# LEVELS OF PCB'S AND DDT'S IN SEDIMENTS FROM THE GUADALETE ESTUARY (SOUTH SPAIN)

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### Introduction

Polychlorinated biphenyls are ubiquitous industrial pollutants formed by 209 possible congeners and DDTs are a group of organochlorine insecticides very used in agriculture until 70's when were banned in most of developed countries. Both organochlorine groups of compounds are present in environmental samples and due to their physico-chemical properties, persistence and toxicity, are considered global environmental pollutants (1).

The estuary of river Guadalete is subjected to a restoration program, with the objective of improving the water quality, including the recovery of the aquatic and benthic fauna. In order to evaluate the effects of the corrective measurements applied in the estuary of river Guadalete, a monitoring program of the estuary aquatic communities, the environmental conditions and the pollution inputs have been established. Sediments were selected as the most adequate samples to evaluate the pollution in the study area since several studies had shown that PCBs accumulate in riverine (2, 3) and marine ecosystems (4).

The objective of the present study is to evaluate the levels of PCBs and organochlorine insecticides in sediments from the Guadalete River and to evaluate their significance and impact on the invertebrate benthic macrofauna of the river.

#### **Methods and Materials**

#### Sampling area

The study area is situated in the estuary of the river Guadalete, which waters flows to Cadiz bay (SW Iberian Peninsula). Three stations in the low-middle estuary were selected (Fig. 1).

#### Samples

Samples were collected seasonally, in January and May of 2001. For benthic communities, sampling was carried out in the intertidal zone using an Ekman dredge ( $0.0225 \text{ m}^2$  effective area) scanning 0.25 m<sup>2</sup>. For the analysis of the benthos, samples were sieved by using a 0.5 mm mesh and fixed in formol 4 % for further identification and quantification of the meiofauna. Samples for the analysis of pollutants were collected by triplicate using the same dredge. Sediment samples were collected in the section corresponding to 0-10 cm. Samples were lyophilized, sieved and divided into two fractions (total and <63 mm). Their granulometric composition and C and N organic content was determined using an elemental analyzer Carlo Erba 1106.

### Residue analysis

The analysis of DDTs and PCBs consisted on an extraction of the dry sample in a Soxhlet apparatus

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during 24 h with toluene. In order to avoid interferences from sulfur, Cu powder was added to cartridges before the extraction. Furtherly, the extracts were and purified through an open glass column filled with anhydrous sodium sulfate, neutral activated silica and basic and acid silica, using n-hexane as solvent. Once concentrated, the extract was passed through a new column filled with anhydrous sodium sulfate and FlorisilÒ. Sample extracts were injected in a GC Agilent 6890 Series equipped with an mECD (Palo Alto, CA, USA). N<sub>2</sub> was used as carrier gas at a constant flow of 1.5 ml/min. A DB-5 column was used (60 m long, 0,25 mm i.d., 0,25 mm, J&W Scientific, USA). All PCB congener standards (PCB# 28, 52, 95, 101, 105, 114, 118, 123, 132, 138, 149, 153, 156, 157, 167, 170, 180, 183, 189 and 194) were obtained from Dr. Ehrenstorfer (Augsburg, Germany) and pp'DDD, pp'DDE and pp'DDT, were purchased to Chem Service (West Chester, PA, USA). TCN (25 pg/mL) from Dr. Ehrenstorfer (Augsburg, Germany) was used as internal standard.

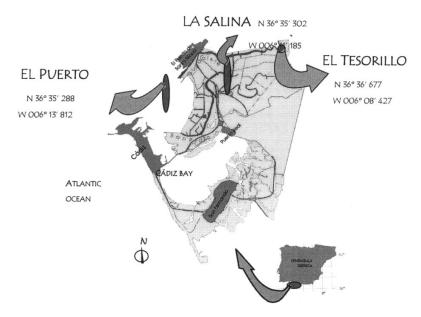


Figure 1. Geographical situation of the study area.

