CHAPAEVSK, RUSSIA: POPs IN THE ENVIRONMENT, FOOD, BREAST MILK AND BLOOD OF LOCAL RESIDENTS. RECOMMENDATIONS FOR ENVIRONMENTAL REMEDIATION

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Introduction.
Environmental pollution and public health in the town of Chapaevsk have been studied since 1994, when local administration put forward a corresponding initiative. Chemical plant is the principal source of emissions of dioxins, gamma-hexachlorocyclohexane (lindane) and hexachlorobenzene (HCB) in this town. This plant produced chlorinated organic pesticides between 1967 and 1987, and later began production of liquid chlorine, dichloropropionic acid, methyl chloroform, vinyl chloride, and pentachlorophenol. In 1994, concentrations of dioxins in ambient air, measured within 3-4 km from the plant boundaries, exceeded 2 MACs every 7-10 days per year. Concentrations of PCDD/PCDFs (I-TEQ) in the soil near the plant were 141 ng/kg, gradually decreasing to 37 ng/kg at the distances 2-7 km, and down to 4 ng/kg at the distances 7-10 km. Besides dioxins, local soils were contaminated by chlorinated organic pesticides [1,2,3].

Materials and Methods
Analysis of hen's eggs was performed using GC-HRMS technique. Eggs were boiled in distillated water directly after sampling and send to the laboratory were stored refrigerated till analysis. After removing of shell, eggs were mixed with anhydrous magnesium sulfate; subsample (~10 g) was spiked with $^{13}C_{12}$-labeled standard and extracted by 150 ml acetone:hexane (20:80 v:v) at in high-performance solvent extraction system. Extracts was cleared by acid silica and on alumina column, if needed. Each analytical run contained a method blank. All solvents, sorbent and reusable glassware were tested to ensure the absence of contaminants and interference. Analyses were performed on GC-HRMS (Hewlett Packard HP 6890 Plus, Finnigan MAT 95XP) at resolution 10000. Others analysis were down by usage routine methods indicated in corresponding papers.

Food. Local population in Chapaevsk, like in many other small Russian towns, dwells on locally grown foods (vegetables, fruit, eggs, milk, meat, and poultry). Fishing in the nearby water reservoirs is also popular. According to surveys of local residents, over 70% of them eat locally produced milk and dairy products, over 50% - eat locally produced meat and eggs (most people eat eggs 4 – 6 times a week)[4]. Besides, fishing is very popular there, and many fishing areas are situated in the immediate vicinity from the chemical plant. About 80% of population regularly eats locally caught fish.

In Chapaevsk Dioxins and PCBs were first found in cow milk and vegetables in 1998. Dioxins were found in all samples of cow milk, with concentrations of 2,3,7,8-TCDD in the range 17,3 – 61,0 pg/g lipids, 1,2,3,7,8-PeCDD – 61,0 pg/g lipids WHO-TEQ. In most cases 1,2,3,4,7,8- and 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD were detected, as well as hexachlorinated furans. PCDD/Fs level in milk exceeded Russian allowable level - 5,2 pg/g lipids I-TEQ. In vegetables and fruit 0,002-10,6 pg/kg WHO-$TEQ_{PCDD/F}$ were found. The highest concentrations of these substances were found in cabbage - 10,6 pg/g, tomatoes - 0,48 pg/g and 2,0 pg/g in carrots. These vegetables were grown in household plots within town limits [2,3].

In the second study, PCBs, lindane and HCB were found in food in 2005, within the framework of IPEN program of comparative study of chlorinated organic substances in chicken eggs[5]. In the given study eleven

samples from local farms and market Chapaevsk were analyzed by Institute of Problems of Ecology and Evolution. Results are presented in Table 1.

The results of POPs measurements in chicken eggs were plotted against the distance of household farms from the chemical plant. POPs concentrations in locally produced eggs were 24-42 times higher than in the eggs from other regions of the Russian Federation. The profile of PCBs was typical for man-caused pollution. But congeners patterns was not stable, and it is possible to conclude that contamination consists at least from two factors - Sovol/Sovtol mixture and trichloro-biphenyl. The ratio of concentrations PCB-28/31 and PCB-52 were wide varied; the first one was typical for “light” mixtures of PCBs, while the second one was typical for moderately chlorinated mixtures. The elevated concentrations of PCB-180 could also indicated contribution of "heavy-PCBs" mixtures.

