Oil Shale, 2004, Vol. 21, No. 4
pp. 333-339
ISSN 0208-189X

https://doi.org/10.3176/oil.2004.4.06

POLYCHLORINATED BIPHENYLS (PCB), POLYCHLORINATED DIBENZO-*P*-DIOXINS (PCDD) AND DIBENZOFURANS (PCDF) IN OIL SHALE AND FLY ASH FROM OIL SHALE-FIRED POWER PLANT IN ESTONIA

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Estonian and Baltic Thermal Power Plants are the world largest thermal power plants burning low-grade local oil shale. During the European Dioxin Project the concentrations of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and polychlorinated biphenyls were measured at Baltic Thermal Power Plant in oil shale and fly ash from electrostatic precipitators. The study of PCB and dioxin was carried out by Landesumweltamt Nordrhein-Westfahlen, Germany. It was concluded that the power plants are probably not major sources of dioxins. It should be noted that the European Dioxin Inventory did not include any measurements of air emission from sources in Estonia.

Introduction

Both North-East Estonia (Ida-Virumaa county) and North-West Russia (the westernmost Slantsy region of Leningrad district) are extremely rich in oil shale. In North-East Estonia, some 13,000 jobs depend on the further mining of oil shale, in North-West Russia (Slantsy) the figure is somewhat lower – 3,500. Nevertheless, the continuation of oil shale mining is an important economic and social issue for oil shale regions. In the short-term, till 2006, world oil shale production may well increase from about 16 million tonnes in 2000 to about 23 million tonnes on account of the production growth in Estonia (from 11.6 to 17 million t) and in Australia (from 0.8 to 7.8 million t) [1].

Unfortunately, there are very few ways to use oil shale economically. One of these is to extract shale oil, the other is to burn it in power plants. In 1959, the oil shale-based Baltic Power Plant and in 1969 the Estonian Power Plant were put into operation. Besides, oil shale is also used in several

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smaller power plants and in plants of oil shale processing and chemistry. Oil shale serves as fuel at Kunda Nordic Cement, which is the major producer of building materials in Estonia. There are two main disadvantages to this: it has a relatively low calorific value and causes an extraordinary high amount of pollution, both in the air and on the ground. The local inhabitants, not only the workers involved in oil shale mining and processing, are exposed to complex mixtures of dusts (ashes), gases and vapors.

There are no other mineral resources, except peat available in surroundings, usable as a source for fuel and energy.

The preliminary information revealed that considering dioxin emissions in Estonia a thermal power plant firing oil shale might be of interest.

Till 1998, the concentrations of polychlorinated dibenso-*p*-dioxins (PCDD), polychlorinated dibenzofurans (PCDF) and polychlorinated biphenyls (PCB) in Estonian oil shale and fly ash have not been analyzed. Therefore, the data presented in this paper should be of interest to the general public.

Materials and Methods

Dioxin present in Estonian oil shale and fly-ash from the electrostatic precipitators (ESP) was determined by Landesumweltamt Nordrhein-Westfahlen, Germany, and quantified according to the European Standard EN 1948:1946. This standard consists of three ultimate parts (sampling, extraction and clean-up, identification and quantification) and is worked out for the determination of mass concentration of PCDDs and PCDFs in stationary source emissions.

The following two modifications were made:

1. The samples were air-dried.
2. 20 g of sample material was extracted for 20 hour with toluene in a Soxhlet apparatus [2].

Two oil shale and two fly ash samples were analyzed with high-resolution GC/MS methods for their content of PCB, PCDD and PCDF [2].

Results and Discussion

Persistent Organic Pollutants (POPs) are chemicals that remain in the environment for long periods of time, accumulating in the fatty tissue of living organisms [3], and they are transported long distances in the environment.

The term ‘dioxins’ covers a group of 75 polychlorinated dibenzo-*p*-dioxin (PCDD) and 135 polychlorinated dibenzofuran (PCDF) congeners, of which 17 are of toxicological concern. PCDD and PCDF are toxic and persistent chemicals whose effects on human health and the environment include dermal toxicity, immunotoxicity, reproductive effects and teratogenicity, endocrine disrupting effects and carcinogenicity. The most toxic congener is 2,3,7,8-tetrachlordibenzo-*p*-dioxin (TCDD), classified by the International Agency for Research on Cancer as a known human carcinogen. PCDD and PCDF have never been produced and have never served any useful purpose [3, 4]. The polychlorinated biphenyls cover a group of 209 congeners, and PCDD/Fs cover a group of 210 congeners. Waste incineration (69% of total emissions in 1995), iron and steel (10%) and non-ferrous metals (8%) industry, etc. [4] are the largest sources of PCDD/Fs releases to the environment in the world.

As dioxins have very long half-lives, their concentrations in soil change very slowly. As a rule, the biodegradation half-life times of persistent organic pollutants (POPs) in real soil environment are very long – from years to decades. Biodegradation of POPs in soil can be considered a minor loss process of POPs in the environment [5].

The sources of polychlorinated dibenzo-*p*-dioxins and dibenzofurans have not been detected in Estonia. Estonia still has no waste incineration factors, which would act as substantial sources of PCDD and PCDF pollution. A dioxin inventory was carried out in Estonia in 2002. The inventory was based on the methodology of the toolkit for identification and quantification of PCDD/Fs releases, developed by UNEP Chemicals in the form of the following designated 'UNEP toolkit' [6].

