

DDT AND PCB LEVELS AND LONG-TERM TRENDS IN SEDIMENTS COLLECTED FROM THE EASTERN COASTAL AND OPEN WATERS OF THE ADRIATIC SEA

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Abstract

From 1976 to 1992, sediment samples were collected from several areas at over sixty stations located in the eastern Croatian coastal and open waters of the middle and the northern Adriatic Sea. Chlorinated insecticide and polychlorinated biphenyl mass fractions in the surface sediment samples ranged from <0.1 to 96.7 for DDT_{Total} and from <0.5 to $294 \cdot 10^9$ for PCB dw.

Introduction

The Adriatic Sea, a semi-enclosed body of water, is of special interest for the evaluation of the entry, extent and fate of chlorinated hydrocarbon pollutants. Bottom sediment is often the best available medium for the long-term monitoring of many contaminants in aquatic recipients. From 1976 to 1992, sediment samples were collected from several areas at over sixty stations located in the eastern Croatian coastal and open waters of the middle and the northern Adriatic Sea (Fig 1). It is very important to stress that all these samples were analyzed from a single analytical group (mostly by the same analyst), using a uniform methodology that had been very successfully intercalibrated during eleven international intercalibration exercises¹⁾.

Experimental Methods

Sediment samples were collected with a corer or by means of the Peterson grab sampler, placed in aluminium foil and frozen. Analysis of 0-3 cm layer of samples were performed. Before analysis samples were freeze dried and extracted with n-hexane in a Soxhlet apparatus for 8 hours. The analytical method used for the analysis of sediment extracts included filtration through a column of Na_2SO_4 anhyd., KCN solution in acetone or elementary mercury for sulphuric elimination and cleaning on an alumina column²⁾ and the separation of the PCBs from organochlorine insecticides on a miniature silica gel column³⁾. After concentration down from 0.3 to 1 cm^{-3} , elutes were analyzed by EC gas chromatography. During all the analytical procedures, the Mirex standard was used as the internal standard⁴⁾.

Results and discussion

Table 1 presents basic statistical data on chlorinated hydrocarbon mass fractions in sediment samples collected from the Adriatic Sea during the 1976-1992 period on the basis of dry weight. The results of the statistical calculations for all the data are presented at the beginning of Table 1. Separate statistical calculations for samples collected from the northern and middle Adriatic open waters and the eastern Adriatic coastal waters were also performed and presented in Table 1. The standardized coefficients of the skewness and the kurtosis test for significant deviations from the normal distribution. When the values for the standardized coefficient are outside the range of -2.0 to +2.0, the data may depart significantly from normal distribution. Because the data depart

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significantly from normal distribution, the arithmetic means of the data in the groups of the samples differ significantly in comparison to the median or geometric means.

