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Organochlorines in Antarctic Marine Food Chain at Terranova Bay (Ross Sea)

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The aim of this study was to evaluate chlorinated hydrocarbon pollution of the Antarctic food chain at Terranova Bay (Ross Sea). Samples belonging to several Taxa, Echinoderms, Molluscs, Fishes, Birds and Mammals, representing different levels in the food chain, were analysed. The organochlorines detected and assayed were hexachlorobenzene (HCB), the *op'* and *pp'* isomers of DDT and of their metabolites DDD and DDE and several congeners of polychlorobiphenyls (PCBs). In muscle the substance occurring at the lowest levels in all three species was HCB. In the DDT group, *pp'*-DDE showed the highest concentrations. PCBs were calculated as the sum of the principal congeners identified (about 20). Wide differences in PCB fingerprint were observed between the various species; the most common congeners were the pentachlorobiphenyls 22'44'5 and 23'44'5, the hexachorobiphenyls 22'344'5' and 22'44'55', and the heptachlorobiphenyls 22'33'44'5 and 22'3'44'55'.

Key words: pollution, organochlorines, food chain, Terranova Bay

INTRODUCTION

In the last decade, there has been much research into the global distribution of persistent organochlorines such as polychlorinated biphenyls (PCBs) and DDT. It has been found that these contaminants can reach the troposphere, mainly as vapours, and may be deposited in remote areas of the world, especially the cold polar regions. Recent studies have revealed unexpectedly high levels of organochlorines in air, seawater and wild animals in the Arctic (Hargrave *et al.*, 1992; Iwata *et al.*, 1992; Muir *et al.*, 1992). This is certainly due to atmospheric transport of persistent organochlorines to the Arctic from lower latitudes. Despite the regulation or prohibition of these chemicals in western nations since the 1970s, their use and disposal are still continuing or increasing in developing countries near the tropical latitudes and this will influence global levels of contamination in the next few years, even in the Antarctic.

Pollution of such a remote area as the Antarctic by organochlorines is mainly due to aerial transport, although ocean currents and scientific stations may play a minor part. Ocean water bodies are believed to be the final sink of these toxic contaminants, after long-range atmospheric transport from emission sources, mass transfer between air and water and scavenging in the deep sea layers by particles.

Hence these contaminants pass from air to water to sediment, entering the marine food chain. Marine invertebrates acquire them by ingestion with food and/or by direct transfer from the water or the surface of mineral particles. The same is also true of fish and it is difficult to establish the relative importance of these two routes in the field. Due to their mobility and lipoaffinity, these substances accumulate in living organisms, in general from lower to higher, practically following the prey-predator hierarchy in the trophic levels, namely from plankton to small fishes to large fishes to birds and mammals. The level of contamination is influenced by individual and specific factors, but mainly by the level that each species occupies in the food chain. In fact xenobiotic concentrations increase by several orders of magnitude from invertebrates and fishes to predators at higher

trophic levels.

Since little information is available on these questions in the Antarctic environment, our research group is collecting data with the aim of evaluating chlorinated hydrocarbon pollution of the Antarctic food chain at Terranova Bay (Ross Sea), near the Italian Scientific Station (74°40′ S, 164°10′ E).

