



# Chlorinated Hydrocarbons in Marine Sediments of the Baja California (Mexico)–California (USA) Border Zone

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Polychlorinated biphenyls and organochlorinated pesticides are widespread on land and in aquatic environments. This is a result of their wide use during the last two decades in industry, agriculture and even health campaigns that use them to counteract diseases such as malaria. Their physicochemical properties make them very resistant to biological degradation and, thus, highly persistent (Fowler, 1990; Wesen *et al.*, 1992; Iwate *et al.*, 1994).

This category of compounds poses serious threats to public health and most life forms; their toxicity is manifested through mutagenesis, teratogenesis, and effects a wide variety of metabolic systems, including those that govern reproduction (Hooper *et al.*, 1990; Brown *et al.*, 1991; Goldberg, 1995). They are extremely liposoluble hydrophobic substances readily absorbed in the organic portion of suspended particles in wastewater and urban runoff, and eventually end up in coastal sediments close to sewage outfalls, bays and harbours. Sediments are sources for these toxics to enter chains, and thus endanger public health and coastal ecosystems (NRC, 1994).

The north-west coast of Baja California forms part of an oceanic bay bordering southern California and includes the USA–Mexico border region and Todos Santos Bay, located at Ensenada, Baja California. In these two areas, discharges of wastewater are the principal means of transport of pollutants from the land to the sea (Nishikawa-Kinomura *et al.*, 1988; SCCWRP, 1990a). Along the coast of southern California, USA, the discharge of wastewater occurs regularly through submarine outfalls located at the 60 m isobath and under the thermocline. In the bays of Ensenada and Tijuana, Baja, California, outfalls occur along the coastline. According to SCCWRP (1992), from 1971 to 1991 some of the more important outfalls

from southern California, USA, discharged 41 255 kg of DDT and 44 909 kg of PCBs to the sea. Recent information about the quality of wastewater from California, USA, shows an improvement relative to the 1970s, particularly a decrease of almost 100% in the discharge of PCBs and DDT. In Mexico, the quality of wastewater with respect to these toxics is unknown, but their potential is great.

Studies of pollutants in coastal sediments in the region are rare, focusing more on the study of heavy metals (Gutiérrez-Galindo *et al.*, 1994; Romero-Vargas, 1995; Villaescusa-Celaya, 1996), PAHs (Macías-Zamora, 1996), TBTs (Macías-Carranza, 1996), and coliform bacteria (Orozco-Borbón and Delgadillo-Hinojosa, 1989). The objective of this study is to describe the degree of pollution from PCBs and organochlorinated pesticides along the north-west USA–Mexico border region and Todos Santos Bay, Baja California, through identification, quantification, and by revealing the geographic distribution of these toxins in the surface sediments.

## Materials and Methods

Sediment samples were collected from each area; the number and distribution of the stations are illustrated in Fig. 1a and b. The sediments from the border region and Todos Santos Bay were collected in April 1992, during the ECOBAC IV cruise, aboard the R/V *Alejandro de Humbolt*. Sediments adjacent to the coastline of Todos Santos Bay were collected using a small craft in January 1992. Sediments were collected with a van Veen grab, they were placed in decontaminated glass jars, and preserved at  $-20^{\circ}\text{C}$  until laboratory analyses.

The quantification of the chlorinated hydrocarbons in the sediment was made according the method of MacLeod *et al.* (1985), modified by Wade *et al.* (1993). A method blank, spiked blank, and spiked sample were run for each group of 12 samples for

