Bull. Environ. Contam. Toxicol. 31, 251–256 (1983)

Levels of Chlordane, Hexachlorobenzene, PCB and DDT Compounds in Finnish Human Milk in 1982

Kim Wickström,[1] Heikki Pyysalo,[1] and Martti A. Siimes[2]

[1]*Technical Research Centre, Food Research Laboratory, SF-02150 Espoo 15, Finland, and* [2]*Children's Hospital, University of Helsinki, SF-00290 Helsinki 29, Finland*

The presence of DDT and its metabolites in human milk has been reported in studies from various countries during recent years (VUORI et al. 1977, WESTÖÖ & NOREN 1972, BAKKEN & SEIP 1976, DILLON et al. 1981, DYMENT et al. 1971, ACKER & SCHULTE 1970, BALUJA et al. 1982, SUVAK 1970, MIYAZAKI et al. 1980). Polychlorinated biphenyls (VUORI et al. 1977, WESTÖÖ & NOREN 1972, BAKKEN & SEIP 1976, DILLON et al. 1981, DYMENT et al. 1971), hexachlorobenzene (MIYAZAKI et al. 1980) and chlordane compounds (MIYAZAKI et al. 1980, TAKAHASHI et al. 1981) have also been detected in this substrate.

The use of DDT in Finland was closely restricted in the early 1970's and totally banned in 1977. Similar steps were taken in many other countries about the same time. As a consequence, a decrease in the concentrations of DDT and its metabolites has been reported in the Baltic environment (MOILANEN et al. 1982) and in Baltic herring which is suspected to be the main source of DDT in the Finnish diet. In Finland the average yearly intake of DDT compounds has been roughly estimated at 1 mg per person (KIVIRANTA et al. 1982).

An increase has been demonstrated (MOILANEN et al. 1982) in the concentration of chlordane insecticides in Baltic fish. Oxychlordane is the main metabolite of chlordane insecticides in mammals (TASHIRO & MATSUMURA 1977) and has been found in human adipose tissue (ATALLAH et al. 1977).

The conventional analytical procedures for the determination of chlorinated hydrocarbons involve solvent extraction, followed by cleanup of the extract with liquid partitioning and column chromatography. VEIEROV & AHARONSON (1980) introduced an efficient extraction and cleanup procedure in which concentrated sulfuric acid is used for the removal of fat and other interfering substances. The detection of the chlorinated compounds has usually been accomplished by electron capture gas chromatography.

This paper describes the determination of polychlorinated biphenyls, DDT and its metabolites, hexachlorobenzene and chlordane components in 50 samples of human milk by a selected ion monitoring technique.

METHODS AND MATERIALS

Fifty individual human milk samples were kindly supplied by the Milk Bank of the Children's Hospital, University of Helsinki, during the period December 1981 to June 1982. All the donors were from the Helsinki city area. The age of the donors was 22-38 years, their length 152-180 cm, weight 48-90 kg and they were mothers to 1-4 children. No data on the dietary habits of the donors was available. All except one were nonsmokers.

Extraction and cleanup of the samples were performed by the method of VEIEROV & AHARONSON (1980). Hexane was used instead of petroleum ether as the extracting solvent. The extract was concentrated to about 0.5 ml before GCMS analysis. o,p'-DDD, previously confirmed not to be present in the samples, was used as an internal standard and added to the milk sample before extraction.

The analysis of the concentrated extracts was made by the selected ion monitoring technique. The instrument used was a Hewlett Packard 5992 gas chromatograph mass spectrometer equipped with an OV 101 fused silica column (25m, i.d. 0.32 mm). The on-column injection technique was applied and the oven temperature was programmed from 120° (delay 0.5 min) to 240° at 15°/min. The ions monitored were 237 (for detecting p,p'-DDT, o,p'-DDD and p,p'-DDD), 248 (p,p'-DDE), 284 (HCB), 326 (penta-, hexa- and heptachlorobiphenyls), 360 (hexa-, hepta- and octachlorobiphenyls), 375 and 377 (α- and γ-chlordane) 387 and 389 (oxychlordane) and 407 and 409 (for nonachlor isomers). In ambiguous cases the identifications were confirmed by monitoring the six most prominent ions in the mass spectrum of the compound in question. Peak heights were used as the basis for quantification.

