Detection of dioxin sources in Kazakhstan

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Introduction

In the Republic of Kazakhstan within the frame of the UNDP/GEF Project «Initial Assistance to the Republic of Kazakhstan to Meet its Obligations under the Stockholm Convention on POPs» a preliminary inventory of dioxin sources was carried out in compliance with the UNEP Standardized Toolkit for Identification and Quantification of Dioxin and Furan Releases[1]. First of all dioxin sources are represented by large enterprises of ferrous and non-ferrous metallurgy, power stations. Potential emission of these most large sources was estimated by experts of UNDP-Kazakhstan at a level of 340 g TEQ/year.

The next stage was experimental confirmation of PCDD/Fs emission by a series of metallurgical enterprises of Kazakhstan and also analysis of pollution of fish caught in a large Lake Balkhash important for fish industry. The Balkhash Lake occupies the area of about 20,000 km^2 and consists of two parts: a part of fresh water and a part of salt water connected by a narrow strait. Water volume is over 100 km^3. Fish catch makes more than 8,000 ton per year.

PCB pollution as a result of production of industrial capacitors in the city of Ust-Kamenogorsk until the end of the 80s was also experimentally confirmed, namely PCB use (trichlorobiphenyl). According to the estimation made by AMAP experts for the period of 1980-1989 over 10,000 ton of trichlorobiphenyl were used[2].

The areas of examination were as follows:

1. Ust-Kamenogorsk: the titanium-magnesium industrial complex, the plant “Kazzinc”, the capacitor plant.
2. Temirtau: the metallurgical works ISC “Mittal Steel Temirtau”.
3. Karaganda: the foundry.
4. Balkhash: the mining and metallurgical complex.
5. A residential block in the city of Balkhash.
6. The Lake Balkhash.

Measurements of PCDD/Fs in the air, fly ashes, soil, filleted fish and PCBs in the material of buildings were performed in the laboratory of the Environmental Research and Protection Centre. The laboratory successfully passes annual international intercalibration procedure on PCDD/Fs determination in soil and ashes of burning (Umea, Sweden) and in food stuff (Oslo, Norway, 2001, 2005).

This is not the first experience of getting experimental data on dioxin content in the environment and biological objects in Kazakhstan. As back as in 1994-1995 by the project of USAID research on pollution with chlororganic compounds including dioxins was carried out in 7 places of the Central and South Kazakhstan[3,4]. Samples of breast milk of 92 women were analysed. The highest PCDD/Fs levels (mean – 57.2 pg I-TEQ/g fat, max – 133 pg I-TEQ/g fat) were found in the South Kazakhstan, in cotton-growing districts where in 1965-1985 2.4.5-T defoliant was dispersed and 2.4-D pesticide produced in Ufa was used.

Besides PCDD/Fs content was analysed in fish from the Lake Chadara in the South Kazakhstan (carp, bream, pike, crucian) as a potential source of human exposure via food chain in this region[5]. TCDD was not detectable in fish samples (WHO-PCDD/Fs-TEQ-was 0.11-0.14 pg/g w. w.).

Material and Methods

1. **Atmospheric air** was sampled in the working zone for 13-18 hours at a speed of sampling 12 m^3/h. The volume of pumped air was 150-200 m^3. US EPA Compendium method TO-9A “Determination of Polychlorinated, Polychlorinated and Brominated/Chlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Ambient Air” was used for sampling and analysis. Quartz filters and cartridges Supelco, ORBO-2000 Large PUF were used. Filters and cartridges right after air sampling were packed into aluminium foil, placed into a container and stored at a temperature of 0-4^{0}C until sample preparation. “Blank” field sample is the same filter and cartridge held without air pumping that was analysed just like filters and cartridges with samples. Standard solution was applied on the analysed filter and cartridge – ^{13}C-labelled PCDD/Fs (CIL Inc., cat. # EDF 8999-4). The samples were extracted in 300 ml of toluene for 24 hours followed by rotary evaporation and multi-step multi-column

clean-up procedure. HRGC/HRMS analyses were carried out at a 10,000 mass resolution on a VG AutoSpec Ultima coupled to a HP 6890 GC system using a 60-m Restek Rtx-Dioxin (Restek Corp., USA) column. The degree of extraction made from 79 up to 94%, the detection limit was 0.005 pg/m^3 of air.

