Time Trend Studies of Chlorinated Pesticides, PCBs and Dioxins in Danish Human Milk

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1. Introduction

Levels of chlorinated pesticides and total PCB were earlier determined in Danish human milk samples from 1982 and 1986[1-3]. In 1986 analysis for dioxins and furans were included. Since then more restrictions have been made in the use of chlorinated pesticides and PCB, and much work has been done to identify and reduce the sources of dioxins. In 1993 new samples were collected together with information on living area, intake of different kind of foods etc.. These samples have been analysed for chlorinated pesticides, PCB congeners and total PCB. The latter in order to compare with earlier measurements of the PCB level. Some of the samples have been analysed for dioxins and furans as well.

2. Analytical methods

Chlorinated pesticides and total PCB:
36 samples were analysed for chlorinated pesticides and total PCB.
Human milk samples were mixed with a potassium oxalate solution and ethanol and solvent extracted with diethylether and pentane. The clean-up was carried out on standardized florisil, which was eluted with dichloromethane/pentane. PCB was separated from most of the pesticides on a silica column, which was first eluted with pentane then with diethylether/pentane. Determination of the chlorinated pesticides was carried out by HRGC-ECD on two parallel capillary columns, while total PCB was determined by GC-ECD on a packed column, using Aroclor 1260 as a standard.

PCBs and dioxins congeners:
10 samples were analyzed for both dioxins and PCBs. These samples were processed at the National Institute of Public Health and Environmental Protection (RIVM) in the Netherlands, which is accepted by WHO for exposure assessment studies. The analytical procedure included liquid-liquid extraction for isolation of the fat fraction and removal of the fat and interfering compounds by clean-up on activated carbon and alumina. PCDDs, PCDDs, and Non-ortho PCBs were analyzed by HRGC/HRMS - other PCBs by HRGC.
36 samples were analyzed for PCBs only. In this analytical work-up scheme[4] fat was removed by silica impregnated with H_2SO_4, and the following fractionations were done by florisil and activated

carbon column chromatography. Instrumental analysis were conducted on HRGC/HRMS. Quantitation and recovery control were performed by adding carbon isotope labelled standards to the milk sample before clean-up.

3. Results

The mean concentrations on fat basis of the dominating chlorinated pesticides and total PCB are shown in figure 1 and 2. The results are compared with the earlier investigations in 1982 and 1986 and a distinct decrease in the concentrations is seen especially for the chlorinated pesticides. A similar decrease is found e.g. in Norway[5].
The levels of PCDDs and PCDFs show no significant change between 1986 and 1993/94. The concentrations and pattern of distribution of individual congeners are comparable for the two sampling periods. As seen in figure 3 the mean TEQ for dioxins and furans in 1993/94 amounts to 16.7 pg/g fat, while the mean TEQ for the planar PCB congeners has a value of 17.2 pg/g fat.

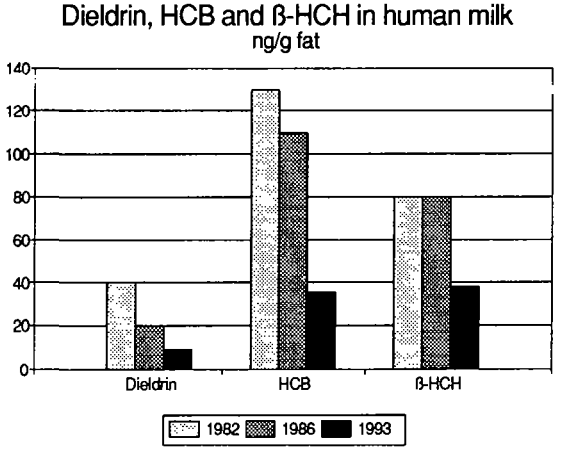

Figure 1. Mean levels on fat basis of chlorinated pesticides: Dieldrin, HCB and ß-HCH in Danish human milk from 1982, 1986 and 1993.

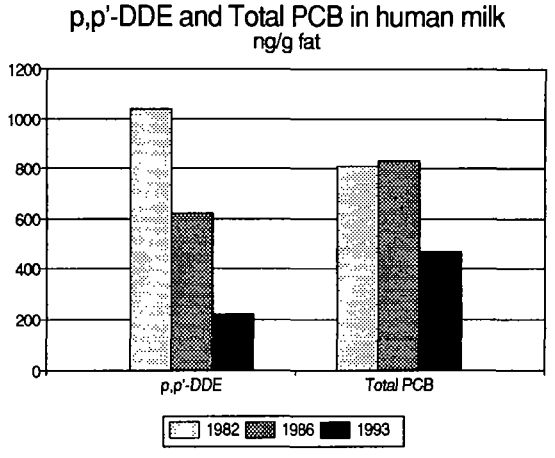

Figure 2. Mean levels on fat basis of p,p'-DDE and total PCB (as Aroclor 1260) in Danish human milk from 1982, 1986 and 1993.

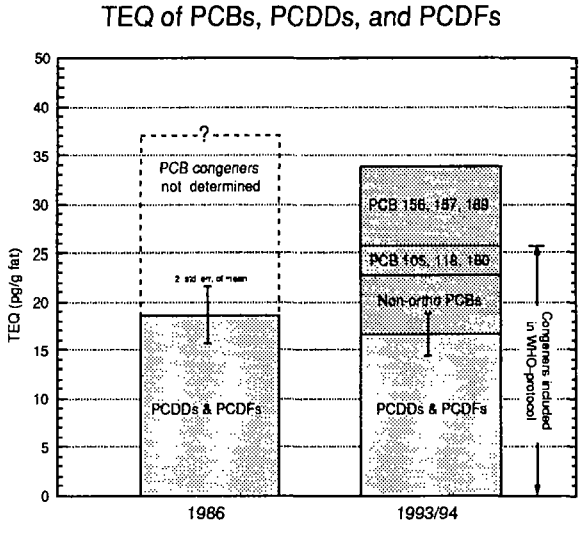

Figure 3. Levels of PCBs, PCDDs and PCDFs in Danish human milk expressed as toxic equivalents.

4. References

1) Sundhedsstyrelsen (1983): Forurening af modermælk med visse chlorerede pesticider og PCB. Hygiejnemeddelelser:3. Bind I,Rapport; Bind II, Bilag (In Danish).

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3) Andersen, J.R. & Orbæk, K.(1984): Organochlorine contaminants in human milk in Denmark 1982. Ambio **13**: 266.

4) Storr-Hansen, E. and Cederberg, T. (1992): Determination of planar polychlorinated biphenyl (CB) congeners in seal tissues by chromatography on active carbon, dual-column high resolution GC/ECD and high resolution GC/high resolution MS. Chemosphere **24**, 1181-1196.

5) Johansen, H.R., Becher, G., Polder, A. & Skaare, J.U. (1994): Congener-specific determination of polychlorinated biphenyls and organochlorine pesticides in human milk from Norwegian mothers living in Oslo. Journal of Toxicology and Environmental Health **42**: 157-171.