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Long-Term Trends of DDTs and PCBs in Sediment Samples Collected from the Eastern Adriatic Coastal Waters

M. Picer and N. Picer

Center for Marine Research, "Ruder Bošković" Institute, Zagreb, Croatia, Yugoslavia

It has been well documented that synthetic chlorinated hydrocarbon residues are widespread throughout the oceanic ecosystem. The Mediterranean Sea, as a semienclosed body of water, is of special interest and there have been many baseline studies to measure the existing levels of these contaminants in various components of the ecosystem. Although declining DDT residues in estuarine mollusks were noted in 1973 (Butler, 1973), to our knowledge there are only a few data describing the long-term monitoring of high molecular weight chlorinated hydrocarbons in coastal sediment samples (Picer M., 1988; Picer N., 1990; UNEP/FAO/WHO/IAEA, 1990,). The aim of this paper is to describe the trends of DDTs and PCBs in sediments collected from the Adriatic Sea eastern coastal waters (Figure 1) monitored over an fourteen-year period. 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 which was very successfully intercalibrated during seven international intercalibration exercises (Picer, M. et al. 1978; Anonymous, 1988).

MATERIALS AND METHODS

Sediment samples were collected with a corer or by means of the Peterson grab sampler. Analysis of 0-3 cm layer of samples collected by corer or by grab sampler was performed. Collected sediment samples were placed in the preheated aluminum foil and frozen. Before analysis samples were freeze dried and extracted with n-hexane in a Soxhlet apparatus for 8 hours. The obtained extracts dried by passing them through a column of Na_2SO_4 anh., evaporated to 1 cm^{-3} and cleaned on an alumina column (Picer N. and Picer M., 1980). KCN solution in acetone or elemental mercury were used for sulfur elimination. Separation of PCBs from chlorinated insecticides was performed on a miniature silica gel column (Picer M. and Ahel, 1978). After concentration down from 0.3 to 1.0 cm^{-3}, eluates were analyzed by EC gas chromatography. During the analytical procedure, the Mirex as internal standard was

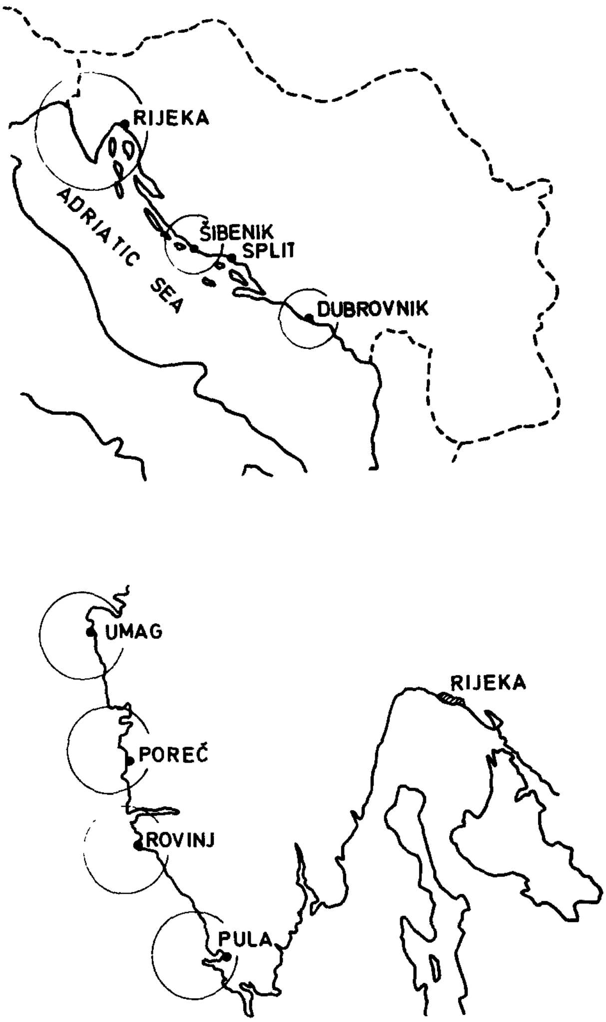

Figure 1. Investigation Area

used (Picer M. and Picer N.). The method employed was intercalibrated by several International intercalibration exercises organized by the IAEA, Monaco, (Picer N., 1990). After summing up all the obtained intercalibration results of the marine sample analysis, the authors decided to employ correction factors (from 1.4 to 2.1) for all their measurements of chlorinated hydrocarbons in the sediment samples. This means that the results presented were obtained after correcting the original data with these correction factors.