2. **Soil samples** were taken in the centre of the city of Balkhash, in a square, and in the outskirts of the city from the area of 5 square metres in 5 points. **Samples of fly ashes and industrial dust** were taken in some points from walls close to working places for which the ambient air had been sampled. The samples were averaged.
To a portion of solid substance (3 g of fly ashes, 10 g of soil) a mixture of standard ^{13}C-labelled PCDD/Fs analogues was introduced (CIL Inc., cat. # EDF 8999-4); everything was mixed and left for 12-16 hours. Ashes samples after treating with hydrochloric acid, washing and drying were extracted with toluene in a Soxhlet for 16 hours with 4-fold rotation of toluene per hour. Soil and dust samples were extracted with a mixture of methylene chloride/acetone in an ultrasonic bath. The extract was concentrated, solved in 2-3 ml of hexane and purified on a modified silica gel column, column with base alumina and on a carbon column (Carbopac C/Celite 545).

3. **Samples of plaster** were taken from a wall of the plant in Ust-Kamenogorsk where in 1968-1989 capacitors were produced and PCB-mixtures, primarily trichlorobiphenyl were used. The sample was taken after removal of a layer of old paint to the depth of 5-6 cm in 5-6 points, the sample was averaged.
HRGC/LRMS PCBs type content analyses were carried out on a MD 800 (VG MassLab.). 40-m Restek Rtx-Dioxin column and standard solutions (cat. # Z-014J, # C-SCA-06, AccuStandard Inc., USA) were used.

4. Fish samples. In order to estimate pollution of the Balkhash Lake 6 species of food fish were selected: cat-fish (*Silurus glanis, Linne),* sazan (*Cyprinus carpio, Linne),* asp *(Aspius aspius iblioids, Kessler),* pike perch *(Lucioperca lucioperca, Linne),* bream *(Abramis brama, Linne),* Aral roach "vobla" (*Ritilus rutilus aralensis, Berg).* Determination of species, sex and age of fish was carried out by specialists of biological museum "Exotarium", Ufa.
Fish carcasses were frozen and kept until analysis. A piece of fillet was cut out from the middle of the fish carcass, entrails, framework bones and scales were removed. Fish fillet was homogenised, for analysis 10 g of sample were used.

Table 1 **Description of fish samples**

Fish	**Cat-fish**	**Sazan**	**Asp**	**Pike perch**	**Bream**	**Vobla**
Species	*Silurus glanis*	*Cyprinus carpio*	*Aspius aspius iblioids*	*Lucioperca lucioperca*	*Abramis brama*	*Ritilus rutilus aralensis*
Sex	male	female	female	male	male	female
Weight, g	3400	1500	740	400	250	220
Age, years	15	7	5	3	8	8
Length, cm	78	44	34	34	25	23

Standard solution (CIL, cat. #EDF 8999-4) was added to the analysed sample, everything was mixed with natrium sulphate in proportion of 1:4, glass columns of 12 mm in diameter, 600 mm of length were filled with the mixture and left for 12-15 hours. The mass in the column was eluted with the mixture of methylene chloride:hexane in proportion of 1:1. Lipid content was determined gravimetrically. Clean-up of the extract was carried out according to the classical pattern. The degree of extraction was from 53 up to 89%. Detection limit was 0.01 pg/g of dry weight of sample or 0.3 pg/g lipids. PCDD/Fs concentrations were determined according to the Methods USEPA 1613 (Autospec-Ultima, VG, 10,000, Restek Rtx-Dioxin, 60 m).