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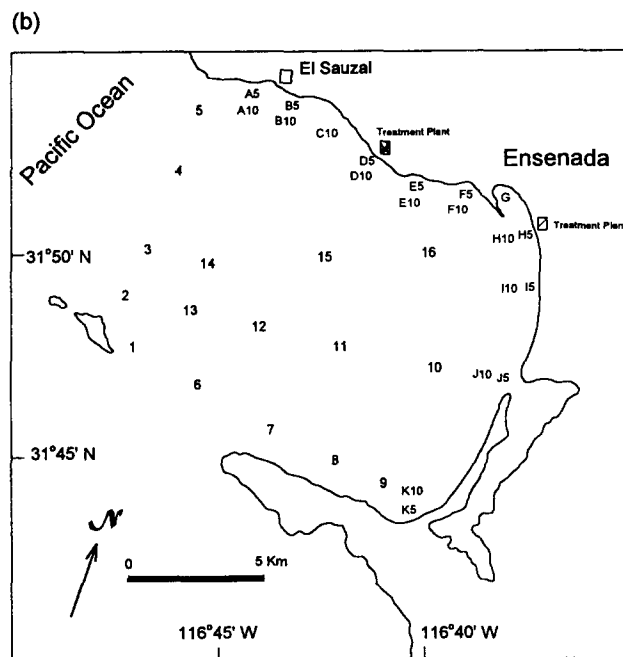
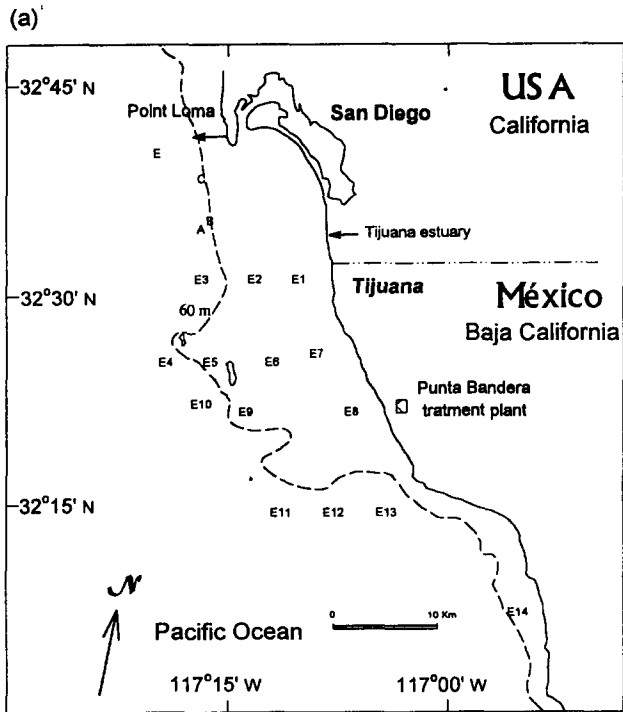


Fig. 1 Study area and sampling stations at (a) Baja California-California border zone; (b) Todos Santos Bay.

quality control purposes. The procedure consisted of adding an internal standard solution of 2,4,5,6-tetrachloro-*m*-xylene (TCMX) and decachlorobiphenyl (PCB-209) to 30 g of dry sediment that was extracted with methylene chloride in a Soxhlet instrument during 12 h (one cycle every 4–5 min). Copper fibre was used to eliminate any elemental sulphur.

The extract was concentrated to 5 ml and the solvent then exchanged for hexane and the extract concentrated to 1 ml, with a gentle flow of  $N_2$  at 50°C. The extract was fractionated with column chromatography, slurry packed with 20 g of silica gel (400°C for 4 h, deactivated 5% with water) over 10 g of neutral alumina (400°C for 4 h, deactivated 1% with water). The column was consecutively eluted with 200 ml of pentane:methylene chloride (1:1 v/v) (f1) and 50 ml of methanol (f2). The first fraction, which contains the chlorinated hydrocarbons, was concentrated as previously described. A solution of 4,4-dibromooctofluorobiphenyl (DBOFB) was added to the final extract as a recovery standard.

The pesticides and polychlorinated biphenyls were analysed in a Hewlett-Packard 5890A gas chromatograph, equipped with a  $^{63}Ni$  electron capture detector and a HP 7673 autosampler. A DB-5 capillary column (J and W Scientific), 30 m  $\times$  0.250 mm i.d., was used for the separation. The carrier gas was  $N_2$  at 42 cm s $^{-1}$ , measured at 200°C. The temperature of the column was programmed at 50°C for 3 min, from 50 to 170°C at 4°C min $^{-1}$  without hold time, from 170 to 210°C at 1°C min $^{-1}$  and from 210 to 300°C at 4°C min $^{-1}$  without hold time, ending at 300°C for 10 min. Temperatures of the injector and detector were 275 and 325°C, respectively. The calibration was made by determining the concentrations and areas relative to the internal standard (TCMX and PCB-209), and calculating the response factor with a non-linear adjustment with four levels. The following are the pesticides examined, with the detection limits given in ng g $^{-1}$ . Isomers  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ -BHC (0.19–0.27), aldrin (0.08), heptachlor, heptachlor epoxide (0.11–0.98),  $\alpha$  to  $\gamma$ -chlordane (0.08–0.09), endosulfan I (0.07), sulphate (0.15), aldehyde endrin (0.32), dieldrin (0.62), and the isomers *p,p'*- and *o,p'*-DDT, DDE and DDD (0.04–0.22).

