# CHLORINE INDUSTRY IN THE FORMER USSR, CHAPAEVSK, RUSSIA

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## Introduction

Molecular chlorine manufacturing and utilization was a significant part of the former USSR industry. Chlorine was absorbed practically in all industry branches including drinking water purification, plastics production and even manufacturing of solid-fuel engines for ballistic rockets manufacturing. Chlorine industry enterprises, as a rule, were combined into industrial complexes, including factories producing miscellaneous target products of civil and military purpose as well as auxiliary production of semi-finished products and raw materials, including molecular chlorine. Basic technology of chlorine manufacturing was and still is electrolysis using graphite electrodes. A considerable part of industrial waste was incinerated on the territory of production complexes. Furnaces with alkaline scrubber were used for burning of organic chlorine waste. Other waste materials were incinerated in furnaces equipped with low-effective cyclone dust separators. Wastes that are not subject to incineration were land-buried near the enterprises. Thus, there were a lot of dioxins emission sources, each of them having a specific profile. Besides, a perceptible contribution to general pollution by PCDD/Fs was made by the high capacity transformers where PCBs were applied.

Near plants the settlements and urban areas were located those inhabitants were engaged in gardening and farming. The furnace heating was used in houses that considering the elevated level of organochlorine compounds constituted an additional source of exposure. The ecological control in the former USSR assumed only emission of the “macro-components” control in which framework no attention was usually attributed to organic pollutants. Semi-military nature of the enterprises also facilitated to conceal medical statistics. After dissolution of the USSR some enterprises were closed, others have reduced their production output or were reorganized, though it didn’t always meant reduction of the environment pollution due to weakening of the State ecological control as well as uncontrollable dismantling and utilization of dangerous equipment, including the containing PCBs transformers.

Currently there are more than ten chlorine sites contaminated by PCDD/Fs and other POPs in Russia. These areas’ effective levels of pollution remain unknown. Before dissolution of USSR no research on evaluation of dioxins levels in the environment was carried out. Only at the end of 80$^{ties}$ the labs capable to analyzed dioxins level were established and the Federal program existing at the end of 90$^{ties}$ allowed to obtain single data from various regions of Russia. Now research is being conducted mainly due to activity of the local governments in several regions or International funds’s support. Multifunctional chlorine production centers in Sterlitomak, Volgograd, Sayansk, Usolye-Sibirskoe, Cheboksary, Ufa, Kemerovo, Bereznyaky, Dzerzhinsk, Chapaevsk may be classified as potential sources of POPs contamination. The sites of PCBs and transformers production, such as Novomoskovsk and Serpukhov, as well as pulp and paper plants in Arkhangelsk, Kotlass, Amursk and Svetlogorsk, also can be identified as potential Russian “hot-spots”.

The long-term research was carried out in Chapaevsk and Ufa only. Chlorine (50 thousand tons/annual) benzol, phenol, hexachlorobenzene (HCB), pentachlorophenol (PCP), hexachlorocyclohexane (HCH), polychlorcamphene (toxaphen), dichlorethane, vinyliden chloride, acetic acid, monochloracetic acid, propionic acid, phosphorus trichloride, methyl chloroform and hexachloroethane were produced at Chapaevsk plant. Thus, there was a complete set of typical sources of POPs emission for chlorine industry. The purpose of this study was evaluation of the PCDD/F/PCB/pesticides levels in Chapaevsk’s samples of environment, food and chemical enterprises areas.

## Material and Methods

5 samples of urban soil, 21 subsamples of plant soil, 6 samples of outdoor plasters, two - of house dust, three samples of air collected using high-volume active sampler, one air sample collected using PUF passive sampler (one filter exposed at 30 days), 4 of fish, 9 samples of eggs and 21 subsamples of human milk were collected in 2005-2007. 21 soil subsamples from plant's area, covered 822.86 acres, were pooled. 11 and 10 individual milk samples were pooled into two samples. Individual and pooled samples were analyzed using standard analytical methods at the Laboratory of Analytical Ecotoxicology of the Institute of Ecology and Evolution by HRGC/HRMS.

