THE CONTAMINATION OF HUMAN MILK WITH POLYCHLORINATED DIBENZO-p-DIOXINS, -DIBENZOFURANS AND -CHLOROBIPHENYLS IN RUSSIA.

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ABSTRACT

A review of the data on human milk contamination with polychlorinated dibenzo-n-dioxins (PCDD, D), polychlorinated dibenzofurans (PCDF, F) and polychlorinated biphenyls (PCB) obtained in the analysis of milk samplings taken in accordance with the WHO/EURO requirements at European certified laboratories shows that a the territory of the former Sviet Union (FSU) is heavily contaminated with both D/F and PCBs. The PCB toxic concentration exceeds dramatically the D/F total toxicity. Profiles of D/F congeners from different cities are similar. This can be accounted for by the leveling of the D/F composition at the penetration to living organisms and noticeable similarity in the food of women-milk donors due to the current situation in these countries.

INTRODUCTION

The first studies on the assessment of milk contamination with dioxins in Russia were carried out in 1988 - 1990 [1]. In 1993 - 1994 another study was done within the second round of exposure studies on levels of PCBs, PCDDs and PCDFs in human milk [2]. Upon the completion of the second round the work within this program in Russia continued and as a result the data on milk contamination in six cities located in the European part of Russia were obtained (Table 1). From three locations (Arkhangelsk, Salavat and Kargopol) analyses were carried out at the Laboratory for Organic-Analytical Chemistry, National Institute of Public Health and the Environment (RIVM) the Netherlands by dr. A.K.D. Liem. The samples from the other locations were carried out at the State Institute for Quality Control of Agricultural Products (RIKILT-DLO) by W.A. Traag. Both Dutch laboratories were "certified" by UN WHO/EURO for the analysis on dioxins in breast milk. In addition to the cities mentioned, analyses were also carried out in the cities of Murmansk and Monchegorsk in the North of Russia [3] and in former republics of the Soviet Union - the Ukraine (Kiev) [2, 4], Kazakstan [5] and Lithuania [6]. During this period Russian researchers performed a few more analyses of milk, though they were done not according to the WHO/EURO rules and at uncertified analytical laboratories. Geographically this study presents the whole territory of the European part of Russia from the White Sea in the North (Arkhangelsk) to Volgograd near the Caspean Sea. Sterlitamak is situated in the East in Bashkortostan adjacent to the Urals, and Suzdal is in 200 km from Moscow. Suzdal and Kargopol are small cities with the population of 10 - 20,000 without any industrial enterprises; Dzerzhinsk and Sterlitamak are developed industrial chemical centers; Arkhangelsk (paper-and-pulp sector) and Volgograd (plenty of chemical and metallurgical plants of various kinds) are typical large cities of Russia.

METHODS AND MATERIAL

A main specific feature of the research project is the standard milk sampling procedure within the WHO/EURO rules. Under current conditions in Russia this is a challenge. Even the first paragraph of the WHO/EURO requirements that reads "A mother must be healthy" is almost impracticable. For instance, in Volgograd 100% of pregnant women suffer from anemia and vitamin deficiency and they are prescribed to take ferrum preparations and vitamins. We did not consider this an obstacle to milk sampling. However anomalies of pregnancy and other pathologies in the health of a pregnant woman, mother or child hindered sampling. The following was presumed as criteria of health: a mother does not take any medicines, normal pregnancy, normal childbirth and healthy baby. This leads to multimonth expectations for appropriate milk donors. It took us from 3 to 6 months to obtain a standard pooled sample from 10 donors. In selecting a donor who would meet the WHO/EURO requirements a large city such as Arkhangelsk provided only two healthy mothers. Yet, a more close study of their medical records showed that one of those "healthy" mothers had had pregnancy toxicosis and this candidate had to be excluded. A study on medical records of other pregnant women with close dates of childbirth in this city gave no appropriate candidate donors for the next two months. There were no healthy mothers who would comply with the WHO/EURO rules in the huge, almost half-million city. It is this infrequency or absolute lack of "standard" mothers in a selected region that is the reason for the fact that random data on the human milk exposure to dioxins in Russia could prove to be "nonstandard" and confusing. It is pointed out in [2] that individual distinctions in contamination levels of milk from different donors could have as large as variations by a factor 3 to 5. One should be very cautious with the data obtained in earlier studies if take into account the fact [7] that random samples could give an inadequate contamination pattern due to both variations in donor's individual features and a casual choice of the donor.

