Chlorobiphenyls and organochlorine pesticides in fish and sediments - the five QUASIMEME interlaboratory studies

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Abstract
A series of five interlaboratory studies on the analysis of chlorobiphenyls (CBs) and organochlorine pesticides (OCPs) has been conducted within the three years EU-QUASIMEME programme. As a result of this programme data produced by monitoring laboratories in Western-Europe are now of known quality, which enables matching of environmental questions and laboratory performance.

1. Introduction

During the three years period (1993-1995) of the EU-QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe) programme five interlaboratory studies on chlorobiphenyl (CB) and four on organochlorine pesticide (OCP) analysis have been organized (Table 1). The first two studies focussed on the long term precision of the laboratories by repeated analyses with intervals of weeks in between[1,2]. The subsequent rounds focussed on the between-laboratory variance. This paper focuses on the overall results of the three-years programme with emphasis on the between-laboratory variance.

In addition to standard solutions of CBs and OCPs, environmental matrices were offered to the participants for analysis, which reflected as much as possible real samples which are normally analyzed in the monitoring programmes. These matrices were lean and fatty fish tissue, shellfish, fish oil and sediments which varied in the degree of contamination. The fish, shellfish and fish liver samples used were wet, sterilized samples. The obvious advantage was that such samples are much closer to natural samples used in monitoring programmes, compared to freeze-dried samples. Using these samples, the studies included in this way the homogenization and extraction steps of the CB and OCP analysis. After each study a detailed assessment of each laboratory's performance was

Table1 Overview of interlaboratory studies carried out in the QUASIMEME programme

Study	Determinands	Matrix	Target
1	9 CBs	Standard solution	Long term precision
		Cod liver oil	Between lab. variation
2	9 CBs	Standard solution	Long term precision
	8 OCPs	Cod liver oil	Between lab. variation
		2 Sediments	
3	9 CBs	Standard solution	Between lab. variation
	8 OCPs	Cod liver	
		2 Sediments	
4	9 CBs	Cod liver	Between lab. variation
	8 OCPs	Mussels	
		Plaice	
		2 Sediments	
5	9 CBs	Standard solution	Between lab. variation
	8 OCPs	Mackerel	
		Cod liver oil	
		2 Sediments	

made. The participants were encouraged to improve their methods to obtain a more accurate result in a next round. A workshop was held between the fourth and the fifth study, in which 15 laboratories, which until then had produced the least good results, participated[3].

2. Materials and methods

Each laboratory was given a protocol with specific instructions for each study. The standard solutions were supplied in ampoules, in quantities of ca. 5 ml. in iso-octane. The CBs (Nrs. 28, 52, 101, 105, 118, 138, 153, 156 and 180) and OCPs (α-HCH, γ-HCH, HCB, p,p'-DDE, p,p'-DDD, p,p'DDT, dieldrin, transnonachlor) used all had a purity of >99%, except α-HCH (purity >98%). The sediment samples, originating from the North Sea, the Baltic and estuaries of European rivers, taken by Rijks Waterstaat, The Hague, The Netherlands and dried and homogenized by the Institute for Environmental Studies, Amsterdam, The Netherlands were supplied in glass jars, in quantities of 100-200 g. One sediment sample was taken form the river Clyde by the Clyde River Purification Board, UK, and was prepared and supplied similarly. The cod liver oils were supplied in ampoules, in quantities of ca. 5 ml. The wet fish, fish liver and shellfish samples were homogenized and packed in tins in quantities of ca. 80 g and immediately sterilized. All samples were tested to confirm the required level of homogeneity.