## Results and Discussion

The results of PCDD/F/PCB/pesticides level analysis are presented in Table 1 and PCDD/Fs level - in Table 2. In the majority of samples PCP and HCB production consequences can be identified based on typical large contribution of OCDD and congeners OCDD/OCDF/HpCDDs specific ratio. Contribution of OCDD/OCDF/HpCDDs in total TEQ in most of the samples ranges within 15-25 %. Thus, the source of basic dioxin pollution in the city is not related to the process of organochlorine compounds synthesis, but other sources of emission. Incinerators for different types of waste and electrolytic production of chlorine using of graphite electrode can be identified as such sources of emission. Due to lack of experimental data regarding emission level from those sources and significant discrepancies of PCDD/Fs profiles in different processes of incineration currently it is difficult to assess the contribution of each source with a high reliability degree. Nevertheless, the following qualities can be identified based on data presented in the Table 1:

- large contribution of TCDF and PeCDFs in total TEQ;
- total concentration of PCDFs no more than in 3-5 times exceeds concentration of 2,3,7,8- substituted congeners;
- low contribution of high-chlorine furans (except OCDF which is a result of HCB/PCP production).

Such signs, as a rule, are not typical for incineration of organochlorine compounds, though existence of such sources of city contamination is obvious. The similar profiles were observed with some deviations when analyzing waste of graphite electrode and technical PCBs that were not produced in Chapaevsk was done, however could be formed as admixtures at chlorination of natural biphenyls, that probably justifies high level of PCBs in biological objects. Thus, the primary sources of Chapaevsk area's high contamination could be identified as the following: 1) production of organochlorine compounds; 2) production of chlorine; 3) incineration of waste. At that, contribution of organochlorine compounds production amounted to no more than 25% of the total pollution.

The level of PCDD/Fs detected in external wall's plaster of buildings demonstrates the level of the city's contamination in the past; and the profile is similar to the same that was detected in soils. There is a significant difference of PCDD/Fs profiles in air samples collected during wet weather in comparison with the soil samples. The air pollution can be attributed more to incineration's and vehicle's emission products. In general, the level of dioxins contamination of the Chapaevsk city is typical for many industrial territories, both in Russia and in other countries. However peculiarity of Chapaevsk is that the contaminated territories are used for habitation and agriculture. The high levels of PCDD/Fs in eggs, house dust and human milk demonstrate the high risk and high population's exposure to these pollutants. Biological samples' analysis proved a high level of most of the samples contamination, at that no correlation between $TEQ_{PCDD/Fs}$ and PCBs was identified, but at the same time there is a correlation between concentration of HCB and WHO-$TEQ_{PCB}$. Besides, the results of hen's eggs samples analysis have shown one more serious problem of modern Russia – there was a medium level of PCDD/Fs, but an excessive level of PCBs in one sample collected at the most remote from the enterprise spot. It can be attributed to uncontrolled dissemination of pollutants following the contaminated by PCBs equipment dismantling.

Thus, using Chapaevsk area as an example, we can suppose that any center of chlorine industry of the former USSR is contaminated by dioxins and other POPs as a "hot-spot". Further research and rehabilitation programs for contaminated areas should be undertaken in these sites.

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**Table 1. Concentrations of PCDD/F/PCBs and organochlorine pesticides in Chapaevsk samples.**