MATERIALS AND METHODS

Specimens of Holothurians, Cephalopods, Bivalves (*Adamussium colbecki*), Fishes (*Pagothenia bernacchii*, *Cryodracus antarticus*, *Dissostychus mawsoni*), Birds (*Aptenodytes forsteri*, *Pygoscelis adeliae*, *Catharacta maccormicki*) and Mammals (*Leptonychotes weddelli*), representing different levels in the food chain, were analysed. Tissues and organs were frozen, homogenized and freeze-dried. For the analysis of chlorinated hydrocarbons, freeze-dried material was extracted in Soxhlet with pesticide-free, vacuum distilled n-hexane; the extract underwent to sulphuric acid clean-up, followed by Florisil chromatography. Analysis was performed with a Perkin-Elmer model 8700 gas chromatograph equipped with Ni^{63} electron capture detector. A SPB-5 bonded phase (0.25 μm film thickness) fused silica capillary column (30 m long, internal diam. 0.2 mm) from Supelco was used. The carrier gas was helium at 110kPa, with a split ratio of 50/1. The detector scavenger was argon/methane (95/5) at a flow of 30 ml/min. Oven temperature was 100°C for 10 min and was then increased by 3°C/min to 280°C. The injector (PTV) was kept at 50°C until the time of injection, after which the temperature was quickly raised to 250°C. Detector temperature was 300°C. A mixture of specific isomers was used for instrumental calibration, recovery evaluation and confirmation.

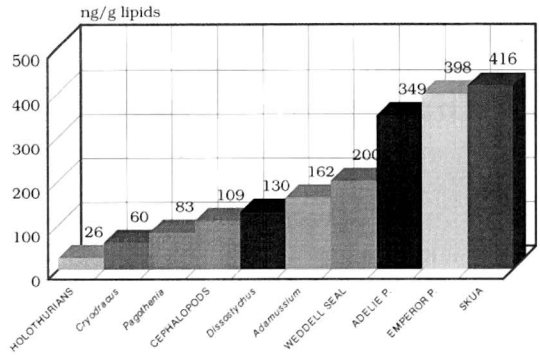

Fig. 1. HCB in muscle.

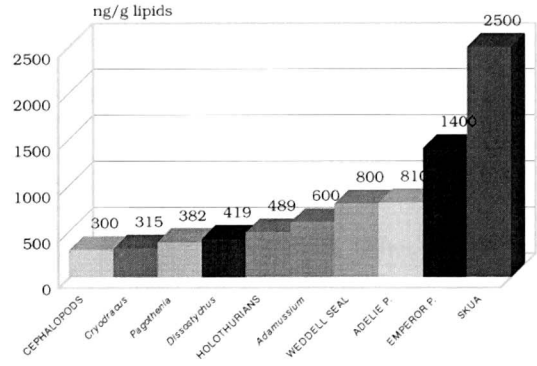

Fig. 2. DDTs in muscle.

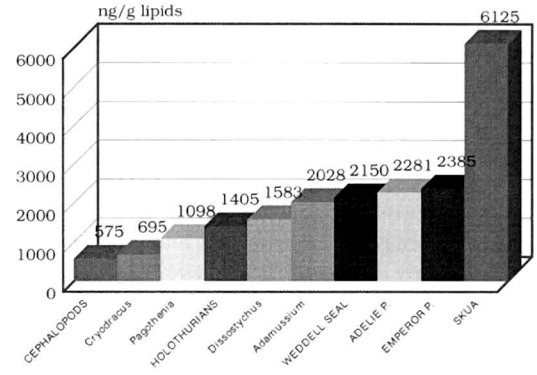

Fig. 3. PCBs in muscle.

RESULTS AND DISCUSSION

The organochlorines detected and assayed (Figs 1-3) were hexachlorobenzene (HCB), the op' and pp' isomers of DDT and their metabolites DDD and DDE, and several congeners of polychlorobiphenyls (PCBs).

In muscle, the substance occurring at the lowest levels in all the species was HCB. The mean levels found were 26 ng/g (fat basis) in holothurians, 60-160 ng/g in molluscs and fish, and 200-420 ng/g in penguins, Weddell seal and South polar skua. These figures are similar to those found in fatty tissue by Schneider *et al.* (1985) in the same species of penguins, and in eggs by Focardi *et al.* (1992).

