PCDD/Fs AND PCBs-WHO LEVELS IN ADIPOSE TISSUE AND BREAST MILK FROM RUSSIAN CITIES

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Abstract
Data have been found on PCDD/Fs/PCBs content in adipose tissue of residents of a large industrial center in the Ural, Russia, the city of Perm (medium level is 21.1 pg TEQ PCDD/Fs per g lipids), which have been compared with those of Ufa and Chapayevsk, two best known zones of dioxin exposure in Russia. This corresponds to data for Chapayevsk (20.7 pg/g lipids) and is more than by two times lower than the data for Ufa (55.5 pg/g)[1]. Tendencies for PCBs are the same. PCDD/Fs/PCBs pollution in Perm is confirmed by examination of breast milk. Found values (6.83 pg TEQ PCDD/Fs /g of fat, 8.68 pg TEQ PCBs /g of fat) are making the average level for industrial cities of Russia: Magnitogorsk (7.16 pg TEQ PCDD/Fs /g of fat and 11.41 pg TEQ PCBs /g of fat), Tobolsk (7.68 pg TEQ PCDD/Fs /g of fat) and Karabash (7.64 pg TEQ PCDD/Fs /g of fat). An exception to this series is the city of Ufa where more than double excess of the regional background level of PCDD/Fs content has been registered, what confirms the existence of a PCDD/Fs active emission source. [2,3]

Introduction
The Stockholm Convention on POPs presumes research on PCDD/Fs and PCBs spreading and also assessment of risk to population health. Obtaining reliable data on exposure levels in different countries, in particular, data on experimental determination of true levels of biological tissues pollution of people is quite necessary for solution of these problems. Russia after signing the Convention is undertaking some measures in this direction. Due to vast areas, nonuniform man-caused load in regions and shortage of experimental data the problem of PCDD/Fs and PCBs monitoring in Russia is of top priority. Levels of human biological tissue pollution are rather good markers of PCDD/Fs exposure in different areas. It is known that toxicants related to POPs group are accumulated in biological tissue (fat) and are in equilibrium concentration in blood during the whole life. Especially high concentration of POPs is observed in tissues of people between 50 and 70 years old and it is the evidence to the history of PCDD/Fs and PCBs exposure in the studied region. PCDD/Fs and PCBs level of pollution accumulated to the age of 20-30 is estimate by the level of breast milk pollution. The cities of Russia that we've studied are characterized by different level and character of industrial load, the history of industrial development, the number of population and as a result the level of people' exposure (Table 1).

Table 1. **Characteristics of studied cities of Russia**

Cities	Perm	Ufa	Chapayevsk	Tobolsk	Karabash	Magnitogorsk
Geographical location	North Ural	South Ural	Povolzhye	West Siberia	South Ural	South Ural
Population	990 200	1 200 000	71 000	104 800	16 100	427 500
Administrative status	Administrative center of the Perm Region	The capital of the Republic of Bashkortostan	A city in the Samara Region	Industrial center, Tyumen Region	Industrial center, Chelyabinsk Region	Industrial center of the Chelyabinsk Region
Area	798 km^2	753.7 km^2	187 km^2	222 km^2	68.6 km^2	375.8 km^2
Industrial load	Chemical, oil-chemical and fuel industry	Chemical, oil-chemical industry	Chlorine chemistry	Chemistry and oil chemistry	Copper production	Ferrous metallurgy
PCDD/Fs exposure sources	Emission of chemical and oil chemical plants	2,4,5-T, 2,4-D, Cl_2, TCP production	Chemical weapons production	Emission from chemical plants	Emission from non-ferrous metallurgy plants	Emission from ironworks

Materials and Methods

Objects for analyses were breast milk samples from 30 women – permanent residents of Karabash, from 18 residents of Tobolsk, 40 residents of Perm and 73 residents of Ufa. Samples were taken in compliance with recommendations of WHO, data given in questionnaires confirm adequacy of sampling. None of the women had ever been connected with unfavorable working conditions at chemical plants and all of them had been living in these cities for 5 years.

Peculiarities of adipose tissue sampling in Ufa and Chapayevsk were described in our paper of 2005. [1] Adipose tissue from Perm was sampled with laparotomy at gynecology departments of city hospitals for a period from September 2006 to February 2007.

PCDD/Fs content in adipose tissue of people living in Perm has been determined in 4 pool samples of fat taken from 10 donors each. Laparotomy in all cases was quite necessary due to pathology that required surgical operation. Laparotomy was carried out with the purpose of: 7 cases - adnexectomy, 12 – hysterectomy, 16 – supravaginal amputation of uterus, 3 – tubectomy, 1 – myomectomy and 1 patient was subject to minor cesarean section at a small period of pregnancy due to premature detachment of placenta. All women provided written informed consent. Information obtained from the interviewer administered questionnaire included age, height, weight, occupational history, residential history, pregnancy history, life style (alcohol intake and tobacco usage). Average donor age was 47 years old.

