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Persistent Organochlorine Pesticides in Coastal Sediments from Petacalco Bay, Guerrero, Mexico

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The use of persistent organochlorine pesticides (POPs) to control agricultural pests and vectors of diseases, like malaria, is a common activity in developing countries, thus, representing a serious environmental risk due to the high persistence and liposolubility of these compounds. Their presence in the environment is tightly related to mechanisms such as bioaccumulation and biomagnification in food chains and humans (Barkatina et al. 2002; Sanpera et al. 2002).

The development of specific analytical techniques currently in use has made it possible to detect their levels in the water, soil, sediments, food from plant and animal sources, blood serum, adipose tissue and maternal milk (Nigam and Siddiqui 2001; Barkatina et al. 2002; Barlas 2002; Covaci et al. 2002; Singh and Gupta 2002; Waliszewski et al. 2002). These compounds are introduced into the coastal system through superficial discharges, either by agricultural runoffs and/or from regions that were sprayed to control endemic diseases.

On the other hand, the coastal ecosystems of the Subtropical Mexican Pacific are among the most productive ones, especially for fisheries of important species as tuna, ray, bonito and yellow-jack. However, the accelerated urbanization and industrialization of the region with increase in human settlements, the discharge of non-treated urban waters and agricultural waste have been rising severe pollution problems, endangering the ecology and biodiversity of this important region (Botello 2001).

Thus, the aim of the present work was to analyze the levels of pollution derived from the presence of POPs in coastal sediments of Petacalco Bay, Guerrero, Mexico.

MATERIALS AND METHODS

The Petacalco Bay belongs to the municipality of La Unión, Guerrero State, Mexico, and the study area is located between 17°57’53’’ and 17°59’14’’ N latitude and between 102°2’5’’ and 102°6’11.4’’ W longitude (Fig. 1). Dominating littoral currents of the region run to the northwest in spring and

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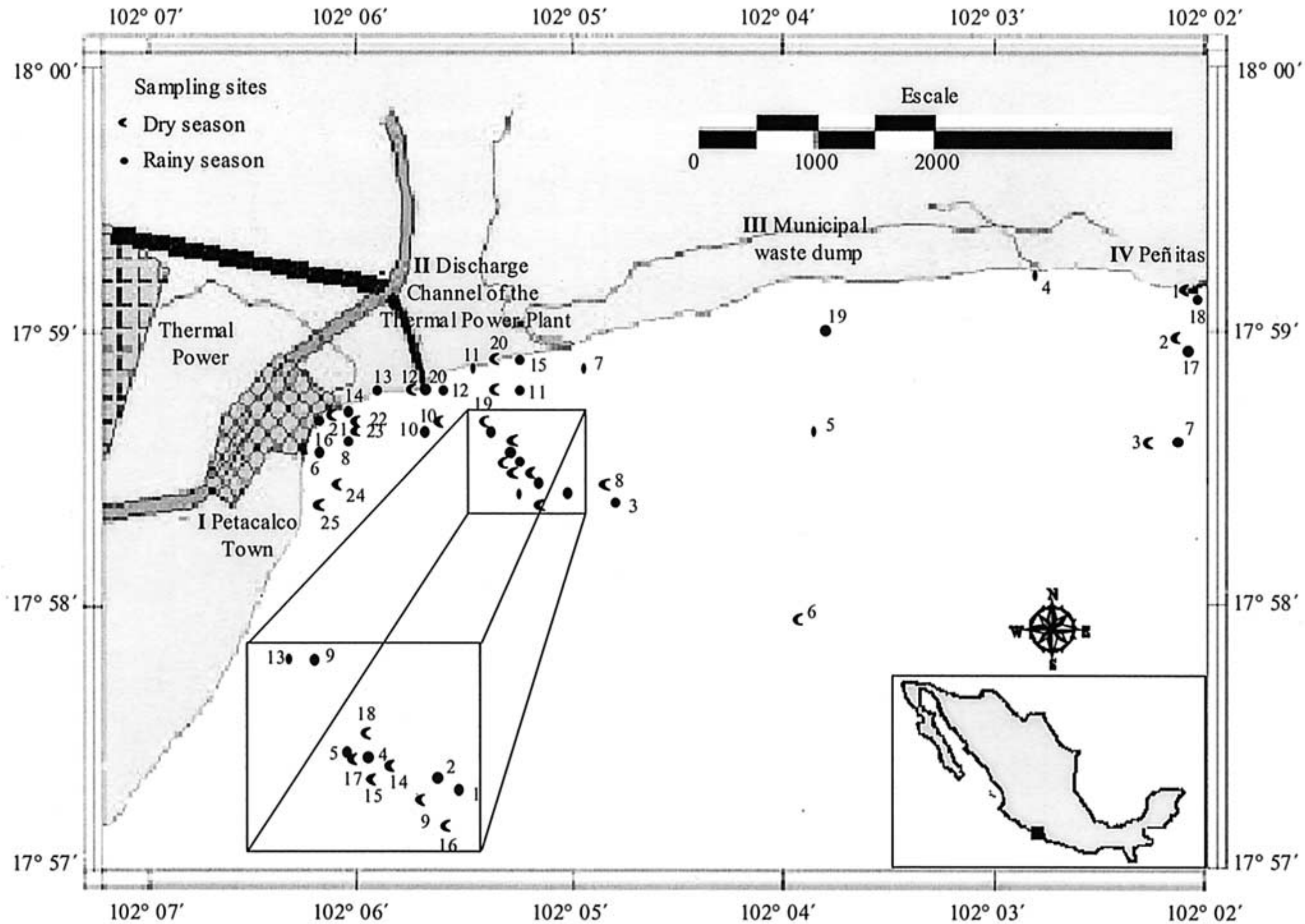