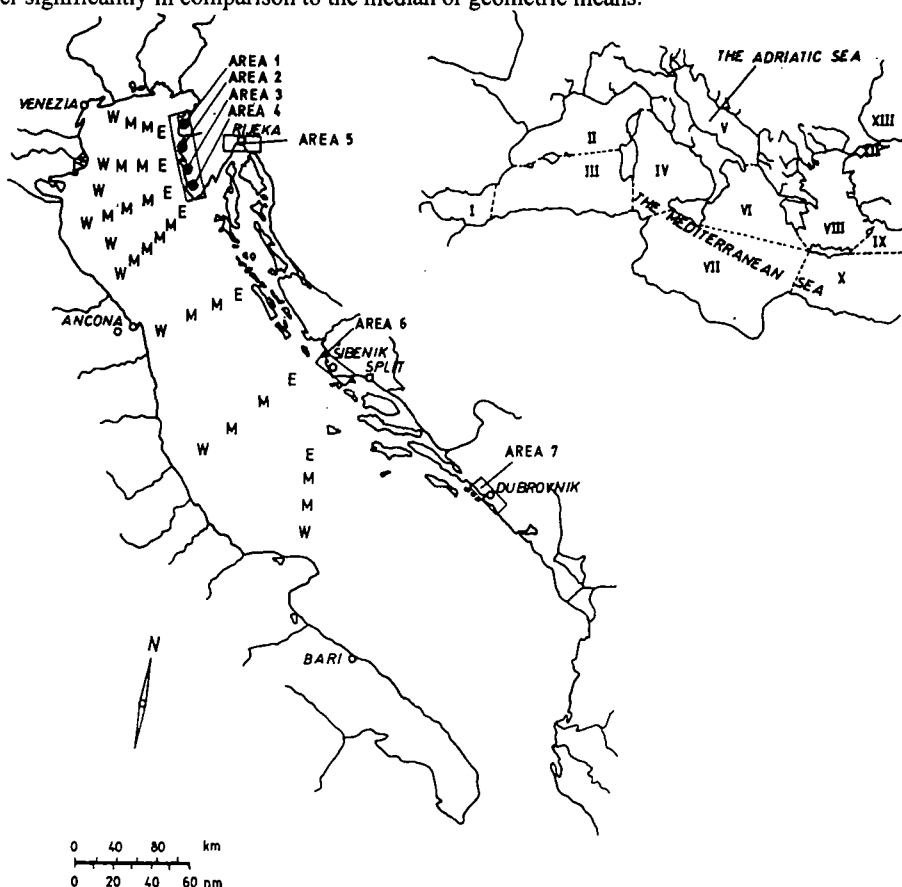


Figure 1. Investigated area and the Mediterranean zones (east (E), middle (M) and west (W) stations).

Table 1
Basic statistical data of mass fraction ($w_{dw} \cdot 10^9$) of chlorinated hydrocarbons in investigated sediment samples collected from the Adriatic sea waters during 1976-1992 period

| Pollutants | DDT _{Total} | | | PCB | | |
|-----------------------|----------------------|---------|---------|---------|--------|---------|
| | A | A | B | A | B | C |
| Area of investigation | | | | | | |
| Number of samples | 220 | 219 | 72 | 219 | 72 | 148 |
| Average | 3.0 | 16.2 | 2.3 | 16.2 | 0.3 | 4.3 |
| Median | 0.7 | 2.7 | 0.8 | 2.7 | 0.1 | 1.5 |
| Geometric mean | 0.6 | 3.1 | 0.8 | 3.1 | 0.1 | 1.4 |
| Stand. deviation | 8.65 | 35.0 | 3.9 | 35.0 | 0.45 | 10.3 |
| Skewness | 6.8924 | 4.4216 | 4.0432 | 4.4217 | 2.8431 | 5.7327 |
| Standardised skewness | 41.7271 | 26.7341 | 14.0423 | 26.7324 | 9.8217 | 28.4241 |
| Kurtosis | 60.2341 | 24.9126 | 21.1217 | 24.9298 | 7.8117 | 41.4256 |
| Standardised kurtosis | 182.423 | 75.2178 | 36.5455 | 75.2145 | 13.543 | 103.126 |

A=All sediment samples; B=Northern and middle Adriatic open waters; C=Eastern Adriatic coastal waters.

