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Original Research

Determining PCBs in Fish and Sediment Samples Related to Intercomparison Studies

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Abstract

This paper reports on the analysis of polychlorinated biphenyls (PCBs) in selected intercomparison materials (IAEA-435 (tuna) and IAEA-159 (sediment)), and presents the author's results against the background of results accepted by the organizer of the intercomparison studies, i.e. the Marine Environment Laboratories of the International Atomic Energy Agency in Monaco. The samples were extracted with a mixture of acetone/hexane (tuna) or acetonitrile (sediment) by sonication, cleaned up using micro-columns packed with different materials (e.g. silica gel, florisil, copper), and analyzed by GC-ECD. The difficulties of PCB determination are indicated and the differences between the analyses of low- and high-molecular-weight PCBs are emphasized.

Keywords: PCB analysis, fish, sediment, interlaboratory comparison

Introduction

Polychlorinated biphenyls (PCBs) are synthetic compounds, once widely used as coolants and insulating fluids in the production of transformers and capacitors, and also as hydraulic fluids, plasticizers, additives in paints, adhesives, lubricants, plastics, and pesticides. PCBs are known to cause adverse effects on humans and the ecosystem, and because of properties such as toxicity, high environmental persistence, solubility in fats, the ability to transfer along the trophic chains, and long-range transport to regions where they have never been used or produced, they have been classified within the framework of the Stockholm Convention as persistent organic pollutants (POPs) [1]. Moreover, PCBs were inserted into the lists of harmful substances of many international programs, conventions, and commissions whose objective is protection of the marine environment, e.g. HELCOM (Baltic Marine Environment Protection Commission), OSPAR (Commission for the Protection of the Marine Environment of the Northeast Atlantic), and MED POL (Program for the Assessment and Control of Pollution of the Mediterranean). For decades, considerable amounts of PCBs were released into various ecosystems and, despite the ban on PCB production (since the 1970s and 1980s), are still found in the environment [2] (although levels are gradually decreasing [3, 4]).

Different methods are applied for the determination of PCBs in marine matrices. The choice of methodology is usually determined by costs and the available laboratory equipment. Moreover, these methods are generally labor-intensive and difficult due to the exceptionally wide range of physical and chemical properties across the class, the trace concentrations of single congeners, and the rich organic matrix. Each step of the analysis – from sampling and storage through extraction, clean-up, and injection, to detection – requires its own level of accuracy and adaptation to an individual laboratory. In such cases interlaboratory comparisons are useful for verifying procedures. Usually, seven PCB congeners (CB-28, CB-52, CB-101, CB-118, CB-138, CB-153, and CB-180) are recommended for routine monitoring [3, 4], although sometimes only CB-138 and CB-153 have been used to represent PCB contaminants [3]. In both cases, however, severe under-

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estimation of total PCB concentration should be taken into account, particularly in abiotic samples [5].

The aim of this work was to present the difficulties of determining PCBs in fish and sediment samples, based on results of the intercomparison exercises, obtained from my own studies, in relation to those presented by the organizer, i.e. the Marine Environment Laboratories of the International Atomic Energy Agency in Monaco.

Experimental

Reagents and Materials

The following solvents were used: distilled acetone (for analysis, ≥99.5%, Chempur – Poland), acetonitrile (for HPLC, ≥99.9%, CHROMASOLV®, Sigma-Aldrich), benzene (for HPLC, ≥99.9%, CHROMASOLV®, Sigma-Aldrich), hexane (for liquid chromatography, ≥98%, LiChrosolv®, Merck), isooctane (for liquid chromatography, ≥99%, LiChrosolv®, Merck), isopropanol (for analysis, ≥99.7%, Chempur-Poland), and methanol (for HPLC, ≥99.8%, Fluka).

The sorbent materials used in this study were: copper (fine powder GR, particle size <63 μm, Merck), Florisil (100-200 mesh, Sigma-Aldrich), LiChrolut® RP-18 (40-63 μm, 500 mg, 3 ml standard PP-tubes, Merck), and silica gel (particle size 0.035-0.070 mm, Fluka).

A standard mixture of PCBs (CB-18, CB-28, CB-31, CB-44, CB-52, CB-101, CB-118, CB-138, CB-149, CB-153, CB-180, CB-194) was obtained from Supelco (CEN PCB Congener Mix 1), and working solutions were prepared in isooctane.

All the glassware was soaked in detergent (Micro Liquid Cleaner Int. Prod. Corp., UK), then rinsed successively in tap and distilled water.

