

THE RESULTS OF OVER THIRTY YEARS OF INTERCALIBRATION EXERCISES OF PCBs AND DDTs ANALYSIS IN THE VARIOUS ENVIRONMENTAL SAMPLES

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Abstract

The accuracy of the results for determination various environmental pollutants are possible to evaluate applying participation in intercomparison runs with the samples of composition similar to the environmental samples. Laboratory for organic pollutants determination of the Centre for Marine and Environmental Research, Rudjer Boskovic Institute, Zagreb, Croatia (CMER) took part in many intercalibration exercises for the determination petroleum and chlorinated hydrocarbons in various environmental samples and here are present and discussed results of intercalibration exercises of determination PCBs and DDTs. Since 1973, the Monaco Laboratory of IAEA has organized regular intercomparison exercises on a worldwide and regional scale. Rudjer Boskovic Institute (CMER) from 1974 took a part in intercalibration exercises organized by IAEA. Based on the frequency of participation and the quality of the data reported, the IAEA had issued a list of selected reliable laboratories around the Mediterranean for trace organochlorine compound analysis in various marine samples. Of the 56 laboratories from 14 Mediterranean countries that participated in the intercalibration runs to determine chlorinated hydrocarbons in marine samples, six were selected for excellent analytical performance. Among them was CMER from Rudjer Boskovic Institute.

Introduction

Analytical methods commonly used in analysis of chlorinated hydrocarbons in environment are time consuming, labour-intensive, costly and often very dubious. This is because the investigated pollutants are present mostly at parts per billion (PPB) levels in soil, sediments and biota, and parts per trillion (PPT) in water, have to be concentrated and separated from the matrix (sample clean-up) so that they can be identified and measured mainly by ECD gas chromatography applied in monitoring programs. Applicability of monitoring data depends on their quality measured in terms of reliability, which depends on precision (reproducibility) and accuracy (true values). The accuracy of the results is evaluated applying participation in intercomparison runs with the samples of composition similar to the environmental samples. To improve the reliability and accuracy of the obtained monitoring data, participating institutions have taken part in standardization and intercalibration exercises organized on national or international levels.^{1, 2, 3} Laboratory for organic pollutants determination of Centre for Marine and Environmental Research, Rudjer Boskovic Institute, Zagreb, Croatia (CMER) took part in many intercalibration exercises for the determination petroleum and chlorinated hydrocarbons in various environmental samples and here are present and discussed results of intercalibration exercises of determination PCBs and DDTs.

Materials and Methods

In the period from 1972 until 1974 CMER developed methods for determination PCBs and chlorinated insecticides in various marine samples by using packed column ECD gas chromatography. Briefly method consisted of next steps: After extraction of samples, extracts were cleaned by Al₂O₃ column chromatography and separation of PCBs from chlorinated insecticides was performed by using silica gel separation. This method has been used until today, only after late eighties ECD packed column gas chromatography was changed by using capillary column ECD gas chromatography. The various adaptations of this basic method were used until nowadays and the results of many investigations have been published in numerous papers.^{1, 4, 5}

Results and Discussion

Since 1973, the Monaco Laboratory of IAEA has organized regular intercomparison exercises on a worldwide and regional scale. Rudjer Boskovic Institute (CMER) from 1974 took a part in intercalibration exercises organized by IAEA. On Figure 1 are present results of 8 intercalibration exercises together with other 5 Mediterranean laboratories which have the best results. Based on the frequency of participation and the quality of the data reported, the IAEA has issued a list of selected laboratories around the Mediterranean for trace organochlorine compound analysis. Of the 56 laboratories from 14 Mediterranean countries that participated in the intercalibration runs to determine chlorinated hydrocarbons in marine samples, six were selected for excellent analytical performance. Among them was only CMER from former Yugoslavia.⁶ Even after these excellent results CMER laboratory continue to take a part in intercalibration exercises organized by IAEA for determination CHCL compounds in 7 various samples (sediment - 2 samples, mussel - 3 samples, seaweed-fucus, and tuna fish in period from 1995 to 2005. In these exercises took a part from 14 to 87 laboratories situated from 8 to 43 countries. Some results of these exercises are presented in Figures 2 and 3. As is seen from the Figures 2 and 3 even after using new methodology by ECD capillary gas chromatography, CMER obtained excellent results in determination various PCB congeners in sediment samples. Besides IAEA intercomparison runs RBI took a part in next intercalibration exercises: 1) QUASIMEME Laboratory Performance Studies (Round 26 and Round 28 - altogether 3 sediments and 3 biota samples. 2) Qualco Danube intercomparison study (waste water extracts and sediment samples) altogether 7 samples. These exercises were international in which took a part many laboratories from Danube region countries. In all these intercomparison exercises results of PCBs and various chlorinated insecticides obtained by CMER always were inside acceptable accuracy. On Figure 4 are presented results of intercalibration 5 laboratories included in the fifth framework Program European Commission (Project APOPSBAL) on certified soil samples. On Figure 5 are presented the levels of PCBs and DDTs obtained in the sediment samples collected in period from 1976 to 1990 from the Eastern Adriatic coastal waters. There were analyzed altogether 241 samples in 5 laboratories, including also the results of CMER laboratory. On Figure 6 are presented only results of CMER laboratory (143 sediment samples). Comparing obtained year trend lines it is obviously that DDTs levels declined significantly when only the results of CMER laboratory was took for regression analysis. This is certainly consequence of using reliable and accurate methods for determination PCBs and DDTs in monitored sediment samples.

