

CONCLUSIONS FROM UFA, RUSSIA DRINKING WATER DIOXIN CLEANUP EXPERIMENTS INVOLVING DIFFERENT TREATMENT TECHNOLOGIES

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Objectives: Widespread environmental contamination, including contamination of drinking water, with dioxins and other xenobiotics is a pressing problem in the Ufa region of Russia.⁽¹⁻⁴⁾ The city of Ufa is home to a number of factories including the Chimprom Agrochemical Complex, the site of several industrial "incidents" which have released 2,3,7,8-TCDD and other polychlorinated dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) into the nearby Ufa River where a total of 0.13 to 0.20 ng/l of PCDDs and PCDFs are regularly present. Elevated dioxins have been found in blood from Chimprom plant workers and their children as well as in pooled blood from the Ufa general population.^(5,6) "Emergency" situations where the concentration of dioxins in river or tap water exceeds the "permissible" level (0.02 ng per liter) by ten to one hundred times occur on a regular basis. In addition, high levels of dioxins have been detected in soil, in waste dumps, and in slime pits and are believed to contribute to contamination of ground and drinking water. Other xenobiotics, including phenols, hydrocarbons, and chlororganic compounds, are regularly present in Ufa tap water in concentrations up to a million times higher than dioxins. These may act as carriers of the dioxins which by themselves have low solubility in water.

The municipality of Ufa initiated a water treatment project that has been supported in part by the John D. and Catherine T. MacArthur Foundation located in the U.S.A. This paper reports the results of experiments designed to evaluate the effectiveness of three methods of water treatment. The most effective treatment was approved and is now in use at the Ufa North water plant.

Methods: To create a solution similar to contaminated water from Ufa, a mixture of six to twelve xenobiotics (hydrocarbons, aromatic substances and their chlororganic compounds such as phenol, anyzol, biphenyl, naphthalene, C12, chlorophenol, and chloroanisol) were dissolved in tap water to create concentrations of 10 to 300 times the maximum allowable concentration (0.02 ng per liter) each. This procedure was implemented by mixing the solution for 0.3 to 2 hours and allowing it to settle for 0.5 to 6 hours, after which suspended particles were removed by filtration. PCDD and PCDF standards were added to this solution which was then mixed. Estimated loss of dioxins during transfer from one vessel to another was ten to twenty percent.

Three different types of solutions were used: A) a mixture of PCDDs, PCDFs and other xenobiotics, B) a mixture of higher chlorinated PCDDs and xenobiotics, C) a mixture of the higher chlorinated PCDDs and xenobiotics plus waste water from the Chimprom factory comprising 0.2 to 3% of the total volume. The concentration of PCDDs and PCDFs in these

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solutions ranged from 0.1 up to 50 ng/l for each congener

To minimize loss of dioxins the experimental equipment was made of glass, organic plastic, stainless steel, and silicone rubber. Three methods of treatment were tested. 1) Ozonization (OZ) was performed in a 1.5 meter column where a high-voltage generator synthesized an air ozone mixture which was pumped into the water solution. The water was then pumped to a deaeration column where excess ozonization was removed. 2) The water solution was mixed in a reactor with a newly developed powder sorbent (PS) for three to twenty minutes and then filtered to remove the sorbent. 3) Water treatment with granulated sorbents (GS) from 0.3 to 3 mm in size was performed as a downwards filtration through a lay of GS of about 0.5 m in height. Water samples of 1 to 5 liters were used to prepare specimens for dioxin analysis. Analyses were performed by the dioxin laboratory in the usual fashion, employing cleanup and extraction followed by high resolution gas chromatography-mass spectroscopy.⁽⁷⁾

Results: The results of dioxin analyses are presented in Tables I, II, and III. All samples in Table I were from the prepared solution "A" as described previously. Table II shows the results of the three different water treatments on the prepared solution "B" previously described. Four samples were treated with the granulated sorbents, one with ozonization, and one with powdered sorbents. The three samples in Table III were taken from the prepared solution "C" described above, two were treated with powder sorbents.

Figure I shows the efficacy of the three types of water treatment. Powdered sorbents removed 70-95% of PCDD and PCDF isomers with di-, tetra-, isomers being approximately 85-90% removed and hepta- and octa- removed by 70-90%, the bars labeled "PS" give results of treating water solution "A," PS II indicates the results of treating water solutions "B" and "C". Ozonization reduced the concentrations of di-, tetra-, and penta-CDD and CDF by 70-80%, while the concentrations of hepta- and octa-CDD and CDF were reduced by only 30 to 45%. Granular sorbents proved to be the most effective for removing dioxins from water: from 90-95% of all PCDD and PCDF isomers were removed from the water.

