

## PCBs and DDTs in Surface Mangrove Sediments from the South of Iran (ID NO. 048)

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**ABSTRACT:** Mangrove sediments were collected during wet and dry seasons from nine stations in Khamir, Laft and natural reservoir mangrove-dense areas of Hormozgan province in the south of Iran.  $\Sigma$  PCBs ranged from 5.33 to 15.5 ng/g dry weight and the dominant congener was no.153. Average  $\Sigma$  DDTs for Khamir and Laft mangroves were  $16.58 \pm 1.51$  and  $18.8 \pm 9.98$  ng/g dry weight. DDT was more abundant than DDE and DDD isomers, which indicated the input of DDT. The sediment quality guideline shows that the concentration of  $\Sigma$  PCBs were below the ER-M guideline, whereas levels of  $\Sigma$  DDTs were between ER-L and ER-M. The mangrove ecosystem in Hormozgan province is suffering from urban and industrial development.

**Key words:** PCB, DDT, Mangrove Sediment, Hormozgan province, Iran

### INTRODUCTION

Persistent organic pollutants (POPs) include organochlorine compounds with high stability which can accumulate in the food web. These pollutants undoubtedly show undesirable effects on humans and wildlife (Sarkar *et al.*, 2008; Terauchi *et al.*, 2009). Chlorine pesticides and polychlorinated biphenyls (PCBs) are known as POP chemicals.

Mangrove forests are globally identified as a link to terrestrial and marine environments, and serve as valuable ecological habitats securing food for animals (Bayen *et al.*, 2005; Vane *et al.*, 2009; Walsh *et al.*, 1974). Surface sediment exhibits behaviors similar to bottom sediment, which causes the sinking of organic pollutants (Tam and Yao, 2002).

The fine particles and accumulation of organic matter in mangrove sediment cause the improvement of water via organic matter. As a result of a special hydrodynamic state, organic pollutants accumulate in the mangrove ecosystem (Souza *et al.*, 2008). Due to their closeness to urban areas in numerous states,

mangrove forests are highly affected by humans through varied avenues (Tam and Wong, 2000) including shipping, industrial activities, rivers, aquaculture, and urban waste input (Shete *et al.*, 2009; Vane *et al.*, 2009).

Dense areas of Iranian mangrove forests have been reported. Iranian mangrove forests occur along three provinces in the south of Iran, namely, Bushehr, Hormozgan, and Sistan and Baluchestan. Mangrove forests in the Hormozgan province are divided into six zones based on their location and area. The total area of mangrove forests in Hormozgan province and Nayband Bay is estimated at 202.67 square kilometers. The international wetland covers 63.17 square kilometers of Qeshm Island, with 10.5 square kilometers of forests found at Khamir port (Zahed *et al.*, 2010). Several mangrove forests in the Hormozgan province are very near urban and industrial sites, such as the Laft port mangrove forests opposite Tabl and Laft village (Zahed *et al.*, 2010).

