ORGANOCHLORINE PESTICIDES, DIOXINS, PCB AND POLYBROMINATED BIPHENYLETHERS IN HUMAN MILK FROM GERMANY IN THE COURSE OF TIME

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Introduction

Contamination of human milk with xenobiotics it of major concern due to its importance as the first food for newborn babies. Because humans are at the top of the food chain, it is obvious that human tissues may contain relative high concentrations especially of those lipophilic, persistent residues and contaminants which tend to bioaccumulate, such as organochlorine pesticides, polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF), polychlorinated biphenyls (PCB) and polybrominated biphenylethers (PBDE). Since more than 25 years, the North Rhine-Westphalian Government offers to all nursing mothers living in that state an analysis of their milk for persistent organic residues and contaminants. This ongoing special service started after the discovery of DDT in human tissues, was then extended to other organochlorine pesticides and their metabolites, such as dieldrin, hexachlorobenzene (HCB), hexachlorocyclohexane isomers (HCH) or heptachlorepoxid. Later on, a congener specific PCB analysis was included and since 1984 human milk samples are also analysed for PCDD/PCDF. Last year, the analytical spectrum was further extended to the congener specific analysis of PBDE. All mothers who are interested in an analysis have to fill out a six page questionnaire. Meanwhile, almost 2000 individual human milk samples have been analysed. Based on the results of these investigations and the information gained from the questionnaires, representative conclusions can be drawn about the parameters which influence the levels in human milk. Moreover, statements can be made concerning the levels of the above contaminants in the course of time.

Materials and Methods

Persistent and lipophilic analytes were extracted along with milk fat after addition of potassium oxalate by liquid/liquid partitioning using ethanol, ethyl ether and pentane. For the determination of dioxins and polybrominated flame retardants, aliquots of the fat were fortified with 17 ^{13}C-labelled PCDD/PCDF and 6 ^{13}C-labelled PBDE congeners. After removal of fat on a silica gel column loaded with sulphuric acid, PBDE were separated along with PCB from PCDD/PCDF by means of a Florisil column. While the PCDD/PCDF fraction was further purified on a mini column consisting of a mixture of Carbopack C/Celite 545, the PBDE fraction was analysed without further clean up. Analytical measurement of PCDD/PCDF and PBDE was performed using capillary gas chromatography/high resolution mass spectrometry (HRGC/HRMS) running in electron impact mode (EI) on a Micromass AutoSpec at a resolution of R=10,000. Organochlorine pesticides and PCB were analysed in a separate run. Gel permeation chromatography (GPC) on a BIO-BEADS S-X3 column with ethyl acetate/cyclohexane 1+1 was used for removal of fat followed by a further clean up step on a mini silica gel column (1,5% water) with various solvents of increasing polarity. Analytical determination of these two compound classes was finally performed by capillary gas chromatography/electron capture detection (GC/ECD) on two capillary columns of different polarity. In all cases, quantification of the analytes was based on the added internal standards and multiple point calibration curves. All methods applied were successfully tested in various national and international quality control studies and proficiency tests.

Results and Discussion

Figure 1 shows the mean values for beta-HCH, hexachlorobenzene (HCB) and p,p'-DDE in 1839 individual human milk samples collected and analysed between 1984 and 2000. DDE represents the persistent metabolite of DDT, formerly widely applied as insecticide around the world. The results for DDE include also the parent compound. While samples from the 80s contained measurable levels of p,p'-DDT, this pesticide can nowadays only be detected occasionally at levels near the detection limit. As can be clearly seen, the levels for the above compounds which represent the predominant OCP residues in human milk have decreased by 80-90% within the past 16 years. The results demonstrate that the ban of these pesticides in the Western World in the early 1970s have had a beneficial effect on the body burden of humans.

A somewhat different situation is found for polychlorinated biphenyls. Figure 2 gives the results for the PCB congeners #138, 153 and 180 which show the highest bioaccumulation of all PCB in humans. While the levels for these three compounds were almost equal in the 80s, the results from samples analysed in the 90s also show a declining trend. Compared to 1984, the levels in samples from 2000 are approximately 60-70% lower. Obviously, this decrease is the result of the ban of PCB usage in open systems and the strict regulations on the use of PCB in closed systems as well as on their disposal.

Figure 3 shows the dioxin levels in human milk in the course of time. All levels are given as pg I-TEq/g fat. The graph demonstrates that from1989 to 1996 the levels followed a clear downward trend. Since then, however, this declining trend has come to a stop and the median concentrations are almost equal. This raises the question, whether the decline observed in the early 90s was only due to regulatory measures taken in the 80s to reduce dioxin emissions and to shut down known dioxin sources or was also (and predominantly) the result of optimised industrial production processes introduced much earlier. In any case, the decline of the average PCDD/PCDF contamination of human milk by 60% since 1984 has beneficial effects on the exposure and body burden of breast fed babies.

