

CHLORINATED DIOXIN AND DIBENZOFURAN CONTENT IN 2,4-D AMINE SALT FROM UFA, RUSSIA

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Objective: In the Bashkortostan Republic of the former Soviet Union, at the Ufa Chimprom Agrochemical plant, 2,4,5-T and 2,4-D were manufactured at various times during the past 30 years. We previously found elevated 2,3,7,8-TCDD levels in workers' blood from exposure 25 years prior to blood collection and dioxin measurement.¹ At this meeting we will report elevated 2,3,7,8-TCDD in the blood of some of these workers' children, which suggests an occupational hazard -- dioxin transfer from mother to child during nursing. At last year's International Dioxin Symposium, Dioxin '92, several papers described dioxin contamination at various sites in the former Soviet Union, including Chimprom.²⁻⁴

During a one week consultation with Chimprom factory officials in Ufa during 1992, one of us (AS) learned that citizen's concern about 2,3,7,8-TCDD contamination from the factory (based partially on results from analyses of 2,4-D by a Moscow laboratory), had led to demands that the factory cease production of 2,4-D and caused a temporary closing of the factory in the early 1990s. A report by Hagenmaler,⁵ is the only published finding of 2,3,7,8-TCDD in 2,4-D, but that was presumably due to previous contamination from 2,4,5-T manufacture in vessels used for 2,4-D. Therefore, we were curious to determine if Russian 2,4-D might possibly be contaminated with 2,3,7,8-TCDD. This seemed to be scientifically improbable, although citizen's concern about dioxin toxicity and contamination does seem reasonable, under appropriate circumstances.

Methods: The sample of 2,4-D amine salt was weighed, dissolved in distilled water and spiked with a carbon 13 standard mixture containing at least one 2,3,7,8-substituted PCDD/F isomer per chlorination group. The sample was extracted repeatedly with dichloromethane, the extracts were combined and the solvent was

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evaporated. The residue was dissolved in hexane and subjected to a multicolumn clean-up procedure.^{6,7} After the clean-up, carbon 13 1,2,3,7,8-Tetra-CDD (recovery standard) was added and the sample was analyzed for PCDD/PCDF with the use of HRGC/HRMS (AUTOSPEC) on 60 m SP-2330 and DB-5 capillary columns.

Results: No 2,3,7,8-TCDD was detected in the 2,4-D sample as shown in Table I, Figure 1, and the chromatogram, Figure 2.

Conclusions: Like 2,4-D manufactured in other countries, the 2,4-D from the Ufa Chimprom factory did not contain 2,3,7,8-TCDD. In this case a chemical factory production line was shut down by concerned citizens when this toxic dioxin was, in fact, not being generated. Previously, a Russian dioxin laboratory analyzed a 2,4-D sample from this factory which may have contained parts of 2,4,5-T (resulting in 2,3,7,8-TCDD contamination), and contributed to the citizens' concerns. It is noteworthy that a true 2,3,7,8-TCDD contamination incident, one occurring over 25 years ago, from 2,4,5-T manufacture (which may or may not have led to dioxin contamination off-site) did not initiate such drastic action.

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References:

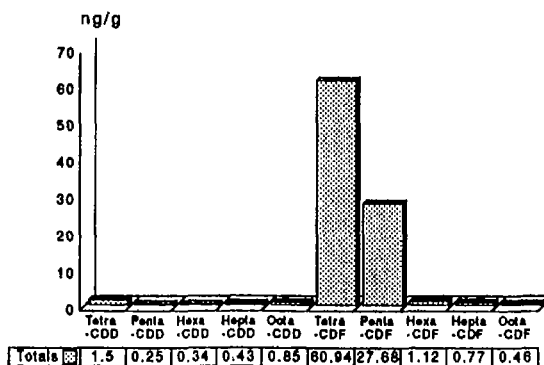
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TABLE I: DIOXINS AND DIBENZOFURANS IN 2,4-D (ng/g, ppb)