At the same time, the heuristic value of a pooled sample is not evident. Actually it reflects only dioxin and PCB levels in a total food ration of women in this region, and besides, not of all women but only of those who give birth in municipal maternity clinics, thus excluding a new class of rich Russians. Individual variations in food menu can be very large, particularly in the cases of vegetarians. Political changes for the past five - six years have led to a drastic drop in the standard of living and thus to the leveling of food by both its fuel value and structure.

Table 1: DIET'S PERFORMANCE OF NURSING MOTHERS ON RUSSIA

Mothers' residence area during last 5 years: Arkhangelsk (1), Kargopol (1), Salavat (10), Suzdal (10), Dzerjinsk (10), Volgograd (10). 42 In all: in urban 92.8 %, suburban 7.2 %. Average age 21.6 (17-29).
Mothers' dietary habits: % mixed 97.6, vegetarian, but with milk and eggs 2.4 (one woman only during pregnancy and baby nursing).
Mothers' smoking habits: % non-smoker (has never smoked) 88.1, ex-smoker (only in school) 11.9, smoker zero.

PRODUCTS	MILK*	CHEESE*	BEEF	FISH
Consumption %				
never	0	19	2.4	7.1
less than once a week	-	-	0	64.4
once a week	-	-	4.8	21.4
twice or less a week	7.1	49.1	-	-
twice a week	-	-	14.3	4.7
more than twice a week	-	-	78.5	2.4
more than twice a week, but not every day	16.7	20	-	-
every day	76.2	11.9	-	-

* Fat content: % low-fat (0.5-1.9%) zero, medium-fat (2.0-2.9%) 78.9, high-fat (3.0% or more) 21.4.
Consumption per day: % less than 250 ml a day 28.6, 250-499 ml a day 42.9, 500 ml or more a day 28.5.
** Fat content: % low-fat 66.7, high-fat 33.3.

This fact can contribute to the understanding of the above discussed alignment in the profiles of congeners in human milk from different regions of the country. This consideration is apparently also applicable to donors from other underdeveloped countries. So, to some extent, data on the human milk contamination obtained in poor countries are statistically more authentic than those from developed countries with a high standard of consumption. A noticeable distinction in menu of Russian donors from Western ones (Table 1) results from the fact that the majority of Russian nursing mothers in their menu have rather much milk (76.2 % - daily) and meat (more than twice a week - 78.5 %), though very little cheese (19 % do not eat it at all) and fish (less than once a week - 64.4 %). The amounts of vegetables and fruit differ greatly. All three diets listed in [8], which comprise daily consumption of meat, cheese, fruit and vegetables, are very unlikely in any region of Russia even in summer. An approximate calculation shows that mothers eat no more than 30 g of beef a day at average. As for fish, it is about 20-30 g a day and it is mostly very cheap sea fish and fish from rivers and ponds. In Russia milk is considered necessary for normal lactation, therefore it fills an important place in the menu - up to 500 ml/day. As a rule, women buy milk at stores, this milk is of medium fatness (2-3 %). Milk with higher fat percentage (more 3 %) was indicated only by Suzdal residents where there are many cows in private ownership. The protein deficiency is compensated by chicken meat (so called "Bush's legs"), mainly imported from the USA and Europe, eggs and regular consumption of "cheese" (curds). An elevated dose of carbohydrates due to a large amount of potatoes, cereals, macaroni and bread results in a considerable weight gain with nursing mothers.

A weight gain of 7-10 kg during pregnancy is considered routine although 15 - 20 kg are not considerd rare. In our study one mother's weight gain was 25 kg and she marked the changes in her diet: "ate more wheat-based food, cookies and sweets." She gave birth to a baby with normal weight. We still do not know how an increase of fat in the mother's body affects the dioxins excretion to milk. We may expect that this could lead to a decrease in the dioxin concentration in milk.