| | Egg, pg/g lipid | | | | Human milk, pg/g lipid | | Fish, pg/g f.w. | |
|---|---|---|---|---|---|---|---|---|
| | >3 km (n=4), mean (min-max) | < 3 km (n=3) | High PCDD/Fs | High PCBs | < 3 km (11 subsamp.) | > 3 km (10 subsamp) | Crucian carp | Pike, (n=3) |
| 2,3,7,8-D | 1.41 (0.35-3.22) | 4.65 | 38.9 | 1.23 | 2.60 | 1.36 | 47.2 | 0.10 |
| 1,2,3,7,8-D | 4.74 (0.9-13.1) | 7.98 | 117 | 0.83 | 3.24 | 1.39 | 27.7 | 0.07 |
| 1,2,3,4,7,8-D | 4.71 (1.33-12.0) | 9.86 | 109 | 1.35 | 2.42 | 1.34 | 36.6 | 0.07 |
| 1,2,3,6,7,8-D | 12 (2.36-30.5) | 25.2 | 248 | 3.52 | 6.10 | 2.72 | 73.1 | 0.07 |
| 1,2,3,7,8,9-D | 5.75 (1.02-17.0) | 9.47 | 58.6 | 1.12 | 1.15 | 0.45 | 9.32 | 0.02 |
| 1,2,3,4,6,7,8-D | 26 (5.82-74.2) | 51.1 | 390 | 7.81 | 3.23 | 2.67 | 34.4 | 0.05 |
| OCDD | 24.4 (10.1-55.7) | 50.1 | 628 | 15.1 | 16.0 | 24.0 | 7.47 | 0.34 |
| 2,3,7,8-F | 10.4 (2.51-20.9) | 9.03 | 51.3 | 9.35 | 1.34 | 0.43 | 0.52 | 0.36 |
| 1,2,3,7,8-F | 11.1 (1.65-33.3) | 7.84 | 69.1 | 4.91 | 4.30 | 0.19 | 0.46 | 0.04 |
| 2,3,4,7,8-F | 16.4 (1.63-53.1) | 6.67 | 56.8 | 6.56 | 11.8 | 4.29 | 8.40 | 0.07 |
| 1,2,3,4,7,8-F | 18.7 (1.87-63.0) | 15.5 | 265 | 4.20 | 18.1 | 3.59 | 19.9 | 0.04 |
| 1,2,3,6,7,8-F | 15.9 (0.97-58.4) | 5.80 | 88.7 | 3.09 | 4.03 | 1.07 | 3.22 | 0.02 |
| 2,3,4,6,7,8-F | 20.3 (0.69-77.4) | 3.79 | 18.6 | 2.49 | 0.40 | 0.36 | 2.00 | 0.06 |
| 1,2,3,7,8,9-F | 2.02 (0.42-7.24) | 1.21 | 29.7 | 0.95 | 0.22 | <0.23 | 0.13 | 0.02 |
| 1,2,3,4,6,7,8-F | 25.5 (1.46-96.7) | 7.42 | 61.6 | 3.99 | 1.23 | 0.82 | 2.47 | 0.02 |
| 1,2,3,4,7,8,9-F | 8.25 (0.46-30.6) | 3.05 | 68.8 | 2.16 | 0.26 | <0.25 | 1.23 | <0.01 |
| OCDF | 4.06 (1.43-9.16) | 5.13 | 242 | <0.11 | 0.99 | 0.95 | 0.29 | 0.11 |
| Total TCDDs | 3.3 (1.24-5.68) | 7.13 | 39.6 | 4.16 | 3.74 | 2.26 | 48.2 | 0.19 |
| Total PeCDDs | 7.17 (0.9-17.0) | 10.3 | 256 | 2.31 | 3.24 | 1.39 | 28.8 | 0.06 |
| Total HxCDDs | 28.1 (5.97-74) | 53.1 | 643 | 11.2 | 9.95 | 5.12 | 120 | 0.22 |