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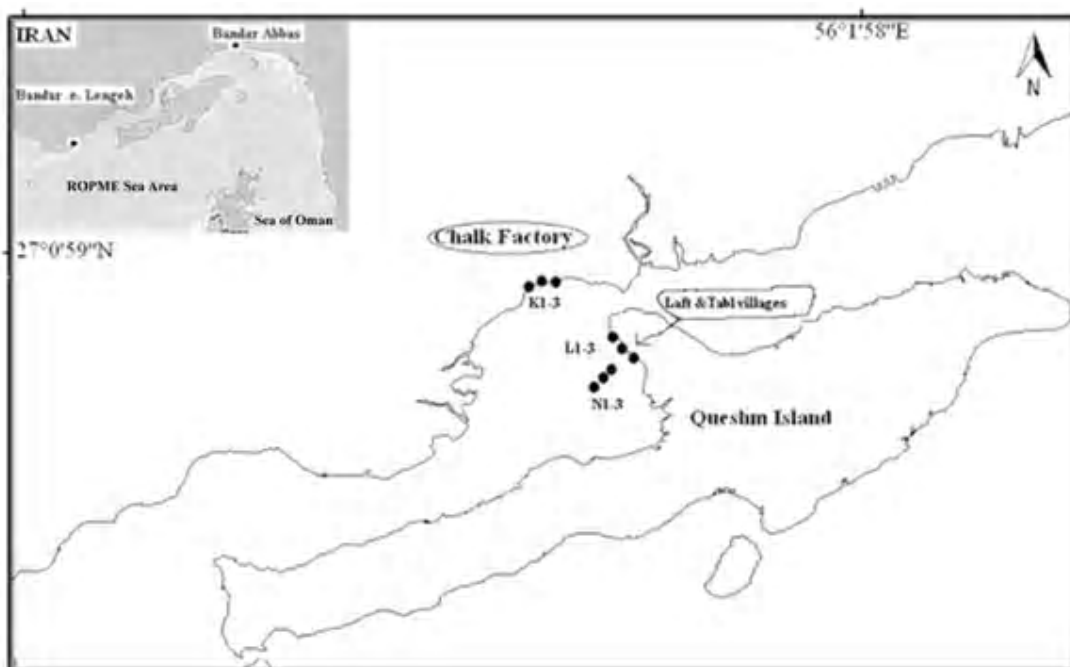


Fig. 1. Sediment sampling areas, Hormozgan Province, Iran

In spite of the urban and industrial progress in Hormozgan province, no study has been published on POPs in the mangrove ecosystem. Thus, this investigation focuses on the distribution and sources of PCBs (congener's nos. 28, 52, 101, 118, 153, and 180) and DDT isomers (DDD, DDE, and DDT) in the Khamir and Laft ports mangrove forests (Fig. 1).

#### MATERIAL & METHODS

Sampling was performed at the three mangrove-dense areas of Khamir and Laft ports. Three separate sampling stations were selected per area. The first area is located opposite the Gatch factory, the second sampling area is positioned near residential villages, and the last one area is found at the natural reservoir. Surface sediment samples were collected with Van Veen grab in duplicate on August 2010 and March 2011 using GPS coordinates to identify the geographical location of nine sampling stations. In the laboratory, the samples were freeze-dried, grounded, sieved, and kept in aluminum foil at  $-20\text{ }^{\circ}\text{C}$  until chemical analysis was performed.

According to the non normal distribution of data, the statistical analyses were performed using non-parametric tests (Kruskall-Wallis), SPSS 18.

##### 1.1. Sample preparation

An analysis of chlorinated and poly aromatic hydrocarbons in sediment was performed based on microwave extraction (De Mora *et al.*, 2010). A total of

15 g of the sample with a mixture of n-hexane and methylene chloride (1:1) was exposed to  $115\text{ }^{\circ}\text{C}$  for 20 min. The sulfur was removed using activated copper.

For the chlorinated hydrocarbons, a silica column was used for fractionation. The PCBs and DDTs were collected by eluting the column with 130 ml n-hexane and 15 ml methylene chloride (EPA, 1996).

##### 1.2. Instrumental analysis

The concentration of target compounds was determined by a gas chromatography system (Agilent 6890N) equipped with a mass selective detector (Agilent 5973N). The used column consists of a capillary column ( $0.25\text{ mm} \times 30\text{ m} \times 0.5\text{ }\mu\text{m}$ ) of DB-5ms (Agilent 122-5536). The mass detector was used in electron impact and selective ion monitoring mode. Helium was used as carrier gas at a flow rate of 1.5 ml/min. The injector was maintained at  $290\text{ }^{\circ}\text{C}$ .

