PCDD/F/PCBs IN MILK OF MAMMALIA INCLUDING HUMAN BEING

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Introduction

Bioaccumulation and biomagnification of POPs in living organisms makes biological tissues a most convenient bioindication object while monitoring background pollution in great areas. Animal and human milk is a most available and traceable matrix. The WHO in the course of several years carried out 3 rounds of analysing PCDD/Fs content in breast milk. The results of this research are now known for the majority of countries including Russia[1].

In 2000 data were obtained on the presence and levels of PCB-WHO[2]. In the region of Bashkiria, Russia, monitoring of food and human biological tissues has been carried out since 1997[3,4].

Cows' milk is widely used as one of the basic elements of human food chain but it is not quite correct to use this kind of samples for characteristic of the area pollution because stabling of cattle presupposes different food additions to vegetable food.

On the other hand, getting milk from wild animals is rather difficult and problematic. From this point of view the study of milk of mares that are fed at pastures is intermediate determination of PCDD/Fs in milk of wild and domestic animals.

The Republic of Bashkortostan situated in the South Ural (Central Russia) is a region of traditional centuries-old horse breeding. The main base for horse breeding is feather-grass and fescue steppe and mountain-forest pastures difficult of access to other livestock. Vegetable food makes 98% of horse ration. Horses obtain their food without assistance at pastures practically all the year round, even in winter.

There are over twenty horse breeding farms in the region where together with elite horse breeding they produce also meat and specific milk products. Meat is exported to European countries, mainly to France, and is also used for producing meat delicacies for the Russian market.

As far as it is known no studies of PCDD/PCDF/DLPCB mares' milk and horse meat pollution were published earlier.

Materials and methods

PCDD/Fs and PCB-WHO determination was carried out in milk and meat of mares, milk samples of cows and human milk in 5 rural districts of the region. Analysis of koumiss – sour milk product made of mares' milk at stud farms – was carried out. All stud farms are situated 20-30 km away from the nearest cities. Mares' and cows' milk samples were received from different milk plants of the same district. The age of the animals was about 3 years old. Breast milk of women living in rural districts was sampled in compliance with WHO instructions. Mean donors' age was 23.7 years old. All samples were analysed individually.

Labelled standards of 15 PCDD/F isomers (CIL) and 12 PCBs (Wellington) were introduced into 100 ml of milk (or 10 g of meat), homogenized and extracted with mixture of hexane-methylene chloride. Purification of the extracts from lipids and proteins was made by gel-penetrating chromatography (Envirogel TM GPC Cleanup, Waters). Registration and measurement were carried out in compliance with methods USEPA 1613, 1668 (Autospec-Ultima, 10000, DB-5 MS,

60m).
The laboratory of the Environmental Research and Protection Centre was certified by the State Authorities of the Russian Federation for carrying out this analysis in food and breast milk. Conformance to international requirements was confirmed by participation in IIR (Norway, Food-2001).

Results and discussion
Obtained data permit to trace the effect of bioaccumulation and to use animal and human milk as an object for background monitoring. Table 1 gives total PCDD/Fs concentration (pg/ml or pg/g lipids) and TEQ-WHO of the sample in the same units.

Table 1. PCDD/Fs content in milk samples (mean value for 5 rural districts of Bashkiria

Indicator (parameter)	Cow milk	Mare milk	Koumiss*	Breast milk
Number of samples	19	5	5	23
Lipids content, g/ml	3.7	1.2	0.35	3.9
Total PCDD/F, pg/ml	0.6	0.3	0.2	2.5
Total PCDD/F, pg/g lipids	13.9	26	59	62.2
TEQ-WHO, PCDD/F, pg/ml	0.08	0.03	0.02	0.98
TEQ-WHO, PCDD/F, pg/g lipids	1.8	2.6	5.8	17.8