Figure 1. Location of sampling sites for sediments in Petacalco Bay, Guerrero, Mexico.

summer and to the southeast in winter (Amezcua 1996). The most important river in the region is the Balsas that flows into this area of the Mexican Pacific. Main activities in the region are agriculture and fisheries (CIBNOR 1995).

Sediments were collected during the dry season 25 samples (November-December, 1999) and rainy season 20 samples (August, 2000) by means of a stainless steel van Veen dredge. After collection all samples were stored in glass jars and frozen (4°C) until analysis. The sampling sites were distributed in four subregions in which the study area was divided: I Petacalco Town, II Discharge Channel of the Thermal Power Plant, III Municipal waste dump site and IV Peñitas (Fig. 1). 100 g of dried sediments from each sampling site were soaked and sieved (250 μm). The purification of organochlorine pesticides (OP) in sediment, was achieved in accordance with the UNEP/IAEA method (1982). 3 g of sediments were extracted in a soxhlet device using n-hexane for 8 hours; one spiked reagents blank was performed for each five samples. The extract was concentrated in a rotovaporator at 30°C and 40 psi; then purified through adsorption chromatography in a column packed with florisil and anhydrous sodium sulfate previously purified, activated and deactivated to separate the polychlorinated biphenyls (PCB, Fraction 1) from the organochlorine pesticides (OP, Fraction 2). The extract was eluted with 60 mL n-hexane to obtain fraction 1 and afterwards with 50 mL of a mixture of n-hexane:anhydrous ethyl ether (9:1) and 20 mL (8:2) to obtain fraction 2; the latter was concentrated under an ultrapure N_2 flow and injecting 1μL of this concentrate into a gas chromatograph (Hewlett Packard mod 5890 series II) equipped with an electron capture detector (ECD^{63}Ni), and a HP-5 capillary column of fused silica, with 5% methyl-phenyl-silicon phase (30 m, 0.25 mm d-i and 0.25 μm layer thickness); He (1mL min^{-1}) was used as carrier gas and N_2 (30mL min^{-1}) was used as auxiliary gas. Working conditions during analyses were: 90°C-2min, 30°Cmin^{-1}-180°C-0min, 3°Cmin^{-1}-270°C-0min. To quantify analytes, the external standard method based on retention time and specific area of the compounds was used. A standard mixture of 16 compounds (Chem. Service, Inc.), at a 20 ng mL^{-1} concentration was used as an internal standard. The recovery percentage was between 90-92%. The organochlorine pesticides assessed were: α-HCH, β-HCH, γ-HCH, δ-HCH (alicyclics), p,p'-DDT, p,p'-DDE, p,p'-DDD (aromatics), Heptachlor, Heptachlor epoxide, Aldrin, Dieldrin, Endrin, Endrin aldehyde, Endosulfan I, Endosulfan II and Endosulfan sulphate (cyclodienes). The analytical performance of results was accredited through the participation of the laboratory in an International Intercalibration Exercise coordinated by the International Atomic Energy Agency (IAEA 1997) for organochlorine pesticides. The obtained concentrations did not follow a normal distribution, therefore we used the non-parametric Mann-Whitney and Kruskal-Wallis tests to assess the differences between both climatic seasons and the four subregions, using Statistica 99 software, level of significance in both cases was set at 0.05; average values with their corresponding standard errors are reported in ngg^{-1} dry weight.