The number associated with each congener or isomer of PCBs is reported according to Ballschmiter and Zell (1980), and is as follows: dichlorobiphenyl: 15; tri: 18, 28, 31; tetra: 40, 44, 49, 52, 54, 60, 70, 74, 77; penta: 82, 86, 87, 95, 97, 101, 102, 103, 105, 110, 114, 118, 121; hexa: 128, 129, 136, 137, 138, 141, 143, 151, 156, 169; hepta: 170, 171, 173, 180, 182, 183, 187, 189, 191; octa: 194, 195, 196, 199, 201, 202, 203, 205; nonachlorine: 206, 207, 208 and decachlorobiphenyl: 209. The detection limit for 30 g of dry sediment was 0.002 ng g $^{-1}$ .

## Results and Discussion

In the US-Mexico border region,  $\Sigma$ PCB were 0.6–36 ng g $^{-1}$ . Greatest values were observed at stations 3 and C (36.3 and 19.72 ng g $^{-1}$ ), close to the sewage outfall at Point Loma, and at station 11 (23.0 ng g $^{-1}$ ) located in Mexican waters. Stations 1, 5, and 13 had intermediate levels of 8.4 ng g $^{-1}$  each. Without taking into account the three highest values, the general

average was  $5.26 \text{ ng g}^{-1}$ , with a coefficient of variation of 50%. Except for station 1, located off the Tijuana River Estuary, the other stations (3, C, 11, 5 and 13) are located close to the 60-m isobath. Twenty-eight congeners of PCBs were identified (28, 70, 74, 82, 87, 95, 97, 101, 105, 110, 118, 121, 128, 129, 138, 141, 143, 151, 159/187, 180, 183, 191, 194, 195, 199, 203, 206), of which 95, 28, 105, 101 and 118 appeared more frequently in the samples analysed. The first in 93% and the last two in 50%. The greatest number of congeners was found at stations C, D and B, close to the outfall of Point Loma, with 20, 13 and 11, congeners,

respectively. Along the Mexican coast, stations 13 and 9 also exhibited a relatively large number of PCB, 13 and 10. Between 6 and 3 congeners were identified at the other stations (Fig. 2a).

Highest concentrations of  $\Sigma\text{PCB}$  were generally located at stations further from the coast, particularly those close to the 60-m isobath, and the sewage outfall at Point Loma, as well as off the Tijuana River Estuary. This can be related to: the proximity of the source; sedimentological characteristics; amount of fine-grain sediment; content, distribution, and nature of the organic matter; and biological productivity associated