RESULTS AND DISCUSSION

The results of the statistical calculations for all the data are presented on Table 1. The average, median, mode and geometric mean measure the central tendency of the data, while the standard deviation, minimum, maximum, lower quartile, upper quartile and interquartile range show the data spread. The skewness coefficient measures the asymmetricality of the data distribution. As seen, all pollutant concentrations show positive values of skewness.

Table 1 Basic statistical data of chlorinated hydrocarbons concentrations in sediment samples collected from the Adriatic sea eastern coastal waters during 1976-1990 period

Pollutants	DDTtotal	PCBs
Number of samples	42	41
Average	4.2	23.2
Median	1.6	5.5
Geometric mean	1.4	5.8
Mode	0.3	0.5
Standard deviation	10.1	41.7
Minimum	<0.1	<0.5
Maximum	93.9	294.0
Lower quartile	0.5	1.5
Upper quartile	3.0	26.8
Interquartile range	2.5	25.3
Skewness	6.11	3.59
Standardized skewness	29.74	17.42
Kurtosis	46.66	16.16
Standardized kurtosis	113.50	39.17

This means that the upper tail of the distribution curve is longer than the lower tail. Kurtosis coefficients reveal the flatness or steepness of the data distribution with respect to a Gausian or normal distribution. For normal distribution, the kurtosis coefficient is 3.0. For the data presented, the kurtosis coefficients are all higher than 3.0 which means that the distribution curve is steep at the center or has relatively long tails. The standardized coefficients of the skewness and kurtosis test for significant deviations from the normal distribution. When using relatively large samples, the standardized coefficient is approximately unit normal. When the values for the standardized coefficient are outside the range of -2.0 to +2.0, it means that the data may depart significantly from normal distribution. As seen, the data presented do depart significantly from normal distribution. This signifies that median and geometric means better indicate the central tendency of the investigated chlorinated hydrocarbon concentrations in the sediment samples collected from the Adriatic sea eastern coastal waters during 1976-1990 period than does the arithmetic mean.

Table 2 presents the results of a one-way analysis of the variance of chlorinated hydrocarbon concentrations in sediments depending upon the collection period.

Table 2 One way analysis of variance of chlorinated hydrocarbons concentrations in sediment samples (collected from the Adriatic sea eastern coastal waters during 1976-1990 period) depending upon collection period.

Response variable	Variance homogeneity Hi_2	p	Homogeneous groups	Significant level for mean difference
DDTtotal (dw)	3.37363	$0.20<p<0.30$	76-79, 80-83, 84-86 and >86	0.0490
PCB (dw)	1.50993	$0.30<p<0.50$	76-79, 80-83, 84-86 and >86	0.4111

Calculations are made using 95% confidence intervals. Figure 2 presents the means of total DDT and PCB concentrations in sediment samples for each investigated intervals for the means using 95% confidence intervals. Means and their 95% confidence intervals are presented as intervals (left side of Figure 2) and as a notched box-and-whisker plot (right side of Figure 2). A notched box-and-whisker plot is a modification of the standard box-and-whisker plot (McGill et al., 1978). 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 overlap. As is seen significantly different results are obtained by one-way analysis of the variance of total DDT and PCBs concentrations depending upon the collection period (Figure 2 and Table 2). Differences are observed for 95% confidence intervals and presented as a box-and-whisker plot. Note some unusually large values of DDT and PCB concentrations in box-and-whisker plot for the 1976-79 and 1980-83 collection period. It is normally expected that other statistical calculations for analysis of variance will also not find significant differences among the levels of PCBs in sediments collected from the Adriatic eastern coastal waters in different collection periods. For DDTs these differences are significant (Table 2).