RESULTS AND DISCUSSION

Average POPs concentration per sampling was 1.96 ± 0.38 ngg^{-1} during the dry season and of 27.43 ± 10.40 ngg^{-1} in the rainy season; global average was 12.8 ± 4.74 ngg^{-1}. During the dry season, the highest concentration of pesticides was located at the subregion III (Municipal waste dump) with 3.12 ± 0.95 ngg^{-1}, followed by the subregion II (Discharge Channel of the Thermal Power Plant), the subregion I (Petacalco Town) and the lowest values at subregion IV (Peñitas); whereas during the rainy season, the subregion II (Discharge channel) yielded the highest average with 37.47 ± 18.59 ngg^{-1}, followed by the subregions III (Municipal waste dump), I (Petacalco Town) and the IV (Peñitas) (Fig. 2). Considering the three chemical POPs families, during the dry season, cyclodienes showed the highest average with 1.60 ± 0.34 ngg^{-1}, followed by alicyclic and aromatic compounds. Concentrations increased during the rainy season, dominated by the alicyclic compounds with 19.33 ± 9.26 ngg^{-1}, followed by cyclodiene and aromatic compounds (Fig. 3).

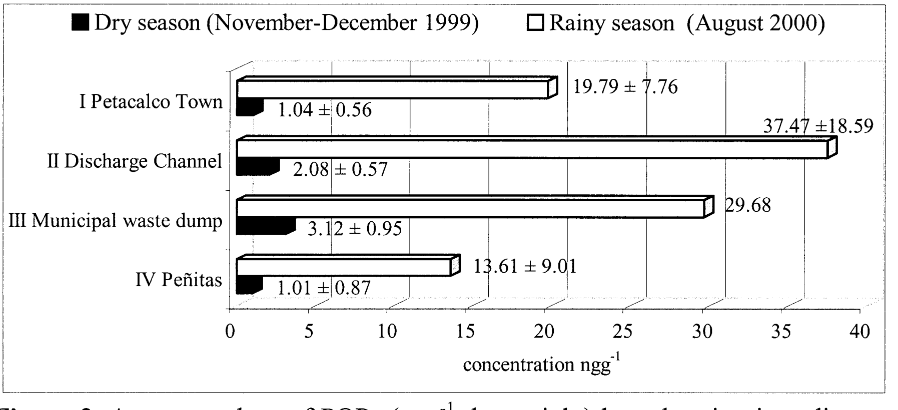

Figure 2. Average values of POPs (ngg^{-1} dry weight) by subregion in sediments from Petacalco Bay, Guerrero, Mexico.

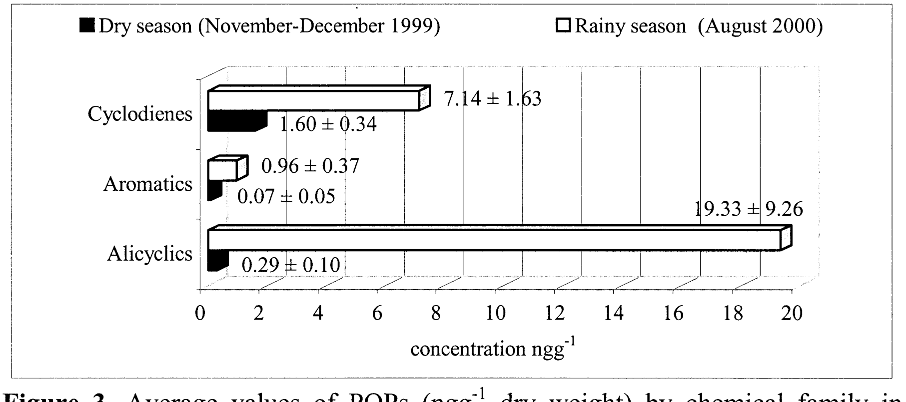

Figure 3. Average values of POPs (ngg^{-1} dry weight) by chemical family in sediments from Petacalco Bay, Guerrero, Mexico.