Acknowledgements

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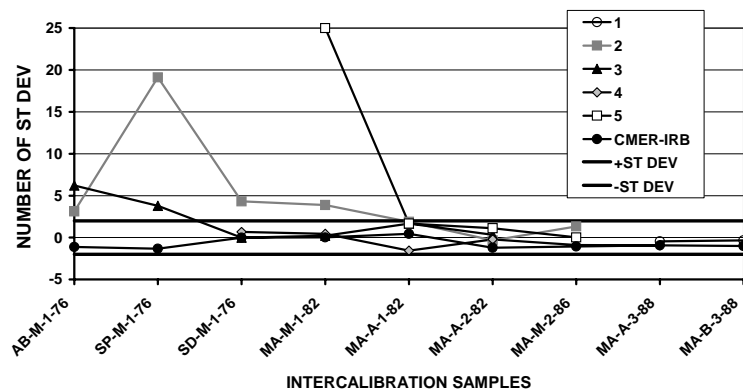


Figure 1. Development data quality in selected Mediterranean labs (Aroclor 1254)

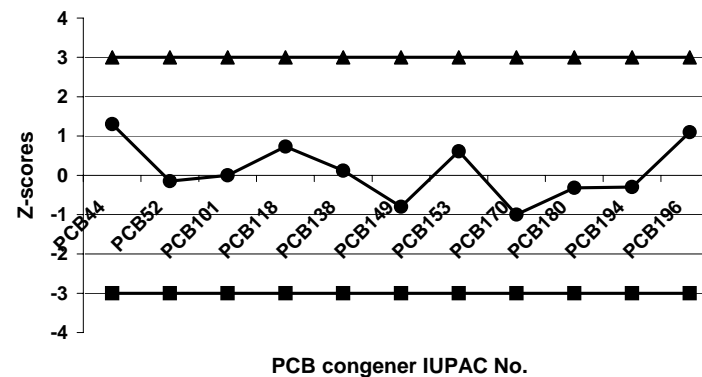


Figure 2. Results of CMER in intercalibration of PCB homologues in sediment, 1999

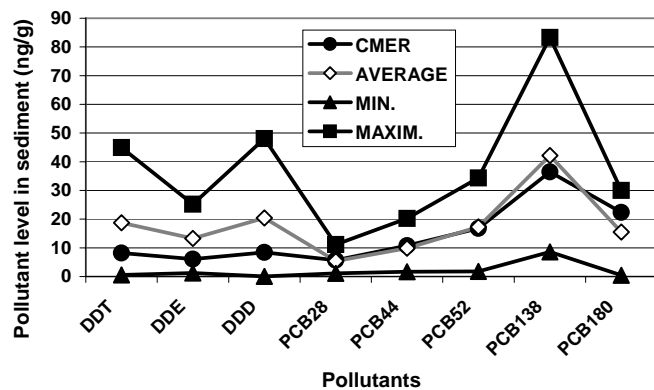


Figure 3. CMER sediment intercalibration, IAEA, 2001 (autl. excl.)

