi-nationally (US-Mexico) shared resource. Chemicals in water and/or sediments are moving in both direction exchanging these and other pollutants across borders. We claim that as a consequence of this natural exchange, mass balances studies are incomplete if no measurements are made simultaneously on both sides of the border. Here we are comparing results of POPs concentrations in marine sediments collected in the first and third monitoring efforts. In particular we are presenting results for DDTs and other old or legacy pollutants under the preconceived idea that in a ten year period, some decreasing in concentration would have to be observed given that, for DDTs, half lives are somewhere near 2 to15 year periods[3,4].

The sampling sites are shown in Figure 1.

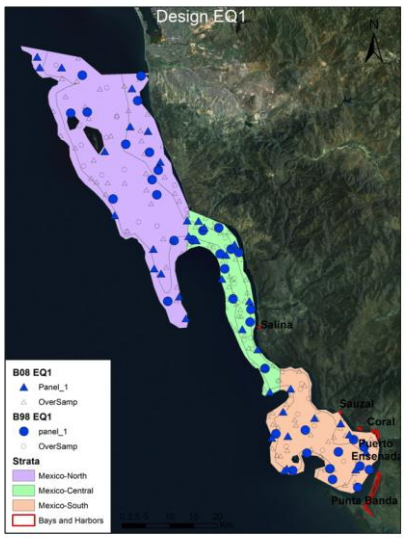

Figure 1. Sampling design for the Mexican Coastal part of SCB in 2008. The three colors indicate three different strata based on closeness to population Centers. The north stratum is near Tijuana, Baja California, Mexico.

South stratum is near Ensenada, Baja California. The central stratum is mostly under populated coastal area.

Surprisingly, 10 years later the worldwide trend has not been reflected in a decrease in concentration typical of what has been reported just north of our study area[2]. We decided to investigate the presence and extent of distribution in coastal marine sediments collected during the project Bight-08 conducted by us in Mexican waters of the SCB. We wanted to respond to the question of what, if any, is the effect of coastal growth during this ten years span but based on two expected facts; assuming better wastewater treatment practices and given the ban on the use of most of these chemicals mainly in the US would result in decreases in concentration loads and a better environmental perspective for the biota living in the area.
In this coastal region, the suspected main routes of entry are the five wastewater-treatment plants in addition to the creeks and semi-permanent rivers draining from inland.

Materials and methods

Field methods. The sampling design has also been extensively explained elsewhere[5]. In short; A stratified-random probability-based approach was used to select about 80 sediment sampling sites within the southern end of the SCB[6,7]. Three strata were selected: (1) Northern strata near Tijuana Baja California; (2) Central strata, mostly un-populated coastal stretch and (3) Southern strata near Ensenada Baja California. Each stratum consisted of samples at three different depths sites including the inner continental shelf (5-30 m water depth), mid-shelf (30-200 m), and upper slope (200-500 m). Samples were collected using a Van Veen grab. Lab Methods; The following 24 compounds were measured in surface sediments collected by using a Van Veen grab sampler: mirex, metoxychlor, endosulfan sulfate, endosulfan I and II, heptachlor and heptachlor epoxide, endrin, endrin aldehyde, dieldrine, aldrine. organo-chlorine pesticides. p,p'-DDT, o,p'-DDT, p,p'-DDD, o,p'-DDD, p,p'-DDE, o,p'-DDE, α-chlordane and γ-chlordane, α- HCH, β-HCH, γ- HCH, δ-HCH and HCB. The methods for Pesticides have been described elsewhere[8]. These methodologies were all tested and inter-calibrated using unknown samples collected from the Bight. Briefly, 40 g of samples were spiked with surrogate standards and soxhlet extracted 12 hrs. The extracted material was concentrated to about 1 mL and separated using column chromatography (11 X 300 mm). Two fractions were obtained from columns containing 12 cm high of silica and 6 cm high alumina both suspended in hexane. Fraction 1 was extracted with hexane and Fraction 2, containing PCB, DDT and PAH was extracted with a hexane:dichlorometane 70:30 (vol:vol). Fraction 2 was concentrated to 0.5 mL and spiked with internal standards. OC were determined and quantified using a GC HP 6890 Plus, coupled with an Electron Capture Detector (ECD), with a 60 m DB-XLB column (0.32 mm i.d. x 0.25 µm film) and He as carrier gas. All OC compounds identified were confirmed by GC/MS on an Agilent GC7890A – 5975C MSD with a 30m DB-5MS column (0.25 mm i.d. x 0.25 µm film), EI mode, and He as carrier gas.

Results and discussion

As we stated, we wanted to respond to the question if the phased-out OC pesticides are showing a decline as reported around the world. We realize that so far, there are only 3 samplings and that change may be difficult to spot, however, taking into account the long half-lives of many of these OC, we decided to compare the 1998 vs the 2008 concentrations at the same northern stratum. The results of both samplings are shown in Figure 2.

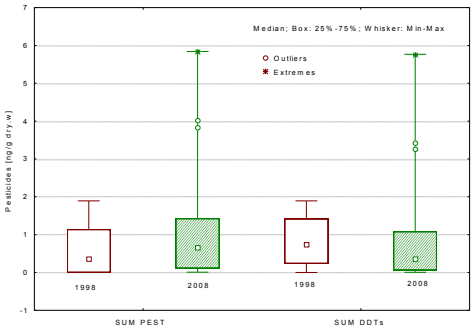

Figure 2. Box and whiskers plot showing the comparison of the sum of pesticides measure in 98 vs 08 and the sum of total DDTs only for the same two samplings.