In the DDT group, *pp'*-DDE showed the highest

concentrations (Figs 4-6); DDTs were about 300-400 ng/g in cephalopods and fish, from 500 to 600 ng/g in benthic invertebrates, 800 ng/g in the Adelie penguin (*P. adeliae*) and Weddell seal (*L. weddelli*), 1400 ng/g in the Emperor penguin (*A. forsteri*) and 2500 ng/g in the skua (*C. maccormicki*). As far as Antarctic organisms of other trophic levels are concerned, *pp*'DDE and *pp*'DDT values between 0.1 and 0.5 ng/g dry weight have been reported in mosses and lichens of the Ross Sea (Focardi *et al.*, 1991). Previous studies on Antarctic fish (Subramanian *et al.*, 1983; Hidaka *et al.*, 1984) measured DDTs in four species collected around the Japanese Antarctic station, Syowa, out of the range of influence of the base; slightly higher concentrations were found around Syowa than in the present study area. In birds these results were similar to those reported in the same and other Antarctic species by Schneider *et al.* (1985), Luke *et al.* (1989) and Focardi *et al.* (1991); in the muscle and fat of the Weddell and Crabeater seals, Hidaka *et al.* (1984) and Schneider *et al.* (1985) reported values between 10 and 500 ng/g.

PCBs were calculated as the sum of the principal congeners identified (about 20): the average was around 600 ng/g in cephalopods and Cryodracus, from 1000 to 2000 ng/g in benthic invertebrates and other fish species, more than 2000 ng/g in penguins and 6000 ng/g in the South polar skua. The PCBs content of these fish samples was higher than in the fish samples of Subramanian *et al.* (1983) and Focardi *et al.* (1992), and lower than in samples from other seas and oceans (Vuorinen *et al.*, 1985; Larsson *et al.*, 1991). Fig. 3 shows a marked difference between the concentrations of these contaminants in the birds; specifically, PCBs were found to be 3 times higher in the South polar skua than in the penguins. Unlike penguins, skuas are long distance migrants, and are known to range over polluted water bodies in winter. Interestingly, PCBs and DDE levels recorded in South polar skua eggs are only a tiny fraction of those in Great skua eggs from the North Atlantic. South polar skuas spend only about 4-5 months in Antarctica, then migrate through the Southern Ocean and are not uncommon in the northern Pacific and northern Atlantic during winter (Devillers, 1977; Furness, 1987). In the Atlantic, they probably mix with groups of Great Skuas during the northern summer

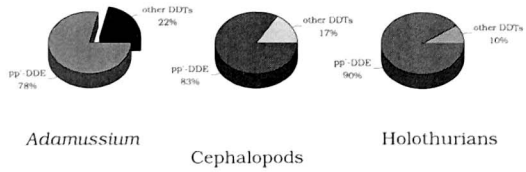

Fig. 4. *pp*'-DDE/DDTs in invertebrates.

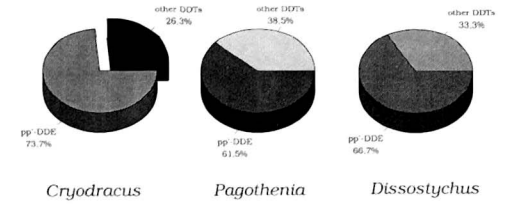

Fig. 5. *pp*'-DDE/DDTs in fish.

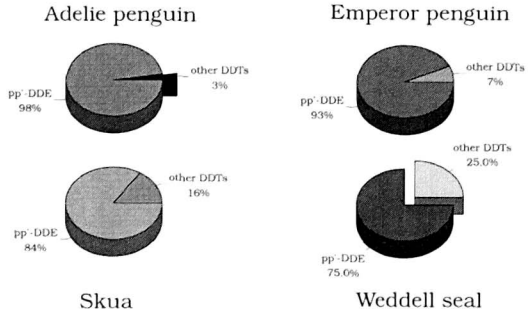

Fig. 6. *pp*'-DDE/DDTs in birds and Weddell Seal.

