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THE FATE OF CHLORINATED HYDROCARBONS IN THE AQUATIC ECOSYSTEMS. CASE STUDY: FOOD CHAIN BIOACCUMULATION IN THE BIOTA OF THE KARAVASTA LAGOON

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Abstract. The chlorinated hydrocarbons like pesticides and polychlorinated biphenyls are chemical substances which are extremely persistent, bioaccumulating, toxic to surrounding environment and to human health. The atmosphere is the major path for the delivery of these pollutants to the oceans. The concentrations and the chemical forms of chlorinated hydrocarbons change once they are added to surface water, as a result of four natural processes: dilution, sedimentation, biodegradation and biological amplification. The last one, the so-called bioaccumulation, is the most effective one. In our case study, the process of bioaccumulation of some chlorinated hydrocarbons in different aquatic species is discussed. The bioaccumulation patterns of chlorinated hydrocarbons in biota of Karavasta lagoon from their sediment source resulted to be largely determined by chlorine content and their lyophility. It is also dependent of the kind of species being analysed and their position in the food chain.

Keywords: bioaccumulation, chlorinated hydrocarbons, food chain, biological magnification, congeners, egestion.

AIMS AND BACKGROUND

The chlorinated hydrocarbons like chlorinated pesticides and PCBs (polychlorinated biphenyls) have become widely distributed all over the globe. Chlorinated pesticides (like DDT, Lindane, Aldrine, Heptachlor, etc.) have been extensively used in agriculture. Polychlorinated biphenyls are a group of 209 compounds with extremely high physical, chemical and biological stability[1,2]. These chlorinated substances which are extremely persistent, bioaccumulating and toxic present a risk of adverse effects to surrounding environment and to human health. The global chemical fate of the chlorinated hydrocarbons is controlled by the point of discharge, movements of the atmosphere and the oceans, the rate of exchange processes between the atmosphere and the Earth's surface, and the rate of chemical loss from various environmental phases (Refs 3-6). In the marine environment the chlorinated hydrocarbons may be physically distributed in two principal ways:

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atmospheric and land-base sources. The atmosphere is the major path for the delivery of these pollutants to the oceans (Refs 2, 3, 5-7). Chlorinated hydrocarbons can be found in true solution, or in vapour phase, or adsorbed in air-borne particles. The chlorinated hydrocarbons dispersed in the atmospheric air are carried by air streams and settle down with precipitation onto the surface of the water basins and the land. The interface between the sea and the atmosphere is a unique environment. Chlorinated hydrocarbons will reside briefly at the water surface as they are hydrophobic compounds, especially if the airborne particles carrying them are not easily wetted. On account of their poor solubility, they mainly dwell in water on the surface of particles and benthos, and precipitate into the bottom sediments causing contamination of the aquatic organisms (Refs 3-9) (Fig. 1).

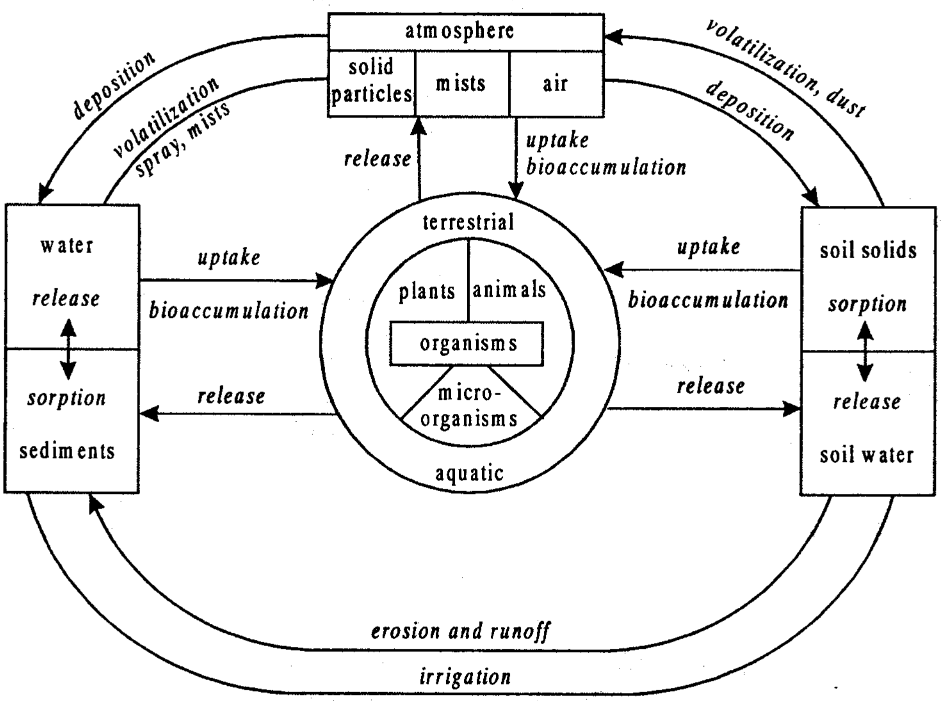

Fig. 1. Interactions of pollutants among the hydrosphere, atmosphere, lithosphere and biosphere[1]

Certain amounts of pesticides and polychlorinated biphenyls are distributed via land-based sources like discharged liquid industrial effluents which are eventually and gradually carried by rivers into the ocean. The run-off process from raining and water used for watering and irrigation is another way that carries these compounds into the water surface[8].

