DIOXINS AND PCBs IN MEAT AND MILK FROM RUSSIAN REGIONS AND IN IMPORTED PRODUCTS FROM GERMANY DURING THE DIOXIN INCIDENT

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Introduction

At the present time the dioxin and PCBs pollution is global, there are practically no countries or territories without local emission sources. Transboundary transfer of toxicants also makes its contribution. But the main cause of polluting animal meat is the use of additives (both vegetable and mineral) to feeding stuff.

Now and then there occur incidents with anthropogenic dioxin pollution of feed stuff and consequently of meat and fat of cattle, swine and poultry. Thus there was pollution of poultry in Belgium (1999) that was caused by the use of PCB and dioxin polluted fats, dioxin pollution of pork in Belgium (2005-2006), in Chile (2008), beef and pork in Ireland in 2008 and there also was the incident with contamination of pork and poultry in Germany (November-December 2010).

Monitoring of livestock products (meat and milk) pollution with dioxins and PCBs is carried out in different countries including Russia[1-3]. But there is no regular control of imported products in Russia.

The fact is that the information on the dioxin pollution of food stuff comes to Russia from abroad, sometimes with a delay. Thus pork and pork fat produced in Germany after November 1, 2010, had got to the Russian market because limitations for import were introduced only on January 20, 2011.

The products that had already come to meat processing and packing factories were detained until clarifying the situation with the dioxin pollution. The paper presents the results of studying 11 lots of pork and pork fat that were to be additionally checked because of the prohibition of their usage. According to the EU norms the determination of PCDD/Fs and PCBs-WHO was made in the same samples.

In whole, production of 1.5 thousand enterprises of Germany is supplied to Russia. The import of pork from Germany in 2010 was about 130-140 thousand tons. The German import to Russia covers 33% of byproducts and over 40% of pork fat of heat-resistant sorts (to 450 thousand tons per year).

A similar situation is observed with control of domestic products. There are only occasional data in regions of Russia. The concentration of dioxin in meat and dairy products is not under control in the country. Trace amounts only of two groups of POPs are being checked: isomers ant metabolites of DDT and HCH. On September 1, 2008 the Resolution of the Government sanitary inspector of the RF dated July 16, 2008 No. 43 entered into force. The Resolution introduced control of dioxins in meat and dairy products[4]. These norms correspond to the European ones only by dioxins, they do not include PCBs, but they still present a progressive step in the way of providing safety of food products.

In the Russian Federation there are regions that due to peculiarities of their industrial and military technogenesis demand special attention directed to the safety of food products in terms of persistent organic pollutants (the aftermath of phenoxy herbicide production, the presence of chlorine chemistry objects, uncontrolled burning of oil hydrocarbons, fires etc.).

These regions are Bashkiria and the Chechen Republic – large-scale producers of livestock products (meat and dairy) that mainly provide their own demand. The most convenient matrixes for study are milk and muscular tissues of domestic animals sampled in private farms at footloose pasture what permits to assess all probable ways of POPs intake. For determination of the background level of PCDD/Fs and PCBs in milk and tissues of animals and for an indirect assessment of agricultural areas of two large regions of Russia the pollution level of beef and pork from 16 private farms and of whole milk from 6 districts of Bashkiria was analyzed. In 6 districts of Chechnya beef and milk were sampled. Pork is not produced in the Chechen Republic.

Materials and methods

In milk and meat samples 29 isomers of PCDD/Fs and PCBs-WHO were determined by the method of a high resolution chromato-mass-spectrometry in compliance with the methods US EPA 1613 and 1668[5,6].

The isomer-specific analysis of PCDD/Fs and PCBs was carried out with the use of a measuring system consisting of a chromatograph Carlo Erba 8035 and a high resolution mass spectrometer Autospec-Ultima (VG) in the mode of electronic impact (36 ev) with the resolution > 10.000. The absolute detection limit of 2,3,7,8-TCDD made 10 fg. Separation of PCDD/F and PCB isomers was performed in a non-polar capillary column Restek RTX-Dioxin 60 m long. The results of PCDD/F and PCB-WHO determination were presented in an international scale of toxicity coefficients (TEQ-WHO) with the use of the system of toxicity equivalency factors (WHO-TEF 1997).

