

Organochlorine Pesticide Residues in Chilean Fish and Shellfish Species

Alfonso Ober,* Mauricio Valdivia, and Inés Santa María

Chemistry Department, Faculty of Science, Santa María University, P.O. Box 110-V, Valparaíso, Chile

Environmental pollution with organochlorine pesticide residues is evident throughout the world, and a great number of data have been reported. These compounds are known to be toxic to biota and to persist both in the aquatic and terrestrial ecosystems where they accumulate.

Organochlorine pesticides (OCP's) enter into the marine ecosystems mainly via agricultural drains, although wastewater discharges may also represent an important source of marine pollution by these compounds (Fytianos et al. 1985; Faust & Aly 1964). In aquatic organisms, they accumulate by direct absorption from water and/or by partitioning into lipids of foods (Bjerk & Brevik 1980).

The use of organochlorine pesticides has been banned in many countries, but in Chile only DDT and its derivatives were banned in January 1986; the other OCP's are still widely used, and only a few data about their levels in the Chilean environment have been so far published.

As part of our marine contamination studies, we have investigated the presence of OCP's in commercially important fish and shellfish species. Presently, data on OCP levels in south eastern Pacifican species are very scarce and we did not find published results on their contents in Chilean marine species. We report here the average contents of OCP's in 11 marine species from the Chilean coastal waters.

MATERIALS AND METHODS

All solvents and reagents used were pesticide grade or equivalent. Analytical standards of organochlorine pesticides were obtained from Environmental Protection Agency (U.S.). Standard stock solutions (200 ug/ul) were prepared in iso-octane and kept refrigerated.

The marine species investigated here were collected by

* Present Address: University of the Sacred Heart, P.O. Box 12383 Santurce, P.R. 00914

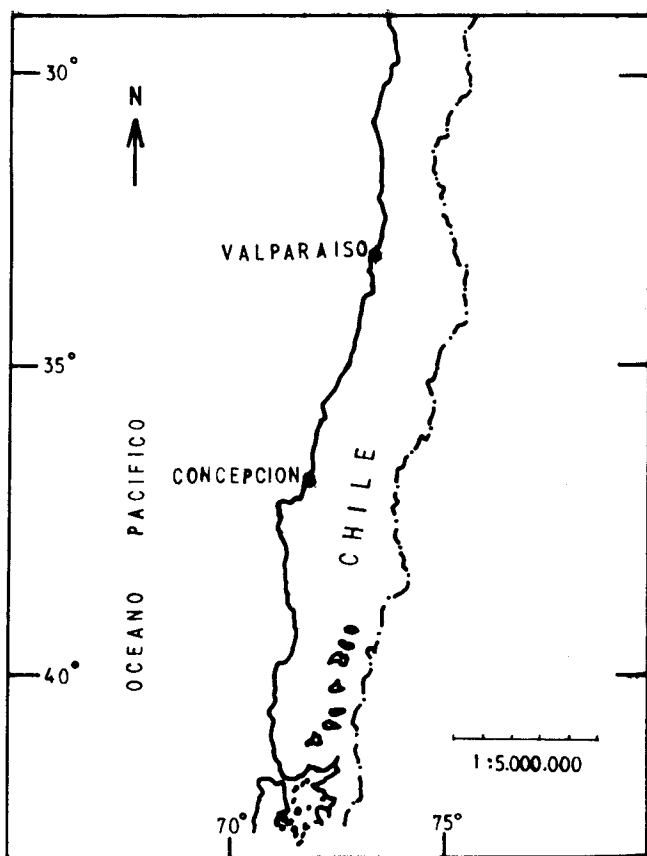


Figure 1. Location of the sampling areas along the Chilean Coast.

professional fishermen from the bays of Valparaíso and Concepción in the period June 1985 to October 1985. After collection the specimens were transported to the laboratory where they were dissected to obtain the muscle tissues. All samples were measured and weighed prior to analysis. Only edible parts were analyzed.

Marine species included 7 fish species from the bay of Valparaíso, and the other two from the bay of Concepción. The investigated species included: Trachurus murphyi (horse mackerel), Merluccius gayi gayi (hake), Genypterus maculatus (black cusk eel), Paralichthys microps (plaice), Seriola violacea (jack), Cilus montti (croaker), Genypterus chilensis (red cusk eel), Mytilus edulis chilensis (mussel), Aulacomya ater (ribbed mussel), Ameghinomya antiqua (clam), and Mesodesma donacium (no simil).