During the dry season, the cyclodienes group depicted the highest averages in the four subregions, the most affected was the III Municipal waste dump with 2.98 ± 0.89 ngg^{-1}, followed by the II Discharge channel (1.44 ± 0.48 ngg^{-1}), the I Petacalco Town (1.04 ± 0.56 ngg^{-1}) and IV Peñitas (1.01 ± 0.87 ngg^{-1}). During the rainy season, alicyclic compounds predominated in the following order: the subregion II Discharge channel (26.60 ± 16.58 ngg^{-1}), the I Petacalco Town (11.80 ± 6.00 ngg^{-1}), the IV Peñitas (9.49 ± 6.82 ngg^{-1}) and the III the Municipal waste dump (6.4 ngg^{-1}). From this group, β-HCH was the compound with the highest values, maximal concentrations were found in the Discharge channel. The general behavior for chemical families was as follows: alicyclics (65%) > cyclodienes (31%) > aromatics (4%).

During the dry season, aldrin depicted the highest average concentration with 0.66 ± 0.18 ngg^{-1}, followed by endosulfan I, α-HCH and heptachlor epoxide as well as DDT metabolites. Metabolite's heptachlor and endrin shown higher levels than their original parents with exception of aldrin whose epoxide, dieldrín, is originated when reacts with peroxides or strong acids, being more toxic and persistent (Arias et al. 1990). Thus the absence of dieldrin would indicate the recent application of aldrin. Whereas during the rainy season the highest value was found for β-HCH with 18.04 ± 8.84 ngg^{-1}, followed by aldrin, heptachlor, endrin and heptachlor epoxide. The number of chlorine compounds was higher in the rainy than in the dry season (100%:62.5%) (Table 1).

Table 1. Average values of POPs (ngg^{-1} dry weight) in sediments from Petacalco Bay, Guerrero, Mexico.

Season	Alicyclics				Aromatics			Cyclodienes									Frecuency (%)
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	
Dry (Nov-Dec 1999)	0.29 ± 0.10	*	*	*	*	0.04 ± 0.04	0.03 ± 0.03	0.02 ± 0.02	0.23 ± 0.10	0.66 ± 0.18	*	*	0.19 ± 0.11	0.30 ± 0.20	0.08 ± 0.04	0.13 ± 0.10	62.5
Rainy (August 2000)	0.37 ± 0.27	18.04 ± 8.84	0.13 ± 0.09	0.79 ± 0.48	0.17 ± 0.17	0.45 ± 0.23	0.34 ± 0.19	1.59 ± 0.48	1.24 ± 0.35	2.03 ± 0.63	0.31 ± 0.17	1.29 ± 0.45	0.31 ± 0.31	0.11 ± 0.08	0.05 ± 0.05	0.21 ± 0.12	100

1(α-HCH), 2(β-HCH), 3(γ-HCH), 4(δ-HCH), 5(p, p'-DDT), 6(p, p'-DDD), 7(p, p'-DDE), 8(Heptachlor), 9(Heptachlor epoxide), 10(Aldrin), 11(Dieldrin), 12(Endrin), 13(Endrin aldehyde), 14(Endosulfan I), 15(Endosulfan II) y 16(Endosulfan sulphate).
* < 0.01 ngg^{-1}

Differences were significant when considering the total POPs concentrations for both seasonal samplings as well as considering each chemical family (alicyclics, aromatics and cyclodienes) and individually among compounds β-HCH, heptachlor, heptachlor epoxide, and endrin. These differences can be attributed to the environmental dynamics of the region, since rainfall is greater in August (CIBNOR 1995) and, consequently, the fluvial supply from the Balsas river; besides, the predominating southeast winds in the summer (Amezcua 1996) and evapotranspiration are also to be considered as important factors for the supply of these substances, whereas during the dry season the decrease of these meteorological events minimize the inputs of these compounds into the adjacent coastal zone.