The assigned values were obtained using the results from a group of eight reference laboratories, which were selected on the basis of their results in previous interlaboratory studies[4-6]. The target value for bias was set at 6%, equivalent to one standard deviation in the standard solutions and at ± 12.5% for the biota and sediment samples. The results were evaluated on the basis of Z-scores, using robust statistics[5]. The Z-value is calculated from the formula

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

in which x_i is the reported value, x is the assigned value, determined by the group of reference laboratories, and s_b is the target standard deviation, mentioned above. Scores of $|Z| < 2$ were considered to be satisfactory, scores of $2 < |Z| < 3$ were considered to be questionable, and scores of $|Z| > 3$ (bias >37%) were considered to be unsatisfactory. In case the analyte concentrations approached the detection limits (generally around 0.1 µg/kg), a constant error appeared to present. Consequently, for example for concentrations of 0.2 µg/kg the laboratories were allowed to have a bias of 50% (error is equal to detection limit of 0.1 µg/kg) . For concentrations below 0.2 µg/kg no Z-scores were calculated.

3. Results and discussion

Most data were produced by GC/ECD (electron capture detection), but a few data sets were obtained by GC/MS (mass spectrometry). No evaluation was made between GC/ECD and GC/MS data. All data were entered by the participants into a data collector programme and returned to the QUASIMEME project office by e-mail or on a floppy disc. Transcription errors and the time to enter these data in the QUASIMEME database were considerably reduced in this way, and the laboratories were made responsible for the data submitted. Z-scores were calculated for each individual laboratory for each determinand. Principal component analysis was also used to aid evaluation of the results[6,8].
A very important point that emerged from this three years programme is that the monitoring data produced by the laboratories are now of known quality. This means that environmental quality and laboratory performance can now be matched.
In Table 2 the best CV (coefficient of variation) values obtained during the programme by the reference laboratories and the whole group of participating laboratories for some selected CBs and OCPs are given for three matrices fish oil, lean fish muscle tissue and North Sea sediments. The table gives an indication of how laboratories involved in monitoring in Western-Europe currently perform. The target value of 15% for all matrices is taken as a minimum target value for a group of laboratories, corresponding with a reproducibility of ca. 50%[6]. This means that when the same group of laboratories would carry out analyses of the same compounds, in similar matrices, for example in a monitoring programme, the ratio between the highest and lowest value produced by these laboratories for one determinand is not higher than 1.5. That again means that differences of more than 50% in concentration can be observed by that group of laboratories. This target is obviously different from the target value set for individual laboratories (12.5%, *cf.* above), for which a satisfactory score of $|Z| < 2$ would mean that the individual laboratory would be able to identify two concentrations that would differ more than 50%.

Table 2 Coefficients of variation (CV) obtained by reference laboratories and whole group of participating laboratories for selected CBs and OCPs

Matrix	CV (%) Whole group	CV (%) Whole group	CV (%) Ref. labs.	CV (%) Ref. labs.	Target CV (%)
	CBs 101, 118, 138, 153, 180	HCB, p,p'-DDE, p,p'-DDD	CBs 101, 118, 138, 153, 180	HCB, p,p'-DDE, p,p'-DDD	
Fish oil	14-14[a]	13-20	4- 7	4-16	15
Lean fish	22-36	27-45	5-16	6-28	15
Sediment	20-24	23-30	12-21	8-22	15

[a] The lowest value corresponds with the best result of the easiest determination, the highest value corresponds with the best result of the most difficult determination.

Table 3 Group category for each laboratory for organochlorine residues in biological tissue and marine sediments (numbers refer to number of laboratories)

Determinands	Matrix	Category			
		1	2	3	4
CBs	Biota	2	16	22	11
OCPs	Biota	4	5	26	8
CBs	Sediments	1	7	16	15
OCPs	Sediments	0	1	11	26

Group 1: > 90% Z scores statisfactory, i.e. $|Z| < 2$; Group 2: 75 - 90% Z scores statisfactory; Group 3: 50 - 75% Z scores statisfactory; Group 4: < 50% Z scores statisfactory.

Table 4 Group category for each compound for organochlorine residues in biological tissue and marine sediments (numbers refer to percentages of all data produced for one compound)

Determinands	Matrix	Category			
		1	2	3	4
CBs	Biota	15-28	5-24	40-44	6-42
OCPs	Biota	12-32	4-25	29-40	8-34
CBs	Sediments	28-35	25-34	27-40	2-10
OCPs	Sediments	30-58	0-18	14-52	0-25

Group 1: > 90% scores statisfactory, i.e. $|Z| < 2$; Group 2: 75 - 90% Z scores statisfactory; Group 3: 50 - 75% Z scores statisfactory; Group 4: < 50% Z scores statisfactory.