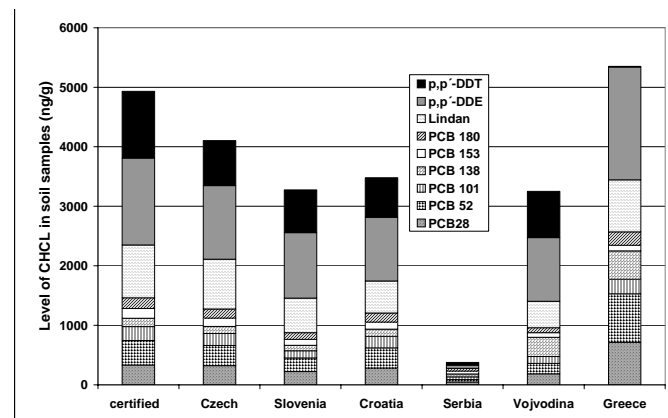


Figure 4. Intercalibration exercise in the soil samples, APOPSBAL - 2003

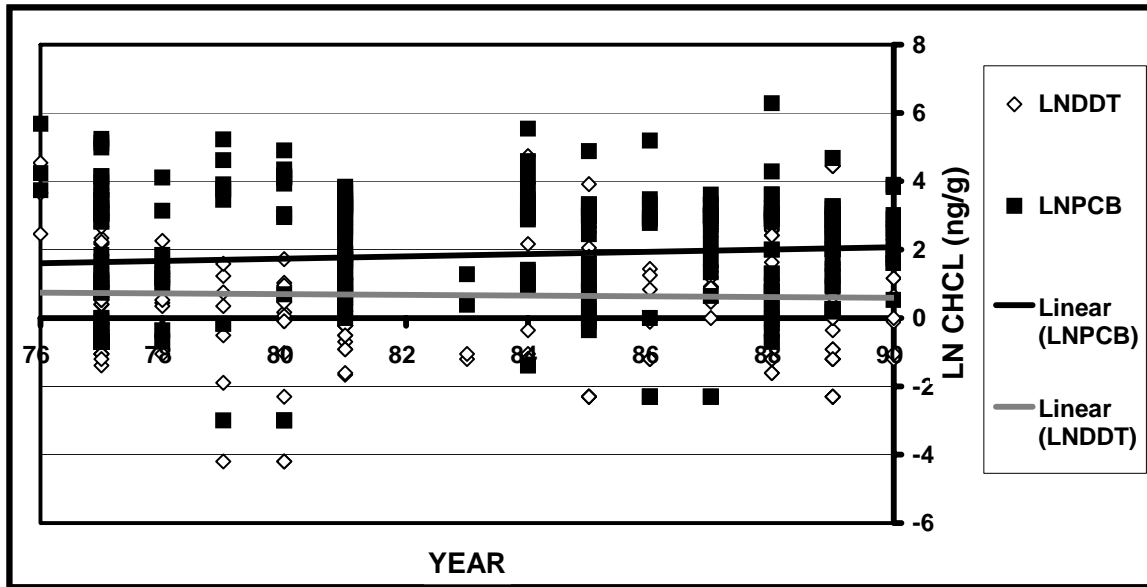


Figure 5. Yearly trend of DDT and PCB level in the eastern Adriatic coastal sediments (241 samples-5 laboratories)

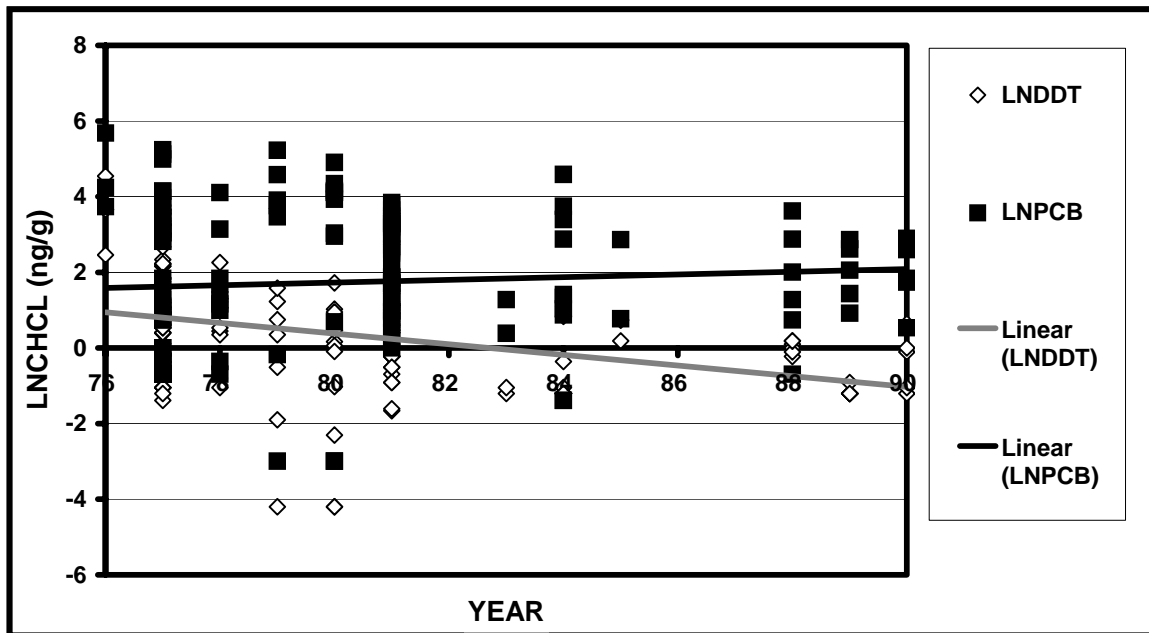


Figure 6. Yearly trend of DDT and PCB level in the eastern Adriatic coastal sediments (143 samples-CMER laboratory)