(Furness, 1987). Furness and Hutton (1979) reported levels of 17.6-25 ppm (wet weight) for PCBs and 1.7-5.9 ppm (wet weight) for DDE in eggs of the Great Skua. The very much lower levels of PCBs and DDE in South polar skuas with respect to Great skuas, indicate that adults of this species may spend a much smaller part of the year in polluted waters than is believed, or, possibly, that birds that winter in the northern hemisphere do not breed there, as suggested in an earlier study on migrant skuas (Devillers, 1977).

The ratio DDTs/PCBs was always less than one confirming the general observation of the worldwide increase of PCBs with respect to DDTs over the last few years, and it shows a substantial change from the earliest measures of these compounds in Antarctica. Risebrough *et al.* (1976) showed this ratio in Adelie penguin eggs to be about 2.5:1 in the mid 1970s.

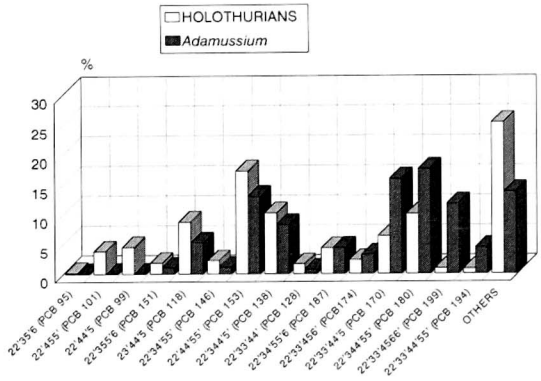

Fig. 7. Percentage of PCBs congeners.

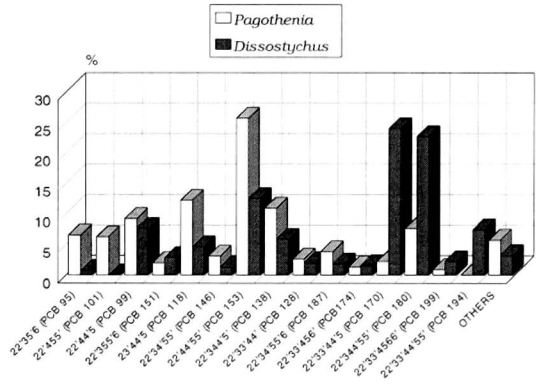

Fig. 8. Percentage of PCBs congeners.

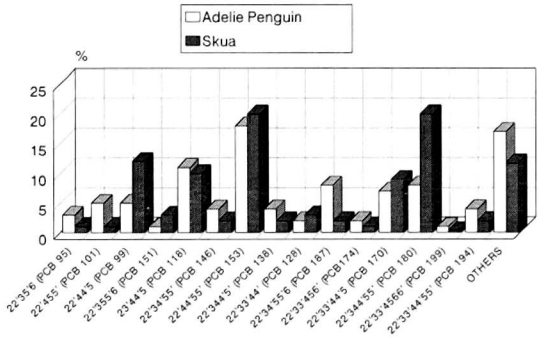

Fig. 9. Percentage of PCBs congeners.

Regarding the composition of PCBs in our samples, a wide range of differences in fingerprint were observed between the various species (Figs 7-9). The most common congeners were pentachlorobiphenyls 22'44'5 and 23'44'5, hexachlorobiphenyls 22'344'5' and 22'44'55', and heptachlorobiphenyls 22'33'44'5 and 22'3'44'55'. Risebrough *et al.* (1976), who first recorded PCBs in Antarctic bird species, noted that the bulk of the residue in their samples consisted of pentachlorobiphenyls. In these samples hexachlorobiphenyls and heptachlorobiphenyls constituted most of the residues; in holothurians, *P. bernacchii* and birds the isomer 22'44'55' predominate whereas in *A. colbecki* and *D. mawsoni* the heptachlorobiphenyl 22'344'55' exceeded 20% of total residue.

In conclusion, these findings confirm the information in the literature on the presence of organochlorines in the Antarctic ecosystem and their penetration into the food chains. The levels found also seem to confirm the world-wide trend of increase in PCBs with respect to DDTs and their metabolites.

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