Samples

Tuna

The tuna homogenate sample was provided as IAEA-435 intercomparison material by the Marine Environment Laboratories of the International Atomic Energy Agency (MEL-IAEA) in Monaco. The tuna (*Thunnus thynnus*) had been caught in the Mediterranean. After collection, a large batch of this fish was freeze-dried, ground and sieved through a 250 μm stainless steel sieve, and then homogenized by mixing in a stainless steel rotating drum for two weeks; this was done at MEL-IAEA in Monaco [6]. In the Marine Pollution Laboratory of the Institute of Oceanology, Polish Academy of Sciences (MPL-IOPAN) four IAEA-435 sub-samples and four IAEA-435 spiked (with the PCB standard mixture – for recovery) sub-samples were prepared for PCB analysis.

Sediment

The sediment sample also was supplied by MEL-IAEA in Monaco as IAEA-159 intercomparison material. Sediment was collected in Kilbrannan Sound, Firth of Clyde, Scotland. The sample was dried, ground, sieved, and homogenized by mixing in a stainless steel rotating drum for three weeks; this was done at MEL-IAEA [7]. In the MPL-IOPAN four IAEA-159 sub-samples and four IAEA-159 spiked (with the PCB standard mixture – for recovery) sub-samples were prepared for PCB analysis.

Extraction and Clean-up

Tuna

The tuna homogenate sample (ca 2 g d.w.) was extracted with a mixture of acetone:hexane 50:50 (v/v) by sonication in an ultrasonic bath (2×3 ml + 8×2 ml, 90 W, 15 min) and centrifuged (2,500 rpm, 10 min) each time. The joined extracts were evaporated to dryness under a stream of argon, then dissolved in hexane (1.5 ml). The solution was passed through three columns packed with Florisil (1 g, bed 9×30 mm) to remove lipids, 0.5 ml through each column (because of the high fat content). All these columns had been conditioned earlier with hexane (2×1.5 ml + 2×1 ml). PCBs were eluted with acetonitrile (3×1 ml + 0.5 ml). The acetonitrile fractions were joined and evaporated to dryness under a stream of argon and the extract was kept frozen until GC-ECD analysis.

Sediment

PCB extraction and purification was carried out using the procedure described earlier [8, 9]. However, the method was modified slightly to reduce the blank load, by replacing the TLC plates with a glass column containing silica gel. Sediment samples (ca 6 g d.w.) were extracted with acetonitrile by sonication in an ultrasonic bath (5×20 ml, 90 W, 15 min) and centrifuged (2,500 rpm, 10 min) each time. The acetonitrile fractions were joined and re-extracted in the acetonitrile:benzene:water (10:1:10 (v/v/v)) system. The collected extract was evaporated to dryness in a rotavapor (Büchi, Labortechnik AG, Switzerland, type R-144) at a pressure controlled by the vacuum system (Büchi, type B-180, 150 mbar) on a water bath (t = 30ºC). Next, the residue was dissolved in 4 ml of acetonitrile, after which the solution was transferred to a vial and evaporated to dryness under a stream of argon. The residue was dissolved in hexane (0.5 ml) and transferred onto a column with silica gel (bed 9 mm × 15 mm) previously conditioned with 2.5 ml of hexane. PCBs were eluted with 3.5 ml of hexane (3×1 ml + 0.5 ml). The hexane extract was evaporated under a stream of argon and purified on the three different types of microcolumn. First, the residue was dissolved in isopropanol (0.25 ml). Water (4.5 ml) was then added and the solution transferred to the RP-18 column (9×13 mm), previously conditioned with methanol (2 × 0.5 ml) and with a mixture of isopropanol (15%) and water (85%) (2×0.5 ml); after the sample had passed through, it was flushed with the same mixture (2×0.75 ml). PCBs were eluted with two portions of hexane (2×1 ml). Next, the hexane extract was evaporated under a stream of argon, dissolved in acetonitrile (0.5 ml)

and transferred to a column packed with copper (bed 9×3 mm) to remove sulphur. The column was flushed with acetonitrile (2×1 ml). The solvent was evaporated to dryness under a stream of argon to a volume of 0.5 ml and transferred to a Florisil column (bed 9×30 mm) conditioned earlier with isooctane (2×2 ml). The PCBs from this column were eluted with acetonitrile (3×1 ml). The solvent was evaporated to dryness under a stream of argon and the extract was kept frozen until analysis by GC-ECD.

Blanks

Four blanks were prepared for each series of samples (tuna, sediment), according to the respective procedures presented above.