The concentrations and the chemical forms of chlorinated hydrocarbons change once they are added to surface water, as a result of four natural processes: dilu-

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tion, sedimentation, biodegradation and biological amplification. In lakes, reservoirs, estuaries, oceans dilution is less effective than in rivers, because these bodies of water frequently contain stratified layers that undergo little vertical mixing. Sedimentation can remove trace amounts of some chlorinated organic pollutants which become attached to the particles that settle and accumulate in the mud, at the bottom of the water column[2]. However, these toxic substances stored in the bottom sediments, can become resuspended and redispersed in water, as well. Biodegradation is ineffective in removing the chlorinated hydrocarbons (Refs 4, 7, 9-12).

Circulation of the chlorinated hydrocarbons in the environment is assisted by the participation of living organisms and the food chain transfer. The accumulation of chlorinated hydrocarbons in aquatic species depends on chemical uptake of these pollutants via food chain (bioaccumulation), direct uptake from water (through gills and skin), elimination via the gills and fecal egestion, and loss by metabolic transformation. The biological magnification or the so-called bioaccumulation, is the increasing abundance of a pollutant in animals from lower to higher trophic levels in a food chain (Refs 3, 9, 10, 12-14). The aquatic organisms ability to concentrate these lipophilic compounds is influenced by numerous factors such as: kind, age, sex, and the lipid content in their tissue[11]. Some aquatic organisms show a greater capacity for accumulation of chlorinated hydrocarbons, than do the others. The degree of accumulation by an organism also depends on the type and amount of the pollutant to which the organism is exposed. The degree of chlorination and the positions of the chlorine atoms in the molecule, are very important, too (Refs 3, 5, 10, 11, 13, 15). Studies on naturally occurring food chains have revealed that species in higher trophic levels have higher concentrations of pesticide residues and polychlorinated biphenyls than the species of each preceding trophic level[11-13].

EXPERIMENTAL

In our case study, i.e. Karavasta lagoon, the process of bioaccumulation of some chlorinated hydrocarbons in different aquatic species is discussed[16]. We compared concentrations in sediments, mussels, fish and pelican eggs. The sediment can be viewed as the source to the overlying water and water as the source to the phytoplancton, zooplancton , fish and birds[12,13].

By analyzing sediments, mussels, fish and birds the object of our study was: a) determination of the bioaccumulation coefficients and patterns for different chlorinated hydrocarbons (pesticides, PCBs) in aquatic biota by trying to guess about their origin as well; b) coming to the conclusions about the extent of endangering of some species of this lagoon as a result of the bioaccumulation of chlorinated hydrocarbons. Sediment samples were collected for three years in the same month, July, from the lagoon of Karavasta. Different kinds of biota samples: mussels

(*Mytilus galloprovincialis*), different fish species (*Marone labrax, Mugil cephalus, Sparus aurata, Mullus barbatus*, etc.) and eggs from pelicans (whole eggs, shell) were taken at the same period as well[16]. The air dried sediment samples and biota samples were treated with sodium sulphate. The samples were extracted with a mixture of *n*-hexane/dichloromethane. The extracts were treated with metallic mercury and separated in two fractions under control by chromatographing mixtures of standard compounds on each batch of Florisil. Gas chromatographic determination of the chlorinated hydrocarbons was made by HP 5890 Series II GC with ECD detector, with silica capillary column, 50 m, i.d. 0.32 mm and stationary phase SE-52 (0.17 μ).

RESULTS

Some of the experimental results are comprised in these histograms[17] (Figs 2-4):

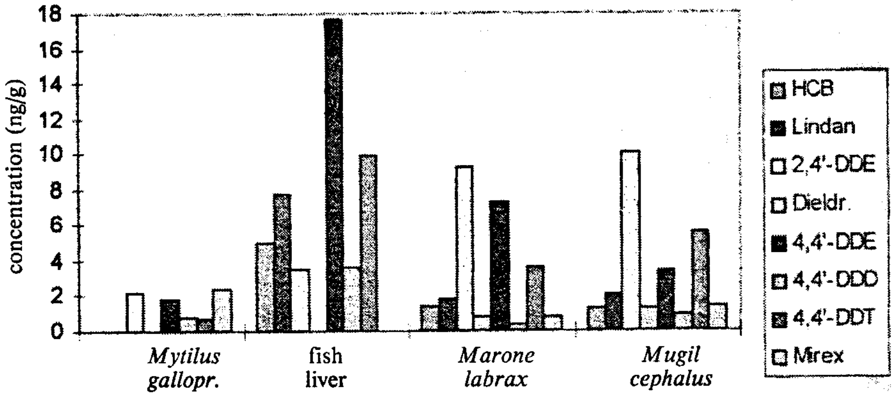

Fig. 2. The concentrations of chlorinated pesticides in biota of Karavasta lagoon (ng/g)