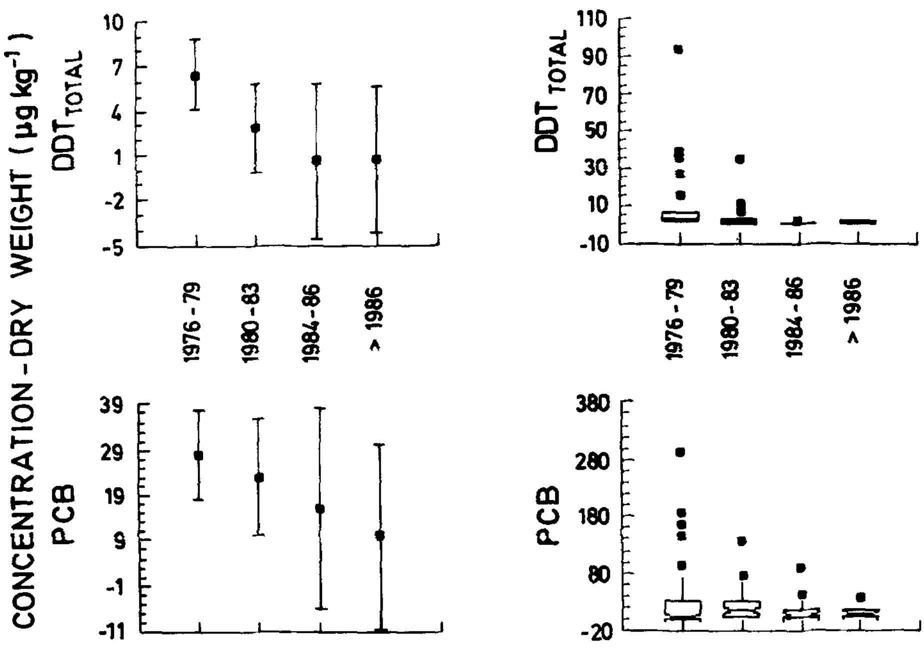

Figure 2. Means and their 95% confidence intervals of total DDT and PCB concentrations in sediment samples depending upon the collection period, presented as intervals (left side) or as a notched box-and-whisker plot (right side)

The Kruskall Wallis one-way analysis by rank facilitates the study of a balanced or unbalanced one-way design for data which are not normally distributed. The results of this statistical investigation of the concentration of chlorinated hydrocarbons in sediments by collection period are presented in Table 3.

Table 3 Nonparametric Kruskall Wallis analysis of chlorinated hydrocarbon concentrations in sediments by collection period.

Pollutants	Average ranks and number of samples				Significance
	76-79(69)	80-83(43)	84-86(14)	>86(16)	level
DDTtotal(dw)	87.254	69.395	33.714	42.281	1.279E-6
PCB(dw)	64.841	83.167	65.571	70.375	0.135

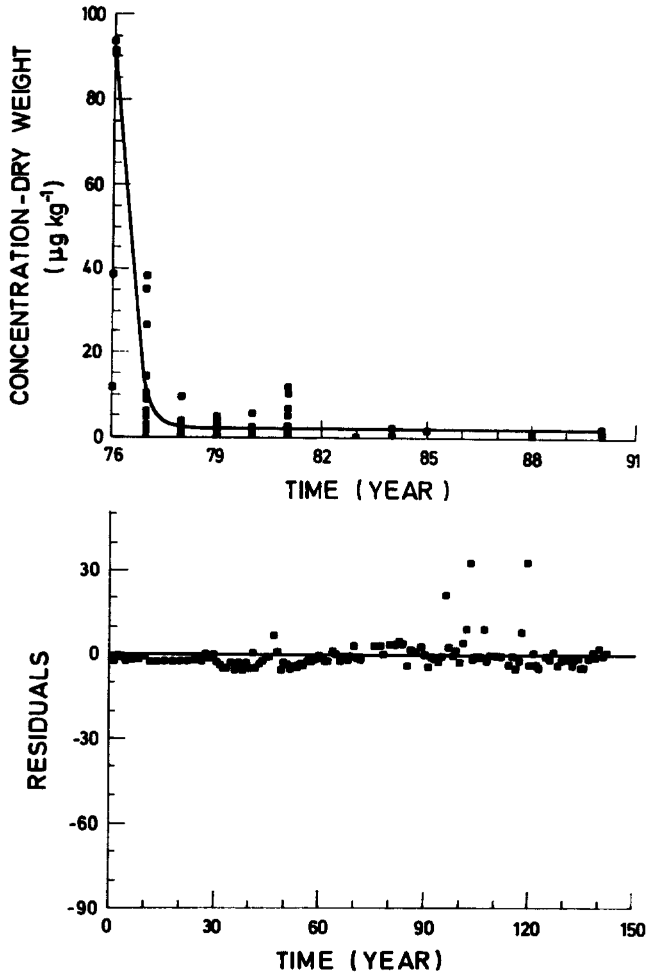

Figure 3. Yearly trend of total DDT levels in sediments with residuals of fitted model