Among DDT metabolites, the most significant differences were established in concentrations of p,p'-DDE. The difference in concentrations of Lindane and HCB in locally produced and imported eggs was the highest. Concentrations of Lindane и HCB in local eggs was higher by factors of 54,2 and 69,6, correspondingly, than that in imported eggs. The contamination level depended upon the distance from the chemical plant. WHO-TEQ_{PCBs} were 3,5 times higher in the eggs taken from the farms next to the plant. The sum of DDT and lindan, in chicken eggs did not show such significant differences. High concentrations of HCB in chicken eggs were observed in the vicinity of the plant, which used to produce these substances in the past.

In the framework of this project, POP concentrations were studies in chicken eggs in the city of Novomoscowsk and others Russian territories. Novomoscowsk chemical works produced PCB oils; also was found that agricultural farms around the city heavily applied pesticides. In comparison with Novomoscowsk eggs, eggs from Chapaevsk had lower concentrations of PCB (by factor of 3.3, or 94 vs. 324 pg/g lipid), and lower concentrations of DDT sum (by factor of 8,6, or 502,3 vs. 4332 ng/g lipid). But concentrations of DDT and its metabolites in Chapaevsk eggs were higher in the eggs taken from the districts where this pesticide had been applied earlier. The differences in concentrations were 4 times for DDT, and 4 times for HCB, (DDT – 502,9 ng/g lipid vs. 126,0 ng/g lipid, HCB – 66,4 vs. 15,5 ng/g lipid).

Comparison of Russian data with the results of major international IPEN study, which involved 17 countries showed that concentrations of PCB in Russian eggs (taken from Chapaevsk and Novomoscowsk) was significantly higher than that in chicken eggs from Helwan, Egypt (11,74 ng/g lipid WHO-TEQ), Lucknow, India (9,40), Bolshoi Trostenec, Belarus (9,83)[6]. HCB content in the eggs taken from private farms of Chapaevsk and Novomoscowsk was higher (66,4 ng/g lipid), than that in the eggs taken from polluted regions of Helwan, Egypt (15,1), Bolshoi Trostenec, Belarus (4,7), Kovachevo, Bulgaria (25,5)[6].

Breast milk. Dioxin content in breast milk of Chapaevsk women was 42,26 pg/g lipids WHO-TEQ[3], which is higher than that in other regions of Russia and some other countries.

Blood. Women workers of Chapaevsk had the highest blood levels of dioxin, and local residents who lived near the plant also had elevated concentrations of dioxin in their blood, according to the study[2], commenced in 1997. The second study (1998) involved 24 blood samples. It also confirmed high blood levels of dioxin (61,2 pg/g lipids WHO-TEQs)[7]. Comparison of the results of these studies with the results of similar studies indicated that adult Chapaevsk residents had higher blood levels of dioxin than residents of other regions of Russia, and the residents of most countries. The third study was sponsored by Harvard School of Public Health and CDC. This study confirmed high concentrations of dioxins in blood of adolescents. Blood levels of dioxins were proportional to the age, and consumption of locally produced meat and fish. The children had the same proportions of dioxins, furans, and coplanar PCBs in total TEQs, as the adults from the previous study. The median (25^{th}, 75^{th} percentile) concentrations for total PCDDs, PCDFs and coplanar PCBs were 95,8 pg/g lipids (40,9, 144), 33,9 pg/g lipids (20,4, 61,8), and 120 pg/g lipids (77,6, 157), respectively. For WHO-TEQs, the median (25^{th}, 75^{th} percentile) for total PCDDs, PCDFs, and coplanar PCBs were 0,29 (0,1, 9,14), 7,98 (5,27, 12,3), and 7,39 (4,51, 11,9), respectively. Although TCDD was largely non-detectable, two boys had high TCDD levels (17,9 and 21,7 pg/g lipid). Elevated levels of dioxin-like compounds in serum were positively

associated with increased age, consumption of fish, local meats other than chicken, and inversely with weeks of gestation. The total TEQs among Chapaevsk adolescents were higher than most values previously reported in non-occupationally exposed populations of comparable or even older ages. Dietary consumption of local foods, as well as age and weeks of gestation, predicted dioxin exposure in this population [8].

