Dioxins, PCBs and some Chlorinated Pesticides in Human Milk from the Kola Peninsula, Russia

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Introduction

The Kola Peninsula in the northern part of Russia is highly industrialized, resulting in considerable pollution of the environment. The Murmansk area is characterized by mixed industries and harbour traffic, while Monchegorsk is dominated by a big smelter complex. These industrial activities may release persistent organochlorine compounds (OCs) such as dioxins and PCBs to the environment. Exposure of the general population to OCs occurs mainly through ingestion of contaminated food. The dietary habits in the two regions are practically the same, based on a modest consumption of fish, meat, and milk products. In the Netherlands, higher levels of dioxins and PCBs are found in human milk of women living in highly industrialized areas compared to more rural districts[1)]. Also the consumption of fish can contribute to the accumulation of OCs in humans[2,3)]. The aim of the present study was to review the contamination level with respect to dioxins, PCBs and other OCs in women from Murmansk and Monchegorsk and to elucidate a possible geographic difference.

Materials and Methods

Sampling and collection. In april 1993, 30 human milk samples were collected in the Second Hospital of Murmansk and the City Hospital of Monchegorsk. From all the mothers, details of health, age, weight, occupation, and dietary habits were filled in on questionnaires. The average age of the mothers was 24 years. The samples were collected 37 to 41 weeks after delivery. The milk was expressed manually in a 50 ml precleaned pyrex bottle with a teflon coated top. All the samples were kept frozen at -20^{0}C until analyzed.

Determination of Chlorinated Pesticides and PCBs.

Sample extraction, clean-up, and GC analysis. Extraction with cyclohexane and acetone and clean-up with sulphuric acid were done according to a method described earlier[4,5)], slightly modified . The milk fat content was determined gravimetrically. TCN (tetrachloronaphtalene) was used as the internal standard. Separation was performed on 60 m SPB-5 and SPB-1701 capillary columns (Supelco, Inc., Bellafonte, Pa). The GC analyses is described in detail elsewhere[6]. Recoveries of pesticides and PCBs varied from 90 to 128. Detection limits were 0.01 ng/g fat for PCBs and 0.01-0.02 for pesticides.

Determination of PCDDs/PCDFs and non-ortho PCBs
Due to the limited amount of samples, determination of PCDDs/PCDFs and non-ortho PCBs was performed on pooled samples from each of the two regions studied. In addition to this, an individual analysis was performed on one sample from Murmansk with a very high content of PCBs.

Extraction, clean-up and GC analyses. After addition of sodium oxalate and methanol to the mothers milk samples, lipids were extracted with diethyl ether/n-heptane[7]. Clean-up of fat was performed according to a method described elsewhere[8], slightly modified. The PCDDs and PCDFs were determined by GC-HRMS[7].

Results and Discussion
Chlorinated pesticides. Moderate levels of hexachlorobenzene (HCB) were found in all the milk samples (Table 1). Significantly higher levels of sum chlordane, pp-DDE and sum DDT were observed in Murmansk compared to Monchegorsk. Of the HCH-isomers, the β-HCH was the predominant isomer, which contributed with 99% to the sum-HCH. pp-DDE contributed 78% to the sum DDT. The ratio DDT/DDE was slightly higher in Monchegorsk compared to Murmansk. 4 individual samples showed a ratio DDT/DDE higher than 0.30. The HCB, sum HCH and sum DDT levels in the two cities correspond well with a study in the Soviet Union in 1990[9], but they are considerably higher than OC levels measured in Norway in 1991[6].

Table 1. Residues (pb. ug/kg fat weight) of HCB, sum HCH, sum chlordane, pp-DDE, pp-DDT sum DDT and ratio DDT/DDE in human milk from Murmansk and Monchegorsk

	Murmansk				Monchegorsk				Monchegorsk
	Mean	S.D.	Range	Median	Mean	S.D.	Range	Median	Mother X
Fat %	**2.77**	**1.39**	**(0.75-5.87)**	**2.8**	**3.56**	**1.29**	**(1.58-5.7)**	**3.34**	**2.9**
HCB	129	83	(51-417)	111	111	47	(64-253)	93	151
sum HCH	858	466	(415-1996)	664	745	295	(475-1569)	612	874
sum chlordane	59	38	(16-167)	52	33	24	(17-90)	21	37
pp-DDE	1269	530	(776-2816)	1159	892	220	(548-1343)	884	1381
pp-DDT	178	174	(17-713)	103	145	71	(59-242)	123	267
sum DDT	1615	690	(886-3474)	1332	1154	265	(676-1664)	1109	1990
ratio DDT/DDE	0.14	0.11	(0.01-0.38)	0.1	0.17	0.09	(0.05-0.35)	0.15	0.19

Di-ortho and mono-ortho PCBs. The sum di-*ortho* PCBs and the sum mono-*ortho* PCBs show no statistical difference between Murmansk and Monchegorsk, even though the levels of some individual PCBs tend to be higher in Monchegorsk. PCB-74, 99, 153, 138 and 180 were the major di-*ortho* substituted congeners and contributed 60-70% to the sum di-*ortho* PCBs. PCB-118 was the main contributor to the sum mono-*ortho* PCBs with a percentage of 64-70% (Table 2). One individual sample (mother X) was presented on its own because the levels of PCBs were about tenfold higher than the other samples.