* koumiss – sour milk product made of mares' milk on industrial basis

As it is seen the least total pollution level is observed in mares' milk and products made of it (<0.03 pg/ml). Cows' milk is polluted nearly by 3 times more and human breast milk – by 30 times more than mares' milk.
Due to different content of lipids in mares' and cows' milk samples the ratio of concentrations converted to lipid component is changed but the values for breast milk remain highest.
All-the-year-round pasture of horses makes horses a more convenient object for monitoring of PCDD/Fs spreading by air transfer as compared with cattle kept in stalls. We assume that the found data testify to the absence of PCDD/Fs emission sources in rural districts of Bashkiria, levels of accumulation may be considered as background levels caused by global PCDD/Fs pollution. If this is really so then breast milk pollution is accounted for by a longer period of exposure as compared to animals and by regular PCDD/Fs intake with fat-containing products, milk and meat. The effect of bioaccumulation for which the lifetime is most important results in considerable PCDD/Fs accumulation even at a background level.
Isomer distribution in milk samples of mammalia and human beings in the same district is given in Figure 1 and Table 2. In addition to data on milk Table 2 gives the results of PCDD/Fs accumulation in a sample of horse meat (stallion, 3.5 years old).
The main difference in isomer accumulation is referred to tetra- and penta-chlorinated dibenzo-para-dioxins and dibenzofurans. Concentration of these compounds is higher than in a breast milk sample. Accumulation of OCDD is maximum in human breast milk and mares' milk while in cows' milk it is minimal.
It should also be noted that Russian norms of permissible fat content 5.2 pg/g lipids PCDD/Fs expressed in I-TEQ are not exceeded for mares' and cows' milk but human breast milk does not meet this requirement due to the effect of accumulation within the food chain.

Figure 1. PCDD/Fs in mammalia milk

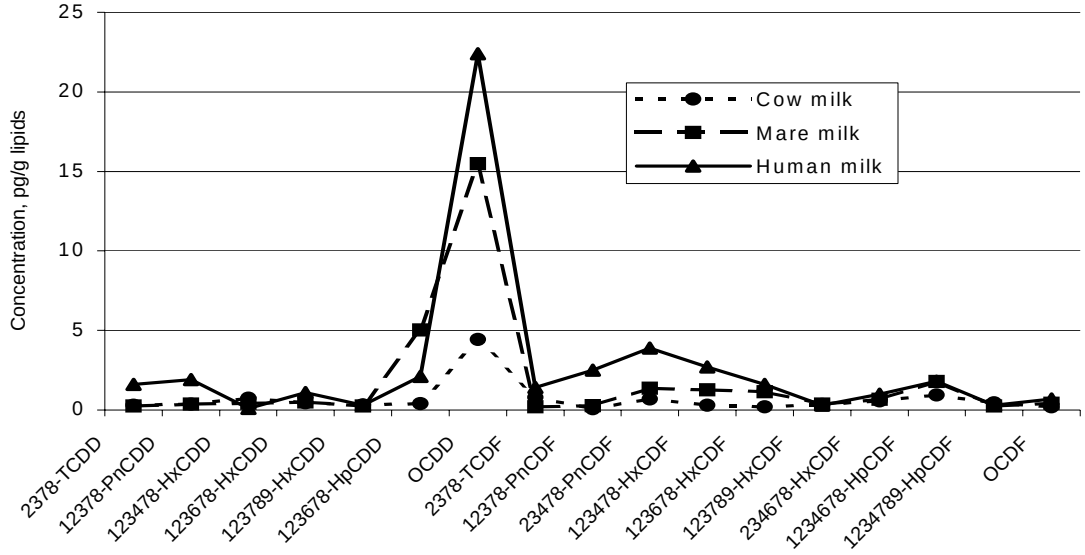

Table 2. PCDD/Fs in milk and meat of horses in comparison with the data for human breast milk and cows' milk from a rural district, pg/g lipids