Chromatographic Analysis

The sample dissolved in isooctane (150-600 µl) was injected (1 µl) into a gas chromatographic system (GC 6000, Vega Series 2, Carlo Erba Instruments) coupled with an electron capture detector (ECD 80/800, Fisons Instruments). Helium was used as carrier gas and nitrogen as make-up gas. The GC system was fitted with a fused silica capillary column with a 5% phenyl-substituted dimethylpolysiloxane phase, 0.25 mm i.d. × 60 m, 0.25 µm film thickness (CP-Sil 8 CB Low Bleed/MS, Varian (1) or HP-5, Hewlett Packard (2)). Injector and detector temperatures were 280 and 320ºC, respectively. The oven temperature programme was held isothermally at 90ºC for 1 min., then programmed at 40ºC·min^{-1} to 210ºC, held for 0.5 min., again programmed at 5.6ºC·min^{-1} (1) or 2.6ºC (2) to 230ºC, held for 10 min., next increased by 5.6ºC·min^{-1} (1) or 2.6ºC (2) to 275ºC and held for 20 min. Peak identification and determination of PCB concentrations were based on comparison of retention times and individual peak areas in the sample chromatogram with the respective peak retention times and areas of standards. Examples of chromatograms for tuna and sediment series (standard mixture, sample, spiked sample, and blank) are shown in Fig. 1.

Results and Discussion

PCBs were determined in two different marine matrices – fish and sediment – from different parts of Europe. The highest content of PCBs was detected in tuna (mean Σ9 PCBs = 194.5 ng·g^{-1} d.w.). The PCB content in sediment was considerably lower (mean Σ9 PCBs = 4.52 ng·g^{-1} d.w.). Even though the samples were collected from different environments (the Mediterranean Sea and the southwestern coast of Scotland), probably contaminated to different extents, these results conform to what is generally known about the environmental fate of PCBs, above all in the food