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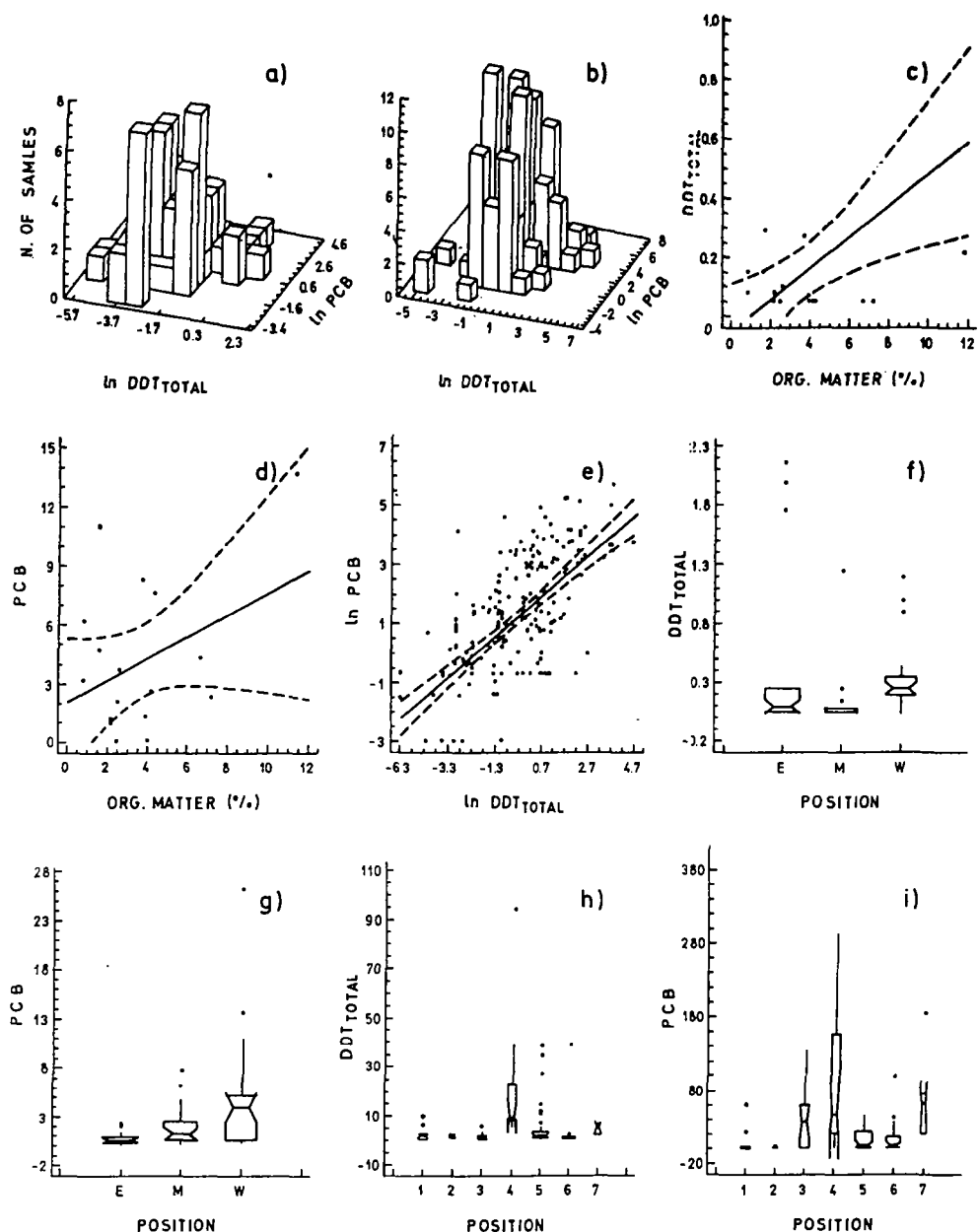


Figure 2. Three dimensional histogram of the PCB and DDT_{Total} (natural logarithmic values) mass fractions in sediments and the frequency of observations. - a) open waters, b) coastal waters; linear regression analysis the mass fractions of DDT_{Total} - c) PCB - d) with organic matter in sediment of the northern Adriatic; - e) linear regression analysis the mass fractions of DDT_{Total} with PCB (natural logarithmic values) in all sediment samples; the means of the mass fractions of DDT_{Total} and PCB are presented as a notched box-and-whisker plot in sediment samples from open waters for east(E), middle(M) and west(W) stations - f) and g); for coastal waters: h) and i).

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Figures 2 a) and b) present three-dimensional histograms with the $\ln \text{DDT}_{\text{Total}}$ mass fractions plotted horizontally along the bottom of the figure, the second variable ($\ln \text{PCB}$) extending back into the figure, and the frequency of the observations (number of samples) are aligned vertically. Due to the abnormal distribution of pollutant data, it was necessary to use logarithmically transformed values to ensure normal distributions of data. The logarithmic values distributed very closely to normal distribution (Figures 2 a) and b). Values for the standardized coefficients of such transformed data are within the range of -2.0 to +2.0.

Linear regression analysis of the mass fractions of total DDT and PCB with organic matter in the sediment of the northern Adriatic (samples collected only during 1990) show significant correlation for total DDT but not for PCB. (Figures 2 c) and d).

Linear regression analysis of the mass fractions of total DDT with PCB (natural logarithmic values) in all the sediment samples (Figure 2 e) show high correlation.