The recoveries were found to be 85-100 % for all the compounds studied.

The data was statistically processed by CDC Cyber 173 computer using Pearson's correction analysis and multiple regression analysis.

Fat content of the samples was analyzed according to the method of AOAC (HORWITZ 1980).

The reference compounds were kindly supplied by the U.S. Environmental Protection Agency.

RESULTS AND DISCUSSION

The results are presented in tables 1 and 2.

Table 1. Concentrations of organochlorine compounds in Finnish human milk samples

	In whole human milk* (mg/kg)			In human milk fat (mg/kg)		
	mean	S.D.	range	mean	S.D.	range
PCBs	0.016	0.008	0.002 -0.041	0.45	0.24	0.065-1.2
DDE	0.030	0.021	0.005 -0.083	0.85	0.61	0.15 -2.7
DDD	0.0003	0.0002	<0.0001-0.0012	0.009	0.006	<0.003-0.024
DDT	0.0012	0.0010	<0.0001-0.0033	0.036	0.026	<0.003-0.10
Total DDT	0.031	0.022	0.005 -0.084	0.89	0.63	0.15 -2.7
HCB	0.0023	0.0013	0.0007-0.006	0.064	0.040	0.014-0.24
*Fat (%)	3.7	1.1	1.6-5.5			

Chlordane components were not detected in the individual samples owing to limited sensitivity. However, when ten randomly selected samples were combined and further concentrated, oxychlordane and nonachlor isomers could be detected in the resulting extract (Table 2).

Table 2. Concentrations of chlordane compounds in Finnish human milk samples (ten individual samples combined)

	Average concentration (µg/kg)	
	Whole milk	Milk fat
Oxychlordane	0.2	5
trans-Nonachlor	0.4	10
Nonachlor isomer (cis-?)	0.08	2
cis-(α) Chlordane	<0.05	<1
trans-(γ) Chlordane	<0.05	<1

The extraction and cleanup procedure was found superior to previously used solvent partition methods. The only drawback was that some pesticides, e.g. dieldrin and endrine, are decomposed by the acid treatment. Efficient cleanup of the extracts is especially important when using capillary columns with their small sample capacity. No chromatographic prefractionation of the extracts was necessary because of the great specificity of the selected ion monitoring technique.

Some results of recently published human milk studies from different countries are presented in Table 3.

Table 3. PCB and DDT concentrations in human milk (mg/kg whole milk)

Country	Year	PCB	Total DDT	Ref.
Finland	1973-74	0.024	0.058	VUORI et al. 1977
Finland	1982	0.016	0.031	this study
Sweden	1967	0.014	0.11	WESTÖÖ &
	1971-72	0.025	0.086	NOREN 1972
Norway	1975	-	0.082	BAKKEN & SEIP 1976
Canada	1975	0.029	0.039	DILLON et al. 1981
USA	1971 publ.	-	0.11	DYMENT et al. 1971
Germany	1970 publ.	0.10	0.11	ACKER & SCHULTE 1970
Spain	1981	0.25	0.25	BALUJA et al. 1982
Soviet Union	1970 publ.	-	0.21	SUVAK 1970

Comparison of the results of this study with the data from the Finnish investigation in 1973-74 indicates that both the PCB and DDT concentrations are decreasing. This is to be expected as a result of the restrictions put on the use of these compounds. The methods of analysis in the two studies also differed, however, and the results must be compared with some caution.

The mean ratio of the DDE and DDT concentrations in the present data is 25, whereas it was less than 3 in the previous investigation. This is an indication of the metabolism of DDT occurring in the environment.

Chlordane compounds have previously been detected in human milk. The concentrations are summarized in Table 4.