During the chlorinated hydrocarbon analysis, the temperature of gas chromatography system oven was gradually increased from  $80\text{ }^{\circ}\text{C}$  (1.5 min hold) to  $160\text{ }^{\circ}\text{C}$  (with  $40\text{ }^{\circ}\text{C}/\text{min}$  ramp), to  $170\text{ }^{\circ}\text{C}$  (with  $10\text{ }^{\circ}\text{C}/\text{min}$  ramp), to  $250\text{ }^{\circ}\text{C}$  (with  $4\text{ }^{\circ}\text{C}/\text{min}$  ramp), and finally to  $300\text{ }^{\circ}\text{C}$  (with  $8\text{ }^{\circ}\text{C}/\text{min}$  ramp and 10 min hold).

##### 1.3. Quality control

All solvents were prepared at chromatography grade. With each set of samples, blanks were run to investigate the possibility of interference or contamination. The quantization of components was performed based on

an external standard method. The internal standards used for recovery calculation included PCB 29, PCB 198, ε-HCH, and endosulfan I- d for chlorinated hydrocarbons. A certified reference material, IAEA-417, served as a sediment sample to confirm quality assurance of the procedure. The average recoveries for PCBs and DDTs were 82 % and 80 % respectively. The method detection limit for PCBs congeners and DDTs were approximately 0.15 and 0.2 ng/g respectively.

**RESULTS & DISCUSSION**

The average concentrations of Σ PCBs and Σ DDTs in sediment collected from the sampling stations during dry and wet seasons are presented in Table 1.

Statistical tests showed no significance differences among the levels of chlorinated pollutants within dry and wet seasons (p < 0.05). Although unsurprising, this result may be due to the very low rain fall in Hormozgan province during the winter of 2011 based on a meteorological report for Hormozgan.

Concentration ranges of Σ PCBs and Σ DDTs among the sampling stations were 5.67 to 15.55 ng/g, and 13.32 to 36.75 ng/g dry weight, respectively.

The detected PCBs showed the average sum concentrations of 8.17 ± 0.61 and 9.04 ± 3.5 for Khamir and Laft angroves, respectively. The similar values for Σ DDTs were 16.58 ± 1.51 and 18.8 ± 9.98 ng/g dry weight.

No previous regional data exist on the level and distribution of chlorinated pollutants in the mangrove sediments of Hormozgan province. Compared with other results, the total concentrations of PCBs and DDTs were reported as nd -3.65 ng/g and nd- 8.64 ng/g dry weight, respectively, for the mangrove sediment samples along the Tanzanian coast (Kruitwagen *et al.*, 2008). Sediments of Guanabara, Brazil, varied greatly at 17.83 to 184.16 ng/g dry weight for a sum of seven PCB congeners; the values for the total DDTs were 10.61 to 37.4 ng/g dry weight (Souza *et al.*, 2008). Tam *et al.* (2002) observed that the concentration of Σ PCBs

**Table 1. Concentration of pollutants in sediments from Hormozgan Province (ng/g dry weight)**

Area	Station	Dry season		Wet season		Average	
		Σ PCB	Σ DDT	Σ PCB	Σ DDT	Σ PCB	Σ DDT
Khamir mangrove	k1	8.0 ± 0.22	16.43 ± 0.07	7.31 ± 0.45	15.33 ± 0.85	8.17 ± 0.61	16.58 ± 1.51
	k2	8.41 ± 0.25	16.98 ± 1	8.57 ± 0.26	16.90 ± 0.82		
	k3	7.91 ± 0.22	15.54 ± 0.13	8.81 ± 0.88	18.3 ± 3.31		
Average		8.11 ± 0.3	16.32 ± 0.78	8.23 ± 0.86	16.84 ± 2.06		
Laft mangrove	L1	7.00 ± 0.19	14.98 ± 0.35	8.08 ± 1.07	16.17 ± 1.72	9.04 ± 3.5	18.8 ± 9.98
	L2	15.55 ± 5.05	36.75 ± 17.42	8.43 ± 0.21	15.27 ± 0.11		
	L3	6.87 ± 0.28	13.32 ± 0.25	8.29 ± 0.13	16.16 ± 1.57		
Average		9.8 ± 5	21.68 ± 14.05	8.27 ± 0.51	15.87 ± 1.14		
Natural reservoir	N1	6.66 ± 0.35	15.89 ± 0.06	6.92 ± 0.04	15.82 ± 1.46	6.79 ± 0.71	15.87 ± 0.6
	N2	5.67 ± 0.24	15.16 ± 0.22	7.21 ± 0.96	15.96 ± 0.04		
	N3	7.00 ± 0.5	16.19 ± 0.5	7.28 ± 0.97	16.2 ± 0.42		
Average		6.44 ± 0.64	15.75 ± 0.53	7.14 ± 0.63	16 ± 0.7		