Results and discussion

Monitoring of biological objects for the content of PCDD/F and PCB-WHO in two large regions of Russia has shown that the pollution level of beef samples taken in districts of Bashkiria and Chechnya does not exceed the norms of the permissible concentration for the RF and the norm for the EU (less than 4.5 pg/g lipids by the sum total of TEQ PCDD/Fs and PCBs). More rigid norms for pork (2.5 pg/g lipids of the sum total of PCDDs/Fs/PCBs) are also sustained in products of Bashkiria. The analysis of caw milk has shown that in whole all samples comply with the norms for the RF and the EU but still bear traces of pollution with dioxins and PCBs. The level of this trace pollution changes depending on the region.

The concentration of dioxins in samples from Chechnya is somewhat higher than that in samples from Bashkiria, probably due to a higher content of fat in meat samples from Bashkiria – 12.8% while the content of fat in samples from Chechnya is by 2 times lower (6.3%). However a similar correlation of TEQ PCDD/F is observed also for caw milk samples what testifies to the existing difference in the background dioxin pollution level of these territories.

In the isomer specter of PCDD/Fs in samples from Chechnya there prevails a group of polychlorinated dibenzofurans – companions of burning processes what may be connected with the effects of large-scale fires at oil fields and accidents at oil pipelines.

In terms of PCBs a reverse correlation is observed: the concentration of PCBs in meat and milk samples from Chechnya is considerably lower what is obviously connected with the level and the history of the anthropogenic load of both regions. In Bashkiria there are powerful energy plants with the equipment of high capacity using PCB-containing oils, in Chechnya there was a pause of almost 10 years before the beginning of rehabilitation of industrial production.

Table 1. PCDD/Fs and PCBs in samples of meat and cow milk from Russia

TEQ PCDD/Fs and PCBs in samples of meat and milk from Bashkiria, pg /g lipids						
Sample	***Beef***		***Pork***		***Milk***	
POPs	**PCDD/Fs**	**PCBs**	**PCDD/Fs**	**PCBs**	**PCDD/Fs**	**PCBs**
Number of samples	16		12		6	
Mean	1.18	1.16	0.28	0.44	1.3	1.26
Max	2.59	3.43	0.55	2.32	2.48	2.36
Min	0.45	0.3	0.06	0.06	0.8	0.68
Median	0.99	0.78	0.24	0.19	1.11	0.95

TEQ PCDD/Fs and PCBs in samples of meat and milk from Chechnya, pg/g lipids				
Sample	***Beef***		***Milk***	
POPs	**PCDD/Fs**	**PCBs**	**PCDD/Fs**	**PCBs**
Number of samples	5		6	
Mean	1.81	0.31	2.41	0.75
Max	2.92	0.63	4.51	0.66
Min	0.71	0.16	1.32	0.32
Median	1.69	0.26	2.04	0.66

In meat samples mainly hepta- and octa-isomers of dioxins and furans are detected; 2,3,7,8-TCDD (a most toxic isomer) is found only in 30% of beef samples, but practically in all pork samples (only from Bashkiria). Among PCBs the indicator isomers are prevailing, their concentration differs by 3-5 times depending on the region.

Table 2. PCDD/Fs/PCBs in beef samples from two regions of Russia (pg/g lipids, mean)