PCDDs/PCDFs and non-ortho PCBs. No difference in levels of sum 2,3,7,8-TEQ PCDDs/PCDFs was seen between Murmansk and Monchegorsk. A slightly higher level (TEQ) of *non-ortho* PCBs was found in Monchegorsk compared to Murmansk. A study of human milk in the Soviet Union in

1990 shows a wide variation on levels of PCDDs/PCDFs between industrial and rural regions[9], also confirmed by a study in the Netherlands[1]. Such regional differences were not found in Norway[10]. The contamination level (TEQ) in the milk from mother X from Monchegorsk was for PCDDs/PCDFs and non-ortho PCBs 2.7 and 3.5 times higher than the mean levels in human milk from this town (table 3). As the woman is working in the smelter complex, the possibillity of occupational exposure cannot be excluded.

Table 2. Residues (ppb, ug/kg fat weight) of di-ortho PCB and mono-ortho PCB in human milk from Murmansk and Monchegorsk

	Murmansk				Monchegorsk				Monchegorsk
PCB IUPAC number	Mean	S.D.	Range	Median	Mean	S.D.	Range	Median	Mother X
28	4.1	2.7	(2.2-12.3)	2.8	6	4.2	(2.3-10.8)	4.4	12.2
52	4.5	3.3	(0-10.7)	3.8	1.9	2.3	(0-8.1)	1.3	6.9
66	4.8	3.1	(2.6-15.7)	4.1	10.1	6.9	(4.3-33.4)	8.2	96.6
74	31.9	16.2	(56.8-79.4)	26.9	53.4	27.9	(18.6-120)	50	1222.8
99	34.6	14.2	(20.2-79.2)	32.5	47.8	20.3	(17.8-88.5)	46	1057.4
101	3.7	2.3	(1.6-11.3)	3.2	4.4	1.8	(2.4-8.4)	3.4	31.3
110	0.5	0.9	(0-2.6)	0	2.6	2	(0-6.6)	2.7	10
128	8.3	4.9	(2.6-22.9)	7.6	4.8	2.7	(2.1-13.6)	4.1	31.6
138	97.1	45.1	(51.8-245.3)	85.1	95.6	31.9	(42.7-173.9)	88.5	865.3
141	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d
149	1.2	0.9	(0-4.0)	1	1.1	0.7	(0-2.5)	1.1	19.8
153	127	59.5	(66.5-318)	115.3	118	37.8	(58.1-196.6)	112	932.5
170	17.1	9.1	(9-47.2)	14.6	14.1	5.1	(7.5-24.2)	14.5	46.3
180	37.9	20.3	(19-104)	33.7	31.1	9.5	(14.9-54.6)	30.1	88.8
187	9.8	5.3	(4.3-24.9)	8.3	8	2.7	(4.1-14.3)	7.3	20.4
194	4.6	2.9	(1.7-13.8)	3.6	3.3	1.2	(0.5-5.6)	3.4	6.5
206	1	0.5	(0.3-2.5)	1	0.6	0.3	(0-0.8)	0.5	1.1
209	1.1	0.7	(0.2-2.5)	1	0.6	0.4	(0-1.6)	0.5	3
Sum *di-ortho* PCB	**389.2**	**191.9**	**(207-993.3)**	**344.5**	**403.4**	**157.7**	**(197.2-652.3)**	**378**	**4452.5**
105	11.8	7.2	(5.1-37.1)	9.8	18.4	7.9	(7.2-33.4)	17.2	492
114	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
118	63.2	36.3	(28-186.6)	52.3	92.2	38.3	(43.2-167.3)	83.4	1596.2
156	14.6	7.3	(7.5-37.6)	14	16.1	5.8	(6.9-28.9)	15.5	144.7
157	5.6	2.9	(2.9-15.1)	5	5.6	2.2	(0-9.3)	6	46.9
Sum *mono-ortho* PCB	**95.2**	**53.7**	**(43.4-276.3)**	**81.1**	**132.3**	**54.2**	**(64.9-238.8)**	**122.1**	**2279.8**
Sum *di-ortho* and *mono-ortho* PCB	**484.4**	**235.9**	**(250.5-1270)**	**429**	**535.7**	**184**	**(262-859.8)**	**511**	**6732.3**

Table 3. Results of sum 2,3,7,8-TEQ (PCDD/PCDF) and (PCB), (pg/g fat weight) in pooled milk samples from Murmansk and Monchegorsk and one individual sample from Monchegorsk

	Murmansk	Monchegorsk	Monchegorsk mother X
Fat %	2.42	3.12	2.9
PCDD/PCDF (TEQ)	15.8	15.7	41.9
PCB (TEQ)	11.7	14.2	38.3

Conclusions

Levels of organochlorine pesticides in human milk from the Kola Peninsula are considerably higher compared to corresponding levels in human milk in Norway. The levels of PCBs, PCDDs/PCDFs in the mothermilk from the Kola Peninsula are higher than levels found in rural areas in the Soviet Union, higher than in Norway, but correspond with levels found in Lithuania. No significant geographical differences in levels of PCBs and PCDDs/PCDFs between Murmansk and Monchegorsk were found. The finding of one particular highly contaminated sample shows the need for analyses of individual samples in the first investigation in a new area.

Acknowledgements

The authors thank the participating mothers, the Hospitals in Murmansk and Monchegorsk and in Norway Sissel Planting and Ole Jørgen Rossland for skillful technical assistance during the analyses of PCDDs/PCDFs and non-ortho PCBs.

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