An absolute absence of smoking mothers is striking. Four women from Volgograd and one from Kargopol smoked only in school years as it often happens to schoolgirls. The others have never smoked. A diet of a Honolulu (USA) woman is extremely simple and did not change before and after the childbirth (she also does not smoke): milk and dairy products — 4 glasses a day (24 ounce}, fish and sea food — once a week 200 g. No beef. Note that it was the first identification of D/F and PCBs in breast milk on the Hawaiian Islands where we had anticipated to receive pure milk for comparison. The samples were analysed for the seventeen 2,3,7,8- substituted congeners and the three planar PCB congeners 3,3',4,4'-tetrachloorobiphenyl (77), 3,3',4,4',5-pentachlorobiphenyl (126) and 3,3',4,4',5,5'-hexachlorobiphenyl(169) using gaschromatography-high reso;ution mass spectrometry. To express the toxic potency of the mixture of dioxins and planar PCB's, the toxic equivalency factor (TEF) appraoch was used. A TEF value was assigned to the dioxin and planar PCB's which represents their relative toxic potency towards 2,3,7,8- TCDD. the most toxic dioxin congener which TEF value is 1.0. By multiplying the TEF value of each congener with the concnetratiuon of that congener in pg/g fat, the toxic value of that congener was calculated (pg TEQ/g fat). Summaryzing the TEQ's of all congeners gives the total TEQ value in each sample.

RESULTS AND DISCUSSION

The analysis of the human milk samples taken in the Arkhangelsk Region (cities of Arkhangelsk and Kargopol) and Bashkortostan (city of Salavat) to detect its D/F contamination revealed that the contamination compositions in these samples from different regions are very close. Note that Arkhangelsk is under the impact of emissions from a paper-and-pulp mill (PPM) complex, Kargopol is located in a rural area without any industrial enterprises, and Salavat is situated in a heavily polluted region with powerful chemical industry having no relation to PPMs. A comparison of D/F congeners profiles in milk from other Russian regions, from Western countries and Vietnam has shown an absolute similarity in contamination profiles of milk from these regions. Table 1 lists data on the D/F composition in human milk and total toxicity of samples in the units of an international I-TEF toxicity scale. From table 1 it is obviously shows that the ratio of D/F congeners in the milk samples is actually identical.

Table 2: ***LEVEL OF TOXICITY POLYCHLORODIBENZO-p-DIOXINS, DIBENZOFURANS AND POLYCHLOROBIPHENYLS IN HUMAN MILK FROM RUSSIA (pg/g fat)***

