LONG-TERM MONITORING (1972-2006) OF PCBs AND DDTs IN MUSSELS FROM THE EASTERN ADRIATIC COASTAL WATERS

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Introduction

The Adriatic Sea is an elongated basin (139 000 km^2) of the northern Mediterranean, extending for 800 km into the heartland of the European continent. Croatian coastal karst region warrants particular attention because of its high ecological sensitivity and the unfortunate unscrupulous destruction during the warfare of 1991–1995[1]. . Bioaccumulation of chemicals in biota may be a prerequisite for adverse effects on ecosystems. Mussels have been used in many parts of the world as indicator organisms because of their ability to sequester lipophilic contaminants such as PCBs and DDTs[2].

The aim of this paper is to describe the levels and trends of DDT's and PCBs in mussels collected from the Adriatic eastern coastal waters (Figure 1) monitored over a thirty years period. All these samples were analyzed from a single analytical group (mostly by the same analyst), using a uniform methodology which was successfully intercalibrated during numerous international intercalibration exercises, where for detection of pollutants ECD gas chromatography were used with packet and/or capillary columns [3,4] . As is seen from global report of UN, UNEP, G.E.F. Regionally Based Assessment of Persistent Toxic Substances[5], such a long term monitoring of persistent organic toxicants are very scarce and for mussels practically unique all over the World.

Materials and methods

Mussels were collected manually or by dredging in inter tidal or shallow waters. The soft tissue was removed from the shell, placed in aluminum foil and frozen. Samples consisted of 20-30 individual organisms with shells 3-6 cm in length. Mussel tissue concurrently homogenized and extracted twice with 75 ml petroleum ether(b.p. 313-318°K)

Figure 1. A map of the sampling areas along the eastern Adriatic Sea coastline

in a Lourdes blender for 3 minutes, then filtered through a 3- cm- high column of anhydrous Na_2SO_4. and Mirex was added as an internal standard. The sample extract was concentrated to 1 ml and applied to a 6-mm-ID column holding 2 g alumina. The separation of the PCBs from organochlorine insecticides were performed on a miniature silica gel column. For ECD GC chromatography until 1991. packed columns were used and after that year capillary glass columns were used in several Hewlett Packard and Varian gas chromatographs. Details of used methods were published in numerous papers[6,7,8] .

Results and discussion

Figure 2 presents the three dimensional histograms with the DDT total wet concentrations plotted horizontally along the bottom of the figure, the second variable (PCB total) extending back into the figure, and the frequency of observations (number of samples) aligned vertically. The part a) of the Figure presents normal values and part b) of the figure presents natural logarithmic values. Due to non normal distribution of pollutants data, it was necessary to use logarithmically transformed values to ensure normal distributions of data. As is seen logarithmic values distributed very close to normal distribution. Values for the standardized coefficients are inside the range of -2.0 to +2.0 for logarithmically transformed data. For that reason all other statistically analysis logarithmically transformed data have been used.