## **Results and Discussion**

Total PCB levels in January 2001 ranged between 3.55 ng/g and 92.55 ng/g dry weight which were found at "El Tesorillo" and "El Puerto" respectively. Regarding the normalized congener composition (Fig 2), it can be observed that in El Tesorillo PCB#153, 138 and 180 were the most abundant (>10%) as found in other studies (5), but other low chlorinated congeners were found at similar levels. However, in "La Salina" PCB#180 had no important contributions (2 %) compared to PCB# 153 and 138 (>15 %), and PCB# 118 showed higher levels than in the other stations. In May 2001, the congener profiles are similar to those found in January for the three locations studied, but some variations were observed. In "El Puerto", PCB#153 had no important contribution (1 %) and in La Salina PCB#180 showed an increasing value. In general it can be said that total PCBs decreased from January to May 2001 in La Salina and El Puerto stations but, on the contrary, levels were found to increase at "El Tesorillo".

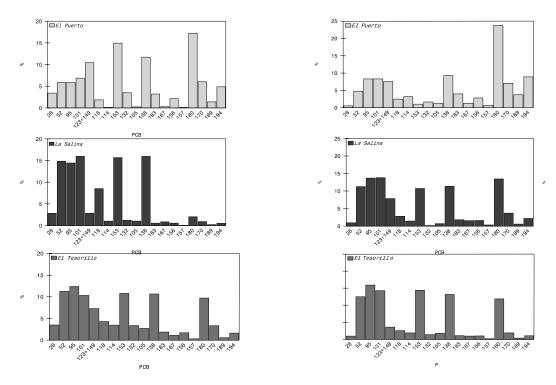


Figure 2. Normalized congener composition of sediments collected in the tree locations in January (left) and may (right).

For DDTs (considered as the sum of pp'DDD, pp'DDE and pp'DDT), in January 2001 the concentrations ranged from 12.44 ng/g d.w. to 58.80 ng/g d.w. corresponding to El Tesorillo and La Salina respectively. In May, levels ranged between 1.52 ng/g d.w. and 19.20 ng/g d.w. corresponding to El Puerto and El Tesorillo respectively. It was found that DDE always exhibited the highest levels, being normally in the order DDE > DDT > TDE. The DDE/DDT ratio was calculated for all samples analyzed and it was found that this ratio was always >1. This value suggests that DDT had not been recently used in the study area. Comparing data obtained in this study with those obtained in different studies in sediments, it can be observed that DDTs levels are lower than obtained by other authors and situated at 248 ng/g d.w. in Argentina (6) or 415 ng/g d.w. in California (7). PCBs do not differ significantly and, in general, levels found in this study were lower that in the other studies: 20.64-52.5 ng/g d.w. in Holland (8) or 1.1-141 ng/g d.w. in Korea (9).

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### References

- 1. Tatsukawa R. (1984) Arch Environ Contam Toxicol. 13, 731
- 2. Hooper, S. Pettigrew C., Sayler G. (1991) Environ Toxicol Chem. 9, 655
- 3. Galassi S., Guzzella L., Battegazzore M., Carrieri A. (1994) Ecotoxicol Environ Saf. 29, 174

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- 4. Zaranko D., Griffiths R., Kaushik N. (1997) Environ Toxicol Chem. 16, 1463
- 5. Nakata H., Sakai Y. Miyawaki T. (2002) Arch Environ Contam Toxicol. 42, 222
- M.L. Menone, J.E. Aizpún de Moreno, V.J. Moreno, A.L. Lanfranchi, T.L. Metcalfe, C.D. Metcalfe. (2001) Arch Environ Contam Toxicol. 40, 355
- 7. L.R. Brown. (1997) Arch Environ Contam Toxicol. 33, 357
- A.J Hendriks, H. Wever, K. Olie, K. Van de Guchte, A.K.D. Liem, R.A.A. van Oosterom, J. van Zorge. (1996) Arch Environ Contam Toxicol. 31, 263
- 9. G.H. Jeong, H.J. Kim, Y.J. Joo, Y.B. Kim, Y. So. (2001) Chemosphere 44, 1403