The results from analyses of human milk samples for polybrominated biphenylethers (PBDE) are depicted in Figure 4. While the data for 1992 represent the results from our quality control pool prepared in 1992 from approx. 1 kg of remaining milk fat from human milk samples then analysed, the data for 2000 are the mean concentrations determined in seven human milk samples. With the exception of PBDE # 153 which shows a somewhat higher mean level in 2000, the concentrations of all other congeners are very similar for the two years where the samples were collected. Although the number of analyses, especially in 2000 is very low, with all precaution, the results do not seem to follow the same trend as reported for human milk from Sweden showing a continuous increase since 1972 with a doubling of the PDBE levels every 5 years[1].

References

1. Noren, K. and D. Meironnyte (1998) Organohalogen Compounds 38, 1

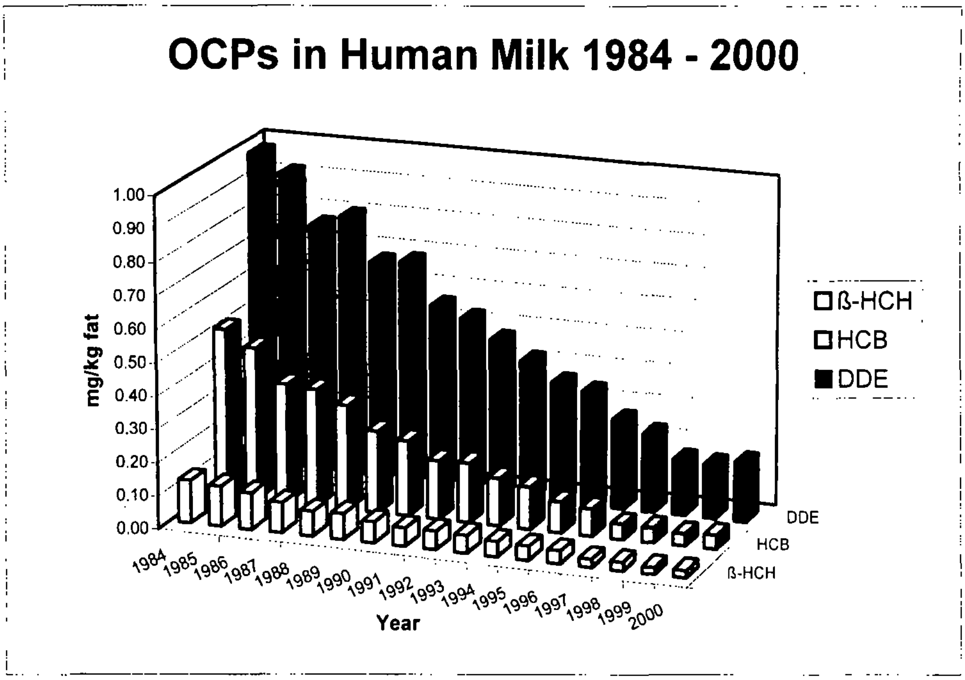

Figure 1

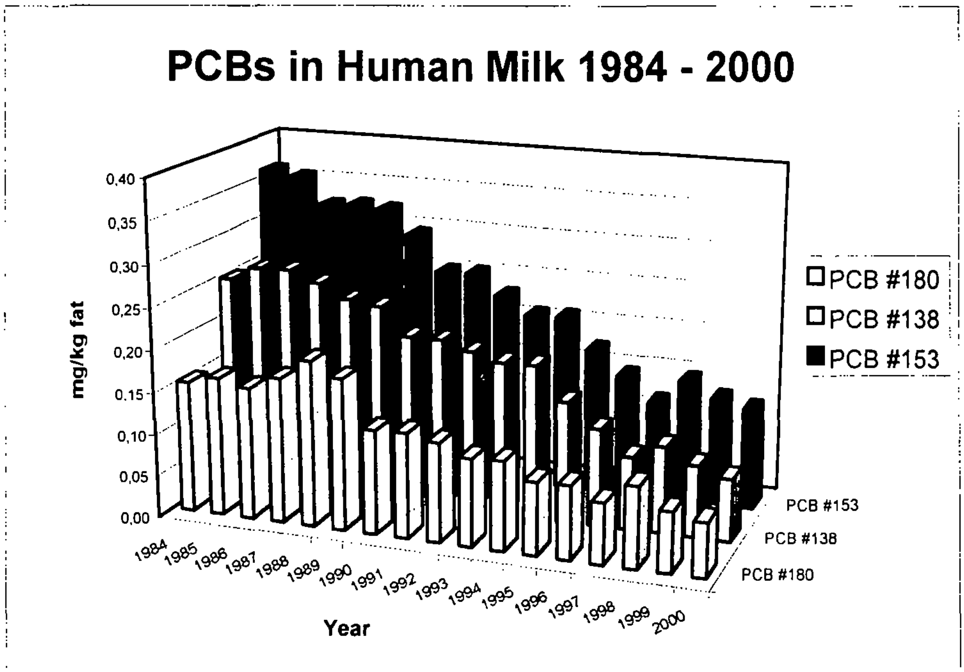

Figure 2

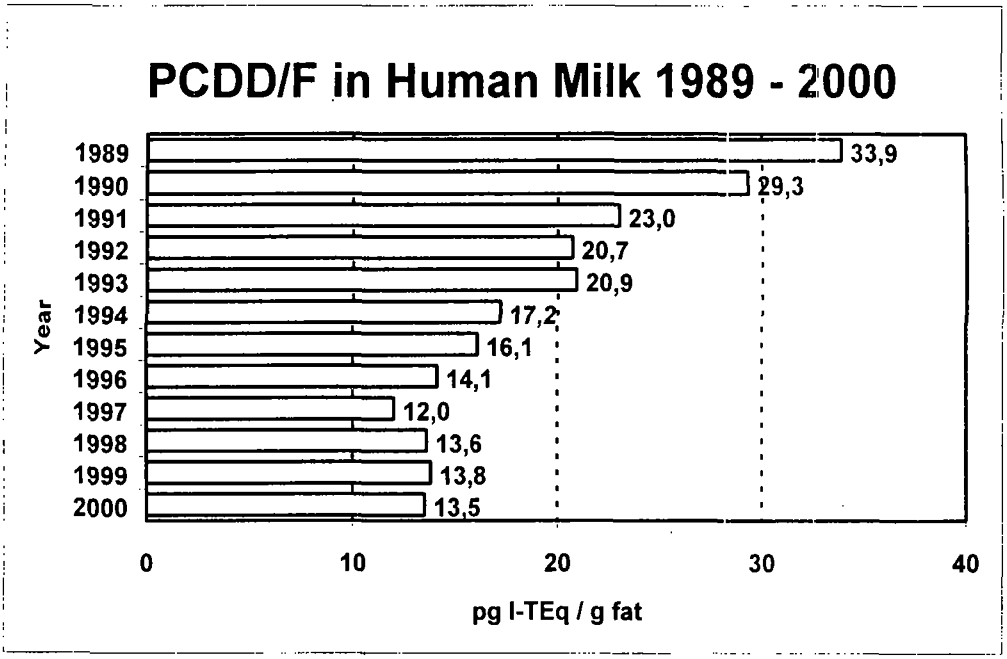

Figure 3

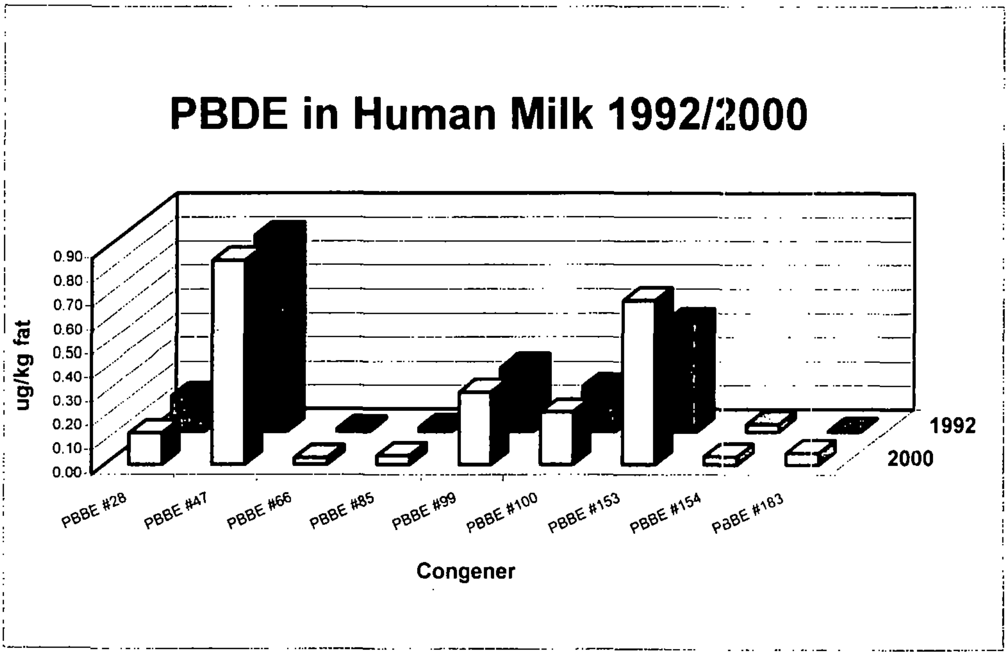

Figure 4