The results of Table 2 show that the reference laboratories meet the target values for CBs in all matrices, whereas for OCPs difficulties are still encountered in lean fish and sediments. The whole group of laboratories can produce acceptable results for cod liver oil, but still has difficulties with

CBs and OCPs in lean fish and sediments. To balance these results to some extent, it should be emphasized that until now the QUASIMEME programme on CBs and OCPs has been a learning programme, which means that laboratories were allowed to make mistakes while learning and improving their methodology.

Table 3 gives an impression of the quality of the individual laboratories. All data produced for the studies 2 - 5 were collected and compared to the assigned values as described above. Four categories were made: laboratories with 90% of acceptable Z scores ($|Z| < 2$), laboratories with 75-90% acceptable Z scores, those with 50-75% acceptable Z scores, and those with less than 50% acceptable Z scores. For biological samples only two laboratories for CBs and three for OCPs had > 90% acceptable results, for the sediment samples only one laboratory had more than 90% of acceptable results for CBs. However, a similar group category per individual compound shows a different picture (Table 4). The percentage of results in category 1 now varies from 10 to 60%. It can therefore be concluded that laboratories can perform well, but that there is still a large variability in the data. This is a plea for a better quality control, the use of quality control charts, and regular participation in interlaboratory studies.

When comparing the results obtained in this three years programme with those reported on comparable studies, it may be concluded that the QUASIMEME results are at least comparable or better. The CV values obtained by the whole group of participants for the fish oils varied between 14 and 18% for the major CBs (101, 118, 138, 153, 180). Seal blubber oil, as comparable matrix, analysed in the ICES/IOC/ OSPARCOM CB interlaboratory study resulted in CV values of 12-27% for these CBs[6] and seal blubber analysed in a German study resulted in CV values of 9-26% for these CBs[9]. For the same CBs in sediment the CV value in the QUASIMEME study varied between 20 and 33%, whereas in the ICES/IOC/OSPARCOM study the range was 15-30%, and in a Dutch study on CBs in sediments 25-50%[10].

An important observation may be that serious difficulties are expected in comparability of the laboratories as soon as the concentrations of the analyses to be measured approach the range of < 1 µg/kg. Both Horwitz and Albert[11] and Mes et al.[12] report on the relationship between CV values in interlaboratory studies and the level of the analytes. Horwitz and Albert expect CV values to exceed 50% at an analyte level of 1 µg/kg. Mes et al. showed that CV values exceeded 20% at a level of 5 pg/µl per injection. It is clear that in these QUASIMEME studies similar problems are encountered. Only by improving analytical techniques and lowering detection limits, which could for example be achieved by large volume injection[13] or comprehensive multidimensional GC[14,15], the performance at the very low level can be improved. It is important for monitoring agencies to be aware of these limitations and not to define tasks for groups of laboratories which can in principle not lead to a satisfactory results.

4. Conclusions

The interlaboratory studies on the analysis of CBs and OCPs carried out under the QUASIMEME programme have resulted in much more insight in the quality of the data produced by monitoring

laboratories in Western-Europe. Some laboratories undertake analyses which are regularly of a high standard, using validated methods that are under control. Monitoring agencies should encourage the development of QA management and measurement structures such as QUASIMEME to (i) identify good performance laboratories for specific tasks whilst (ii) allowing other laboratories to improve to a level where their data are acceptable for marine monitoring purposes, (iii) providing a continuous assessment to (iv) eliminate data which can be shown to be unreliable.

Two recommendations are given to managers of marine monitoring programmes. To obtain a good agreement between laboratories producing results in monitor programmes, it is recommended to select a group of laboratories which have a proven, accceptable level of quality measurement to carry out such a task. Secondly, the analytical methods which are used with the present sample mass do not provide data with an accuracy of better than ±50% when analyte concentrations decrease much below 1 µg/kg.

5. References

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