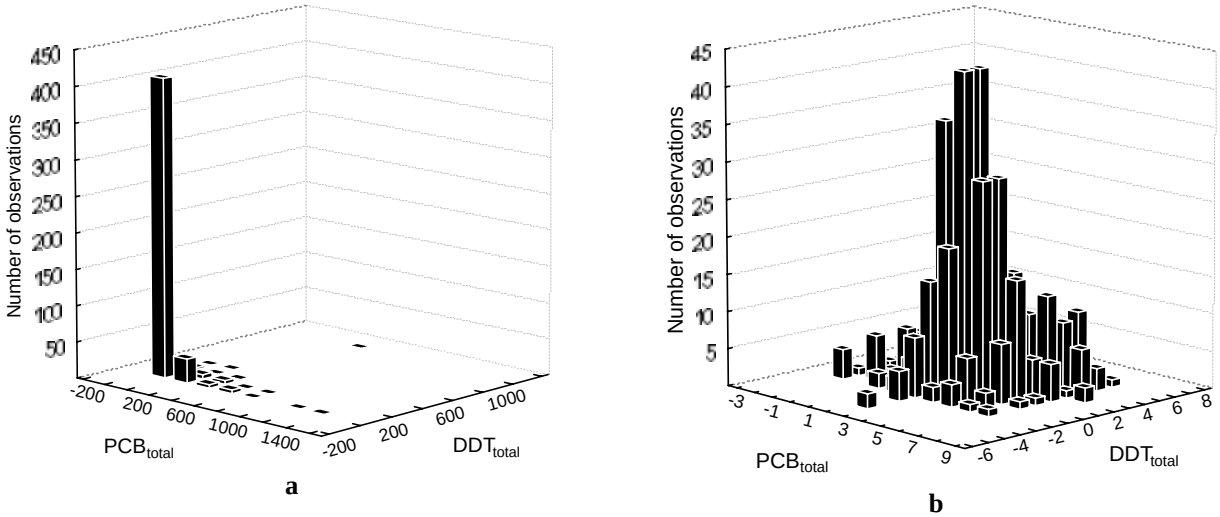

Figure 2. Distribution of a) true PCB_{total} (Aroclor1254+1248) and DDT_{total} levels and b) ln values (ng/g wet mass)

During the total monitoring period altogether over five hundred mussel samples were collected and analyzed. The following ranges of levels of chlorinated hydrocarbons were determined in mussels on the wet sample mass: PCB ranges from below method sensitivity (0.1) to 1510 ngg^{-1}, respectively DDT ranges from 0.1 to 1088 ngg^{-1}. On Figures 3 and 4 comparison of a) PCB levels and b) DDT levels at different areas along the eastern Adriatic coastal waters are present. On Figure 3 levels are present (logarithmic values) on wet basis and on Figure 4 on EOM (Extracted organic matter) basis. Figures presents means and their 95% confidence intervals of total DDT and PCB mass concentrations (natural logarithmic values) in mussel samples depending upon the collection areas. As is seen there were not observed significant difference for PCBs levels between investigated areas except for Šibenik area which are lower in comparison with other areas. Levels of DDTs are lower in Šibenik , Split and Dubrovnik areas in comparison with Istria, Kvarner and Zadar areas. Comparing wet weight basis levels with EOM basis levels (Figure

4) it is observed lower standard deviation with nearly the same conclusions about the pollutants levels as was described for wet basis levels.

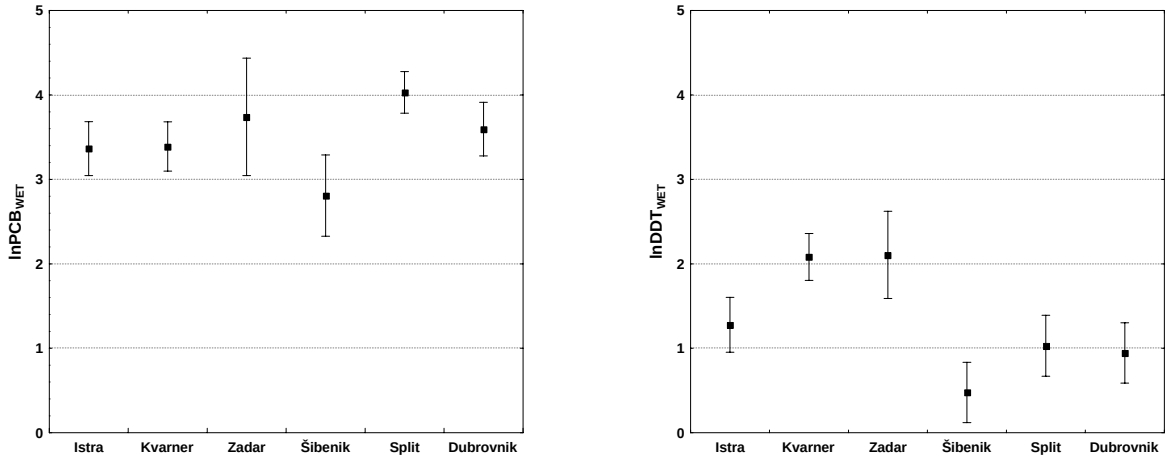

Figure 3. Comparison of a) PCB levels and b) DDT levels at different areas along the eastern Adriatic Sea coastline

