STUDY OF DIOXIN SOURCES IN KRASNOYARSK, RUSSIA

Kucherenko A.V., Klyuev N.A.[1], Yufit S.S.[2], Cheleptchikov A.A.[1] and Brodskj E.S.[1]

SLA "Ecology", 660097 Krasnoyarsk, Russia
[1] Institute of Ecology and Evolution RAS, Leninsky prosp. 33, 117701 Moscow, Russia, kluyv@online.ru
[2] Institute of Organic Chemistry RAS, Leninsky prosp. 47, 119992 Moscow, Russia

Introduction.

Russia is the only industrial country, which does not estimate its annual dioxin emission. Previous studies were only monitoring the pollution level in Russia. One-time measurements of incinerator emission were also carried out to obtain work permission. Incidentally, such data is classified and can't be published. This work is directed towards local monitoring of industrial emission of PCDDs/PCDFs in the city of Krasnoyarsk, a large industrial center in Siberian region and being the main producer of aluminum metal in Russia. Aluminum is isolated from the crude ore by electrolysis, a very energy-consuming process. There is also a necessity of heating a city populated by a million people during the cold season (usually winter lasts for 6 mo. with temperatures falling below -50 °C). A hydropower electric plant along with three large fuel plants and several boilers burning brown coal supplies electric power and heat. Several other factories including a paper mill, non-ferrous metals factory may produce dioxin byproducts. These manufactures are historically located close to populated areas along Enisey, one of the largest rivers in Russia. A program directed toward the decrease of the level of dioxins and dioxin-like compounds in the environment was started in Krasnoyarsk region in 1998. In this paper is presented an estimation of annual emissions from the main industrial sources. A total of 80 samples were studied: 21 air samples, 35 solid waste (mainly industrial), 22 sewage water samples and 2 samples of the end products.

Methods and Material

Sample collection was carried out during normal functioning of the plants using methods certified in the Russian Federation. Stock gas samples were taken by a device, based on Staplex TFIA-2 high volume air sampler, equipped with a transfer line and a trapping system (quartz fiber filter (2 μm id, 5 mm thickness) and 100 ml of XAD-2 resin). Kinetic characteristics of chimney exhaust were measured simultaneously.

The aqueous solutions were extracted by methylene chloride (3 x 50 ml). The solid samples were extracted in special apparatus for contentious-flow extraction by hot solvents. This

method utilized the same advantages, as the accelerated solvent extraction (ASE), but does not require usage of expensive high-pressure equipment (samples placed into an extraction cell were washed with a continuous flow of solvents fed in from a reservoir by gas pressure (0.5-2.0 atm, flow rate 15-25 ml/min) [2]. The solid waste samples (10 g) were 200 ml of toluene, filters and resins used for air sampling were extracted by 500 ml of toluene at 98 °C, sediments and other samples with low sorbtion activity were extracted with 200 ml hexane:acetone (50/50 v:v) at 60°C.

Fly ash samples (10 g) were refluxed in a mixture of 70 ml toluene, 10 ml of HCl and 50 ml of ethyleneglycole dimethyl ether. After 6 hours 300 ml of distilled water were added and the organic phase was separated. The organic solvent was evaporated on rotary evaporator, next the residue was dissolved in 100 ml hexane:dichlormethane (50/50 v:v) and cleaned-up consistently in multilayer silica, FAS-MD carbon microcolumn, multilayer silica and alumina columns. Recovery was estimated to be 70-85% using 2-fluoro-6,7,8,9-tetrachlorodibenzo-p-dioxin, the analyses were performed on GC-MS (HP 6890 Plus, Finnigan MAT 95XL) at resolution 10000 [2].

Results and Discussion.

For the first time the estimation of PCDDs/PCDFs emission in large industrial city in a Russia was provided. The main target of the following investigation was the identification of the major sources of dioxin pollution and the estimate of their annual emission into the environment. The results of this study are summarized in Table 1 and 2.