Results and Discussion

1. Dioxins in ambient air of working places at enterprises of ferrous and non-ferrous metallurgy

WHO-PCDD/Fs-TEQ levels in ambient air samples of working places is high in the copper-smelting shop of mining and metallurgical complex in the city of Balkhash (over 4 pg/m^3), close to the sintering machine at the plant "Mittal Steel Temirtau" (about 4 pg/m^3) and at the engineering plant in the city of Karaganda (about 2 pg/m^3). This is respectively by 8 and 4 times more than Russian maximum allowable concentrations norm in the air (0.5 pg PCDD/Fs-I-TEQ /m^3)[6]. The conditions under which people are working at the hydrometallurgy plant of JSC "Kazzinc" are at the edge of permissible.

The preliminary found data permit to make a conclusion about considerable emission at these enterprises and the necessity of more detailed analysis of emission. Low concentrations found at the by-product coke plant of the "Mittal Steel Temirtau" are probably explained by technological peculiarities connected with high concentration of coal dust in the air adsorbing PCDD/Fs. But this does not excludes long-term pollution of the territory near the coking plants. The ambient air in the buffer area of the former capacitor plant (Ust-Kamenogirsk) corresponds to the norms of the Russian Federation in terms of dioxin pollution.

2. Dioxins in dust and fly ashes of metallurgical plants in Kazakhstan

The results found for the air of polluted working zone of metallurgical plants were confirmed by the analysis of dust taken from the walls of these shops (Table 2). As it follows from Table 2, the highest values of the current dioxin pollution (the air) correlate with those for the long-term pollution (dust, fly ashes). Evidently industrial waste of these enterprises may be a source of pollution for the environment and the population.

Table 2. PCDD/Fs levels in air (pg/m^3) and fly ash (pg/g) from the metallurgical enterprises of Kazakhstan

City	Balkhash		Karaganda		Temirtau			Ust-Kamenogorsk	
Production	**copper-smelting**		**foundry iron**		**sintering machine**		**coke**	**hydrometallurgy**	
	air	ash	air	ash	air	ash	air	Air	
2378-TCDD	0.04	1.56	0.05	0.10	0.01	5.32	ND	0.01	1.57
12378-PnCDD	0.44	6.70	0.25	0.45	0.19	41.06	0.01	0.03	1.59
123478-HxCDD	0.58	13.22	0.19	ND	0.21	43.90	ND	0.03	1.26
123678- HxCDD	0.69	16.00	0.33	0.42	0.41	60.91	ND	0.05	1.88
123789-HxCDD	0.23	10.17	0.16	ND	0.10	21.25	ND	0.02	0.88
1234678-HpCDD	3.04	175.16	1.13	2.67	2.20	217.90	0.03	0.20	9.99
OCDD	4.43	335.64	1.87	12.86	2.80	219.37	0.09	0.52	28.59
2378-TCDF	0.97	16.05	0.63	12.09	0.31	141.93	0.06	1.34	29.97
12378-PnCDF	1.74	58.34	1.37	2.51	2.24	367.02	0.02	0.31	13.61
23478-PnCDF	3.16	44.63	1.47	2.92	3.51	551.78	0.04	0.29	13.38
123478- HxCDF	4.22	81.13	1.27	2.15	3.40	596.65	0.01	0.31	13.92
123678- HxCDF	9.37	175.50	3.02	2.71	8.88	1123.35	0.04	0.57	28.15
123789- HxCDF	0.13	2.02	0.13	0.20	0.46	75.10	ND	ND	0.69
234678- HxCDF	3.31	81.17	1.07	1.32	3.81	472.24	0.03	0.20	9.71
1234678-HpCDF	15.49	405.57	3.36	2.97	8.79	950.95	0.10	1.32	49.02
1234789-HpCDF	0.73	25.15	0.38	1.44	1.34	178.77	0.02	0.33	5.24
OCDF	2.79	165.12	1.13	1.71	3.98	352.21	0.02	0.80	79.92
TEQ-WHO	**4.29**	**263.78**	**1.84**	**4.06**	**3.95**	**607.88**	**0.05**	**0.47**	**19.83**

3. Dioxins in urban soil

The found values for soil taken in the places 1-3 km away from the industrial zone of Balkhash are less than 1 pg/g what testifies to the absence of active pollution by air transfer from the chimneys of the power station and the plant. At the same time the value of pollution over 6 pg WHO-PCDD/Fs-TEQ/g within the city border, in the central park of Balkhash, may testify to the presence of local pollution sources: traces of leaves burning and emission from chimneys of individual houses and from automobile transport. The level of 9 pg WHO-PCDD/Fs-TEQ/g is often registered in the areas of European industrial cities, but for Russian cities as a rule this is a considerable pollution level, because the average level is usually 1-3 pg WHO-PCDD/Fs-TEQ/g[7].