PCDD/Fs	Bashkiria	Chechnya	PCBs-WHO	Bashkiria	Chechnya
2378-TCDD	0.40	0.55	33'44'-TCB(77)	22.28	6.31
12378-PnCDD	0.22	0.42	344'5-TCB(81)	2.91	0.61
123478-HxCDD	0.54	0.15	233'44'-PnCB(105)	857.5	132.5
123678-HxCDD	0.17	0.15	2344'5-PnCB(114)	64.24	11.7
123789-HxCDD	0.14	0.2	23'44'5-PnCB(118)	2470.84	433.1
123678-HpCDD	0.61	0.78	2'345'5-PnCB(123)	46.23	7.78
OCDD	4.59	1.99	33'44'5-PnCB(126)	6.84	2.83
2378-TCDF	1.29	1.35	233'44'5-HxCB(156)	149.17	35.91
12378-PnCDF	0.36	1.99	233'44'5'-HxCB(157)	37.33	8.96
23478-PnCDF	0.39	1.11	23'44'55'-HxCB(167)	65.25	14.07
123478-HxCDF	0.41	1.87	33'44'55'-HxCB(169)	0.75	0.35
123678-HxCDF	0.27	0.3	233'44'55'-HpCB(189)	6.57	2.05
123789-HxCDF	0.3	0.13	**TEQ-WHO**	**1.81**	**0.31**
234678-HxCDF	0.25	0.15			
1234678-HpCDF	0.42	0.46	In case of non-detectable isomers the calculations were made with the use of ½ of LOD.		
1234789-HpCDF	0.34	0.38			
OCDF	1.82	1.7			
TEQ-WHO	**1.18**	**1.16**			

In general the environmental situation in the Republic of Bashkortostan and in the Chechen Republic in terms of PCDD/Fs and PCB-WHO pollution of meat and dairy products may be assessed as relatively safe but the presence of toxicants in tissues and milk of animals testifies to the existence of local pollution sources.

Table 3. PCDD/Fs/PCBs in samples from Russia (Bashkiria) and from Germany (pg/g lipids, mean)

PCDD/Fs	Russia	Germany		PCBs-WHO	Russia	Germany	
Sample	pork	pork	pork fat	Sample	pork	pork	pork fat
Number	12	5	8	Number	12	5	8
2378-TCDD	0.15	0.13	0.05	33'44'-TCB(77)	8.43	10.17	3.72
12378-PnCDD	0.08	0.07	0.04	344'5-TCB(81)	1.0	2.45	0.24
123478-HxCDD	0.06	0.12	0.04	233'44'-PnCB(105)	415.15	469.77	212.26
123678-HxCDD	0.10	0.12	0.06	2344'5-PnCB(114)	26.00	22.53	12.12
123789-HxCDD	0.08	0.09	0.04	23'44'5-PnCB(118)	840.97	865.37	441.73
123678-HpCDD	0.25	0.34	0.38	2'345'5-PnCB(123)	15.09	18.16	7.3
OCDD	1.38	4.35	2.15	33'44'5-PnCB(126)	0.04	4.34	0.85
2378-TCDF	0.74	0.71	0.42	233'44'5-HxCB(156)	66.41	31.06	17.48
12378-PnCDF	0.31	0.41	0.26	233'44'5'-HxCB(157)	16.06	6.16	5.1
23478-PnCDF	0.18	0.11	0.06	23'44'55'-HxCB(167)	18.89	9.11	6.09
123478-HxCDF	0.48	0.76	0.30	33'44'55'-HxCB(169)	0.05	0.05	0.05
123678-HxCDF	0.09	0.23	0.16	233'44'55'-HpCB(189)	2.61	4.02	105.17
123789-HxCDF	0.08	0.12	0.06	**TEQ-WHO**	**0.19**	**0.92**	**0.27**
234678-HxCDF	0.08	0.08	0.03				
1234678-HpCDF	0.22	0.22	0.08	In case of non-detectable isomers the calculations were made with the use of ½ of LOD.			
1234789-HpCDF	0.20	0.14	0.09				
OCDF	0.30	0.91	0.47				
TEQ-WHO	**0.28**	**0.50**	**0.25**				

The results of the analysis of German pork and pork fat in comparison with similar measurements from 12 districts of Bashkiria are given in Table 3.
Pork (boneless, shoulder) and pork fat were supplied under codes DE EZ 906 EG, DE EZ 917 EG, DE NI EUZ 518 EG, PE EZ 906 EG, DE NI EUZ 201 EG DERPEZ 306 EG, PE NI EUZ 532 EG by providers D&S Fleisch GmbH, B&C Tonnels Fleishwerk, MUR Logistik GmbH.
No excess norm of the EU and the RF was found in lots of pork and pork fat from Germany supplied to Privolshsky and Uralsky federal districts of Russia in Nov.-Dec. 2010. It was worth mentioning that pork samples from Russia (Bashkiria) contain considerably lower concentrations of PCBs.

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