INDUSTRIAL EMISSION FACTORS IN THE CITY OF KRASNOYARSK

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Introduction
Russia and former Soviet republics still lack emission factors (EF) values, causing the absence of reliable data about dioxin emission into the air. Earlier data is scarce and partially outdated.[1] The resistance of the business owners, exemplified by forbidden exhaust sampling and the underreporting of business productivity, complicates collection of the new emission data. In general, the result is the raise of EF numerical value. **OOO** 'Ecology' managed to overcome these difficulties and retrieved information for EF determination. These results are presented in the following article.

Experimental Section.
Exhaust gases were sampled using a sampling probe inserted into the center of the chimney if possible. The length of the probe (0.5 – 4 m) depended on the chimney diameter and the temperature inside. The compounds of interest were collected from the stream of gas by a polysorbent analogous to XAD-2. About 100 g of sorbent was placed downstream of a glass wool filter containing internal standards, ^{13}C-labeled PCDDs and PCDFs. The rate of the gas and the temperature of the sorbent (<140 °C) were continuously monitored. The sampling time varied from 5 to 20 min. Analysis of the collected compounds was carried out on Finnigan MAT 95 XL and HP 6890 chromato-mass spectrometer as described in earlier works.[2]

Results and Discussion
Table 1, 2 and 3 show the emission factors (EF) from the studies carried out in March 2000.

Cement manufacturing. During cement manufacturing the 'clinker' is roasted in rotating furnaces. The amount of PCDDs and PCDFs increases if waste is simultaneously incinerated. The Krasnoyarsk cement furnaces differ by burning coal, not gas or fuel oil as usual. Our data, as well as the data from other sources, is shown in Table 1. The values obtained in our study match perfectly with values from cement furnaces (Germany) using non-toxic waste as fuel.[3] This coincidence may result from burning (non-toxic) coal in Krasnoyarsk.
Aluminum Production Krasnoyarsk factories produce aluminum using the electrolytic process. Emission factor of 11.2 ug I-TEQ/ton was calculated. Remelting of aluminum scrap not contaminated with PBCs or other additives is carried out in IAK-40induction flue furnaces. The emission factor was equal to 1.4 ug I-TEQ per one ton of aluminum metal in this department, a value close to one reported earlier (1.51 ug I-TEQ/ton. An anode-manufacturing factory gave an *EF of 1114.1* ug I-TEQ per ton of coke. No previous data was available for comparison. The high EF for coke used to make anodes may contribute to high dioxin emission during electrolysis. Earlier analysis of anode contamination during a separate chlorine production run showed a high

level of dioxins.[4] The contamination was attributed to a chemical reaction between the electrode and chlorine gas, while our results showed that the electrodes themselves could contain the dioxins. ***Steel Production*** Steel-making in arc furnaces resulted in an EF of 1.15 ug I-TEQ/ton, while other furnace types gave 1.26 ug I-TEQ per ton of steel.[1] Steel plants in Germany reported corresponding values of EF: arc and induction furnaces produced only 0.032 ug I-TEQ per ton of steel, while electric melting devices gave off 0.48 ug I-TEQ/ton. Similar arc furnaces in Krasnoyarsk had EF of 17.18 ug I-TEQ/ton. Thus, Russian furnaces yielded 500 times more dioxins than in Germany and 15 times more than in the USA. High dioxin levels may result from either a high contamination of the starting product or the absence of air emissions purification.
Burning coal/ Five heating boiler plants in Krasnoyarsk use coal for fuel. Measured emission factors were summarized in Table 2. If the highest/lowest values are rejected, than average EF was 19 ± 4 ug I-TEQ/ton. Similar value was magnitudes lower in the US (0.087 – 0.6 ug I-TEQ/ton),[5] probably, due to an inadequate clean-up system in Russia. US purification systems completely remove process dust though a system of electric and cloth filters, while Krasnoyarsk heating plants use multicyclons that do not catch particles less that 10 microns in diameter.
Crude oil burnin. Emission factors were calculated for two boiler plants: 46.7 ug I-TEQ/ton for a boiler plant and 43.4 ug I-TEQ/ton for power plant #3. The average value of 45 ± 4 ug I-TEQ/ton could be used for emission estimation for similar plants in Russia. German data indicated that EF for crude oil (0.4 ug/J)? was twice as large as for coal (0.2 ug/T Joules).Using this relation, a value of EF for coal was calculated (45.0 : 2 = 22.5 ug I-TEQ/ton) which is within the order of magnitude with our data above (19 ± 4 ug I-TEQ/ton) received independently from the studies of burning coal.
Burning of wood waste. A woodworking plant emitted 13,146.8 ug I-TEQ per 1 m^3 of waste into the atmosphere. Assuming that the specific gravity of wood is 0.8 m^3/ton, EF equaled 16.43 ug I-TEQ/ton of wood. The presence of tree bark in waste resulted into 10-fold increase in EF (133.3 ug I-TEQ/ton). Available data for small wood-burning furnaces is similar to that obtained in this study.[3] A better purification systems should be applied in systems for burning tree bark.
Other industrial processes. Several other industries were investigated in Krasnoyarsk. Their EFs, determined for the first time, included the following processes:

1. Chlorine bleaching at a paper mill. The measured EF value (0.6 ug I-TEQ/ton) is significantly larger than one obtained earlier for a sodium regeneration boiler (SRB). This is an important distinction since SRBs were considered an important source of dioxins in paper mills (typically 0.2 ug I-TEQ/ton in the USA).[1] Earlier OOO 'Ecology' demonstrated the closeness of the EF of SRBs in both countries.[6] From data collected at the Krasnoyarsk paper mill, we conclude that chlorine bleaching, not SRB, is the main source of air emission of dioxins during the manufacturing of cellulose.

