

## Levels and Profiles of PCDDs and PCDFs in Soils and Sediments from Chapaevsk, Samara province, Russia

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### Abstract

In this paper we report on results from isomer specific analyses of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in samples of soils and sediments collected in Chapaevsk (Samara province, Russia). Many of the samples contained significant concentrations of dioxins derived from a nearby chemical plant. Samples taken in the area surrounding the plant show a decrease in concentration with distance.

### Introduction

The Russian chemical industry remains a major source of toxic emissions. In the past, many plants have been used extensively for the production of chemical weapons. Although production has been kept secret, it is evident that significant dioxin formation has occurred through the manufacture of toxic agents using chlorine and other halogens. Poor control over process efficiency and by-product disposal has resulted in serious environmental contamination by dioxins. Despite the cessation of chemical weapons production at many of these plants, toxic emissions containing dioxins from other chlorine processes still continue unabated.

This paper reports the results from the first dioxin monitoring survey at Chapaevsk. Chapaevsk is a small industrial town in Samara province, southern Russia. The major industrial plant in Chapaevsk is the Plant of Chemical Fertilizers of Chapaevsk (PCFC) situated approximately 3km from the town. In the past PCFC has been used extensively for the production of toxic agents (mustard gas, lewisite etc.).

For economy, waste disposal at PCFC including dioxin contaminated waste, has been

mainly by open surface dumps which has allowed leaching into rivers and groundwater and airborne dispersal to surrounding soils. Little data is currently available on the levels of PCDD and PCDF contamination in the vicinity of PCFC and other Russian chemical plants resulting from these methods of waste disposal<sup>1-3</sup>.

Recently it has been discovered that the production of sodium pentachlorophenate between 1967 and 1990 had been generating 2,3,7,8 substituted PCDDs and PCDFs in significant quantities. In 1990, 2,3,7,8-TCDD (together with HxCDD and HpCDD) at ppq levels was found in an artesian drinking water well in Chapaevsk. This work has attempted to provide an initial picture of dioxin distribution at PCFC and in the surrounding area and to assess the persistence of PCDDs and PCDFs in soils and sediments.

## Sampling and Analysis

Samples for analysis were taken in 1992 and 1993. Figure 1 shows the locations of samples taken for analysis. In total, 13 samples have been subjected to full congener specific analysis. Samples were solvent extracted and the extractant was concentrated. LC was used to elute the extractant and the PCDDs/PCDFs collected and concentrated to a suitable volume. PCDD/PCDF analysis was carried out by passing the samples through a GC directly interfaced to a HR mass spectrometer operating in the SIM mode. Homolog groups and specific 2,3,7,8- substituted congeners were identified and quantified by reference to <sup>13</sup>C PCDDs/PCDFs IQS.

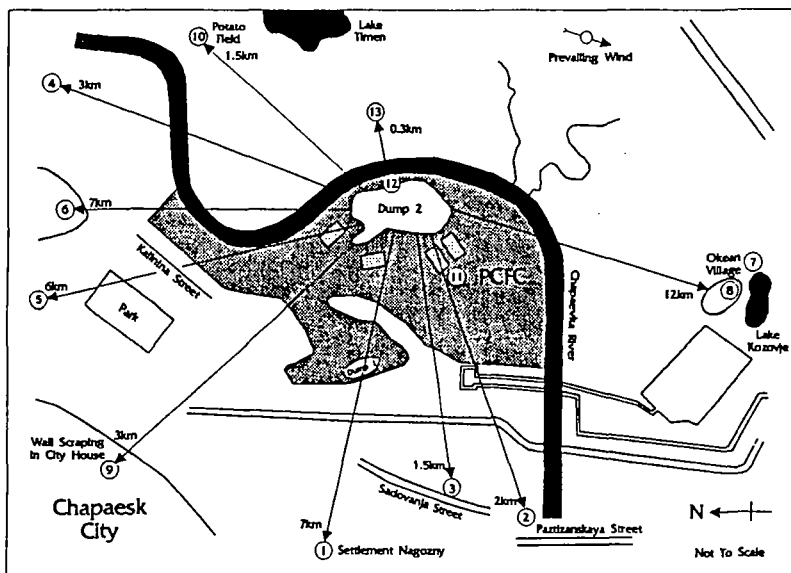


Figure 1. Sample locations at PCFC and in the surrounding area.

## Results and Discussion

Considerable variability was observed in PCDD/DF concentrations at PCFC and in

the surrounding area. Table 1 summarises the results from the analyses. The highest concentration, 1 436 500 ppt total PCDD/DF (46,200 ppt TEQ), was observed at site 12 in close vicinity to the major PCFC waste dump. This contrasts with sample 8 at Okean village (12km from PCFC) where the concentration was below the limit of detection. The distribution of dioxins in the surrounding area exhibits a clear trend of decreasing concentration with distance from PCFC (shown in Figure 2).