At least two things are obvious from the Figure, first; concentrations have not changed significantly in this period of ten years (and at least 8 years since Mexico declared that was phasing out DDTs even for vector

control of malaria). Second, more than 90 % of total OC pesticides are DDTs. This last point can be best explained by observing Figure 3.

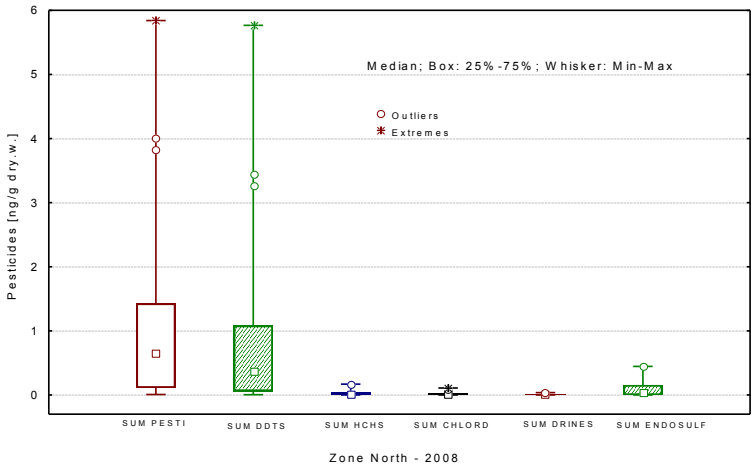

Figure 3. Box and whiskers plot for the sum of the different groups of OC pesticides including DDTs, HCHs, Chlordanes, drins and Endosulfanes. The largest concentrations correspond to DDTs.

Two questions that we would like to address before attempting to explain why there are no significant changes in concentrations of DDTs are; first, if there is evidence of new use of DDTs in the area. To address this question, we will use the ratio of the sum of the DDT metabolites to that of DDT previously used elsewhere[9]. The results are shown in Figure 4 below.

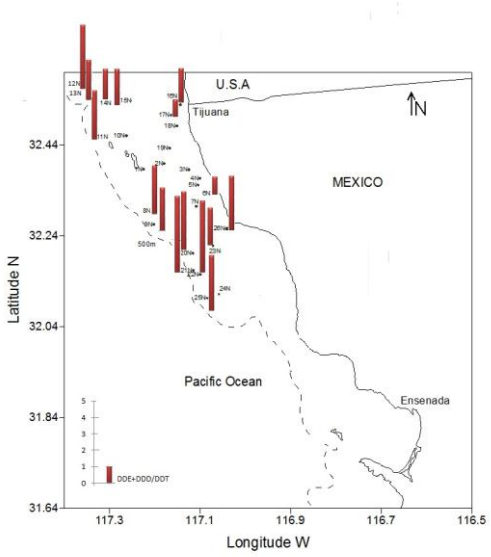

Figure 4. Ratio of DDE+DDD to DDT for all samples in the northern Stratum. All ratios found are >1.

These results suggest that there appears to be no use of new DDT. One would expect that for recent use of DDT, given that technical formulations usually contain around 70% DDT[10] the ratio would be <1 for technical DDT. The second question is, where are these compounds distributed? We offer Figure 5 below to show the distribution of the DDT and metabolites distribution for the norther stratum. This Figure will probably help in

explaining why we think that few to no change has been observed in the concentration over this ten year period in this part of the world.

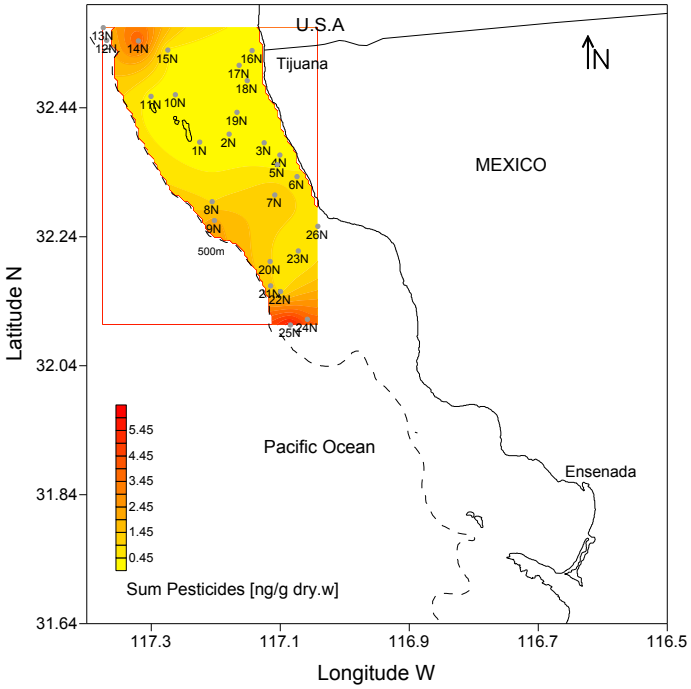

Figure 5. Sum of DDT and its metabolites. The distribution expands about 30 km from the US-Mexico international border to the south.

Briefly, we suspect that there are at least three factors that may have contributed to this apparent constant concentration for OCs in coastal sediment of this area. In no particular order, first; 98 was an " el niño" year with larger than usual load of particles introduced by rain into the ocean. Second, the international wastewater treatment plant discharging jut at the border started operating till 2000. Its effect is clearly visible at station labeled 14N in Figure 5. And third, there is more permissively use of pesticides in Mexico than in the US in general.

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