PCDD/PCDFs levels in drinking and surface water in Republic Bashkortostan

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Abstract

This report summarises a systematic 3-year monitoring of drinking and natural water for PCDDs and PCDFs levels in industrial regions and in background sites of the Republic Bashkortostan.

Introduction

In most industrialized countries world-wide with significant ecological problems the programs of the inspection of the supercontaminants-PCDDs and PCDFs in various environmental media including drinking and natural waters are realized.

Because of the mobility of natural water systems, the cyclic and seasonal water bodies filling, the atmospheric precipitations of various intensity and also because of the low background level it is these water systems, that have been studied not sufficiently well for the background level of PCDD/PCDFs.This was observed practically by all the researchers dealing with the complex programs of large areas studing.

The potential sources of PCDDs and PCDFs getting into the water system are the industrial and municipal wastes, the bleaching of pulp in paper-making, the organochlorine herbicides production and the by-products of their synthese, drainage and street flows and also the runoffs from agricultural areas treated by chemicals.

The most significant data on the water contamination in various countries are known from US EPA report [1], for New York St. [2],Sweden [3] (Eman river),Canada [4] (Ontario St.), for two prefectures of Japan [5], and also for rivers of GB and Wales.

On the limited data base in the report [1] the following conclusions were drawn:

-in drinking water the PCDD/Fs were not often detected on the level of 1 ppq and above;

-in unprepared water samples the contamination of the PCDD/Fs was higher than in prepared one;

-in surface water the concentration of PCDD/Fs is increasing usually from tetra-to octa-chlorinated groups and congeners.

In the same report the results of drinking water study in North America are summarized. 214 samples were collected as the background ones, the average level (0,0056 ppq) of I-TEQ was calculated. The background levels for Europe are not reported because of the limited information.

In study of Rose C.L.[6] initiated by the National Rivers Authority of Grait Britain the PCDD/Fs level in fresh water of UK and Wales was accounted for < 6 ng /L for total PCDD/Fs, which corresponds to 0,08 ng I-TEQ/L.

Miyata [5] has shown the PCDD/Fs levels in drinking and spring waters in two prefectures of Japan. The detection limits (0,03-0,05 ppq) were exceeded only for two isomers -HpCDD and OCDD (1,39 and 1,91 ppq, respectively).

Objective and Methods

Our study in 1994-1997 was aimed to evaluate the PCDD/Fs distribution in surface water in Republic Bashkortostan (RB) and in drinking waters of urban and rural regions as well. In the flood time and summer period the river water was sampled with the suspended particulate material in it both from the contaminated areas near the industrial centres and sites with the background contamination.

One of the basic waterways of Bashkortostan - Belaja river is affected by main industrial centres: Ufa-oil refining, petrochemistry, chlorine productoin, major heat power stations, railway transport; Sterlitamak-Production Association "Caustic", oil refining; Meleus- "Khimprom", railway transport; Salavat-oil refining; Sim- rail junction, metallurgy (Figure 1, sample 5).

Ufa river is of a special importance for Ufa city as a watersupply source. It was the getting into Ufa river the effluents of "Khimprom", containing mainly phenol and probably PCDD/Fs, that resulted in a well known "phenol disaster" in 1991. From six water supply systems in Ufa three of them are located on Ufa river (sample 1).

Some other rivers of RB cited in this study are relatively small ones, not affected by large industrial contaminations, but they can be affected by transborder transfer from the neighbouring enterprises of Cheljabinsk, Tatarstan etc.(samples 2,3,4). The rivers beyond the Urals without the evident industrial contamination sources can be considered as the background points just like the drinking water from the artesian wells in this region (samples 6,7,8).

During 1994-1997 more than 250 drinking water samples were collected in Ufa city and other regions of RB. The flood time (April-May) as a most unfovourable sampling period is associated with an increase of water flows, with an abundant snow melting, runoff of agricultural inputs into brooks and small rivers, with an increased water turbidity and consequently with an increasing the loading of the cleaning systems. In addition because of increased bacteriological activity the higher amounts of chloride of lime are used in all water supply systems of Ufa city to provide the necessary water quality according to the bacteriological requirements. The analysis of water and suspended in it particles was performed according to the standard method EPA 1613.