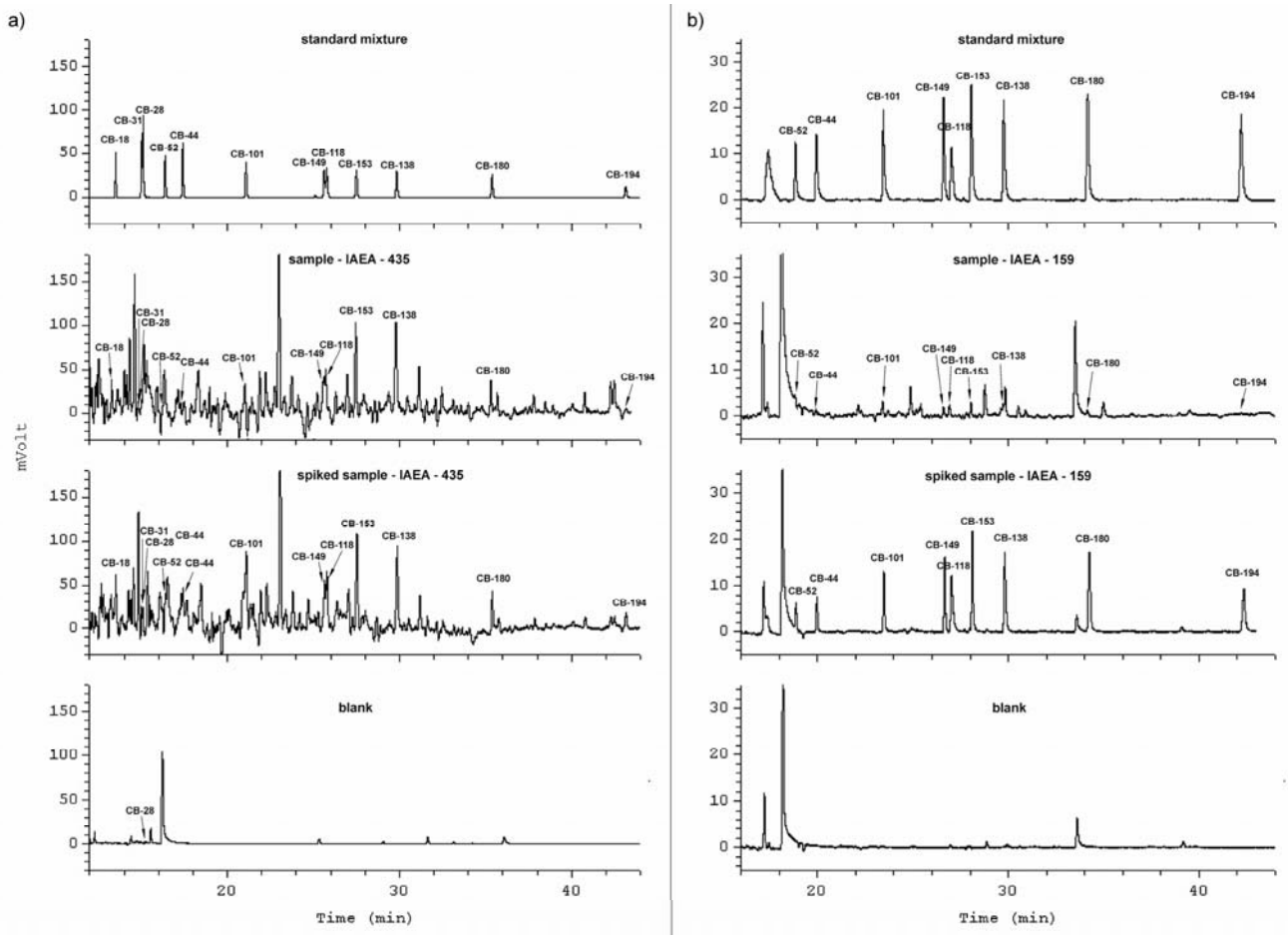

Fig. 1. Chromatograms of standard mixture, sample, spiked sample, and blank for a) tuna and b) sediment series of PCB analyses.

Table 1. Recovery and blank load of PCBs for tuna and sediment samples.

Samples	CB-18	CB-31	CB-28	CB-52	CB-44	CB-101	CB-149	CB-118	CB-153	CB-138	CB-180	CB-194	S 12* PCBs	S 9** PCBs
IAEA-435 (tuna)														
Recovery (n=4) [%]	36	42	34	62	47	108	86	110	131	110	76	85	77	90
Blank (n=4) [ng]	0.00	0.00	0.29	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.29	0.00
IAEA-159 (sediment)														
Recovery (n=4) [%]	-	-	-	42	50	77	84	101	89	115	94	74	-	81
Blank (n=4) [ng]	-	-	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	0.00

*CB-18, CB-31, CB-28, CB-52, CB-44, CB-101, CB-149, CB-118, CB-153, CB-138, CB-189, CB-194;
**CB-52, CB-44, CB-101, CB-149, CB-118, CB-153, CB-138, CB-189, CB-194

chain as a result of their properties, such as persistence, ability to bioaccumulate, and solubility in fats [10, 11].

The determination of PCBs, especially low PCB contents, requires exhaustive analysis of blank samples in each series of the study. It is an important aspect of good analytical practice to carry out the proper blank correction. In this study the PCB extraction was modified to reduce the blank load. Fig. 1 shows two of the blank chromatograms obtained for tuna and sediment samples. In both cases there are a few clear, high peaks, but their retention times are not the same as the peaks of the PCBs under study. Many of them are due to the presence of phthalates (e.g. DBP – dibutyl phthalate), because of the ubiquitous nature of these contaminants, proven by GC/MS analysis. Blank loads of PCBs for tuna and sediment samples are presented in Table 1.

The greatest difficulties in determining PCBs in many marine matrices are due to the low contents of those compounds. Hence, the lower the concentration of the analyte, the greater the chances of inaccurate results. Some authors, who have analyzed the QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) laboratory performance studies report, for example, that current analytical methods for PCBs do not yield very accurate results when analyte concentrations are < 1 $\mu g \cdot kg^{-1}$ [12]. At the same time, other researchers have presented results of PCB determinations in $pg \cdot g^{-1}$ [13, 14]. The analytical methods and instrumentation presented in this study do not allow the limits of determination of individual PCBs to be reduced below 0.05 $ng \cdot g^{-1}$; other authors, however, give these, for example, as 0.05 $pg \cdot l^{-1}$ [14] and 0.01 $pg \cdot l^{-1}$ [13] in suspension or 0.5 $pg \cdot g^{-1}$ in sediment [13, 14]. Despite the serious difficulties in comparing laboratory performances, especially when analyte concentrations are low or if only the sum of PCBs is shown, interlaboratory comparisons are useful for verifying and improving one's own methods.

Fig. 2a shows the PCB concentrations in the IAEA-435 sample, determined in this study, against the background of results accepted by MEL-IAEA (without outliers). Additionally, Fig. 2b shows *Z*-scores for my results [6]. *Z*-scores are calculated for the assessment of laboratory performance according to the formula:

$$Z = (x_i - x)/s_b$$

...where x_i is the reported value, x is the assigned value (the mean value of the accepted results), and s_b is the target standard deviation. Performance is considered acceptable if $|Z| \leq 2$; $|Z|$ between 2 and 3 is considered questionable, and when $|Z| > 3$ the measurement is regarded as unacceptable. The procedure has been accepted as standard by ISO/IUPAC [15]. Three of the twelve PCB congeners determined were not accepted, as can be seen by comparing the results presented in Fig. 2a and taking the *Z*-scores in Fig. 2b into account. These are the trichlorinated congeners CB-18, CB-28, and CB-31, low-molecular-weight PCBs determined in this study. The concentrations of the remaining PCBs (CB-44, CB-52, CB-101, CB-118, CB-138, CB-149, CB-153, CB-180, and CB-194) in the tuna homogenate were determined correctly and, based on *Z*-scores ($|Z| < 2$), can be regarded as acceptable. Generally, the highest concentrations of PCBs in the IAEA-435 sample were determined for those with five (CB-101 and CB-118), six (CB-138, CB-149, and CB-153), and seven (CB-180) atoms of chlorine, from 23 to 81 $ng \cdot g^{-1}$ d.w. (from 17 to 43 $ng \cdot g^{-1}$ d.w. – my results). The contents of tri- (CB-18, CB-28, and CB-31), tetra- (CB-44 and CB-52), and octa- (CB-194) PCBs were lower, up to 10 $ng \cdot g^{-1}$ d.w. (from 6 to 41 $ng \cdot g^{-1}$ d.w. – my results). In spite of the quite high PCB contents in the tuna homogenate, the range of means accepted by MEL-IAEA (without outliers) is extraordinarily large, especially for CB-138 and CB-153 (from 3.9 to 136 and from 4.1 to 152, respectively), which seems to be inadmissible from a strictly analytical point of view.

The results of the intercomparison for the determination of PCBs in the IAEA-159 sample are shown in Fig. 3. Comparing the results presented in Fig. 3a and taking into account the Z-scores in Fig. 3b, eight of the nine PCB congeners determined were accepted ($|Z| \leq 2$). The one exceed-

ing the accepted range of means ($Z = 3.41$) was CB-44, containing four chlorine atoms [7]. Concentrations of individual PCBs in the IAEA-159 sample were similar and ranged from 0.35 to 0.67 ng·g^{-1} d.w. (from 0.31 to 0.92 ng·g^{-1} d.w. – my results) for PCBs with four, five, and six atoms of chlorine, whereas the contents of higher-molecular-weight PCBs (CB-180 and CB-194) were somewhat lower – 0.26 ng·g^{-1} d.w. for CB-180 and 0.09 ng·g^{-1} d.w. for CB-194 (0.14 and 0.09 ng·g^{-1} d.w., respectively – my results). Like the IAEA-435 samples, the range of means accepted by MEL-IAEA (without outliers) is particularly wide for CB-138 (from 0.01 to 1.27).

Concentrations of PCBs in the tuna homogenate were 'convenient' for determination by GC-ECD, and chromatographic analysis was not exceptionally complicated. Unfortunately, a high content of PCBs quite often also means a rich matrix, so sample preparation is more labor-consuming. In this case, lipid removal proved to be the most difficult, whereas in the sediment sample the problem was the appearance of unidentified compounds, overlapping the PCB peaks, thereby making correct chromatographic analysis difficult. This necessitated additional purification of the sample; one should be mindful that every such step can lead to a loss of analytes. However, if the PCB concentrations in the sediment were higher, this would not be so significant. In general, overlapping peaks appeared in the low-molecular-weight PCB section, which is probably the reason for the erroneous determination of CB-18, CB-28, and CB-31 in the tuna sample, and of CB-44 in the sediment sample. Note, too, that recoveries of these congeners were only half as good as those of the other, high-molecular-weight PCBs (Table 1), which demonstrates that the method presented here provides favorable conditions for the losses of more volatile compounds. In this case PCB recoveries were not based only on one, two or three internal standards (e.g. CB-29, CB-103, CB-198), which is the usual practice [16-18], but the recovery of each congener was considered separately. This seems a reasonable solution, given the diversity of physico-chemical properties within such a large group of compounds.

In spite of long-standing studies on PCB determination, congener specific PCB analyses at trace levels still seem to be a challenge to the analytical and environmental