As is seen, very highly significant differences are obtained for DDTs in comparing the data obtained in various collection periods. Such differences are not obtained for PCB concentrations. The yearly trend of DDTtotal based on dry weight in the analyzed sediment samples and residuals of the fitted model are presented in Figure 3.

As seen, the trend of DDT and its metabolites DDE and DDD is more similar to an exponential function than a linear one, so a nonlinear model is used to calculate the functional relationship between the DDT concentrations and time of collection. Since an analytical solution is not available in this case, the computer procedure employs a search algorithm in an attempt to determine the estimates which minimize the residual sum squares. To run this procedure, the function and estimates of the parameters have to be defined to attempt to fit the system to the data (Anonymous, 1986). The best fit is obtained using the following function and parameters:

$$Y = A + (conc._{max} - A)\, e^{-B(x - beg.\ year)}$$

The parameters are: A = 2; B = 1

Regression analysis is used to quantify the nature and strength of the relationship among the concentrations of the investigated pollutants in sediment (dependent variable) and the time of collection (independent variable). Table 4 presents the linear correlation coefficients and their significance levels obtained by linear regression analysis of pollutant concentrations in the sediment samples collected during the forteen-year period from eastern Adriatic coastal waters.

Table 4. Results of the linear regression analyses of the values of pollutant concentrations in sediments with time of collection

Pollutants	Concentration base	Time	Number of pairs	Correl. coeffic.	Significance level
DDTtotal	Dry weight	Year	141	(-0.248)	$p<0.01$
DDTtotal	Log(dry weight)	Year	141	(-0.368)	$p<0.01$
PCB	Dry weight	Year	140	(-0.153)	$p>0.05$
PCB	Log(dry weight)	Year	140	(0.073)	$p>0.05$

Statistically significant negative correlation coefficients are obtained by comparing the values of total DDT concentrations. For PCBs, negative correlation coefficient is also obtained but it is not statistically significant (Figure 4).

As seen, the trend of concentration is more similar to an exponential function than to a linear one, so the linearization of the concentration data is achieved by transforming the data logarithmically. Figure 5 presents a scatter plot of the logarithmic values of the total DDT and PCB concentrations in the sediment samples in comparison with the collection year with the estimated linear regression line and a pair of dotted lines representing the 95% confidence limit. By using logarithmic transformations of concentration values, a higher negative correlation coefficient for total DDT is obtained. In the case of PCB concentration, nonsignificant correlation coefficients are obtained even after the logarithmic transformation of the data.