Conclusions: Granulated sorbents constitute a relatively inexpensive approach to removing dioxins from drinking water. These experiments indicate that, with the proper treatment, even the most toxic 2,3,7,8-CDD and 1,2,3,7,8-CDD isomers can be efficiently removed from drinking water. It is hoped that removal of dioxins from drinking water will reduce the exposure of the population to these highly toxic chemicals.

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**Table I: PCDDs and PCDFs in Water Samples from Ufa, Russia
Mixture "A"
(Measured in parts per trillion)**

Sample #	Y 201	Y 202	Y 203	Y 204	Y 222	Y 232	Y 210
Treatment	GS	GS	GS	GS	OZ	PS	None
PCDDs							
Tetra	0.07	0.16	0.34	0.91	0.77	2.17	8.3
Penta	0.22	0.56	1.19	2.59	0.82	2.12	15.6
Hexa	1.05	2.34	4.34	9.43	2.77	5.74	37.3
Hepta	1.89	4.2	5.64	1.24	4.33	8.33	42
Octa	2.69	3.67	4.55	9.77	3.49	10.1	45.8
Total	5.92	10.82	16.06	23.94	12.18	28.46	149
PCDFs							
Tetra	<0.02	<0.02	<0.03	<0.03	<0.03	<0.03	<0.03
Penta	<0.004	<0.006	<0.006	<0.01	<0.005	<0.006	n.d.
Hexa	n.d.	n.d.	n.d.	0.003	n.d.	n.d.	n.d.
Hepta	<0.003	<0.003	<0.010	<0.014	<0.005	<0.004	<0.004
Octa	<0.03	<0.03	<0.03	<0.03	<0.03	0.28	<0.03
Total	0.0285	0.0295	0.038	0.0435	0.035	0.16	0.032

n.d. = not detected. None= no treatment.
OZ = water treated through ozonization

GS = water treated with granular sorbents.
PS = water treated with powder sorbents

**Table II: PCDDs and PCDFs in Water Samples from Ufa, Russia, Mixture "B"
(Measured in parts per trillion)**

Sample #	Y 301	Y 311	Y 312	Y 313	Y 314	Y 315	Y 316	Y 321	Y 322	Y 331	Y 332	Y 333
Treatment	None	GS	GS	GS	GS	GS	GS	OZ	OZ	PS	PS	PS
PCDDs												
Tetra	15.4	0.06	0.45	0.08	0.08	0.07	0.52	11.3	1.4	1.04	0.29	0.05
Penta	10.8	0.07	0.8	0.11	0.16	0.2	1.12	17.5	0.4	4.93	0.15	0.2
Hexa	24.9	0.25	1.55	0.38	0.68	0.52	2.62	47.8	1.36	25	0.6	1.09
Hepta	32.7	0.53	1.22	0.83	1.69	0.3	3.98	55.1	1.53	36.7	0.99	2.92
Octa	31.8	0.54	1.1	0.78	1.51	0.45	2.95	50.5	1.26	27	1.51	1.6
Total	115.6	1.45	5.12	2.18	4.12	1.54	11.19	182.2	5.95	94.67	3.54	5.86
PCDFs												
Tetra	22	0.11	0.58	0.12	0.07	0.02	0.05	10.2	0.53	0.18	0.73	<0.005
Penta	11.5	0.1	0.47	0.06	0.04	0.02	0.08	6.6	0.12	0.12	0.12	n.d.
Hexa	1.7	0.02	0.15	0.02	<0.008	<0.003	n.d.	1.7	0.03	0.08	0.2	n.d.
Hepta	0.99	0.15	0.05	0.01	<0.009	<0.004	<0.008	1.4	0.03	0.12	0.14	<0.003
Octa	0.52	<0.30	<0.04	<0.03	<0.03	<0.02	<0.03	0.61	<0.04	0.12	0.08	<0.03
Total	36.71	0.53	1.27	0.225	0.1335	0.0535	0.149	20.51	0.73	0.62	1.27	0.019

n.d. = not detected None= no treatment.
OZ = water treated through ozonization

GS = water treated with granular sorbents.
PS = water treated with powder sorbents

TABLE III: PCDDs and PCDFs in Water Samples from UFA, Russia Mixture "C" (Measured in parts per trillion)

Sample Code	Y 51	Y 52	Y 54
Treatment	Non	PS	PS
PCDDs			
Tetra	20.4	0.42	2.21
Penta	32.5	0.80	1.10
Hexa	70.3	2.38	0.69
Hepta	56.1	1.83	0.22
Octa	63.5	2.13	0.46
Total	242.8	7.56	4.68
PCDFs			
Tetra	<0.03	<0.03	<0.03
Penta	0.39	0.02	0.01
Hexa	0.16	<0.004	<0.003
Hepta	<0.003	<0.004	<0.003
Octa	<0.03	<0.03	<0.03
Total	0.58	0.054	0.043

PS = water treated with powder sorbents
 None = water received no treatment.