Assessment of the geographical distribution of POPs in the four studied subregions revealed no significant differences among them in any of the samplings. However, in particular, the subregion I Petacalco Town depicted important differences between the dry and the rainy season, which was reflected in the total concentration of POPs and especially in that of heptachlor and endrin. This difference was also observed in the Discharge Channel of the Thermal Power Plant, mainly in cyclodienes and, specifically, for β-HCH, heptachlor and heptachlor epoxide.

According to the Mexican legislation, the use of endosulfan is permitted to some crops and restricted to coffee crop; the use is restricted to lindane (γ-HCH) and DDT, and banned for aldrin, dieldrin and endrin (CICOPLAFEST 1998). In the rural development district of Apatzigan, pertaining to the important agricultural region of Tierra Caliente, in the State of Michoacan, and which exerts influence on the Petacalco Bay through the Balsas river discharge, endosulfan is widely applied to control the white fly on cantaloupe and watermelon crops, as well as the mango plague. However, its use in the latter crop is not authorized. Regarding the alicyclic family, β-HCH has been reported as the most persistent isomer (ECO/OPS/OMS 1995), it was the compound with the highest concentration with its consequent accumulation in the fatty tissue of marine organisms and humans (Barkatina et al. 2002). To minimize the environmental pollution derived from the presence of α and β-HCH, lindane should be used (> 99 % of γ-HCH) instead of the technical HCH (ECO/OPS/OMS 1995). The restriction imposed on DDT use is only for sanitary campaigns. It is important to note that the study area is located between the States of Michoacan and Guerrero and is considered as high risk for malaria transmission (OPS 1997), and could therefore be the polluting source of this pesticide through the runoffs to the Balsas river and from there to the Petacalco Bay, although its illegal use in agriculture due to its low cost cannot be discarded. According to official data on DDT consumption in various municipalities of the State of Guerrero during malaria campaigns, its application has decreased from 1995 to 2000. Regarding the banned pesticides, governmental regulations are not complied with, since aldrin, dieldrin and endrin residues were detected in the Petacalco Bay. It must be emphasized that aldrin was found in all four subregions, both in the dry and rainy seasons indicating its recent and constant use. Finally, heptachlor use is not banned nor restricted officially.

To place into perspective the role of pesticides determined in this study with respect to their toxicity in marine environments, we used the guidelines established by Long et al. (1995) and Buchman (1999). The average concentrations of p,p'DDT, p,p'DDD, p,p'DDE and DDT_{total} , of the whole study area and of each of the zones, were below the ERL (1, 2, 2.2, and 1.58 ngg^{-1}, respectively), i.e., the adverse effects could rarely be observed. Dieldrin was only observed in the rainy season and its concentration exceeded the ERL value (0.02 ngg^{-1}) but did not reach the ERM (8 ngg^{-1}), indicating that biological damage could occur occasionally. However, this does not mean that there is no long-term risk, since benthic organisms that are in greater contact with the polluted sediments, can bioaccumulate and biomagnify them.

Comparing the POPs levels determined in this work with the available information for sediments of other similar environments in the Mexican Pacific, the Petacalco Bay, State of Guerrero; could be considered as a low polluted area, since the average POPs values in the lagoonal systems of the State of Chiapas (Chantuto-Panzacola and Carretas-Pereyra) revealed higher averages of 29.42 ± 9.93 and 70.21 ± 33.29 ngg^{1} (Rueda 1997). Other reports on the Subtropical Mexican Pacific, such as from the Mexcaltitán lagoon in the State of Nayarit, the Port of Mazatlán, the Lobos lagoon, the Ohuira Bay in the State of Sinaloa, and the Guaymas Bay in Sonora, reveal average values above those detected in this study (58.07 ± 35.53, 60.99 ± 55.63, 71.31 ± 52.40, 368.00 ± 141.72 and 1382.15 ± 1350.36 ngg^{-1} respectively) (Osuna-López et al. 1998; Osuna-Flores and Riva 2002).

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