| Total HpCDDs | 28.7 (6.81-80.6) | 56.4 | 535 | 12.1 | 4.25 | 3.58 | 34.8 | 0.08 |
| Total TCDFs | 16.2 (3.82-35.7) | 11.9 | 75.2 | 13.3 | 1.43 | 0.63 | 4.45 | 0.46 |
| Total PeCDFs | 52.9 (6.2-160) | 21.1 | 478 | 18.9 | 16.4 | 4.81 | 13.0 | 0.24 |
| Total HxCDFs | 78.5 (5.44-280) | 32.4 | 680 | 14.1 | 22.8 | 5.02 | 26.8 | 0.09 |
| Total HpCDFs | 39.4 (3.13-146) | 13.4 | 164 | 10.8 | 1.49 | 0.82 | 4.05 | 0.04 |
| PCB-77 | 414 (149-753) | 579 | 2400 | 162000 | 32.2 | 10.7 | | |
| PCB-81 | 11(17-28) | 147 | 46 | 26400 | 2.55 | 2.74 | | |
| PCB-105 | 15200 (6060-28600) | 29900 | 128000 | 449000 | 7270 | 4620 | | |
| PCB-114 | 1150 (597-2160) | 1930 | 9160 | 30500 | 948 | 1150 | | |
| PCB-118 | 32200 (14100-57800) | 58400 | 251000 | 588000 | 22500 | 16000 | | |
| PCB-123 | 1070 (194-2060) | 1370 | 4920 | 33000 | 119 | 206 | | |
| PCB-126 | 83 (47-181) | 405 | 1190 | 4800 | 55.7 | 43.7 | | |
| PCB-156 | 4530 (2170-8740) | 7760 | 31890 | 46600 | 4500 | 4390 | | |
| PCB-157 | 957 (385-1920) | 1580 | 6563 | 10500 | 1120 | 1110 | | |
| PCB-167 | 1960 (1030-3360) | 2580 | 15697 | 23100 | 1100 | 921 | | |
| PCB-169 | 30 (45-76) | 53 | <35 | 1330 | 15.6 | 14.1 | | |
| PCB-189 | 403 (66-766) | 259 | 2900 | 2690 | 158 | 145 | | |
| PCB-28/31 | 11300 (3600-24800) | 37600 | 122000 | 10038000 | 5000 | 5000 | | |
| PCB-52 | 4340 (2270-8740) | 5000 | 18300 | 740000 | 338 | 338 | | |
| PCB-138 | 49800 (17500-101000) | 62600 | 450000 | 241000 | 48000 | 44700 | | |
| PCB-153 | 37400 (9030-73400) | 35000 | 230000 | 198000 | 62000 | 51800 | | |
| PCB-180 | 56700 (4290-110000) | 18800 | 535000 | 66800 | 16000 | 13900 | | |
| HCB, ng/g | 32.5 (11.4-63.2) | 65.7 | 365 | 8.87 | 82.9 | 69.5 | | |
| β+γ HCCH, ng/g | 287 (7.35-1050) | 225 | 610 | 135 | 194 | 114 | | |
| WHO-TEQ$_{DF}$ | 24.5 (3.3-75.2) | 25.0 | 280 | 8.33 | 15.5 | 5.94 | 93.9 | 0.23 |
| WHO-TEQ$_{PCB}$ | 16.9 (9.27-28.3) | 41.9 | 182 | 664 | 12.1 | 9.94 | | |
| HCB/WHO-TEQ$_{PCB}$ | 2040 (792-4090) | 2490 | 2010 | 13.4 | 6880 | 7000 | | |