2. Graphite mining turned out to be another unexpected source of dioxins. In Krasnoyarsk, after mined graphite is dried using an open flame (gas, fuel oil) (EF = 3.6 ug I-TEQ/ton); the dried graphite is ground and packed (EF = 4.5 ug I-TEQ/ton). the graphite chemical structure is a good trap for dioxins. As graphite looses very little weight after drying, the total emission factor adds up to 8.1 ug I-TEQ/ton. This number is twice as small as obtained from a power plant burning coal.

3. Rubber production for tires was an important source of dioxins (EF = 0.6 ug I-TEQ/ton), on par with paper bleaching.

4. Varnish/paint manufacturing plant did not contribute significantly (EF = 0.03 ug I-TEQ/m^2).

Conclusions

New data regarding emission factors in Russia was obtained, including several industries were never investigated as dioxin emission sources before. All of the EFs were significantly higher than similar EFs in Europe or the US. This fact may reflect the poor condition of waste stream clean-up systems in Russia.

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Table 1. Emission factors obtained at cement factories (ug TEQ/ton).

Reference	**No additives**	**With non-toxic waste**	**With toxic waste**
[7]	0.045	-	-
[3,5]	-	200	2600
[8]	0.27	-	1004-28580
Krasnoyarsk	202.2	-	-

Table 2. Emission factors at power plants burning coal mined at Kansko-Achink (ug TEQ/ton).

Power plant	**With non-toxic waste**	**Power (tons/hr)**
PK-10SH	443	25.7
BKZ-500/140	22.6	72.0
KVTK-100	14.9	28.1
NZL-450	18.9	13.0
Municipal ?	1.6	2.5

Table 3. Emission factor for Krasnoyarsk dioxin sources.

#	Dioxin Sources		EF (ug TEQ/ton)
1	Cement	Clinker	202.2
2	Coal	Power plant	18.8 4 (0.35 ug I-TEQ/TJ)
3		Small boilers	1.6
4	Fuel oil	Power plants	45 1.7
5	Wood	Without bark	16.4
6		With bark	133.3
7	Aluminum	Electrolysis	11.2
8		Remelting	1.4
9		Anode coke	1114.1
10	Paper mill	Bleaching	0.6
11	Steel	Arc furnace	17.2
12	Graphite	Drying	3.6
13		Grinding	4.5
14		Total	8.1
15	Tire	Resins	0.6
16	Varnish		0.03 ug I-TEQ/m^2

References

1 .Pervunina, R.I.; Samsonov, D.P.; Kiruhkin, V.P.; Rahkmanova, T.I.; Zhiryuhina, N.P. Environmental study of pollution by dioxin and related compounds in several cities and areas of Russia in 1988-1996.In *Dioxins - The Supertoxicants of the XXI century*. VINITY, Federal Commitee of Russian Federation on Environmental Policy: Moscow, **1998**, p.64-81.

2.Soboleva, E.I.; Soifer, V.S.; Mir-Kadyrova, E.Ya.; Brodski, E.S.; Feshin, D.B.; Kluyev, N.A.; Polyakov, N.S.; Petukhova, G.A. New clean-up procedure for determining PCDD/PCDFs in lipophylic matrices. *Intl. J. Environ. Anal. Chem.*, **1997**, 68(4), p. 511-522.

3. Ifeu (1998): Ermittling von Emissionen und Minderungsmabnamen fur persistente organische Schadstoffe in der Bundesrepublik Deutschland. Stoffband A: Polychloriete Dibenzodioxine und -furan (PCDD/F) und polycyclische aromatische Kohlenwasserstoffe (PAH). Ifeu-Institut, Heidelberg, Marz **1998**. Forschungsvorhaben Nr. 104 02 365. Im Auftrag des Umweltbundesamten, Berlin.

4. Brzuzy, L.P; Hites, R.A. Global Mass Balance for Polychlorinated Dibenzo-p-dioxins and Benzofurans. *Environ. Sci. Technol.*, **1996**, 30, p.1791-1804.

5. UNEP Dioxin and Furan Inventories. National and Regional Emissions of PCDD/ PCDF, May **1999**.

6. Yufit, S.S.; Kluyev, N.A.; Brodski, E.S. Distribution of dioxin pollution in Arkhangelsk region. In Dioxin-The supertoxins of the XXI century. Regions of Russia. M., **1998**, p. 10-36.

7. US EPA Report *Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-p-dioxine and Related Compounds*. Path 1, Vol. 2, - Washington DC, EPA/600/P-00/001Ab, **2000**, 628 p.

8. The Inventory of Sources of Dioxin in the United States; EPA/600p-98/002 April **1998** External Review Draft.