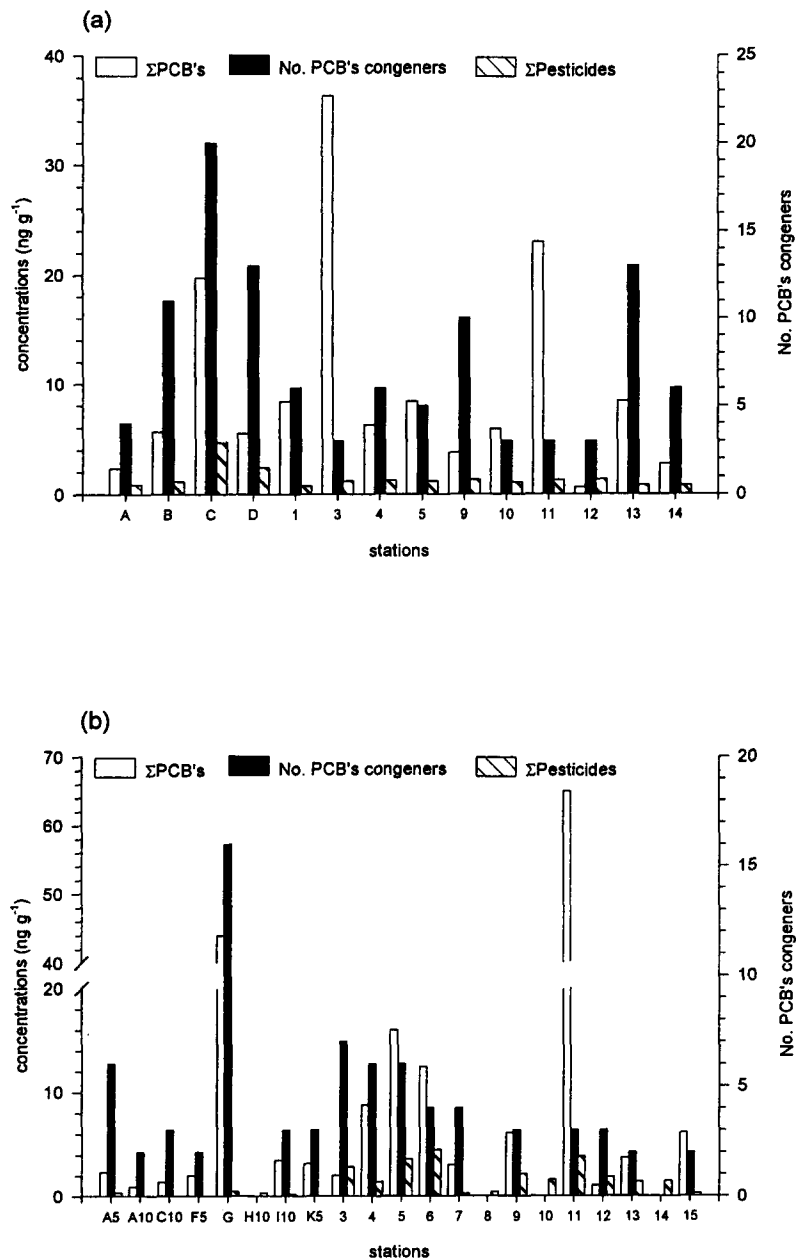


Fig. 2 Bar graphs of the concentrations ( $\text{ng g}^{-1}$  dry wt) of  $\Sigma\text{PCBs}$ ,  $\Sigma\text{Pesticides}$ , and number of congeners in sediments samples from: (a) Baja California—California border zone; (b) Todos Santos Bay.

with upwelling processes, as well as to the predominant flow and transport of the current system in this area (Segovia-Zavala, 1994). Similar behaviour has been observed in trace metals (Villaescusa-Celaya, 1996), PAHs (Macías-Zamora, 1996), and coliform bacteria (Patrón-Mas, 1992).

The relative abundance of the PCB congeners at stations B, C and D, close to the outfall at Point Loma, and at stations 9 and 13 in Mexican waters, close to the 60-m isobath, can indicate the variety of commercial PCB mixtures used in the adjacent urban areas, and also reflect the proximity of their entry to the zone (SCCWRP, 1990b).

Pesticides in the border area ranged from 0.7 to 4.7 ng g<sup>-1</sup> with a mean of 1.47 ng g<sup>-1</sup> and a coefficient of variation of 68%. Greatest concentrations were observed at stations C and D, close to the outfall at Point Loma, 4.7 and 2.4 ng g<sup>-1</sup>, respectively. Lowest concentrations were observed at station 1, off the Tijuana River Estuary, and at stations 13 and 14, close to Punta Descanso, with 0.8 ng g<sup>-1</sup> each (Fig. 2a). A concentration of 1.3 ng g<sup>-1</sup> was observed at five stations, four of which are close to the 60-m isobath. The pesticides quantified in this area were β-BHC, γ-chlordane, p,p'-DDE, endosulfan-sulphate, γ-BHC, endrin, p,p'-DDD, and o,p'-DDE. Of these, p,p'-DDE, γ-chlordane, and β-BHC were more frequent in the samples analysed at 100, 21 and 14%, respectively. Station C had the greatest number of pesticides, five, whereas most had one to two.

The spatial distribution of the pesticides in the area was similar to that of PCBs, with greater concentrations at stations adjacent to the 60-m isobath (C, D, 3, 4, 5, 9 and 11) or close to the sewage outfall at Point Loma (C and D), and lower concentrations at sites close to the coastline (1, 13 and 14). This might be related to many of the factors mentioned in the paragraph on the PCBs (Fig. 2a).

In Todos Santos Bay, ΣPCB were 0.9 to 65.0 ng g<sup>-1</sup> (Fig. 2b). Greatest values were found at stations 11, G, 5 and 6 at 65.0, 44.0, 16.0, and 12.4 ng g<sup>-1</sup> respectively. Without considering these atypical values, an average of 3.4 ng g<sup>-1</sup> was calculated with a coefficient of variation of 70%. In the composition study, 26 congeners of PCBs were identified (28, 74, 87, 95, 101, 103, 110, 114, 118, 121, 138, 141, 143, 151, 153, 154, 156, 173, 180, 182, 185, 189, 194, 196, 205, 206). Of these, 58% were also found in the US Mexican border zone. In samples analysed, congeners 95, 28, 74, 118, 121 and 153 were the most frequent; the first in 82%, and the last four in 29% of all samples. The greatest number of congeners was found at stations G and 3, 16 and 7, respectively, the lowest at stations A10, F5, 13 and 15, with two each.