The means of the mass fractions of total DDT and PCB are presented as a notched box-and-whisker plot in sediment samples from the open waters for the east (E), middle (M) and west (W) stations - Figures 2 f) and g). For the coastal waters, the means are presented in Figures h) and i). A notched box-and-whisker plot is a modification of the standard box-and-whisker plot. A notch is added to each box corresponding to the width of a confidence interval for the median, while the width of the box is proportional to the square root of the number of observations in the data set. The confidence level on the notches is set to allow pairwise comparisons to be performed at the 95% level by examining whether two notches overlap⁵⁾. It is evident that the levels of DDT and PCB are higher in samples obtained from the west stations (especially for PCB) in comparison with levels obtained from the east stations of the open waters of the northern and middle Adriatic.

Notches overlap for total DDT and PCB levels in sediment samples collected from the Umag (Area 1), Poreč (Area 2), Pula (Area 4) and Šibenik (Area 6) areas. Higher PCB levels were observed in sediment samples collected from the Rovinj area (Area 3) and significantly higher levels were in samples from the Pula and Dubrovnik (Area 7) areas. The box-and-whisker plots show significant differences in the total DDT mass fractions in the sediment samples collected from the Rijeka area in comparison with other areas. Such differences are not observed for the PCB levels. There are some unusually large values of DDT and PCB mass fractions in the box-and-whisker plot for the Pula and Rijeka areas ($\text{DDT}_{\text{Total}}$) and for the Umag, Šibenik and Dubrovnik areas for PCB.

We compared data (as arithmetic means) on the chlorinated hydrocarbon levels in sediment samples collected from the Adriatic waters during the 1976-1992 period on a dry weight basis with data obtained from samples collected from various zones in the Mediterranean⁶⁾. The zones of the Mediterranean Sea are presented in Figure 1. The PCB levels for the Mediterranean sediment samples are significantly higher in areas II, IV and VIII in comparison with the sediment samples collected from the Adriatic waters, in a similar range with areas I, and lower in areas III, VII and X. The levels for DDT's are comparable with areas I, II, III, IV and VI, and significantly lower in area VII. From the data presented, it seems that the levels of DDT and its metabolites are significantly higher in areas VIII and X in comparison with the investigated sediment samples from the eastern coastal and open waters of the Adriatic Sea.

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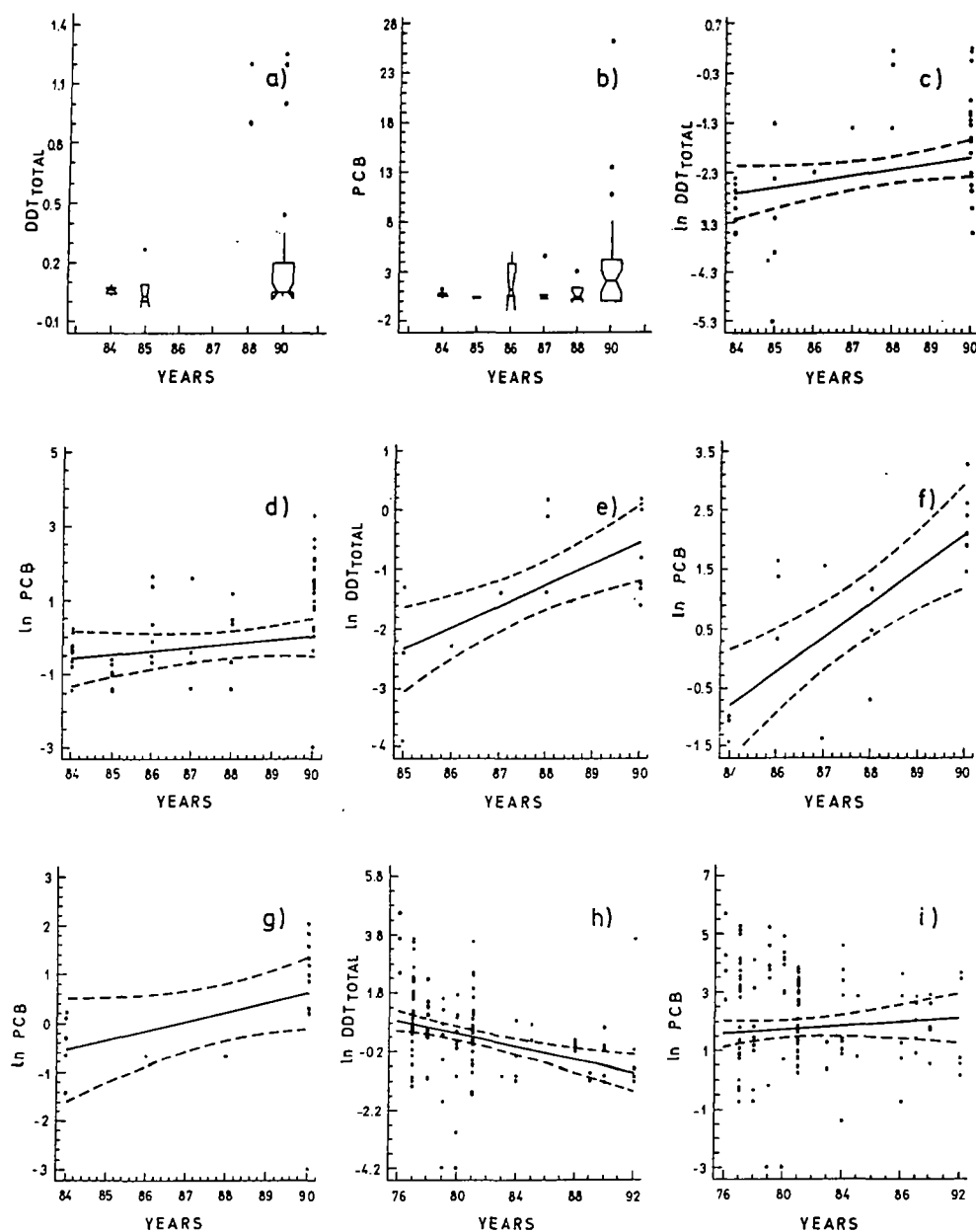