PCDD/FS	Cow milk	Mare milk	Human milk	House meat
2378-TCDD	0.3	0.26	1.6	<0.1
12378-PnCDD	0.38	0.36	1.9	<0.1
123478-HxCDD	0.75	0.42	0.4	<0.1
123678-HxCDD	0.45	0.49	1.1	<0.1
123789-HxCDD	0.33	0.24	1.3	<0.1
123678-HpCDD	0.39	5.02	2.1	<0.1
OCDD	4.43	15.49	22.4	22.1
2378-TCDF	0.8	0.2	1.4	<0.1
12378-PnCDF	0.07	0.28	2.5	<0.1
23478-PnCDF	0.7	1.37	3.9	<0.1
123478-HxCDF	0.3	1.26	2.7	<0.1
123678-HxCDF	0.2	1.13	1.6	<0.1
123789-HxCDF	0.35	0.38	0.3	<0.1
234678-HxCDF	0.58	0.68	1.0	<0.1
1234678-HpCDF	0.94	1.78	1.8	<0.1
1234789-HpCDF	0.45	0.24	0.3	<0.1
OCDF	0.21	0.41	0.7	0.25
Lipids. %	3.2	1.32	3.72	28
TEQ-WHO w.w.	**0.04**	**0.025**	**0.24**	**0.14**
TEQ-WHO, l.w.	**1.21**	**1.87**	**6.5**	**0.5**

DLPCBs were determined in human breast milk and in milk and meat of horses from the same rural district. Concentrations of 12 isomers PCB-WHO in animal and human milk differ more considerably than PCDD/Fs isomers. Difference in concentration of PCB-126 that is making the main contribution into TEQ samples may serve as an example.
Comparing the distribution of PCB isomers in milk and muscle tissue of horses one can see that some of them (105,114, 157,189) are concentrated in tissues more intensively than in milk. Probably this fact explains increased concentrations of the same isomers in human breast milk from this rural district due to many years of background exposure of people.
We did not find any considerable difference in samples of mares' milk and human breast milk from different rural districts. But comparison with PCBs concentration in breast milk of women from the city of Ufa living in the district near chemical plants, namely 5-20 times exceeding for some isomers (118,105, 156 and especially 123) permits to make a conclusion about pollution of the urban area near the plants that have large transformer substations.

Table 3. DLPCBs in mare milk and meat and human milk from rural and urban districts

DLPCBs, pg/g lipids	House-flesh	Milk mare	Human milk	
			rural	urban (Ufa)
33'44'-TCB (77)	47.16	4.93	7.36	52.08
344'5-TCB(81)	5.96	1.17	3.81	17.44
233'44'-PnCB (105)	1852.03	160.24	328.73	9686.19
2344'5-PnCB(114)	194.19	2.56	642.47	1927.41
23'44'5-PnCB (118)	5412.16	993.02	1595.93	34787.79
2'345'5-PnCB (123)	0.18	0.67	3.87	491.62
33'44'5-PnCB (126)	0.23	0.17	22.64	128.93
233'44'5-HxCB (156)	755.99	24.05	2317.69	6953.07
233'44'5-HxCB (157)	152.56	2.88	539.80	1619.39
23'44'55-HxCB (167)	388.22	6.30	648.93	1946.78
33'44'55'-HxCB(169)	1.37	2.23	6.65	19.95
233'44'55'-HpCB(189)	75.71	0.48	85.93	257.79
TEQ-WHO DLPCBs, pg/g lipids	**1.33**	**0.171**	**4.28**	**22.9**
TEQ-WHO DLPCBs, pg/g w.w	**0.052**	**0.002**	**0.16**	**0.92**

Comparison with the data on PCB concentration in human breast milk in Russian and Scandinavian cities (III round WHO)[1,2] allows for considering the background pollution of the region as inconsiderable but there is some difference of isomers 77, 105, 118 and 126 in the sample from Ufa characteristic for the industrial PCB – Sovtol earlier produced in Russia. So far we failed to state the causes of somewhat increased PCB #123 level.

References:

1. van Leewen FXR, Malish R. Organohalogen Compounds (2002), 56, 311
2. Yufit S.,van Leewen R., Malisch R., Samsonov D. Organohalogen Compounds (2002), 56, 333
3. Amirova Z., Kruglov E., Loshkina E., Khalilov R. Organohalogen Compounds (1999), 44, 75
4. Maystrenko V,. Kruglov E., Amirova Z., Khamitov R. Chemosphere (1998), 37, 9-12, 1699