The extract prepared[7] was analyzed on the analytical system capillary gas chromatography (GC Carlo Erba 8035)-high resolution mass spectrometry (MS VG-Autospec-Ultima) in electron impacting mode (36 ev) with resolution 10000. Mass numbers were setted upon PFK, 2 ions for native and isotope-labelled isomers were registrated. The gas chromatograph was operating as follows: column DB-5 J&W Scientific 60 m, temperature programming: from 140°C (1 min) to 220°C at 15° C/min, 220° C(20 min) to 300° C at 4° C/ min , 300° C (15 min); ingector temperature 270° C, splitless sample injection, sample volume 1μL.

The detecting minimum of absolute concentration, at which all requirements of US EPA 1613 to isomer separating are fulfilled, amounts to 10 fg. The detection limits for tap and river water samples ranged for the tap water from 0,01 to 0,3 pg/l depending on the isomer and 0,3-1 pg/L for PCDD/Fs isomers in the river water. The recovery was in the range of 55-100 %

depending on the sample and particular isomer. The relative measuring error for water samples accounted for 30 %.

Results and Discussion

During 1994-1997 more than 250 drinking water samples from urban and rural regions of RB were analyzed for PCDD/Fs levels. The studies have shown that the real PCDD/Fs content in drinking water in Bashkortostan approaches to the analytical detection limit or below it (Table 1).The toxicity coefficient in none of 250 measurements does not exceed 1 ppq (for concentration calculating the not-detectable isomers the one-half detection limit was used).

Table 1. The PCDD/Fs content in drinking water of Ufa city and the backdround level in RB, ppq.

PCDD/PCDFs	Ufa,n=250,1994-1997	Background of RB,n=5,1996
TCDD	ND(0,1-0,3)	ND(0,06)
PnCDD	ND(0,1-0,4)	ND(0,09)
HxCDD	ND(0,3-1,6)	ND(0,1)
HpCDD	ND(0,2-2,72)	ND(0,45)
OCDD	1,11-4,95	0,97
TCDF	ND(0,1-)3,23	ND(0,05)
PnCDF	ND(0,07)-3,95	ND(0,05)
HxCDF	ND(0,6)-2,23	ND(0,04)
HpCDF	ND(0,1)-1,64	ND(0,3)
OCDF	ND(0,4)-4,25	0,52

In other centres of RB the PCDD/Fs level is also within the detection limit, except for OCDD (11,5 pg/L).

The tap water samples from the rural regions beyond the Urals may be considered as being background, here only the OCDD is detected on the 0,3-0,5 pg/L level. In river water samples the PCDD/Fs content is higher and achieves the value of 5 pg TEQ/L (Figure 1). It is interesting that practically in all samples the contribution of furan compounds group into the total concentration is about twice as large as that of dioxins.According to I-TEQs the samples represent two groups of rivers: so-called "clean rivers" and those affected by contamination sources.The procentage part of PCDD/Fs, associated with a particulate material, suspended in the river water, amounted to 50-60 % from the total contamination of sample.

The main monitoring results are the followings :

- Analyzing the PCDD/Fs in samples of natural water both in prepared and in original ones with suspended particles showed, that the toxicants content in rivers, lakes and rills in Bashkortostan is at the detecting limit by HRGC/HRMS methods.The backdround level is 1 pg/L (I-TEQ) for drinking water and < 6 pg/L for rivers.