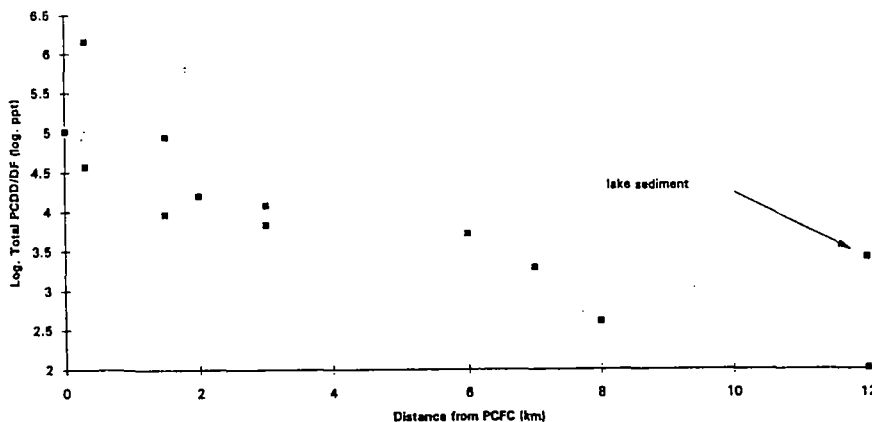


Figure 1. Log. Total PCDD/DF vs Distance from PCFC

This pattern suggests that the waste dump at PCFC is the major source of dioxin contamination in the area. The second sample (site 11) from PCFC was taken from a store of distillation residues from methylchloroform production. This sample also shows elevated concentrations; 102 700 total PCDD/DF (2800 ppt TEQ).

The PCDD/DF distribution in the area surrounding PCFC, suggests that wind dispersion is the major mechanism in the transport of contaminated material from the waste dump. High concentrations in the dust found on a house wall in Chapaevsk (site 9) also indicate airborne transport. Concentrations found in Sadovaja Street (site 3) and Paptizanskaya Street (site 2), downwind (northeast prevailing wind) of PCFC are higher than those found just east of the waste dump at site 13. This may be due to cultivation of the field at site 13 where potatoes are grown.

A close examination of the homolog profiles for these samples produces a confusing picture. Close to the waste dump (site 12) the sample contains significant proportions of each homolog (tetra- through octa-) but is dominated by HxCDD and HxCDF. This profile is not evident in any of the other samples which all tend to be dominated by the octa- chlorinated homologs. There is also no clear pattern evident from the samples taken in the surrounding area either on the basis of distance from PCFC or the sample matrix.

The production of dioxins has continued at PCFC for many years. Many different processes have been responsible for dioxin synthesis thus creating variations in the dioxin profile over time. Contamination dispersed in the environment surrounding PCFC will reflect

the 'integration' of years of production with the consequential variation in homolog profiles. In addition to this source related variation, dioxins deposited by atmospheric wet and dry scavenging will be subject to degradation processes which will tend to change the homolog profile.

Despite the locality of the dioxin source, the pattern of dioxin contamination in the region of Chapaevsk is complex, reflecting changes in source and environmental transformation. This survey has provided the first reliable analysis of environmental levels in this region and has highlighted areas of concern. Further data is urgently required for Chapaevsk and the many similar regions within the former USSR to elucidate sources and determine the impact of historical pollution on the environment.

## References

1. Federov, L. Ecological problems in Russia caused with dioxin emissions of chemical industry. *Extended abstracts of 12th International Symposium on dioxins and related compounds*. Tampere, Finland: 1992;9 75-78.
2. Federov, L. Epidermiological aspects of the dioxin problem in Russia. *Extended abstracts of 12th International Symposium on dioxins and related compounds*. Tampere, Finland: 1992 10: 49-52.
3. Federov L. Dioxin problem in Russian chemical industry. *Extended abstracts of 12th International Symposium on dioxins and related compounds*. Tampere, Finland: 1992; 10:313-316.

PCDD/PCDF Concentrations in Environmental Soil/sediment Samples (ppt)													
(distance from PCFC plant, km)													
Congener/Homolog	11	12	13	3 (1.5)	10 (1.5)	2 (2)	4 (3)	9* (3)	5 (6)	1 (7)	6 (8)	8 (12)	7* (12)
2,3,7,8-TCDD	100	3000	20	7.5	<1	1.5	<1	45	<1	<1	<1	<1	<1
TCDD	700	40000	100	145	15	40	<10	165	<10	<10	<10	<10	<10
PeCDD	10200	197000	200	610	<10	60	<10	20	<10	<10	<10	<10	<10
HxCDD	4500	160000	720	2125	340	385	<20	350	<20	<10	<20	<20	<10
HpCDD	2400	43000	2000	7080	1015	670	485	575	165	570	<4	<4	645
OCDD	40000	134000	30000	64000	3900	13000	4800	8500	4310	960	200	<5	1625
Total PCDD	57800	774000	33020	73960	5280	14155	5325	9655	4515	1560	244	<49	2300
TCDF	6000	8500	100	3400	530	230	335	245	300	18	120	<10	<10
PeCDF	7200	175000	590	1350	<10	300	230	150	155	<10	<10	<10	<10
HxCDF	10200	282000	720	1620	840	240	155	110	<20	<10	<20	<20	<10
HpCDF	1500	130000	310	625	365	86	248	110	24	310	<8	<8	248
OCDF	20000	67000	2200	6350	2200	910	600	1800	225	50	<5	<5	10
Total PCDF	44900	662500	3920	13345	3945	1766	1568	2415	724	398	163	<53	288
Nato/CCMS TCDD TEQ	2800	46200	100	298	50	40	30	71	14	10	4	<4	10

9\* - Scraping taken from house wall

7\* - Silt from Lake Kozovje

Table 1. PCDD/PCDF Concentrations (ppt dry weight) in soil/sediment at the PCFC plant, Chapaevsk, Samara province.