Adipose tissue and human milk samples were analyzed at the laboratory of the Environmental Research Center, Ufa, using HRGC/HRMS. Target analytes included 7 PCDDs, 10 PCDFs, 4 non-ortho substituted polychlorinated biphenyls, and 8 mono-ortho substituted PCBs. Individual adipose tissue samples of 20-30 g were frozen at -20^0C and kept until analyzing. Standard solutions C^{13} – PCDD/Fs (CIL, EDF 8999-4) and C^{13} – PCBs (Wellington) were introduced into the samples.

Extraction of the fat sample (10g) was made by the mixture of methylene chloride/hexane=1/1 with 5% ethyl ether. Extraction of the milk sample (50g) was made by the mixture of methylene chloride/hexane=1/1. The extract was concentrated to lipids. The amount of lipids was determined gravimetrically then lipids were solved in a mixture of solvents and cleaned with SiO_2*H_2SO_4 (40%). The extract was purified from lipids, proteins, steroids with the use of a preparation column Envirogel™ GPC Cleanup (Waters) separating the fractions containing PCDD/Fs and PCBs. Registration and measurement were carried out in compliance with the Methods US EPA 1613 and 1668 using the measurement system Autospec-Ultima (10000), RTX-DIOXIN, 60m. The recovery was 57-100% depending on PCDD/Fs/PCBs isomer.

Results and Discussion

The results of analyzing PCDD/Fs and PCBs content in adipose tissue and breast milk are given in Table 2.

As it follows from Table 2, PCDD/Fs content in adipose tissue of Perm (from 15.8 to 35.6 pg TEQ PCDD/Fs/g lipids and medium level for the city is 21.1 pg TEQ PCDD/Fs/g lipids) and Chapayevsk (20.7 pg TEQ PCDD/Fs/g lipids) residents is at the same level while for Ufa residents this value (55.5 pg TEQ PCDD/Fs/g) is by more than 2 times as much. TEQ-WHO DLPCBs in Perm is about 20 pg/g lipids, in Chapayevsk and Ufa – 58.8 and 125.2 pg/g lipids respectively. Thus data for Perm and Chapayevsk may be considered as medium level for industrial cities of Russia and levels found in Ufa confirm a conclusion about the existence of a dioxin pollution zone and of exposure to dioxin not only of the cohort of exposed workers described earlier in our papers[4,5] but of the whole Ufa population.

Medium level of PCDD/Fs and PCBs pollution in Perm is confirmed by examination of breast milk of 40 donors. Found values for Perm (PCDD/Fs – 6.83 pg/g of fat, PCBs-WHO 8.68 pg/g of fat) are making the average level for industrial cities of Russia. Data are given for other cities of Russia: Magnitogorsk (n=25; 7.16 pg TEQ PCDD/Fs /g of fat and 11.41 pg TEQ PCBs/g of fat), Tobolsk (n=18; 7.68 pg TEQ PCDD/Fs/g of fat and Karabash (n=30; 7.64 pg TEQ PCDD/Fs /g of fat). An exception to this series is the city of Ufa where for 5 years of analyzing more than 70 individual breast milk samples (n=73, 18 pg TEQ PCDD/Fs /g of fat) more than double excess of the regional background level (6 pg TEQ PCDD/Fs /g of fat) of PCDD/Fs content has been registered, what confirms the existence of a PCDD/Fs emission source[2,3]. Analysis of data on PCDD/Fs and PCBs content in breast milk reveals similar tendencies though PCBs content in breast milk is equivalent to dioxin pollution in Ufa as well. Probably in this case age difference is significant: 55 years old for fat tissue donors and 25 – for breast milk donors. It may also be explained by reduction of current PCB exposure in Ufa in comparison with previous decades.

Table 2.

PCDD/Fs and PCBs-WHO content in adipose fat tissue and breast milk of Russian cities residents