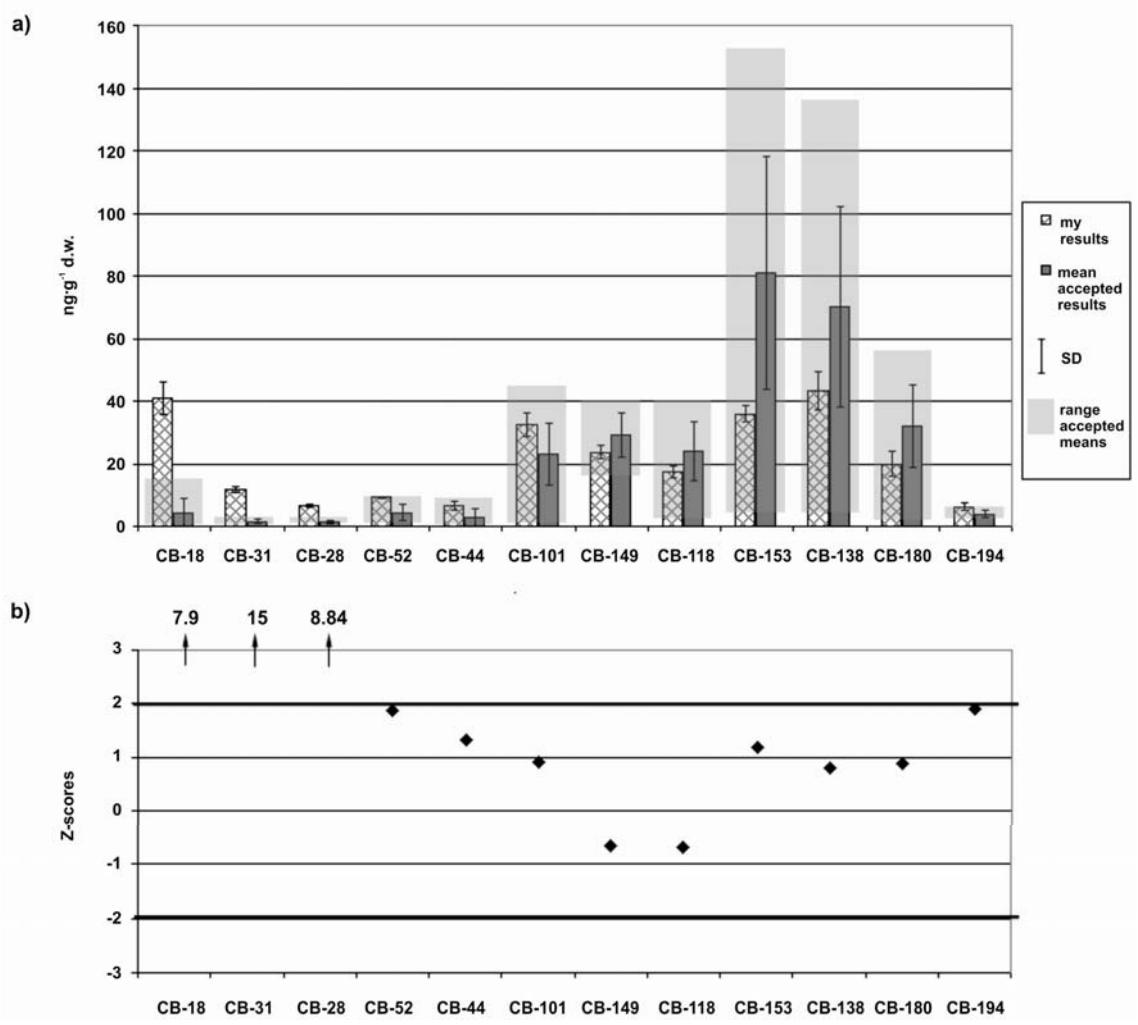

Fig. 2. PCB in the IAEA-435 sample (tuna). a) my results against the background of results accepted by MEL-IAEA, b) *Z*-scores for my results.