With regard to the pesticides in the bay, Σpesticides ranged from 0.2 to 4.5 ng g<sup>-1</sup> with an average of 3.23 ng g<sup>-1</sup>, a coefficient of variation of 85%. Highest values were observed at stations 6, 11, 5 and 3 at 4.5,

3.8, 3.6 and 2.8 ng g<sup>-1</sup> respectively (Fig. 2b). The pesticides p,p'-DDE, α-BHC, β-BHC, δ-BHC, γ-BHC, γ-chlordane, heptachlor epoxide, endrin and endrin aldehyde were identified. Of these, p,p'-DDE, γ-BHC and γ-chlordane were the most frequent in the samples (88, 29 and 24%, respectively). The greatest number of pesticides were found at stations 6 and 3, with five and four pesticides, respectively. The most abundant pesticide in the study area was p,p'-DDE, except at stations 5 (β-BHC) and 11 (γ-BHC).

With respect to the geographic distribution of the PCB, there were three areas that stood out because of the levels and/or relative abundance of the congeners. The first was located at station G, with a ΣPCB of 44 ng g<sup>-1</sup> and 16 congeners, the greatest number. This station is surrounded by ship yards and fish-processing plants. It is also close to the area where the Ensenada creek empties into the ocean, which carries runoff water from the city and discharges municipal wastewater. These high values might also be associated with the use of anti-fouling paints, as observed in harbours of California, USA (SCCWRP, 1990b). Other studies show relatively high levels of heavy metals and organic matter, (Romero-Vargas, 1995), polyaromatic hydrocarbons (Villegas-Jiménez *et al.*, 1996), TBTs (Macías-Carranza, 1996) and coliform bacteria (Orozco-Borbón and Delgadillo-Hinojosa, 1989). These results support the hypothesis that this area possibly functions as a trap for contaminants and sediments (Gómez-Morín and Lizárraga-Arciniega, 1982).

The second area is located north of the bay at stations 5, 4 and A5, close to the harbour at El Sauzal, where there is a fish-processing plant as well as a small industrial park. The Del Carmen and Sauzal creeks empty into the ocean close to this area. Here, intermediate concentrations of ΣPCB were found (16, 8.8 and 2.2 ng g<sup>-1</sup>), a total of six congeners per station. These contaminants might be related to small accidental leaks of PCBs from ships and the industrial park.

The third area is located close to the islands, and includes station 6 with a concentration of ΣPCB of 12.4 ng g<sup>-1</sup> and four congeners. Station 3 could also be included in this area, even though it presented a low concentration (2 ng g<sup>-1</sup>) and seven PCB congeners, the second in abundance of congeners in the entire bay. Other studies indicate relatively high values of organic matter and heavy metals in this area (Romero-Vargas, 1995) and PAHs (Mendoza-Vega, 1996). The results indicate that the area functions as a basin for the accumulation of natural and anthropogenic materials. This behavior might be related to the predominant current pattern in the bay (Argote *et al.*, 1991), which transports and distributes these materials. This system consists of two principal currents, one that flows from Punta San Miguel and displaces along the north coast of the bay until reaching the mouth of the Punta Banda Estuary, and another in the southern part of the bay, which displaces along Punta Banda until reaching the

mouth of the estuary. At this point, both currents converge and create a flow towards the Todos Santos Islands.

The distribution of pesticides in the bay also indicated relatively high values at stations 6 ( $4.5 \text{ ng g}^{-1}$ ) and 3 ( $2.8 \text{ ng g}^{-1}$ ), close to the islands. There were intermediate levels at stations 10 ( $1.6 \text{ ng g}^{-1}$ ), 11 ( $3.8 \text{ ng g}^{-1}$ ) and 12 ( $1.8 \text{ ng g}^{-1}$ ), at the mouth of the Punta Banda Estuary. This distribution can also be explained by the current pattern described for the PCB and also by the proximity of an agricultural area located to the south of the bay. Stations 5 and 4, close to El Sauzal, also showed relatively high values of pesticides, with  $3.6$  and  $1.4 \text{ ng g}^{-1}$ , respectively. This might be associated with rainwater runoff of particulate matter, which is transported through streams crossing small vineyards.

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