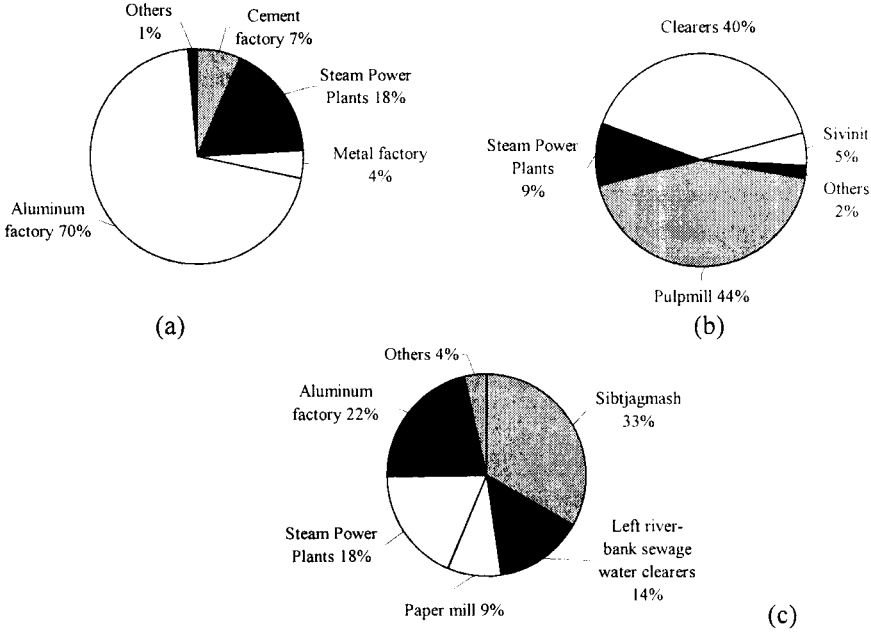

Figure 1. Percentage contribution per sector to the overall PCDDs/PCDFs air (a), water (b) and land (c) emission inventory in Krasnoyarsk in 1999.

Emission of dioxins into the air from major industrial sources in Krasnoyarsk was equal to 560 g I-TEQ in 1999, which is equivalent to almost 20 % of the annual air emission in the entire USA (2744 g I-TEQ for 1995 [3]). Krasnoyarsk aluminum factory contributes 70.5 % of the total value, three steam power plants - 17.5%, cement factory - 6.5% and non-ferrous metals factory- 4.3 %. The annual emission into the water was estimated to be close to 7 g/year. Solid waste (including particles caught by stock gas purification systems) contained only 7.0 - 7.5 g I-TEQ in 1999, which demonstrated the low efficiency of gas cleaning systems. This study did not include vehicle exhaust and emission from factories closed during the sample collection. The total emission from these sources should not exceed several grams I-TEQ. Others dioxin sources, such as private woodstoves, uncontrolled backyard incineration, and trash dump fires, exist. Their contribution can be significant but difficult to measure. For example, soot from a woodstove chimney in a private residence contained 8899.5 ng/kg I-TEQ. The subsequent step in proposed research is a more detailed examination of the air exhaust from different factories as well as the collection of samples from the manufacturers omitted in the presented study. The high values of the estimated dioxin emission require an immediate action from the local authorities towards the protection of the environment. More efficient gas purification should result in a significant decrease in the dioxin emission into the atmosphere.

Acknowledgments

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Table 1. A quantitative inventory of PCDDs/PCDFs emission in Krasnoyarsk air and water in 1999.