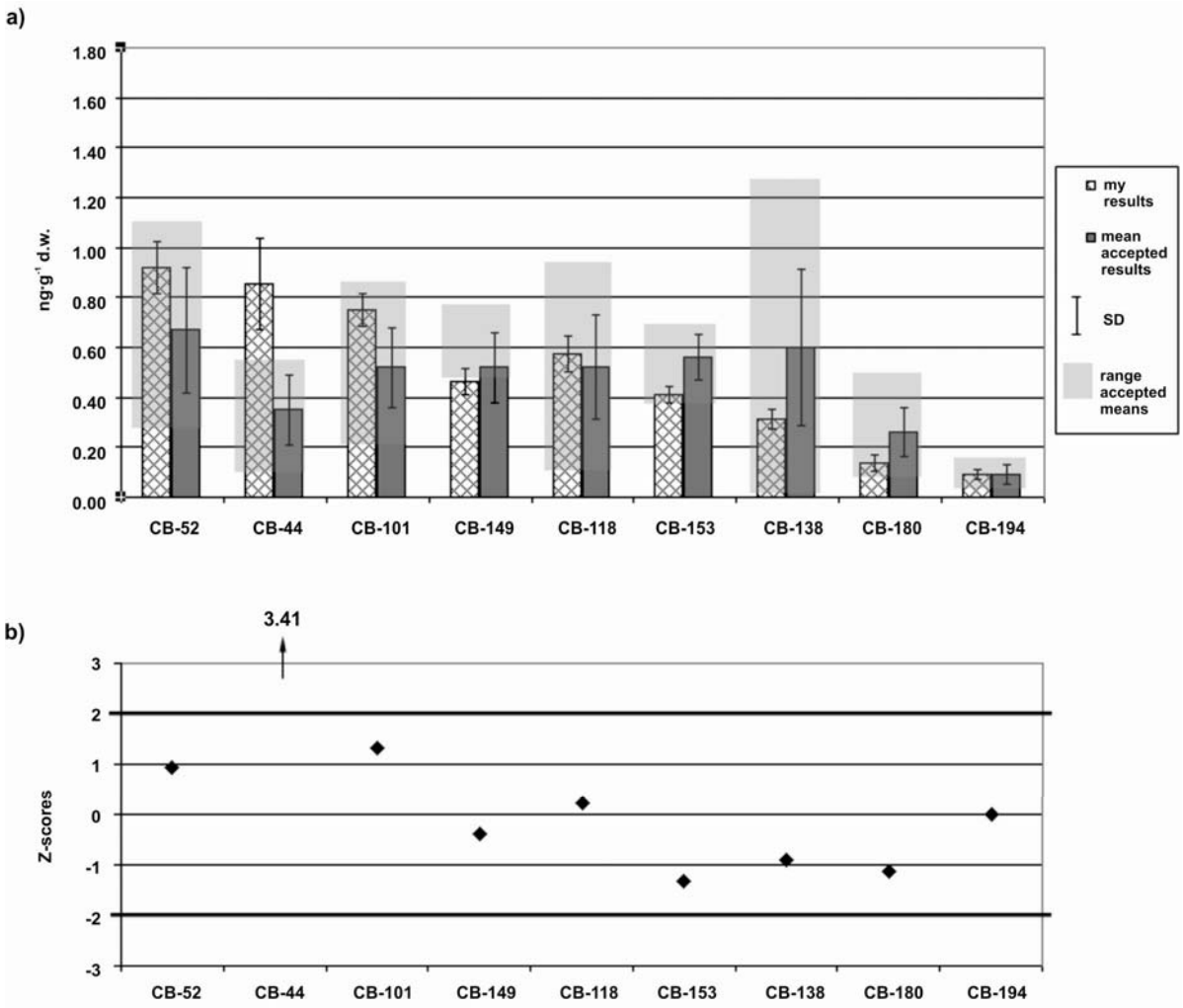

Fig. 3. PCB in the IAEA-159 sample (sediment). a) my results against the background of results accepted by MEL-IAEA, b) *Z*-scores for my results.

chemists. It is common to determine PCBs and PAHs (polycyclic aromatic hydrocarbons) at the same time [19-21]. Both these two groups of compounds are large and their analyses in marine matrices involve many problems [22, 23]. However, it is more difficult to determine PCBs than PAHs [24].

Conclusions

Difficulties of determining PCBs in this study were caused mainly by the overlapping peaks (substances resistant to purification, e.g. phthalates) that appeared in the low-molecular-weight PCB section and relatively high volatility of low-molecular-weight PCBs (loss of analytes in spite of the gentle evaporation of solvents). On the basis of both tuna and sediment samples, it can be stated that the determination of low-molecular-weight (tri- and tetrachlorinated) PCBs in marine matrices is more difficult than in the case of higher-molecular-weight PCBs (from five to eight atoms of chlorine). This is demonstrated not only by my own results, but also by a number of results accepted by MEL-IAEA: in general, about 10 results for low-molecular-weight PCBs, but > 30 results for higher-molecular-weight PCBs. Notice that the ranges of results accepted by MEL-IAEA are often extraordinarily wide, especially for higher-molecular-weight PCBs in tuna homogenate, which confirms that it is still not easy to determine the real level of PCB in a sample.