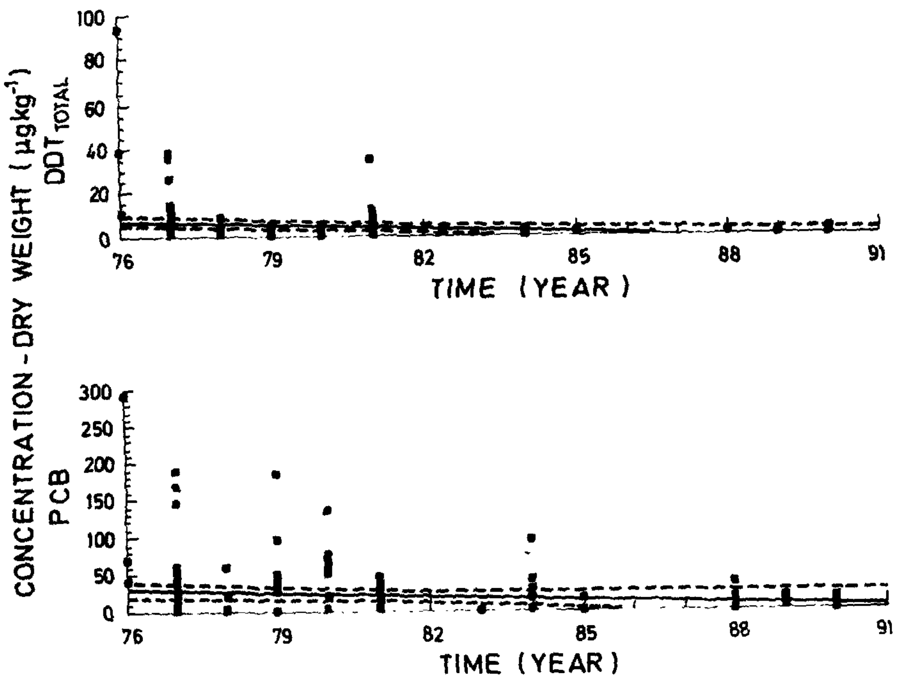

Figure 4 Results of the linear regression analyses of the values of pollutant concentrations in sediments with time of collection.

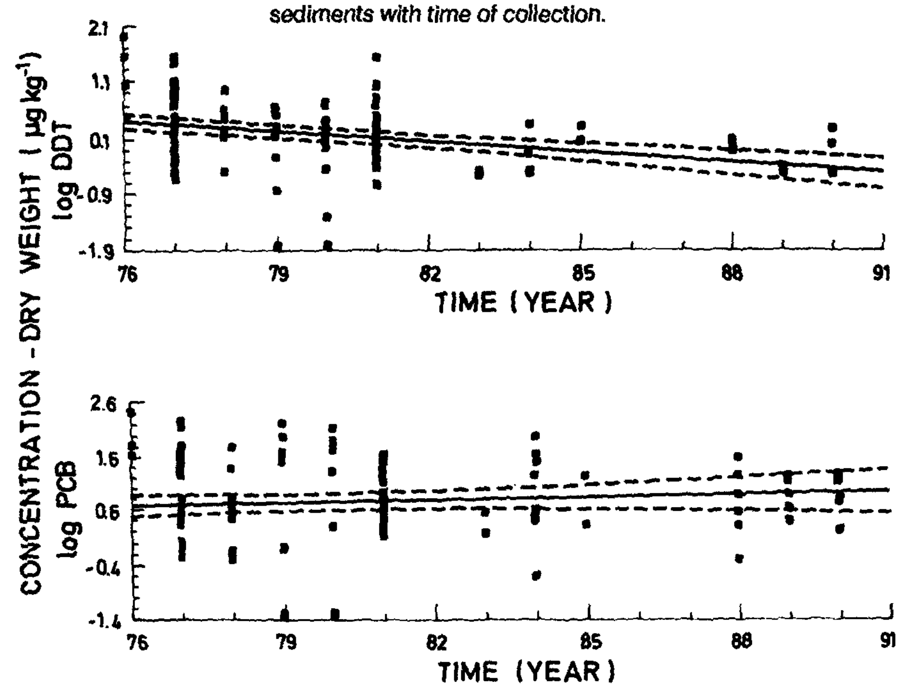

Figure 5. Linear regression analysis of the logarithmic values of the pollutant concentrations in sediments with time of collection.

Analysis of the chlorinated hydrocarbons in sediments from the eastern Adriatic coastal waters in various areas during long-term period led the authors to form the following conclusions:

Total DDT and PCB concentration do not exhibit Gausian distribution in the investigated area and collecting period, so it is necessary to be very careful in interpreting the concentration data using parametric statistics. This frequently has a considerable influence on the means and their confidence intervals. By using the nonparametric Kruskall Wallis one-way analysis by rank, significant differences were found in the levels by period of collection for DDTtotal concentration but not for PCBs concentration. The trend of concentrations of DDT and its metabolites DDE and DDD is more similar to an exponential function than to a linear one, so a nonlinear model is used for the calculation of the functional relationship between chlorinated hydrocarbon concentration and the time of collection. The logarithmic values of total DDT concentrations in the sediment samples in comparison with collection years show a higher negative correlation coefficient in comparison with original data. In the case of PCB concentration, nonsignificant correlation coefficients are obtained after the logarithmic transformation of data.

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