World Health Organization 3rd International Intercalibration Study on PCBs, Dioxins and Furans in Human Milk, Blood, Cows' Milk and Fish

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Summary

Under the sponsorship of the World Health Organization (WHO), an interlaboratory calibration of the analysis of PCBs, PCDDs and PCDFs in human milk, blood, cows' milk and fish was carried out which included 40 laboratories from 16 countries. The study design involved the analyses of each matrix in triplicate. Selected samples were spiked with native standards of certain 2,3,7,8-substituted congeners and certain PCBs congeners at concentrations known only to the WHO staff. The study design resulted in approximately 40 000 individual pieces of PCB, PCDD and PCDF data generated by a variety of analytical methods, at various concentrations. This is, by margin, the largest intercalibration study.

Introduction

For the past several years the WHO Regional Office for Europe (WHO/EURO) has been coordinating a comprehensive project on PCBs, PCDDs and PCDFs, aiming to control and prevent exposure to these toxic chemicals and to assess the possible health risks especially to infants association with contamination of breast milk. One of the important activities within this project is the international quality control study between chemical laboratories producing research data to improve the basis for health risk assessment[1,2,3,4]. Within this context, (WHO/EURO) has been conducting interlaboratory quality control studies on levels of PCDD/PCDFs in human milk and blood within its overall project on the health effects of these chemicals.

ANA

On the basis of recommendation from earlier intercalibration studies, WHO/EURO established a Coordinating Committee to plan the detailed implementation of the third round. The final consultation for this study was held in Volterra, Italy, 1992

The main purpose of the meeting in Volterra was to evaluate the results received, using statistical methods, and to agree on the criteria to be applied to evaluate which of the laboratories are qualified to perform analyses required. Other aims were to discuss the analytical procedures used, to identify weak points and advise on improvements and to consider the need for further activities to ensure the reliability and comparability of the laboratory analyses.

Study design

The study was designed to take into account both the short term and the long-term variation of the data, which was described as the repeatability and the reproducibility, respectively. For each of the three matrices, human milk, blood and cows' milk, a single homogeneous pool was prepared and divided into three sub-pools. Prior to the division into three sub-pools, a quantity of ^{14}C-labeled [1-^{14}C] polydodecane was added to allow homogeneity to be checked. The radioactivity present in the three pools agreed within 10%. Two of the sub-pools were fortified with certain PCB, PCDD and PCDF congeners, the third sub-pool being unfortified. The fortification levels were planned to be approximately 40% and 80% of the expected levels in the collected pools.

After careful mixing the sub-pools were divided into portions to be distributed to participating laboratories in packages containing dry ice to keep them frozen also during shipping. Triplicate analyses of each sub-pool were required and it was the responsibility of each laboratory to divide the material into suitable portions.

For fish samples the procedure was slightly different due to the difficulty in mixing small quantities of spiking congeners into a large bulk of homogenized tissue. In this case the pooled material was divided into individual portions of 25g and the fortification was completed directly onto these samples.

All participating laboratories were requested to analyze for all 2,3,7,8 - substituted dioxins and furans and the following PCB congeners; IUPAC no. 77, 126, 169, 105, 118, 28, 52, 101, 138, 153 and 180. Participating laboratories were also requested to use common $^{12}C_{12}$ standards which were supplied by the coordinating laboratory.

All results from laboratories were sent to WHO/EURO by using special reporting forms. In WHO/EURO all the forms were coded before any further treatment of the data for statistical analyses. After entry of the raw data into a data base each participating laboratory received a copy of that data in order to proof-read it. Only misprints in the figures were allowed to be corrected by laboratories.

Statistical Methods

Statistical analyses were carried out based on whole sample weights rather than fat weight although fat results were requested from laboratories. In entering data whenever the detection limit was reported without corresponding results, half of the detection limit was used. The statistical analyses of data from laboratories was based on calculations of coefficient of variation (CV) for repeatability and reproducibility. This calculation was made for each matrix and each group of chemicals.

The criteria for acceptance of results was based on combination of CV-values for repeatability and reproducibility by calculating the square root of the sum of the squares, e.g.

$$CV\ comb = \sqrt{(CV\ repeat)^2 + (CV\ reprod)^2}$$

For PCDDs and PCDFs in human milk the proposed criteria for acceptance of results was set for CV comb ≤ 30. This equal to the value of 86.46 if the results are recalculated by using the I-TEF values. The criteria for PCDDs and PCDFs in other matrices were set respectively for CV comb ≤ 40 which is equal to 115.28 as I-TEF value.

For PCBs in human milk the criteria for acceptance was set for CV comb ≤ 30 for other matrices it was set for CV comb ≤ 40.

Results and Discussion

The study produced a substantial PCDD/PCDF and PCB data base, upon which assessment of laboratory and analytical method performance could be made. In all about 40 000 separate measurements were submitted by participating laboratories. As a result, this study represents, by far, the largest controlled interlaboratory calibration for PCDD/PCDFs and PCBs.

The total number of laboratories that met the agreed criteria were:

Matrix	Number of accepted laboratories		
	PCDDs/PCDFs	PCBs 77,126,169 105,118	PCBs 28,52,101 138,153,180
Human milk	7	3	4
Blood	5	0*	0*
Cows' milk	11	3	2
Fish	15	6	7

*The total number of laboratories that submitted results for PCBs in human blood was insufficient for the statistics to be applied

Rather large variations were also found between the laboratory standards used by participants.

Further intercalibration studies were regarded highly desirable by the participants.

References

1 WHO Regional Office for Europe. *Environmental Health Series 29*; WHO: Copenhagen, 1988

2 WHO Regional Office for Europe. *Environmental Health Series 34*; WHO: Copenhagen, 1989

3 WHO Regional Office for Europe. *Environmental Health Series 37* ; WHO: Copenhagen, 1991

4 Stephens R.D., Rappe C., Hayward D. G., Nygren M., Startin J., Ersboell A., Carlé J., Yrjänheikki E. J. World Health Organization International Intercalibration Study on Dioxins and Furans in Human Milk and Blood. *Analytical Chemistry, 1992;64:3109-17*