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References

1. Stockholm Convention on Persistent Organic Pollutants, http://chm.pops.int/Convention/ConventionText/tabid/2232/Default.aspx, **2009**.
2. Scientific Report of EFSA – Results of the monitoring of non dioxin-like PCBs in food and feed, EFSA Journal, **8**, (7), 170, http://www.efsa.europa.eu/de/efsajournal/doc/1701.pdf, **2010**.
3. HELCOM, Hazardous substances in the Baltic Sea – An Integrated Thematic Assessment of Hazardous Substances in the Baltic Sea, Balt. Sea Environ. Proc. 120B, **2010**.
4. OSPAR Commission, Status and Trend in Marine Chemical Pollution, http://qsr2010.ospar.org/media/assessments/p00395_Chemical_status_and_trend_HA-6.pdf, **2009**.
5. MUIR D., SVERKO E. Analytical methods for PCBs and organochlorine pesticides in environmental monitoring and surveillance: a critical appraisal. Anal. Bioanal. Chem. **386**, 769, **2006**.
6. VILLENEUVE J.-P., De MORA S.J., CATTINI C. World-wide and regional intercomparison for the determination of organochlorine compounds and petroleum hydrocarbons in tuna homogenate IAEA-435. International Atomic Energy Agency, Marine Environment Laboratory, Report No. 78, **2006**.
7. VILLENEUVE J.-P., OH J.R., CATTINI C. World-wide and regional intercomparison for the determination of organochlorine compounds, petroleum hydrocarbons and sterols in the sediment sample IAEA-159. International Atomic Energy Agency, Marine Environment Laboratories, Report No. 80, **2007**.
8. KOWALEWSKA G., KONAT J. Determination of polychlorinated biphenyls in the marine sediments using gas chromatography. Chem. Anal. (Warsaw) **44**, 223, **1999**.
9. KONAT J., KOWALEWSKA G. Polychlorinated biphenyls (PCBs) in sediments of the southern Baltic Sea – trends and fate. Sci. Total Environ. **280**, 1, **2001**.
10. LANG V. Polychlorinated biphenyls in the environment. J. Chromatogr. **595**, 1, **1992**.
11. SKARPHEDINSDOTTIR H., GUNNARSSON K., GUDMUNDSSON G.A., NFON E. Bioaccumulation and Biomagnification of Organochlorines in a Marine Food Web at a Pristine Site in Iceland. Arch. Environ. Con. Tox. **58**, 800, **2010**.
12. De BOER J., WELLS D.E. Chlorobiphenyls and organochlorine pesticides in fish and sediments – three years of QUASIMEME Laboratory Performance Studies. Mar. Pollut. Bull. **35**, 52, **1997**.
13. BLANZ T., SCHULZ-BULL D.E., EMEIS K.C., PETRICK G., DUINKER J.C. Chlorobiphenyls in suspension and sediment of the southern Baltic Sea: a mass balance calculation since the onset of PCB-production. Cont. Shelf Res. **19**, 891, **1999**.
14. SCHULZ-BULL D.E., PETRICK G., KANNAN N., DUINKER J.C. Distribution of individual chlorobiphenyls (PCB) in solution and suspension in the Baltic Sea. Mar. Chem. **48**, 245, **1995**.
15. THOMPSON M., WOOD R. The international harmonized protocol for the proficiency testing of (chemical) analytical laboratories. Pure Appl. Chem. **65**, 2123, **1993**.
16. CLEEMANN M., RIGET F., PAULSEN G.B., KLUNGSØYR J., DIETZ R. Organochlorines in Greenland marine fish, mussels and sediments. Sci. Total Environ. **245**, 87, **2000**.
17. STEPHANSEN D. A., SVENDSEN T. C., VORKAMP K., FRIER J.-O. Changes in patterns of persistent halogenated compounds through a pelagic food web in the Baltic Sea. Mar. Environ. Res. **73**, 17, **2012**.
18. HELGASON L.B., BARRETT R., LIE E., POLDER A., SKAARE J.U., GABRIELSEN G.W. Levels and temporal trends (1983-2003) of persistent organic pollutants (POPs) and mercury (Hg) in seabird eggs from Northern Norway. Environ. Pollut. **155**, 190, **2008**.
19. HILLER E., ZEMANOVÁ L., SIROTIAK M., JURKOVIĆ L. Concentrations, distributions, and sources of polychlorinated biphenyls and polycyclic aromatic hydrocarbons in bed sediments of the water reservoirs in Slovakia. Environ. Monit. Assess. **173**, 883, **2011**.
20. THOMPSON S., BUDZINSKI H., LEMENACH K., LETELLIER M., GARRIGUES P. Multi-residue analysis of polycyclic aromatic hydrocarbons, polychlorobiphenyls, and organochlorine pesticides in marine sediments. Anal. Bioanal. Chem. **372**, 196, **2002**.
21. HONG Y., YU S., YU G., LIU Y., LI G., WANG M. Impacts of urbanization on surface sediment quality: evidence from polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) contaminations in the Grand Canal of China. Environ. Sci. Pollut. Res. **19**, 1352, **2012**.
22. FILIPKOWSKA A., LUBECKI L., KOWALEWSKA G. Polycyclic aromatic hydrocarbon analysis in different matrices of the marine environment. Anal. Chim. Acta **547**, 243, **2005**.
23. WOLSKA L., RAWA-ADKONIS M., NAMIEŚNIK J. Determining PAHs and PCBs in aqueous samples: finding and evaluating sources of error. Anal. Bioanal. Chem. **382**, 1389, **2005**.
24. KOWALEWSKA G., KONAT J., DOBROWOLSKA Ś. Why is it easier to determine PAHs than PCBs in marine sediments? Chem. Anal. (Warsaw) 47, 189, **2002**.