Nos	CODES	CONGENERS	I-TEF	SALAVAT#		VOLGOGRAD		DZERJINSK		SUZDAL		HONOLULU*	
				Level	TEQ	Level	TEQ	Level	TEQ	Level	TEQ	Level	TEQ
DIOXINS													
1	D4	2378-TCDD	1	5.3	5.3	2.73	2.73	3.58	3.58	6.37	6.37	2.59	2.59
2	D5	12378-PeCDD	0.5	3.9	1.95	1.47	0.74	2.32	1.16	3.27	1.64	2.87	1.43
3	D6(1)	123478-HxCDD	0.1	1	0.1	1.14	0.1	0.86	0.09	1.48	0.15	5.31	0.531
4	D6(2)	123678-HxCDD	0.1	2.7	0.27	3.26	0.3	2.47	0.25	3.81	0.38	34.81	3.48
5	D6(3)	123789-HxCDD	0.1	0.7	0.07	n.d.**	-	0.75	0.08	0.79	0.08	5.56	0.556
6	D7	1234678-HpCDD	0.01	3.4	0.034	3.98	0.04	4.72	0.05	2.74	0.03	55.45	0.554
7	D8	OCDD	0.001	16.4	0.016	18.32	0.02	10.09	0.04	12.33	0.012	251.39	0.251
FURANS													
8	F4	2378-TCDF	0.1	0.8	0.08	1.44	0.14	1.11	0.1	0.74	0.074	0.56	0.06
9	F5(1)	12378-PeCDF	0.05	0.4	0.02	0.62	0.03	0.34	0.02	0.29	0.0014	n.d.	-
10	F5(2)	23478-PeCDF	0.5	6.9	3.45	8.37	4.2	8.79	4.4	8.19	4.1	6.26	3.13
11	F6(1)	123478-HxCDF	0.1	3.7	0.37	4.64	0.46	3.78	0.38	3.13	0.313	3.35	0.34
12	F6(2)	123678-HxCDF	0.1	2	0.2	2.32	0.23	1.83	0.18	2.25	0.225	2.56	0.256
13	F6(3)	123789-HxCDF	0.1	0.7	0.07	n.d.	-	n.d.	-	n.d.	-	n.d.	-
14	F6(4)	234678-HxCDF	0.1	0.1	0.01	0.82	0.08	0.66	0.07	1.08	0.108	1.44	0.144
15	F7(1)	1234678-HpCDF	0.01	1.5	0.015	1.34	0.01	1.74	0.02	1.16	0.012	3.35	0.034
16	F7(2)	1234789-HpCDF	0.01	0.1	0.001	n.d.	-	n.d.	-	n.d.	-	n.d.	-
17	F8	OCDF	0.001	0.3	0.0003	n.d.	-	0.78	0.001	n.d.	-	n.d.	-
SUM TEQ					11.90		9.10		10.70		13.46		13.24
1	PCB 77	33'44'-TCB	0.0005			397.64	0.2	507.93	0.25	110.06	0.06	58.16	0.029
2	PCB 126	33'44'5-PeCB	0.1			113.06	11.3	142.96	14.3	137.89	13.789	59.26	5.9
3	PCB 169	33'44'55'-HxCB	0.01			36.64	0.37	54.47	0.545	51.15	0.51	31.86	0.032
SUM TEQ							11.87		15.10		14.35		5.96
TOTAL SUM TEQ					11.90		20.97		25.80		27.80		19.20
Fat content wt%				3.5		3.39		3.56		3.1		2.17	

\# Data Dr A.K.D Liem's Laboratoy. * For to be compared. **n.d. = Below the limit of detection.

Comment 1: Data of Arkhangelsk and Kargopol (Arkhangelsk region) see: A.K.D Liem, U.G. Ahlborg, H. Beck, F Haschke, M. Nygren M. Ypunes and E. Yrjanheikki. Levels of PCBs, PCDDs and PCDFs in human milk. Results from the Second Round of a WHO-coordinated Exposure Study. Dioxin '96. Organohalogen compounds Vol. 30 (1996), pp. 268 - 273.

Comment 2. Codes of PCB are IUPAC nomenclature. Toxicity equivalency factors (I-TEF) of PCB taked from WHO-TEFs.

Comment 3. Toxicity equivalency factors (I-TEF) and Nos congeners taked from the International convention list

The comparison of a toxicity contribution even more facilitates the D/F congeners profile and virtually the total toxicity of the samples is determined by two congeners D4 and F5(2) and partially by D5. For Arkhangelsk D4 contributes 31% of the total toxicity, F5(2) — 42%, D5 — 13%, and as little as 14% is left for other congeners. The ratio of D4:F5(2) does not vary much, the ratio of D4:D5 is always more than one.In the comparison of the milk contamination from Song-By (South Vietnam) [9] with that from Arkhangelsk and Salavat it is observed that D4 predominates and a D6(2) peak appears, which is seen in the milk from Russia.

Absolutely the same distinctions are noted in the comparison with the milk from Moscow: a marked increase of the D4 contribution into the sample toxicity and a better view of the D6(2) peak. For the other samples studied by A. Schecter the pattern is similar: D4 and F5(2), the most toxic congeners by the I-TEF scale, prevail. It is evident from table 1 that in case the concentration (quantity) of maximum toxic D4 can vary greatly, F5(2) is stable in prevailing over the other D/F congeners. As the process of the milk accumulation takes many months, the ratio of D/F congeners in milk ought to reflect the structure of the environmental pollution or, to be more specific, food contamination, if assumed that we absorb 90% of the total D/F amount with food. This, however is most unlikely. Indeed, a great amount of heavily chlorinated congeners — D8 and F8, D7 and F7 — are characteristic of PPM emissions. There can be so much of octachlorinated furan F8 that it makes a marked contribution into the total toxicity of soils, sediments and air in the vicinity of a PPM [10]. Yet, these congeners either make a small contribution to the total toxicity of samples, or are absent at all. To differentiate samples from various regions not the presence of this or that congener but its absence can serve as a characteristic feature. The absence of D6(3) in milk from Volgograd and F5(1) in milk from Honolulu that make them dramatically different, and the lack of F6(3) and F7(2)

