PCBs and DDTs at the South of the Southern California Bight. Distribution and origin.

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Introduction.

The Southern California Bight (SCB) is a well-known oceanographic feature of the California-Baja California coast which originates from a change in the direction of the continent. Because of this change of the coastline, the normal north to south California Current circulation, changes its course resulting in a complex circulation pattern near the coast. About 20 million people live along the coast (Schiff and Gosset, 1998) and, on both sides of the international border; tens of millions of people use it yearly. The natural drainage of the basin with its large storm water runoff, the industrial and municipal wastewater discharges, the atmospheric transport of pollutants, the dredge material disposal and related processes, result in an increased threat to this very rich ecosystem. It is characterized by a relatively low winter precipitation. Consequently, there are few permanent rivers and/or creeks, most of which only run during rainy season. At the same time, the scarce vegetation coverage results in large sedimentary material, wastes, trash and in general large amounts of sedimentary loads that are transported to the sea.

The normal circulation of the California Current is complicated by topographic features and by the presence of countercurrents of variable magnitude (Chereskin and Niiler, 1994; Winant *et al*., 1999). It includes the presence of up-welling events along the coast adding the complication that particulate and dissolved materials including nutrients and other chemicals, can be brought up to surface waters from water deeper than 100 m (Gomez-Valdez, 1983).

The municipal discharges in Baja California, Mexico are characterized by releases of wastewater directly on the sea surface, along the beach. The most important discharges are; Punta Banderas, with volumes of about 2.60 x 10^8 L/day, El Sauzal de Rodriguez, just to the north of Ensenada, with volumes near 5.2 x 10^6 L/day and El Gallo and El Naranjo with discharges of about 2.16 x 10^7 L/day into Todos Santos Bay. Additionally, many unregistered smaller discharges exist along the coast. It is believed that most of them are raw sewage releases.

It has been considered that lack of treatment and/or a reduced capacity for municipal waters treatment on the Mexican side of the border would result in a more polluted coastal region and an exportation of these pollutants across the border into San Diego, region. Previous studies on this area have suggested otherwise (Sañudo-Wilhelmy and Flegal, 1992, Macías-Zamora, 1996, Segovia-Zavala, *et al.,* 1998).

However, previous lack of QA/QC controls, equivalent methods as well as inter-calibration exercises not allowed direct comparison of values measured at the border. The goals of this study included. Use of similar methodologies and quality controls to measure persistent organic pollutants (POP) and trace metals. Also, to get valid comparisons measured at both sides of the border near municipal discharges.

Material and methods.

The following compounds were measured in surface sediments collected by using a Van Veen grab sampler: i) 41 PCB congeners. Congeners numbers by UPAC: 18, 28, 37, 44, 49, 52, 66, 70, 74, 77, 81, 87, 99, 101, 105, 110, 114, 118, 119, 123, 126, 128, 138, 149, 151, 153, 156, 157, 158, 167, 168, 169, 170, 177, 180, 183, 187, 189, 194, 201, 206. ii) 8 organochlorine pesticides. p,p'-DDT, o,p'-DDT, p,p'-DDD, o,p'-DDD, p,p'-DDE, o,p'-DDE, α-chlordane γ-chlordane.

The methods for PCB and DDT used have been described elsewhere (Zeng and Vista, 1998). These methodologies were all tested and intercalibrated using unknown samples collected from the Bight. Briefly, 15 g of dry sediment were extracted with dichloromethane using a soxhlet system. 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 1 mL and divided into two equal volumes. One part was analyzed for organochlorine pesticides using GC (Gas chromatograph from Hewlett Packard 5890 series 2) using electron capture detector. We used a capillary column DB-XLB 60 m long, 320 µm diameter and 0.25 µm thick of stationary phase.

Results and Discussion:

PCBs were found widely distributed in our study area. They were present in 61% of sampled stations (Fig 1a). However, concentrations found were below the Effects Range Low (ERL), its concentration range was from 0.05 to 8.4 ppb, with an average of 0.7 ppb. Long et al (1995) reports the limit for ERL for PCBs at 22.7 ppb and of 180 ppb for Effects Range Median (ERM) . In this study, only the station labeled E59 at the south of the central strata had a value of 138 ppb (located near Salsipuedes). A concentration well above the ERL but below the ERM. Additionally, almost all stations (98%) had mostly the heavier PCBs (75-209) rather than the lighter ones (18-74). This may suggest remote transport or long residence time of PCB. Both would explain the decomposition/dissolution/ evaporation of the lighter PCB.

Total DDT concentration ranged from 0 to 30 ppb. The pesticides found were mainly constituted by the DDT and its metabolites, DDE and DDD. The total pesticides concentration was 15, 30 and 18 ppb, at the north, central and south strata respectively. The center zone contained the highest concentrations of total chlorinated pesticides follow by south and last north zone. The DDE was the most concentrate metabolite in all three zones.

