A State of Research on Treating Drinking Water from Dioxins and Other Xenobiotics in Russia.

Smirnov, A.D.[A], Alifanova, N.N.[B], Onoprienko V.V.[C], Safarov,M.G.[D] Fjodorov,L.A.[E]

[A] VODGEO Institute, 42 Komsomolsky av., Moscow, 119826, Russia
[B] NITIUS Institute, 8 Galperina str., Perm, 614113, Russia
[C] Institute of bioorganic chemistry of the Russian Academy of Science, 16/10 Miklukho-Maklaya str., Moscow, 117871, Russia
[D] Bashkir State University, 32 Frunze str., Ufa, 450074, Russia
[E] Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Science, 19 Kosygin str., Moscow, 117975, Russia

A real ecological situation in various regions of Russia as well as the ways and means of protecting people from toxic technogenic substances, especially dioxins and xenobiotics of organic and hetero-organic types, have recently become subjects of open investigations and discussions.
The amounts of various toxic xenobiotics, considerably exceeding the maximum permissable concentrations, have been registered in surface and ground waters of Bashkortostan, Kuzbas, and Ural regions. Exceeding concentrations of dioxins in soil and water have also been noticed in the city of Ufa. All this requires additional security measures, including an urgent elaboration of technology and equipment for treatment of drinking water from dioxins and dioxin-like xenobiotics. Investigations in this field are presently being conducted by the authors.

Ufa is one of the main sources of dioxin contamination of all the components of the environment, which is due to 30 years of gas ejections, sewage and burried sludge, all containing dioxins. It is the diversity of pollution sources, some of them unidentified or lacking proper data, that is special about this region.
Besides the polluted area is very large, the ways the toxins invade the environment are numerous, their chemical composition is multi-component, and people mostly get infected by dioxins through water. The situation is aggravated by inhabitants and municipal structures being unprepared to face ecological emergency, as well as by ineffective means of timely chemical control of microconcentrations of toxic substances in water.

To resolve the problem the municipality of the city of Ufa initiated a special project last fall, which has later been supported by MacArthur Foundation (USA). It is being carried out by cooperative efforts of scientists from 12 scientific centers of Russia, including specialists in the field of environmental monitoring, chemical analysis, sorbent and water treatment technologists, hydrogeologists, equipment designers and "green" protagonists.
It has been determined that only 40%-60% of contaminations are caused by identified sources, the rest are washed out of the polluted soil, dumps, slime pits, fertilized and pesticided fields. The pollution is so severe, that even if the the main source of dioxins (a chemical manufacturer "Chemprom") is closed down that will not help much.
Based on a number of tests the most likely total background amount of dioxins in the Ufa river has been determined. It equals 0.0002 ppb. In emergency situations the expected concentrations of dioxins in river water is up to 0,0002-0.1 ppb, and in water pipes -- 0.004-0.026 ppb. The range of dioxins in the Ufa river considerably increases in the industrial zone (where "Chemprom" is located) with highly toxic 2,3,7,8-TCDD appeared among them.
In this region dioxins are present in water along with other xenobiotics, total concentration of which comes up to 10-300 ppb. Besides being highly toxic themselves, these substances act both as carriers of dioxins in the environment and as their competitors with regards to adsorbers. This impedes the analyses and the removal of dioxins from water by conventional treatment.

The peculiar situation in the Ufa region makes it necessary to try and test both destructive and adsorptive technologies of treating water from dioxins. The tests were performed with model solutions and with real water. Substances were added to the water to achieve the most probable concentrations of dioxins and xenobiotcs. The investigated multi-component mixture had the following ingredients: water, dioxins, dioxin-like xenobiotics, technogenic organic matters ("technogenic background"), natural organic matters ("natural background").
Dioxins were represented by four-component mixture typical of the Ufa region: 2,7-dichlorodibenzo-p-dioxin, 1,3,6,8-tetrachlorodibenzo-p-dioxin, 1,3,7,9-tetrachlorodibenzo-p-dioxin, and octachlorodibenzo-p-dioxin in concentration range of 0.001-1 ppb.
Dioxin-like xenobiotics were represented by mixture containing 2,4-dichlorophenylbutyl ether, trichlorodiphenyl ether, and tetrachlorodiphenyl ether in concentrations of 2-10 ppb.
"Technogenic background" contained phenol, benzene, toluene, naphthalene, diphenyl, anthracene, benzpyrene, 2,4-dichlorophenol, and 2,4-dichloroanisol in concentration range of 10-1000 ppb.
"Natural background" was created by organic substances of natural origin with total amount up to 3-8 ppm and total salinity of 100-200 ppm.
The main efforts were directed to the testing of adsorptive technology of water treatment, because it allows to fulfill advanced water treatment

disregarding the toxicity and chemical resistance of impurities and without final byproducts, which might function as secondary contaminants.
The fraction of dioxins and other highly toxic xenobiotics in water does not normally exceed 0.001%–1% of all the impurities. Their target-oriented removal represents a special problem and has required the creation of new carbon sorbents with micropore volume of 0.11–0.44 cm^3/g, total pore volume of 0.58–1.08 cm^3/g and ash content of 2–19% .

Based on bench- and pilot-scale tests the following conclusions have been made:
1. Adsorptive water treatment 60–400 fold reduces the concentrations of dioxins and dioxin-like xenobiotics in water.

2. When dioxins are present in water along with other xenobiotics they are removed more effectively.

3. The coefficient of distribution of toxic substances in "adsorbent--aqueous solution" systems is about 30,000 for dioxins and about 1,000–4,000 for other xenobiotics.

In most of the cases the pollution of water supplies by dioxins and other toxic xenobiotics is eventual. In emergency cases the concentration of 2–10 toxic substances in raw water increases 10–1,000 fold and more, whereas the other 40–60 pollutants remain at the same level. Such situations normally range from 2 to 40 hours per year. In the rest of the time the deviation of contaminant concentrations in water does not exceed 50%–80%. This is typical of Ufa and other industrial regions, where extraordinary ecological situations are often caused by industrial or traffic accidents.
At the same time, design, size and cost of water treatment plants are determined by the type and the level of contamination of raw water supplies. Normally the impurities are easy to remove and the plants are designed to ensure long-duration treatment of the utmost contaminated water. To remove dioxins and xenobiotics from water expensive materials and equipment are required, but their actual implementation may be needed only few days per year. The direct dynamic pilot-tests has shown that after the peak load some adsorbate happens to be washed out from the sorbent by water and hydrocarbons. This secondary background ranges from 0.001% to 3% of the initial.

Thus some new ideas concerning the creation of dioxin and xenobiotic protection systems have been developed.

1. Materials, which have adsorbed extraordinary quantities of dioxins and other xenobiotics from water, should immediately be removed from the technological cycle. Powdered hydrocarbon adsorbers meet this main technological requirement.

2. Efficient removal of dioxins and dioxin-like xenobiotics from real water bodies in concentrations of about 0.001-1 ppb for the former and 10-500 ppb for the latter is possible only by multiphase operations of differentiated treatment, when 95%-99% of toxins are removed at each stage.

3. Barrier systems, resistant to extraordinary concentrations of dioxins and other toxic xenobiotics in water, must have dynamic command-operated pretreatment units with feasible replacement of adsorbers to separate impurities from water, as well as constructions of permanent function for tertiary water treatment and removal of background impurities.