is specific of all of them. F7(2) presence in milk from Arkhangelsk, Salavat and Kargopol distinguishes these cities from Suzdal, Volgograd, Honolulu and Dzerjinsk where this congener is lacking. Congener F6(3) is, as a rule, absent and it was detected only in the samples from Arkhangelsk and Salavat. An excellent coincidence of the congener profiles points out the alignment of contaminations once they get into human milk. As for F8, the reason for this could be its extremely low solubility in water and equally low lipophility. F5(2) is more challengeable as it is never present in PPM emissions in marked amounts. Dry sediments of the Arkhangelsk PPM that could be a major source of the D/F emission in the region contain 180,000 pg/kg of D8 and as little as 430 pg/kg of F5(2). Therefore, the contribution of the latter into the general toxicity is as low as 10 %. The same pattern is observed for other PPM emissions [10]. At the same time, the contribution of F5(2) into the milk toxicity in all samples is rather high. As this congener cannot be generated in a mother's organism during lactation, we have to admit a probability of a D/F selective absorption (excretion) by an living organism. In this case meat, all dairy products and fish are carriers of D/F congeners with a leveled composition. This is likely to be reflected in a relative stability of the D/F congeners composition in the human milk toxicity in various regions.
As a wholeregarding its toxicity, the human milk contamination with dioxins and furans in Russia is close to current levels in Europe.

PCBs CONTRIBUTION
Although the issue of the contribution made by dioxin-like PCBs into the total dioxin toxicity has been so far discussed it is evident that its extent is substatial. Milk in Russia is characterized by a high content of dioxin-like PCBs expressed in toxic equivalents. Almost everywhere PCBs concentrations are higher or close to those of D/F. In all the cities surveyed, including Arkhangelsk and Kargopol, the ratio of PCBs to D/F in TEQ concentrations is notably higher than one (1.1-1.8), and in Suzdal, Dzerzhinsk and Volgograd this ratio can be even higher if other toxic PCBs, in addition to nos. 77, 126, 169, are taken into account. In Arkhangelsk the sum PCBs toxicity equal to 17.5 pg TEQ/g includes only 2.9 pg TEQ/g "no-PCBs" (non-*ortho* PCBs nos. 77, 126, 118) and 5.7 pg TEQ/g "mo-PCBs" (mono-*ortho* PCBs, nos. 105, 118). The same holds for Kargopol: sum toxicity of PCBs are 9.2 pg TEQ/g including "no-PCBs" 2.0 and "mo-PCBs" 2.9 pg TEQ/g [2].
A similar result is observed on the Kola Peninsula [3]: the ratio of the PCBs and D/F toxicity contribution varies from 0.7 to 0.9, in Kazakstan [5] it is equal to 0.7. This ratio is also much higher than one in Lithuania [2], and it is equally high for both a resort area (1.2) and cities (1.5). Both samples from Kiev (Ukraine) have ratios 0.9 and 1.4. Thus we can assume that in all FSU republics the PCBs contribution into the total toxicity of human milk is comparable and exceeds that of dioxins/furans. This differs greatly from highly developed European and American countries (See Table in [2]). For example, in Glasgow (UK) and in Denmark the ratio is 0.3, in Netherlands 0.5 and in Canadian provinces 0.35. In the USA [11] the ratio is 0.25, and in Japan 0.5 (30.8 pg TEQ/g from D/F and 15.5 pg TEQ/g from PCBs) [12]. It is evident that the ratio about one or higher can be expected across the whole FSU territory. This indicates a high level of the PCBs contamination if compared with its moderate exposure to D/F.

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