For residue analysis, 20 to 25 specimens of the shellfish species, and 4 to 8 specimens of the fishes were homogenized in a mortar with anhydrous sodium sulfate and the appropriate amount of the homogenate was taken for analysis.

The OCP's were extracted by sonication of the homogenate (50-100g) with 75 ml of n-hexane/acetone (4:1) for 5 minutes. This operation

Table 1. Mean values * of OCP levels in Chilean fish species. (ppb on a wet basis).

| Species | HCB | Lindane | Aldrin | p,p'DDE | Dieldrin | Heptachlor |
|---------------------|------|---------|--------|---------|----------|------------|
| <i>T. murphyi</i> | 43 | 9 | 226 | n.d. | n.d. | n.d. |
| <i>M. gayi</i> | n.d. | n.d. | 300 | n.d. | 10 | n.d. |
| <i>G. chilensis</i> | n.d. | 8 | 22 | n.d. | n.d. | n.d. |
| <i>G. maculatus</i> | n.d. | n.d. | 40 | n.d. | n.d. | n.d. |
| <i>P. microps</i> | n.d. | 7 | 10 | n.d. | n.d. | n.d. |
| <i>S. violacea</i> | n.d. | 740 | 120 | n.d. | 3000 | 900 |
| <i>C. montti</i> | n.d. | n.d. | n.d. | 360 | n.d. | n.d. |

*Mean value of a sample run in duplicate.

n.d.= not detected

was repeated twice with the same amount of solvent. The combined extracts were washed twice with 125 ml of an aqueous sodium sulfate solution (2% w/v) and dried up with granular anhydrous sodium sulfate.

The clean-up procedure was performed by column chromatography on partially deactivated alumina. Alumina was prepared by heating it up to 550 C for 4 hours, following by the addition of 10% by weight of distilled water. An appropriate aliquot of the OCP's extract, containing less than 0.5 g of fats, was concentrated by means of a Kuderna-Danish concentrator, and quantitatively transferred to the top of a column packed with 22g of alumina (10% deactivated) and overlaid with 1 cm of anhydrous sodium sulfate. The column was eluted with 150 ml of n-hexane. Finally the extract was concentrated to 0.5 ml in a K-D concentrator. Control blank solutions on reagents and equipments were run with each sample.

The OCP gas chromatographic analysis were performed on a Perkin-Elmer Sigma 38 gas chromatograph, equipped with a Ni-63 electron capture detector and a 3.5 m by 2.0 mm i.d. glass column packed with 1.5% OV-17 / 1.95% QF-1 on Chromosorb W HP (100-120 mesh). A second chromatographic column, 2 m by 2.0 mm i.d. glass column packed with 3% OV-225 on Chromosorb W HP (100-120 mesh) was utilized to confirm the peak identities. Injector, column and detector temperatures were set at 220, 200, and 300 C respectively. Nitrogen was used as carrier gas at a flowrate of 35 ml/min. Quantitations were performed with a Perkin-Elmer Sigma 15 Data Station.

Table 2. Mean values* of OCP residues in Chilean shellfish (ppb on a wet basis).

| Species | Lindane | Aldrin | p,p' DDT | p,p' DDE | Dieldrin | o,p' DDT |
|---------------------|---------|--------|----------|----------|----------|----------|
| <i>M. chilensis</i> | 3 | 4 | n.d. | 6 | n.d. | n.d. |
| <i>A. ater</i> | 43 | 10 | n.d. | n.d. | n.d. | n.d. |
| <i>A. antiqua</i> | 113 | 7 | 14 | n.d. | 5 | 15 |
| <i>M. donacium</i> | 11 | 33 | n.d. | 56 | n.d. | n.d. |

* Mean value of a sample run in duplicate.

n.d.= not detected

RESULTS AND DISCUSSION

Figure 1 shows the sampling sites of the marine species examined here. All the species were collected in the bay of Valparaíso, except *M. chilensis* and *A. ater* which were from Concepción. The latter location was taken for comparison purposes since it is also a highly urbanized and industrialized zone.

Average concentrations of the OCP's in the fish tissues are summarized in Table 1. The OCP contents of the examined bivalve molluscan species is shown in Table 2. To avoid differences in the OCP contents due to the different fat contents in the investigated species, the presented data are based on body weight rather than on fat weight.