in the sediment mangrove of Hong Kong varied from <0.1 to 25.1 ng/g dry weight. Collected sediments from stations at the ROPME Sea Area (RSA) including the Bandar Abbas station showed the highest concentration of  $\Sigma$  DDTs, at 312 pg/g dry weight, and  $\Sigma$  PCBs at 155 pg/g dry weight. Our results are more larger than the detected value available from the RSA survey. Such differences are expected because, in this study, collected samples from the mangrove ecosystem possess a high capacity for accumulation of organic matter according to their special ecological characteristics (Souza *et al.*, 2008). In most of stations, the silt percentages were above 50% (Fig. 2), also these mangrove areas are very close to the cement and chalk

factory industries. The studied mangrove ecosystems receive much of their discharge from domestic sources due to their location (opposite Tabl and Laft villages). High shipping and heavy concentrations of shipping activities in the Khamir and Laft ports possibly contribute to the high concentration of PCBs. The significant difference ( $p < 0.05$ ) of measured pollutants concentrations between the Khamir, Laft mangroves with natural reservoir, is confirming the fact of land influence (Table 1).

According to distribution patterns (Fig.3), congener no. 153 has the highest abundance, followed by 28, 118, and 108. Similar results were observed on

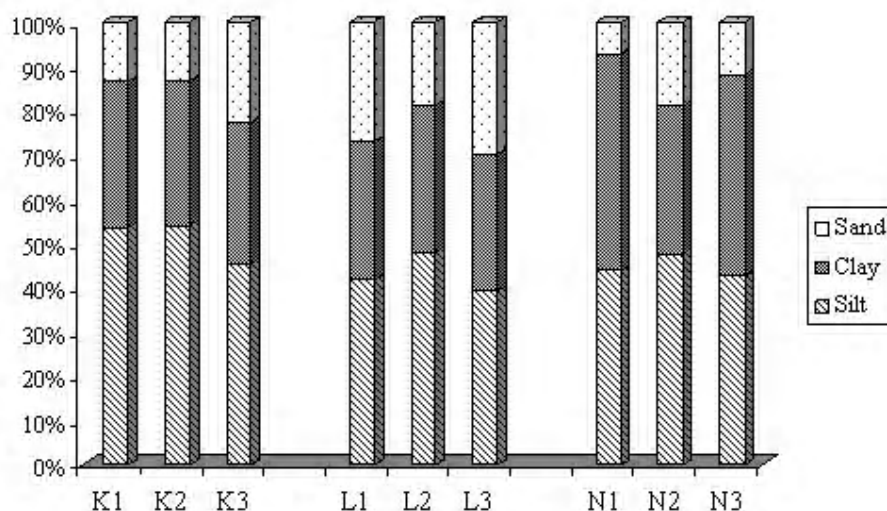


Fig. 2. Sediment texture of sampling stations

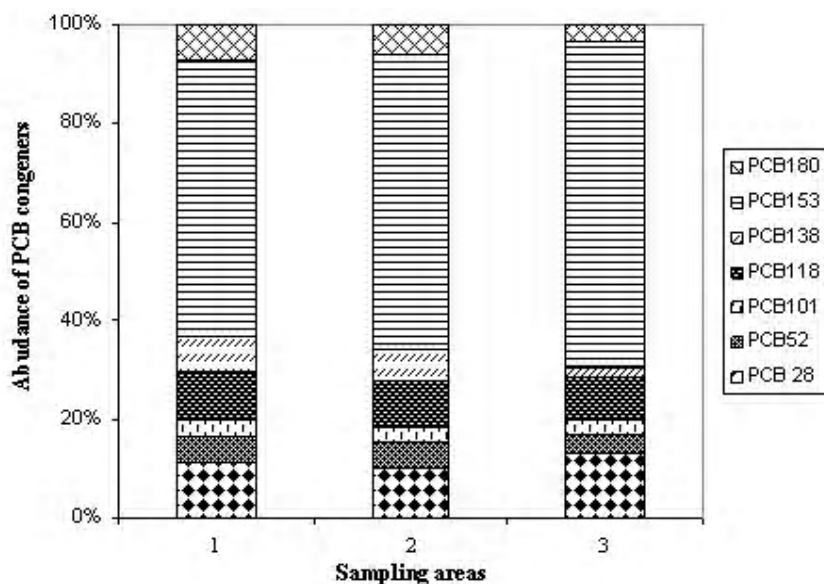


Fig. 3. Distribution patterns of PCBs in mangrove sediment of Hormozgan Province

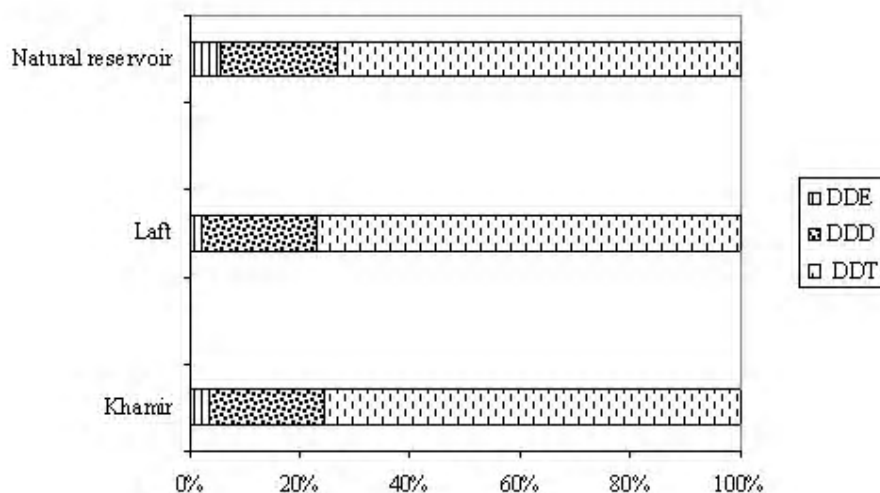


Fig. 4. Distribution patterns of DDTs

the sediment from Shadegan wetland in the northwest of the ROPME Sea Area (Zahed *et al.*, 2009).

All sediment samples contained a higher abundance of DDT than its isomers, DDE and DDD (Fig. 4) which indicate recent input of DDT in the subject area. This can be related to the healthy application of DDT to control malaria, which is a main health problem in Hormozgan and its neighbor province, Kerman (Hanafi-Bojd *et al.*, 2011; Vatandoost *et al.*, 2004).

Despite high PCB concentrations, the values did not exceed the sediment quality guideline value of 22.7 ng/g dry weight, although the values detected for  $\Sigma$ DDTs fell within the ERL and ERM guideline values of 1.58 and 46.1 ng/g dry weight, respectively (Long *et al.*, 1995b).

## CONCLUSION

With emphasis on the high concentration of chlorinated hydrocarbons, considerable inputs of urban and industrial waste are present in the mangrove ecosystem of Hormozgan province. Hot spots will likely occur if the uncontrolled industrial activities and untreated urban waste are allowed to continue.

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