4. Dioxins in food fish of the Balkhash Lake

The found WHO-PCDD/Fs-TEQ$_{fish}$ levels (0.04-0.38 pg/g w.w., Table 3) in fish fillet from the Lake Balkhash as calculated for the wet weight are low in comparison with EC[8] norm, with norms of Russia (11 pg PCDD/Fs-I-TEQ/g)[9] and with true PCDD/Fs content in wild freshwater fish from lakes of Russia (for example Baikal[10] and Russian Arctic[11]) and from Bavaria, Germany[12].

Table 3. PCDD/Fs levels (WHO-TEQ_{fish}) in wild fish from the Lake Balkhash, Kazakhstan (pg/g w.w.)

Species of fish	**Cat-fish**	**Sazan**	**Vobla**	**Pike perch**	**Asp**	**Bream**
2378-TCDD	ND(0.1)	ND(0.1)	ND(0.09)	ND(0.1)	ND(0.07)	ND(0.1)
12378-PnCDD	ND(0.05)	0.06	ND(0.07)	0.04	ND(0.05)	ND(0.1)
123478-HxCDD	ND(0.07)	ND(0.1)	ND(0.08)	ND(0.1)	ND(0.07)	0.05
123678- HxCDD	ND(0.07)	0.02	0.02	ND(0.05)	ND(0.1)	ND(0.1)
123789-HxCDD	ND(0.08)	ND(0.1)	ND(0.08)	ND(0.1)	ND(0.07)	ND(0.1)
1234678-HpCDD	ND(0.07)	0.28	0.26	0.17	0.16	0.33
OCDD	0.51	0.56	0.33	0.31	0.35	0.33
2378-TCDF	0.56	0.97	0.83	ND(0.07)	0.69	ND(0.2)
12378-PnCDF	0.23	0.42	0.33	0.03	0.24	0.25
23478-PnCDF	0.29	0.58	0.43	ND(0.07)	0.26	ND(0.2)
123478- HxCDF	0.28	0.56	0.49	ND(0.07)	0.26	ND(0.1)
123678- HxCDF	0.22	ND(0.05)	0.34	ND(0.15)	0.23	ND(0.1)
123789- HxCDF	ND(0.05)	ND(0.1)	0.04	ND(0.1)	0.02	0.06
234678- HxCDF	ND(0.05)	0.13	0.12	ND(0.1)	ND(0.05)	ND(0.1)
1234678-HpCDF	0.24	0.40	0.38	ND(0.05)	ND(0.05)	ND(0.2)
1234789-HpCDF	ND(0.05)	0.15	0.16	ND(0.1)	ND(0. 08)	ND(0.1)
OCDF	0.35	0.38	ND(0.1)	ND(0.3)	0.22	ND(0.1)
WHO-TEQ_{fish}	**0.24**	**0.5**	**0.38**	**0.04**	**0.23**	**0.05**

5. PCBs in industrial buildings

A sample of plaster from a wall of the Ust-Kamenogorsk capacitor plant, assembling and impregnating section, is a special one. As a result of many years of pollution the plaster contains about 10 g/kg of PCBs, 50% of them are trichlorobiphenyls, 28% - tetrachlorobiphenyls, 9.5% - pentachlorobiphenyls. The total PCBs concentration by 200 times exceeds the boundary level of PCB-containing materials – 50 ppm. Thus the material of the examined industrial building should be classified as especially dangerous material and after liquidation of the building its remains should be utilized taking the required measures[13].

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