Emission Source	I-TEQ Emission Factor	Emission Factor	Annual Emission g I-TEQ/yr
Releases to Air			
PC "Krasnoyarsk paper mill" – bleaching – boiler plant	566 133	ng/t pulp ng/kg wood and shave	0.004 2.739
PC "Cement" – cement kilns coil burning	202231	ng/t clinker	36.777
PC "KraMZ-Lit" SLA "KrAMZ" – melting of aluminum	1442	ng/t aluminum	0.00826
PC "Krasnoyarsk petrochemicals" – boiler plant	46.7	ng/t black oil	0.075
PC "Krasnoyarsk tire factory" (dust from rubber mixer)	658	ng/t mixing	0.0044
Steam Power Plant #1	under investigated		>50
Steam Power Plant #2	22.6	ng/kg coal	41.401
Steam Power Plant #3	14.9 43.4	ng/kg coal ng/kg black oil	6.376 0.352
PC "Krasnoyarsk metal factory" – refinery stock gas	Unpublished information		24.255
SF "Krasmashzavod" – boiler plant	18.9	ng/kg coal	3.167
PC "Krasnoyarsk aluminum factory" – primary aluminum – manufacture and recycling of anodes	 11169 1.11	 ng/t aluminum mg/t coke	 9.382 384.741
PC "Krasnoyarsk metallurgical plant" "Sibelectrosteel" Arc steel furnace #1	17179	nt/t secondary alloy steel	0.164
Municipal boiler plant #6	1.65	ng/kg coal	0.081
PC "Krasnoyarsk woodworking factory" – boiler plant	13147	ng/m^3 wood	1.132
SF "Krasnoyarsk-graphite" – drying drum, propane burning	3575	ng/t graphite	0.027
Releases to Water			
PC "Sibelectrosteel"	7.03- 31.25	pg/l	0.051
PC "Krasnoyarsk pulp – cleaned sewage	10.44	pg/l	0.362
– bleaching sewage	382.53	pg/l	2.050
– mud fields	20590	pg/l	unestimated
– not cleaned sewage	490.04	pg/l	1.204
SLA "KrAMZ"	25.67	pg/l	0.00015
PC "Krasnoyarsk aluminum factory" – desilter sewage	141.1	pg/l	0.092
Steam Power Plant #1 – mixing chamber	21.80	pg/l	0.655
Steam Power Plant #2 – floodway	3.34	pg/l	0.127
Right river-bank sewage water clearer #1	8.99	pg/l	0.544

Right river-bank sewage water clearer #2	2.35	pg/l	0.1465
Left river-bank sewage water clearers - total	25.82	pg/l	2.664
SF "Krasmashzavod" – sewage to Enisey	22.50	pg/l	0.006
PC "Sivilit" – sewage #1	56.02	pg/l	0.002
– cleaned sewage #2	45.06		0.424
PC "Sibtjagmash"	13.55	pg/l	0.0065
PC "Birusa" Chemical factory – sewage #1	1.64	pg/l	0.0002

Table 2. A quantitative inventory of PCDDs/PCDFs emission in Krasnoyarsk land in 1999.

Emission Source	I-TEQ, pg/g	Object	Annual Emission (mg I-TEQ/yr)
SF "Krasmashzavod"	19.68	boiler plant ash	223.26
PC "Sibtjagmash"	1359.56	open-hearth furnace dust	~ 1395.18
	103.42	used pouring form "burnt land"	995.33
Left river-bank sewage water clearers	75.72	mud	~ 1039.78
Right river-bank sewage water clearers	58.08	mud	unestimated
PC "Krasnoyarsk metal factory"	9.61	presscake	12.80
PC "Krasnoyarsk paper mill"			
– sewage water clearers	61.29	mud	~ 612.90
– boiler plant	4.67 / 5.86	ash / cinder	0.609 / 0.085
PC "Krasnoyarsk synthetic rubber factory"	117.87	rubber cinder	11.79
PC "Sibelectrosteel"	471.29	arc steel furnace dust	unestimated
Steam Power Plant #1	1.57 / 0.87	ash / cinder	184.36 / 34.05
Steam Power Plant #2	11.45 / 2.08	ash / cinder	1047.6 / 43.90
Municipal boiler plant #6	33.06	cinder	4.046
PC "Krasnoyarsk aluminum factory"	72.51	mud	1566.43