As it is shown in the tables, all the marine species contained detectable amounts of OCP's. However, as all the values fall below the tolerance levels prescribed for Chilean foods, it appears that the contamination of the marine species with organochlorine residues is not a problem in Chile yet.

Lindane and aldrin were present in almost all the species investigated, while the other organochlorine residues were unequally distributed. The average levels of lindane ranged from 0 to 740 ppb in fishes and from 3 to 113 ppb in the shellfishes, whereas aldrin ranged from 0 to 300 ppb in fishes and from 4 to 33 ppb in the shellfish species. These values are similar to contents reported for fishes from other geographic locations (El-Edib & Badawy 1985; Brevik 1981; Kilikidis et al. 1981), but biologically insignificant since they are below the levels known to have adverse effects in marine species. We found no other published results concerning OCP contents in Chilean species.

The differences in the residue levels among the 7 fish species examined in our study seem to be related to the differences in feeding habits of the species; *G. chilensis*, *G. maculatus*, and *P.*

microps, which are bottom species presented the lowest OCP levels.

The migratory nature of C. montti could explain the presence of DDE in it, because the specimens could have accumulated the pesticides in other geographic areas. The higher OCP levels in S. violacea may at least be partially explained by the habitat of these specimens that develop and grow around the urban and industrial drainages along the coast.

The OCP levels in the examined shellfish species, with the exception of the bottom fish species, were lower than the ones found in fishes. Again, the difference in diet and the non-migratory nature of the molluscan species could partially explain the lower contaminat levels of these species. Comparatively, the shellfish species from the bay of Valparaíso present a higher OCP's content than the ones from Concepción. The levels of OCP determined here for the Chilean molluscan species are considerably lower than the values reported for shellfishes from other latitudes (Hartley & Johnston 1983; Rosales & Escalona 1983).

From the results presented in Table 1 and 2, it can be seen that the species from the bay of Valparaíso and Concepción are not accumulating large quantities of OCP's. Several factors may contribute to this condition: (1) a lessened used of organochlorine pesticides in Chile after DDT and its derivates were banned in 1983; (2) a too limited sampling of marine species in our study; (3) a possible unavailability of OCP's to fishes and shellfishes via foodchain; and (4) species exposed to OCP's may have suffer heavy mortality and therefore were not represented in the analyzed samples.

The low levels of OCP's found in all the marine species investigated in our study seem to indicated that pollution by organochlorine pesticides has no significance in the Chilean central coastal marine species.

Acknowledgements. The authors thank Maria Cecilia Moragas for technical assistance. Thank are due to Prof. Benito Santana for helping with the manuscript preparation.

REFERENCES

- Bjerk JE, Brevik EM (1980) Organochlorine compounds in aquatic environments. Arch Environ Contam Toxicol 9: 743-750
Brevi EM (1981) Organochlorine residues in fish from lake Mjøsa in Norway. Bull Environ Contam Toxicol 26:679-680
Brun H, Berlich HD, Muller FJ (1985) Residues of pesticides and polychlorinated biphenyls in game animals. Bull Environ Contam Toxicol 34:527-532
Crosby OG (1973) The fate of pesticides in the environment. Ann Rev Plant Physiol 24:467-492
El-Dib MA, Badaway MI (1985) Organochlorines insecticides and PCB's in water, sediment, and fish from the Mediterranean Sea. Bull Environ Contam Toxicol 34: 216-227

- Faust SD, Aly DM (1964) Water pollution by organic pesticides. J Am Water work Assoc 56: 267-279
- Fytianos K, Vasilikiotis G, Weil L (1985) Identification and determination of some trace organic compounds in coastal seawater of northern Greece. Bull Environ Contam Toxicol 34:390-395
- Hartley DM, Johnston JB (1983) Use of freshwater clam Corbicula manilensis as a monitor for organochlorine pesticides. Bull Environ Contam Toxicol 31: 33-40
- Kilikidis SD, Psomas JE, Kamarianos AP, Panetsos AS (1981) Monitoring DDT, PCB's and other organochlorine compounds in marine organisms from the north Aegean Sea. Bull Environ Contam Toxicol 26: 496-501
- Rosales MTL, Escalona RR (1983) Organochlorine residues in organisms of two different lagoons of northwest Mexico. Bull Environ Contam Toxicol 30: 456-463

Received May 10, 1986; accepted November 10, 1986