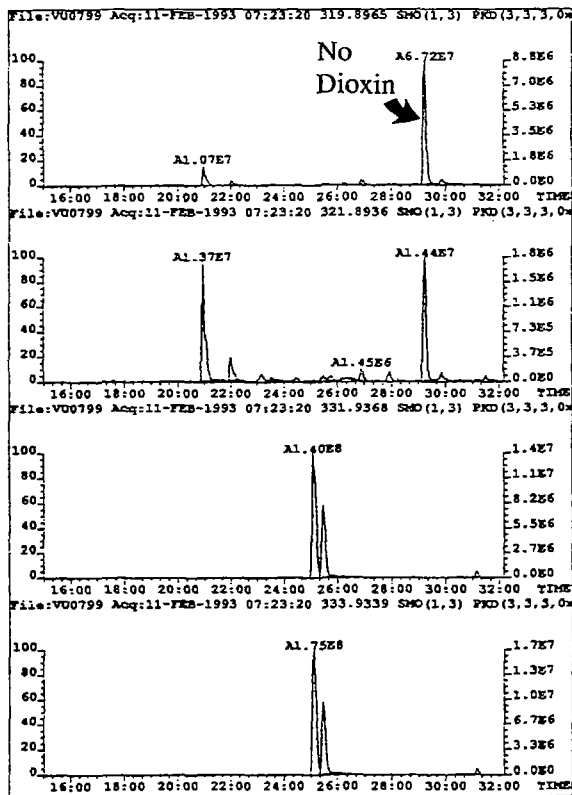
	Concentration	TEQ
2,3,7,8-TCDD	ND	0.02
Total Tetra-CDD	1.5	
1,2,3,7,8-PeCDD	0.03	0.53
Total Penta-CDD	0.25	
1,2,3,4,7,8-HxCDD	0.02	0.002
1,2,3,6,7,8-HxCDD	0.05	0.005
1,2,3,7,8,9-HxCDD	ND	0.001
Total Hexa-CDD	0.34	
1,2,3,4,6,7,8-HpCDD	0.23	0.0023
1,2,3,4,6,7,9-HpCDD	0.2	0.002
Total Hepta-CDD	0.43	
OCDD	0.85	0.00085
2,3,7,8-TCDF	ND	0.1
Total Tetra-CDF	60.94	
2,3,4,7,8-PeCDF	0.06	0.03
1,2,3,7,8/1,2,3,4,8-PeCDF	1.2	0.06
Total Penta-CDF	27.68	
1,2,3,4,7,8/1,2,3,4,7,9-HxCDF	0.08	0.008
1,2,3,6,7,8-HxCDF	0.11	0.011
2,3,4,6,7,8-HxCDF	0.05	0.005
1,2,3,7,8,9-HxCDF	ND	0.001
Total Hexa-CDF	1.12	
1,2,3,4,6,7,8-HpCDF	0.24	0.0024
1,2,3,4,7,8,9-HpCDF	0.02	0.0002
Total Hepta-CDF	0.77	
OCDF	0.46	0.00046
Total PCDDs	3.37	0.04
Total PCDFs	90.97	0.12
PCDDs/Fs	94.3	0.16

ND = not detectable with detection limits shown, Totals include nontoxic isomers.

Figure I: Chimprom Agrochemical Plant, Ufa, Russia
2,4-D (Amine Salt)



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$^{12}\text{C}_{12}$

$^{13}\text{C}_{12}$

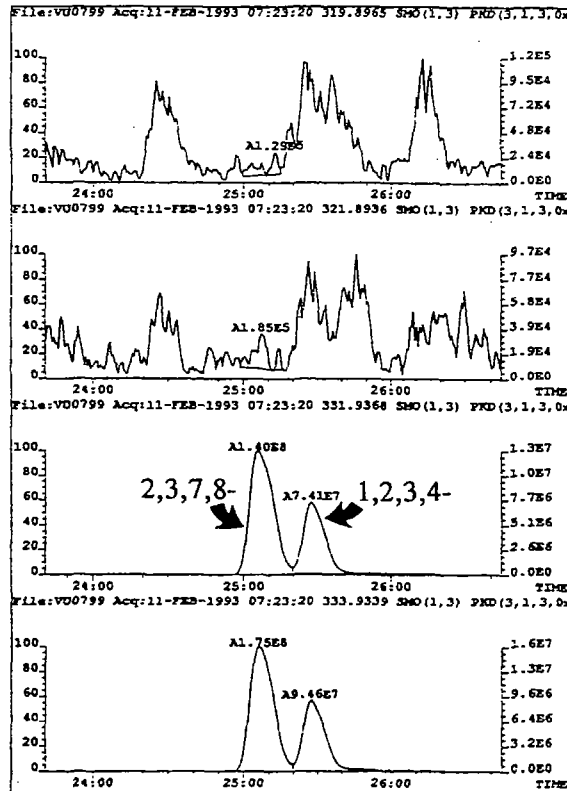


Figure 2 Tetrachlorodioxins in 2,4-D (SP 2331)