DDT degrades to DDD and DDE under anaerobic and aerobic conditions, respectively. The DDT/(DDE+DDD) ratio is frequently used as indicator of recent or historic source of DDT. A ratio >1.0, suggest a recent DDT aplication. In our results, DDE was found in higher concentration that DDD but less than DDT. These results indicate a weathering process favoring the formation of DDE instead to DDD.

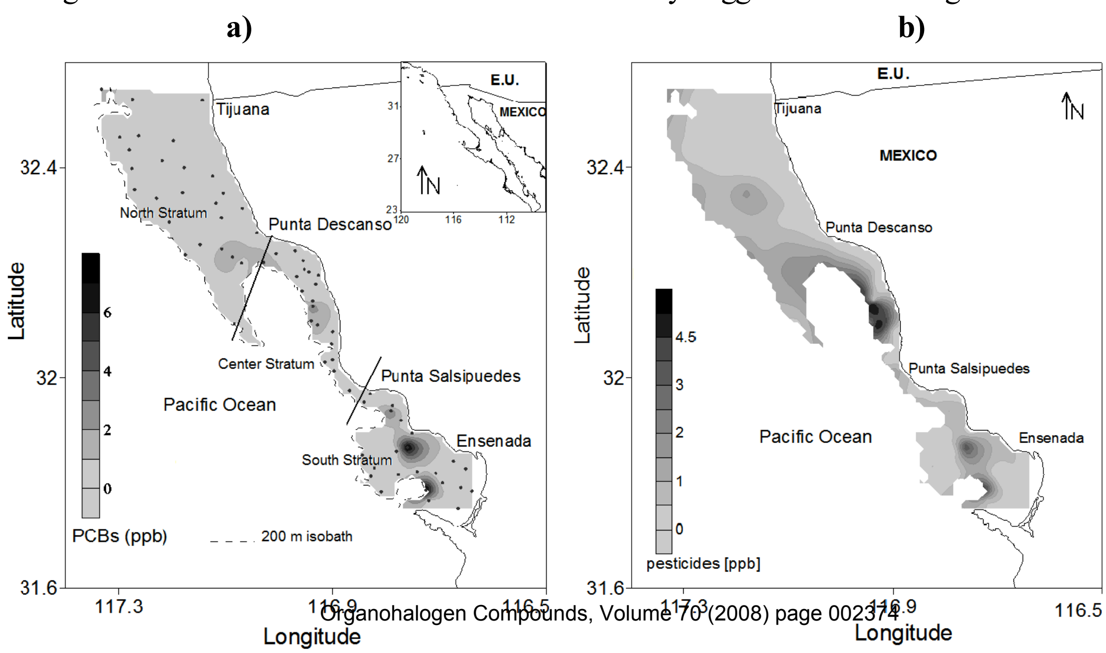
In the northern stratum the high average concentration of DDT may be influenced by the discharges of sewage from Tijuana City and San Diego, USA. The DDT found in center zone gives to an evidence of the importance in dispersion and deposition mechanisms us of DDT's in this zone. Central zone was initially considered as a reference zone because smaller population and no evidence of local agricultural fields in the area. The distribution pattern of the ratio DDT/(DDE+DDD) on the sediment samples in south stratum is related to historical use of these contaminants south of Ensenada. The hydrological conditions and land erosion resulting from urbanization are also contributing factors.

Zeng and Tran (2002), suggest that the sediments from SBC close to Los Angeles may become an important source or contamination, they found ∑DDT ranging from <0.33 to 9,923 ng/g. In Santa Monica Bay, California was reported ∑DDT from 31 to 290 ng/g in different strata (Bay, *et.al*., 2003). They concluded that temporal trends of contamination were greatest in sediments collected from areas near the Hyperion treatment plant outfall system and on the slope of Redondo Canyon. It was indicative of a dispersal mechanism remobilizing historically deposited contaminants to areas relatively remote from the point of discharge. Partida-Gutierrez, *et al*., (2003) reported pesticides in cores en SCB (Mexico) in the range of 0.09 to 19.71 ng/g, concluded that the main source was wastewater discharges from San Diego and Tijuana. Historically, DDT has been a problem in Southern California Bight (Zeng *et al*., 1999).

Conclusions.

The DDTs and its metabolite ratios suggest that there has been recent utilization of these compounds in agricultural sites that drain into the sea. Concentrations at several stations (14) were above the ERL but well below ERMs. A similar situation was detected for PCBs were the heavier congeners were more prevalent than the lighter ones. The maxima found for ∑DDTs in the central stratum is associate to a creek draining from agricultural land.

Figure 1. Distribution of PCBs (a) and DDTs (b) at the south of the Southern California Bight. The no coincidence in their distribution may suggest different origins.



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