Figure 3. The means of the mass fractions of DDT_{TOT} and PCB are presented as a notched box-and-whisker plot in sediment samples from open northern Adriatic waters for investigated year - a) and b); Linear regression analysis the mass fractions of DDT_{TOT} and PCB (natural logarithmic values) with investigated year in sediment samples from open northern Adriatic waters - c) and d); Open waters but only west stations - e) and f), For PCB - middle stations - g), For coastal stations h) and i).

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Table 2

Significant results of the linear regression analyses of mass fraction ($w_{dw} \cdot 10^9$ - natural logarithmic values) of chlorinated hydrocarbons in investigated sediment samples with year of collection

| Eastern Adriatic coastal waters | | | | |
|---|----------------------|-----------------|-------------------------|--------------------|
| Dependent variable | Independent variable | Number of pairs | Correlation coefficient | Significance level |
| $\ln \text{DDT}_{\text{Total}}$ | Years | 146 | - 0.3347 | 0.00003 |
| Northern Adriatic open waters | | | | |
| $\ln \text{DDT}_{\text{Total}}$ | Years | 68 | 0.2386 | 0.04830 |
| Northern and middle Adriatic open waters(west stations) | | | | |
| $\ln \text{DDT}_{\text{Total}}$ | Years | 17 | 0.6603 | 0.00286 |
| $\ln \text{PCB}$ | Years | 17 | 0.7232 | 0.00070 |

The means of the mass fractions of the total DDT and PCB are presented as a notched box-and-whisker plot in the sediment samples from the open northern Adriatic waters for the year investigated - Figures 3a) and b). Linear regression analysis of the mass fractions of total DDT and PCB (natural logarithmic values) with the year investigated in the sediment samples from the open northern Adriatic waters are presented in Figures 3 - c) and d); open waters but only west stations - e) and f). for PCB - middle stations - g), for coastal stations h) and i). From Figures and Table 2. it is evident that by using logarithmic transformations of mass fractions of total DDT values. a highly significant negative correlation is obtained in the coastal waters. This means that from these data, only DDT and its metabolites show a statistically significant yearly trend of decrease. In the case of the PCB levels, nonsignificant correlation coefficients are obtained even after the logarithmic transformation of the data. For the open waters, significantly positive correlation coefficients are obtained for $\ln \text{DDT}_{\text{Total}}$. For the west stations they are obtained for $\ln \text{DDT}_{\text{Total}}$ and $\ln \text{PCB}$.

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