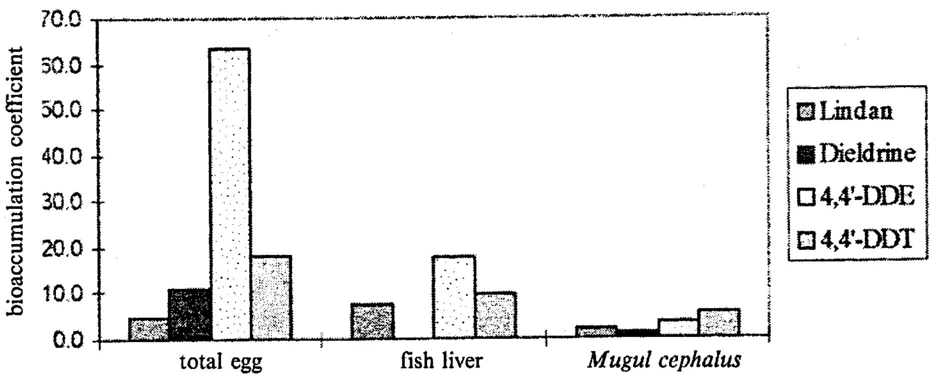

Fig. 3. Bioaccumulation of some pesticides in different species of the food chain in Karavasta lagoon

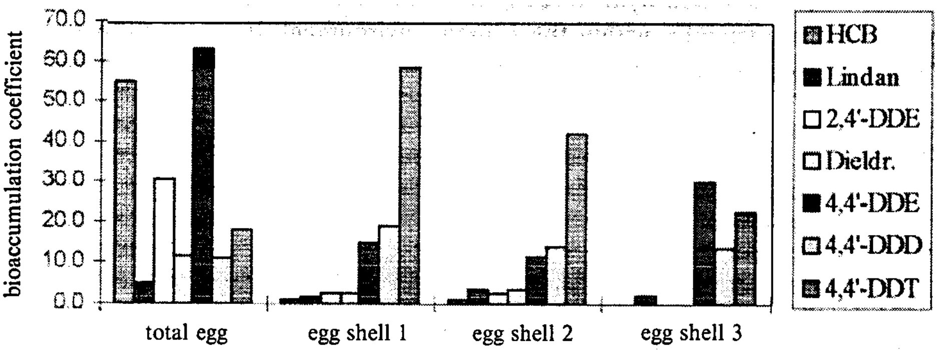

Fig. 4. Bioaccumulation pattern of some chlorinated pesticides in the biological material of *Pelicanus crispus*

DISCUSSION

1. From Fig. 2 the sharp difference between species and liver tissues can be seen. There is a difference between the levels of DDT and its metabolites, too. The highest concentration of 4,4'-DDE is found in fish liver.

2. Different bioaccumulation coefficients are found in different species that represent different levels of the aquatic food chain (Fig. 3). This is obviously dependent on the liophility and chlorine content of the compound and the trophic level, as well. Considering the biological function of liver in the organism, the higher values of bioaccumulation factors than in fish tissue, are acceptable. Pelican is in the top of the aquatic food chain, this can explain the higher level of the bioaccumulation and the difference in distribution patterns of chlorinated pesticides between pelican species and others.

3. Similar distribution of chlorinated pesticides has been found in different egg-shell samples (Fig. 4), but different from that of total egg. This is probably related to their different lipid content. The highest levels are found for 4,4'-DDT and its metabolites. This is due to their extended use in our country.

CONCLUSIONS

The bioaccumulation patterns of chlorinated pesticides in biota of Karavasta lagoon from their sediment source resulted to be largely determined by chlorine content. Bioaccumulation of the chlorinated hydrocarbons has shown to be selective. It is dependent on their liophility and the kind of species being analyzed and their position in the food chain. The levels of the chlorinated hydrocarbons pollution in the Karavasta lagoon is still low to be detrimental to the biodiversity of the lagoon. No correlation was found between the bioaccumulation patterns of chlorinated hydrocarbons in pelicans and other biota species of the lagoon that is suggesting that in pelicans they originate from outside the lagoon. The bioaccu-

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mulation of chlorinated hydrocarbons in biota via food chain is very important factor in their dynamics within the aquatic environment, beside the others, like direct uptake from water, metabolic transformation and egestion.

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