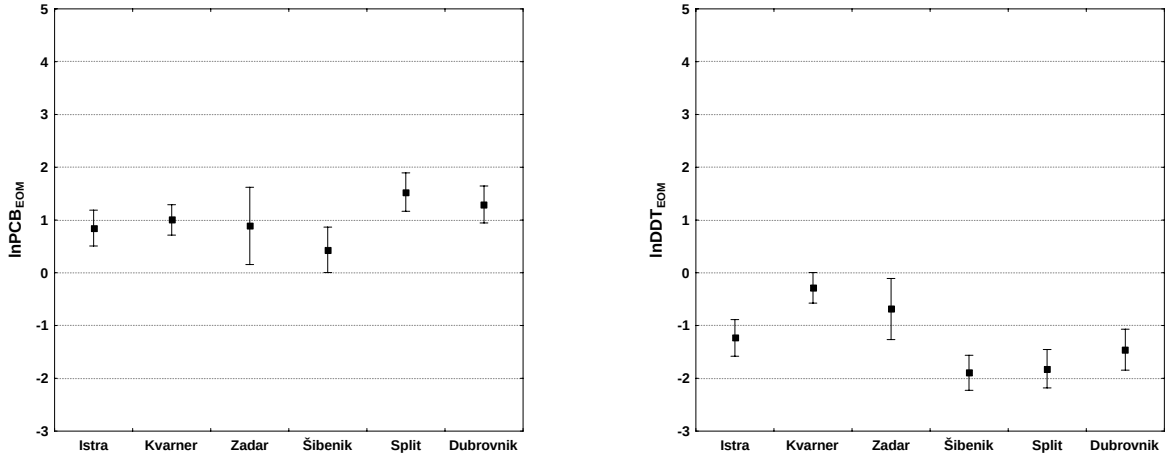

Figure 4. Comparison of a) PCB levels and b) DDT levels at different areas along the eastern Adriatic Sea coastline (EOM mass)

Due to non-normal distributions of the elaborated data, temporal trends are investigated through regression analyses and it was necessary to use log-transformation. Results of linear regression analysis of the logarithmic values of the total DDT and PCB mass fractions and PCB/DDT ratios in the same mussel samples with the years of collection are presented on the Figure 5. Statistically highly significant negative correlation coefficient is obtained by comparing the values of total DDT mass fractions. For PCBs, there were not obtained any correlation and as is seen the levels were not statistically significantly changed during all observed years of investigation. For PCB/DDT total ratios

significant positive correlation coefficient is also obtained. This regression line proved that the levels of DDTs significantly decreased in mussels collected from the eastern Adriatic coastal waters in comparison with PCBs levels.

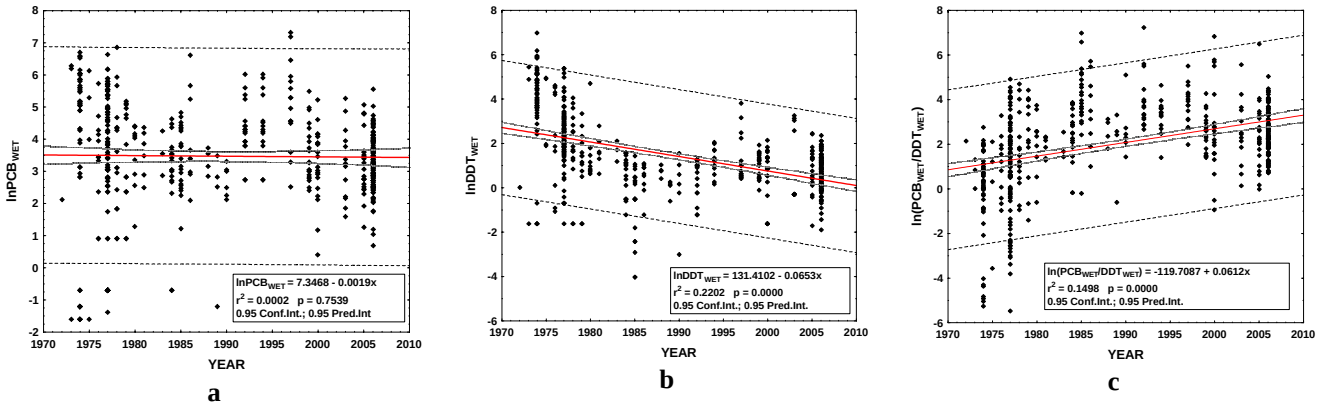

Figure 5. Yearly trends of: a) PCBs, b) DDTs and c) PCB/DDT ratio in mussels from the eastern Adriatic Sea coastline (wet mass)

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