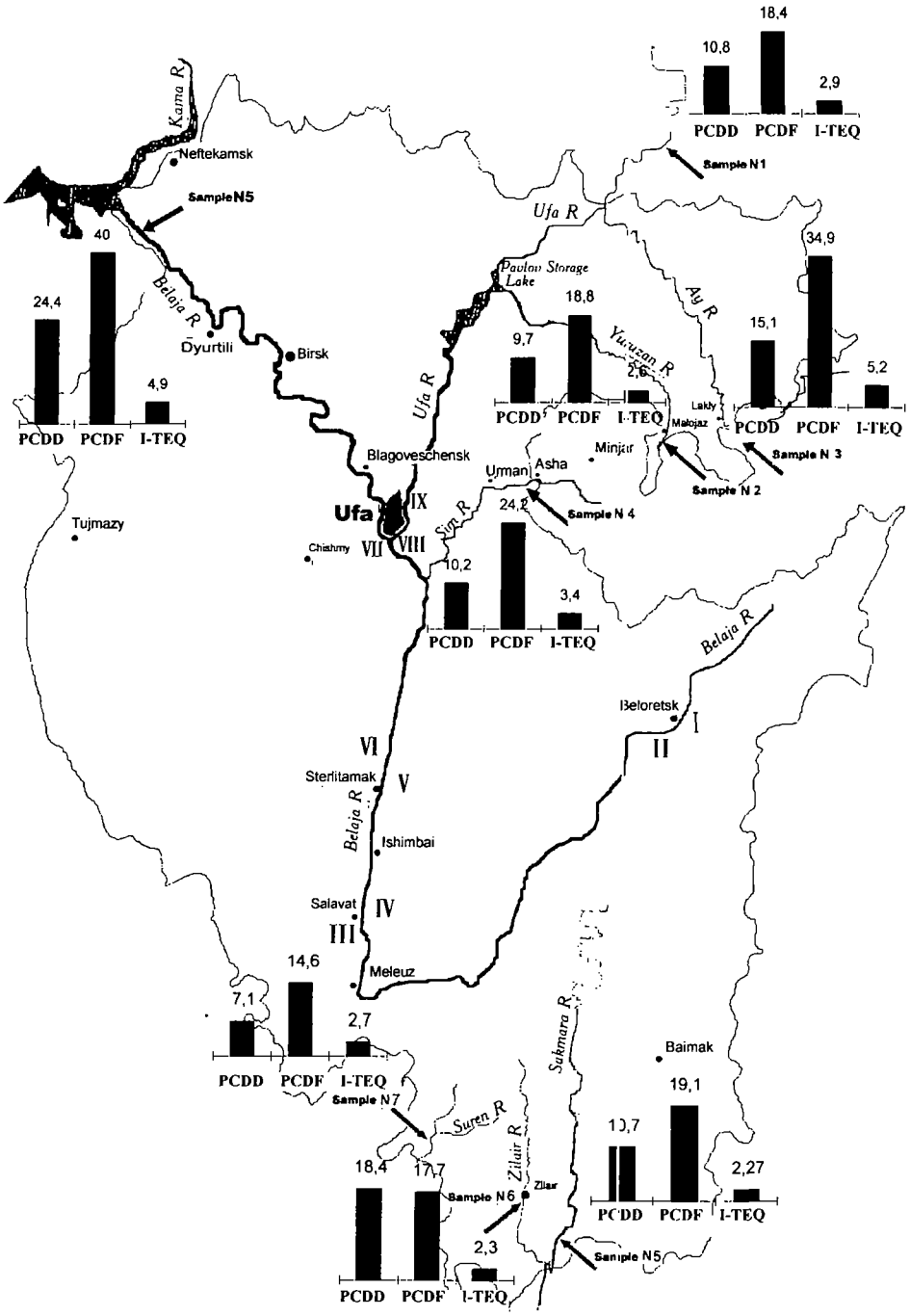

Fig. 1. Sampling sites from rivers of Bashkortostan and their contamination levels.

- Isomer profile of the PCDD/Fs distribution in rivers of RB doesn't allow the main point source to be identified on base of limited data. But it is clear that the contribution of combustion process as one of the known sources of dioxins into the waterways contamination in Bashkortostan is of relatively low importance because of the low content of Cl_7- and Cl_8 - PCDD/Fs isomers, registrated in all samples.

- Analyzing the samples from downstream sites affected by industrial contamination pointed to the sources of technogenic character, but for their identification the information only on water samples is not sufficient.

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