Table 4. Concentrations of chlordane compounds in human milk (μg/kg whole milk)

Country	Year	Oxychlor-dane	Nonachlors cis-	Nonachlors trans-	Chlordanes cis-	Chlordanes trans-	Ref.
Japan*)	1979	0.53	0.18	0.79	0.13	0.16	**)
USA,Hawaii	1979	1.9	-	2.5	-	-	***)
Finland*), present study	1982	0.2	0.08	0.4	<0.05	<0.05	

*) analysis by the selected ion monitoring technique
) MIYAZAKI et al. 1980; *) TAKAHASHI et al. 1981

Chlordane insecticide has never been used in Finland or Scandinavian countries whereas it was heavily used in Japan and especially in the USA. Chlordane and nonachlor isomers are components of technical chlordane, while oxychlordane is a metabolite of chlordane isomers.

Equation (1) mathematically expresses the dependence of the DDT concentration on the age of the donor, number of childbirths and fat percentage of the milk. This was obtained by computer processing of the data.

$$\sum DDT = 0.249 \cdot 10^{-2}(\text{age}) - 0.971 \cdot 10^{-2}(\text{number of childbirths}) + 0.590 \cdot 10^{-2}(\text{fat\%}) - 0.500 \cdot 10^{-1} \quad (1)$$

Similar equations were also obtained for PCB and HCB concentrations. These dependences were, however, not significant.

It can be calculated that the average daily intake of total DDT of a Finnish child weighing 5 kg and consuming 1 kg of milk a day is 0.006 mg/kg. Although low compared with many other countries this value exceeds the ADI value of 0.005 mg/kg proposed by WHO.

Acknowledgements. This study was supported by the Finnish Research Council for Natural Sciences and by National Board for Trade and Consumers Interests. The statistical analysis was kindly carried out by S. Piepponen, M.Sc., Technical Research Centre of Finland.

REFERENCES

ACKER, L. and SCHULTE, E.: Deut. Lebensm.-Rundsch. 66, 385 (1970)

ATALLAH, Y.H., WHITACRE, D.M. and POLEN, P.B.: Chemosphere 1, 17 (1977)

BAKKEN, A.F. and SEIP, M.: Acta Paediatr. Scand. 65, 535 (1976)

BALUJA, G., HERNANDEZ, L.M., GONZALES, M.J. and RICO, M.C.: Bull. Environm. Contam. Toxicol. 28, 573 (1982)

DILLON, J.C., MARTIN, G.B. and O'BRIEN, H.T.: Fd. Cosmet. Toxicol. 19, 437 (1981)

DYMENT, P.G., HEBERTSON, L.M., DECKER, W.J., GOMES, E.D. and WISEMANN, J.S.: Bull. Environm. Contam. Toxicol. 6, 449 (1971)

HORWITZ, W. (ed.): Official Methods of Analysis of the Association of Official Analytical Chemists,Method No 18043, Washington D.C., 1980.

KIVIRANTA, A., KORPI-TASSI, A-M., MALMSTEN, T., NIEMI, E-L., PENTTILÄ, P-L. PYYSALO, H. and RAUTAPÄÄ, J.: Kemia-Kem 3, 202 (1982)

MIYAZAKI, T., AKIYAMA, K., KANEKO, S., HORII, S. and YAMAGISHI, T.: Bull. Environm. Contam. Toxicol. 25, 518 (1980)

MOILANEN, R., PYYSALO, H., WICKSTRÖM, K. and LINKO, R.: Bull. Environm. Contam. Toxicol. 29, 334 (1982)

SUVAK, L.N.: Zdravookhranenie 13, 19 (1970); CA 74, 110883a (1971)

TAKAHASHI, W., SAIDIN, D., TAKEI, G. and WONG, L.: Bull. Environm. Contam. Toxicol. 27, 506 (1981)

TASHIRO, S. and MATSUMARA, F.: J. Agric. Food Chem. 25, 872 (1977)

VEIEROV, D. and AHARONSON, N.: J. Assoc. Off. Anal. Chem. 63, 532 (1980)

WESTÖÖ, G. and NOREN, K.: Vår föda 24, 41 (1972)

VUORI, E., TYLLINEN, H., KUITUNEN, P. and PAGANUS, A.: Acta Paediatr. Scand. 66, 761 (1977)

Accepted April 4, 1983