Human fat tissue				**Breast milk**				
City of Russia	Perm	Chapayevsk	Ufa	Perm	Magnitogorsk	Karabash	Tobolsk	Ufa
Donors (number)	40	6	6	40	25	30	18	73
2378-TCDD	4.40	3.72	18.63	1.66	2.33	1.56	2.16	7.44
12378-PnCDD	4.26	6.46	22.77	1.91	0.51	1.88	1.73	6.15
123478-HxCDD	8.12	14.05	8.88	0.08	2.02	ND(0.04)	0.24	1.53
123678-HxCDD	1.56	16.68	9.32	1.87	4.00	2.44	2.76	3.25
123789-HxCDD	ND(0.1)	1.59	3.60	0.12	0.94	ND(0.03)	0.72	1.12
1234678-HpCDD	11.10	11.24	12.19	3.25	5.59	2.74	4.20	4.22
OCDD	33.55	39.16	45.73	11.98	23.13	10.58	22.66	20.9
2378-TCDF	9.77	6.15	4.89	2.61	1.05	0.04	0.81	0.98
12378-PnCDF	7.31	2.13	1.85	0.57	0.91	1.01	1.55	ND(0.2)
23478-PnCDF	14.40	12.86	19.56	4.05	5.67	6.65	5.40	6.27
123478-HxCDF	12.02	6.87	7.94	2.76	3.73	2.53	2.38	3.17
123678-HxCDF	9.67	7.36	5.93	2.04	0.08	2.07	1.70	2.05
123789-HxCDF	2.94	ND(0.1)	1.29	0.23	0.08	ND(0.02)	0.10	0.21
234678-HxCDF	2.22	1.82	2.85	1.88	1.71	0.64	0.72	1.95
1234678-HpCDF	12.77	1.55	3.40	1.77	2.57	1.32	1.45	2.32
1234789-HpCDF	1.97	2.16	1.86	0.08	ND(0.05)	0.21	0.50	0.35
OCDF	8.90	1.05	0.99	0.1	0.09	0.81	1.57	0.16
TCB(77)	35.10	13.09	47.56	10.63	16.87	NA	NA	6.62
TCB(81)	ND(0,1)	13.48	12.42	22.25	7.74	NA	NA	4.23
PnCB(105)	18380.14	12513.2	26585.0	6273.8	12232.7	NA	NA	6509.7
PnCB(114)	4123.37	3963.44	11060.6	1169.54	1775.0	NA	NA	1235.8
PnCB(118)	59590.12	55018.6	94823.9	19916.7	39973.85	NA	NA	23452
PnCB(123)	919.61	815.20	1766.67	342.1	664.39	NA	NA	344.68
PnCB(126)	ND(0.1)	162.47	253.37	30.28	ND(0.1)	NA	NA	51.88
HxCB(156)	15840.9	20418.95	41283.6	3639.43	8285.53	NA	NA	5585.9
HxCB(157)	3128.37	4237.79	9251.95	898.34	1812.38	NA	NA	1258.8
HxCB(167)	3712.41	4758.51	8811.61	999.34	2018.09	NA	NA	1167.9
HxCB(169)	27.52	51.66	78.16	11.9	14.28	NA	NA	13.73
HpCB(189)	458.35	1343.22	1701.17	144.07	232.65	NA	NA	196.42
TEQ PCDD/Fs	**21.13**	**20.68**	**55.51**	**6.83**	**7.16**	**7.64**	**7.68**	**18.23**
TEQ PCB	**20.1**	**37.45**	**69.66**	**8.68**	**11.41**			**12.43**
Sum TEQ PCDD/F/PCBs	**41.1**	**58.1**	**125.2**	**15.51**	**18.57**			**30.66**

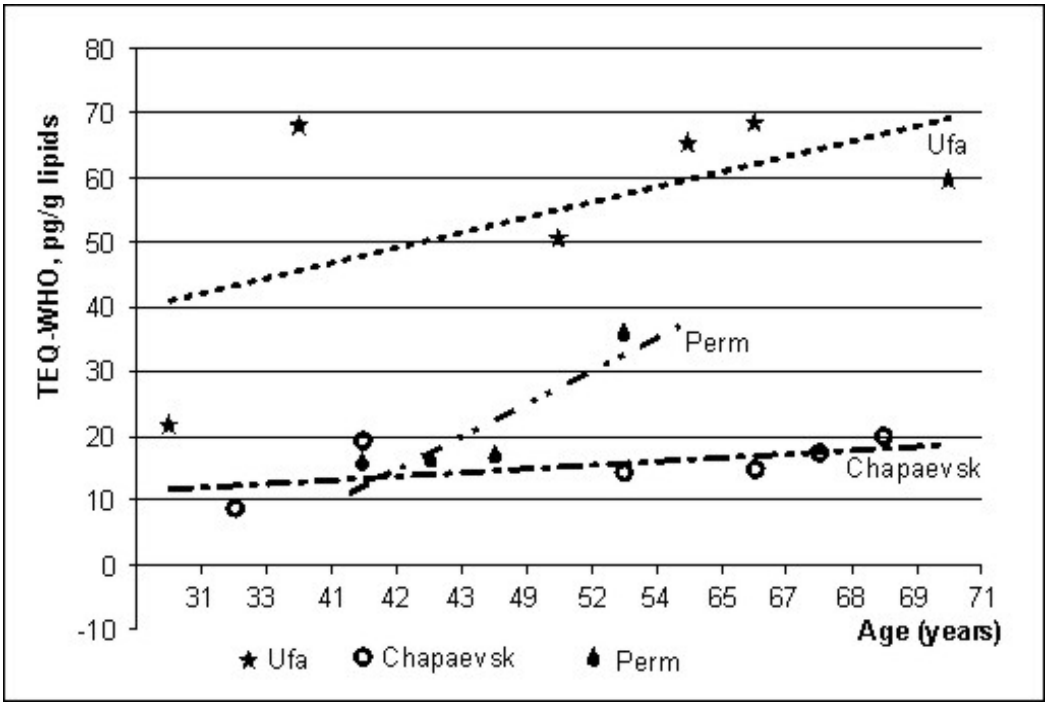

Figure 1. **Age - dependent PCDD/Fs level in the samples of adipose tissue from the cities of Russia**

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