**Table 2. Concentrations and TEQ-1998 of dioxins and furans in Chapaevsk samples, 2006-2007.**

| | Urban soil (n=5), pg/g mean (min-max) | Industrial soil, pg/g (21 subsample) | Sediment (n=4), pg/g mean (min-max) | River sediment near sludge tank | Outdoor plaster n=5, pg/g mean (min-max) | Outdoor plaster most contam. | Air (n=3), pg/m$^3$ | PUF pg/sample (30 day exposition) | House dust | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | 0.5 km from plant, pg/g | 2 km from plant, pg/g |
| 2,3,7,8-D | 0.48 (<0.03-1.71) | 88.50 | 0.14 (0.27-0.28) | 13.7 | 0.14 (0.12-0.3) | 18.0 | 0.007 | 0.83 | 1.15 | 2.08 |
| 1,2,3,7,8-D | 3.25 (0.21-11.8) | 1420 | 0.75 (0.12-1.99) | 101 | 0.24 (0.08-0.95) | 25.7 | 0.011 | 1.46 | 1.88 | 13.8 |
| 1,2,3,4,7,8-D | 6.42 (0.69-21.6) | 7560 | 2.72 (0.13-5.71) | 488 | 0.21 (0.02-0.71) | 62.5 | 0.017 | 0.56 | 5.44 | 27.6 |
| 1,2,3,6,7,8-D | 17.6 (1.31-62.5) | 20700 | 6.97 (0.24-13.9) | 1010 | 0.47 (0.01-1.8) | 102 | 0.027 | 1.78 | 16.2 | 84.4 |
| 1,2,3,7,8,9-D | 10.2 (0.86-35.8) | 10400 | 3.96 (0.17-7.97) | 575 | 0.25 (0.01-0.95) | 61.6 | 0.015 | 0.64 | 8.92 | 45.7 |
| 1,2,3,4,6,7,8-D | 188 (18.5-654) | 311000 | 64.2 (3.05-159) | 12900 | 2.73 (0.22-10.5) | 999 | 0.217 | 10.1 | 186 | 970 |
| OCDD | 836 (78.8-2890) | 243000 | 186 (16.3-468) | 64000 | 10.3 (2.5-37.8) | 3190 | 0.842 | 1050 | 1290 | 4530 |
| 2,3,7,8-F | 4.2 (1.24-13.8) | 258 | 5.55 (0.06-21.3) | 21.1 | 1.05 (0.07-1.84) | 17.9 | 0.027 | 6.26 | 23.1 | 25.6 |
| 1,2,3,7,8-F | 4.65 (0.86-16.8) | 530 | 3.28 (0.04-12.2) | 70.5 | 0.5 (0.01-1.27) | 13.6 | 0.017 | 5.58 | 10.1 | 28.4 |
| 2,3,4,7,8-F | 5.09 (0.9-18.6) | 2770 | 2.57 (0.07-8.4) | 158 | 0.53 (0.02-1.26) | 19.8 | 0.042 | 5.91 | 9.08 | 31.9 |
| 1,2,3,4,7,8-F | 15.1 (1.93-54.5) | 11800 | 7.3 (0.15-24.3) | 550 | 0.63 (0.08-1.67) | 34.6 | 0.044 | 6.87 | 20.0 | 89.9 |
| 1,2,3,6,7,8-F | 3.75 (0.97-12.1) | 2180 | 1.97 (0.07-6.33) | 116 | 0.4 (0.07-0.72) | 13.7 | 0.025 | 4.38 | 6.76 | 29.2 |
| 2,3,4,6,7,8-F | 3.29 (0.81-11.3) | 2420 | 1.21 (0.06-3.6) | 107 | 0.14 (0.03-0.44) | 18.0 | 0.022 | 3.97 | 5.67 | 30.2 |
| 1,2,3,7,8,9-F | 3.58 (0.44-12.7) | 4250 | 1.49 (0.06-4.09) | 140 | 0.1 (0.04-0.31) | 15.8 | 0.010 | <0.7 | 4.78 | 26.4 |
| 1,2,3,4,6,7,8-F | 29.1 (6.89-96.1) | 25500 | 9.46 (0.4-26.1) | 1270 | 0.73 (0.15-2.35) | 145 | 0.177 | 9.50 | 30.7 | 216 |
| 1,2,3,4,7,8,9-F | 6.03 (0.73-21.6) | 1530 | 1.9 (0.1-5.22) | 224 | 0.08 (0.04-0.31) | 19.8 | 0.033 | 2.52 | 7.54 | 55.7 |
| OCDF | 66.6 (8.21-232) | 17600 | 13.1 (0.78-36.5) | 2460 | 0.77 (0.19-3.03) | 358 | 0.456 | 4.94 | 160 | 718 |
| Total TCDDs | 18.1 (4.08-49.9) | 2770 | 4.27 (0.51-8) | 543 | 9.18 (0.97-15.8) | 94.4 | 9.48 | 109 | 20.1 | 70.6 |
| Total PeCDDs | 44.0 (7.57-146) | 28900 | 16.1 (0.74-32.2) | 1950 | 5.23 (0.14-17.0) | 216 | 0.572 | 70.1 | 46.1 | 227 |
| Total HxCDDs | 119 (13.8-406) | 147000 | 52.0 (1.97-101) | 7130 | 4.33 (0.31-13.1) | 723 | 0.561 | 32.4 | 121 | 594 |
| Total HpCDDs | 312 (33.2-1060) | 625000 | 109 (5.67-259) | 21400 | 5.0 (0.55-18.2) | 1660 | 0.434 | 20 | 333 | 1570 |
| Total TCDFs | 37.6 (12.8-115) | 3620 | 16.6 (0.58-52.9) | 668 | 14.8 (1.47-26.6) | 111 | 0.716 | 351 | 95.8 | 237 |
| Total PeCDFs | 54.2 (12.0-180) | 36500 | 23.5 (0.85-66.4) | 1840 | 8.66 (0.99-20.1) | 365 | 0.808 | 174 | 88.0 | 365 |
| Total HxCDFs | 68.2 (11.3-234) | 83400 | 28.5 (1-79.8) | 2700 | 2.72 (0.22-9.55) | 405 | 0.354 | 48.9 | 78.4 | 447 |
| Total HpCDFs | 60.9 (10.6-207) | 57900 | 19.2 (0.79-51.2) | 2790 | 1.3 (0.23-4.54) | 312 | 0.291 | 16.3 | 63.8 | 381 |
| I-TEQ | 14.4 (1.79-51.0) | 1180 | 6.03 (0.18-17.1) | 658 | 0.92 (0.05-2.44) | 89.2 | 0.059 | 8.53 | 19.9 | 79.9 |
| WHO-TEQ$_{98}$ | 15.3 (1.81-54.1) | 12300 | 6.23 (0.17-17.7) | 649 | 1.03 (0.05-2.88) | 98.8 | 0.063 | 8.31 | 19.6 | 82.1 |