Environmental rehabilitation efforts in Chapaevsk: dioxin clean-up

The results of abovementioned studies in Chapaevsk showed significant contamination of the environment by dioxins, and contributed to the decision of State environmental expertise to grant this town special status of "extremely polluted zone" (eleven Russian towns, and Chernobyl territory, have obtained this status). The town of Chapaevsk is characterized by difficult social and economic situation, and receives donations from the regional budget. In the framework of environmental remediation program, Chapaevsk receives regional and federal financing since 1999[9]. Bankruptcy of Chapaevsk chemical plant – the source of dioxin pollution – rendered it insolvent and incapable to finance environmental remediation measures.

There are several types of measures, financed through federal and regional programs of rehabilitation of Chapaevsk territory:

1. Protection of watersheds and surface water bodies (rivers and lakes):
   - Construction of flood prevention dam;
   - Construction of storm water disposal systems on the main roadways in the town.
2. Enhancement of drinking water quality: construction of new water supply network which takes water from the new underground source.
3. Clean-up of soils:
   - Remediation of soils contaminated by dioxins. Contaminated soil is disposed of at industrial landfill, and new soil is added in reclaimed territories.
   - The town bought new public cleansing vehicles.
   - Bushes are planted around the plant.
4. Improvement of public health;
   - Construction of new building of children health care center is being completed;
   - New preschool health-care center is being constructed out of the town limits;
   - Public health care centers received new equipment for diagnosing and treatment of local residents. Child death rates decreased in Chapaevsk.
5. The residents of the house next to the plant will be relocated to another residential block, which is being constructed now.

Local businesses temporarily received tax incentives.

Acknowledgments: The authors of this study thank Mr. N. Malakhov, the head of municipal administration, and Mr. V. Ivanov, the head of environmental department of Samara regional government, for their unfailing support.

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Table 1. PCB, Hexachlorobenzene, Hexachlorocyclohexane and DDT/DDE in chicken eggs, Chapaevsk city, ng/g lipid

	Location		Local farms - Distance from chemical plant	
	Local farms	Market	< 3 km, n=5	> 3 km, n=5
PCB-77	15 325	362.2	852.3	540.8
PCB-81	2 432	77.40	68.14	9.13
PCB-105	67 444	2 311	43 939	14 635
PCB-114	4 727	196.2	3 028	1 275
PCB-118	108 225	4 485	86 176	34 253
PCB-123	4 278	123.6	1 831	978.2
PCB-126	648.6	< LOD (15)	400.2	66.35
PCB-156	13 023	468.5	11 184	8151
PCB-157	2 650	109.8	2 304	1424
PCB-167	5 760	169.9	4766	3 297
PCB-169	136.9	< LOD (15)	10.55	24.17
PCB-189	1 353	7.63	739.5	1700
WHO-TEQ (PCB)	96.39	1.13	61.79	17.55
PCB-28/31	939 233	31 746	47 118	11 501
PCB-52	72 502	1 828	6 929	4 564
PCB-153	93 686	3 122	69 225	97 189
PCB-138	138 692	3 418	129 758	127 110
PCB-180	147 595	918.6	118 823	192 529
HCB	66 417	912.5	113 615	30 728
Lindane	252 183	4 651	259 106	268 721
o,p'-DDE	4 720	382.6	6 315	3 291
p,p'-DDE	372 393	3 632	366 527	427 059
o,p'-DDT	5 098	4 567	8 317	2 064
p,p'-DDT	120 639	92 225	143 837	72 753
Sum DDT and DDE	502 850	100 808	524 996	505 167