The uncontrolled burning processes, power generation and heating are the biggest sources of the direct release of dioxins to the air [7] (Table 1).

Table 1. **Potential Mean Release of Dioxins and Furans (mean g I-TEQ/year) from All Sources in Estonia [7]**

Main Category	Air	Water	Land	Product	Residues
Waste incineration	0.19				0.47
Ferrous and non-ferrous metal production					
Power generation and heating	4.90				5.80
Production of mineral products	0.39			?	0.06?
Transport	0.04				?
Uncontrolled combustion processes	8.10	?	0.12?		4.40?
Production and use of chemicals and consumer products	0.004?			0.03	0.60?
Miscellaneous	0.04			0.002	0.009?
Disposal and waste water		0.15			3.90
Hot spots	?	?	?		
Total	14?	0.15?	0.12?	0.03?	15?

Notes: 1. An empty cell indicates that the release route is considered insignificant.
2. A question mark "?" indicates that the release route may be significant, but no emission factors are available.
3. A number followed by a question mark indicates that the number may be underestimated as some subcategories have not been quantified.

Table 2. **Concentrations of PCDDs and PCDFs in Oil Shale (EOIL1 and EOIL1B) Combusted in the Baltic Thermal Power Plant Furnace, as well as in Fly Ash (EOIL2 and EOIL2B) Caught by Electrostatic Precipitators [8]**

PCDD and PCDF isomers*	Concentration, ng/kg			
	EOIL1	EOIL1B	EOIL2	EOIL2B
Sum TCDD	n.d.	n.d.	n.d.	n.d.
Sum PeCDD	n.d.	n.d.	n.d.	n.d.
Sum HxCDD	n.d.	n.d.	n.d.	n.d.
Sum HpCDD	3.6	3.0	13	n.d.
OCDD	<0.89	2.0	19	<1.6
PCDD	4.4	5.0	32	1.6
2,3,7,8-TCDD	<0.28	<0.33	<0.62	<0.28
1,2,3,7,8-PeCDD	<0.24	<0.46	<0.65	<0.51
1,2,3,4,7,8-HxCDD	<1.0	<1.0	<2.3	<2.2
1,2,3,6,7,8-HxCDD	<0.92	<0.86	<2.0	<1.9
1,2,3,7,8,9-HxCDD	<0.86	<0.81	<1.9	<1.8
1,2,3,4,6,7,8-HpCDD	1.8	1.4	6.4	<0.66
Sum TCDF	n.d.	n.d.	n.d.	n.d.
Sum PeCDF	n.d.	n.d.	n.d.	n.d.
Sum HxCDF	1.3	1.0	3.2	n.d.
Sum HpCDF	1.0	n.d.	4.7	2.7
OCDF	<3.4	n.d.	<18	<8.5
PCDF	5.7	1.0	26	11
2,3,7,8-TCDF	<0.15	<0.27	<0.59	<0.37
1,2,3,7,8/1,2,3,4,8-PeCDF	<0.36	<0.62	<1.3	<0.59
2,3,4,7,8-PeCDF	<0.30	<0.51	<1.1	<0.49
1,2,3,4,7,8/1,2,3,4,7,9-HxCDF	<0.37	<0.51	<0.96	<0.50
1,2,3,6,7,8-HxCDF	<0.33	<0.43	<0.86	<0.43
1,2,3,7,8,9-HxCDF	<0.45	<0.43	<0.84	<0.42
2,3,4,6,7,8-HxCDF	0.98	0.85	2.9	<0.36
1,2,3,4,6,7,8-HpCDF	0.53	<0.74	3.7	1.7
1,2,3,4,7,8,9-HpCDF	<0.73	<1.2	<1.5	<1.2
PCDD+PCDF	10	6	58	13
TE BGA excl. NWG	0.13	0.10	0.42	0.018
TE NATO/CCMS excl. NWG	0.12	0.10	0.41	0.017
TE BGA 1/2 NWG	0.49	0.54	1.30	0.60
TE NATO/CCMS 1/2 NWG	0.61	0.75	1.66	0.83
TE BGA incl. NWG	0.86	0.98	2.18	1.18
TE NATO/CCMS incl. NWG	1.11	1.40	2.92	1.64

Notes: 1. * analyzed by Landesumweltamt Nordrhein – Westfalen laboratory 20. 04. 1998.
2. n.d. – not detected.

Table 3. **Concentrations of PCB in Oil Shale (EOIL1 and EOIL1B) Led to the Baltic Thermal Power Plant Oven, as well as in Fly Ash (EOIL2 and EOIL2B) Caught by Electrostatic Precipitators [8]**

PCB* isomers	Concentrations, μg/kg			
	EOIL1	EOIL1B	EOIL2	EOIL2B
Trichlorbiphenyl	0.49	0.52	0.20	0.06
Tetrachlorbiphenyl	2.2	2.1	0.54	0.22
Pentachlorbiphenyl	4.7	4.4	1.0	0.43
Hexachlorbiphenyl	1.2	1.1	0.41	0.25
Heptachlorbiphenyl	0.36	0.31	0.19	0.14
Oktachlorbiphenyl	n.d.	n.d.	n.d.	n.d.
Nonachlorbiphenyl	n.d.	n.d.	n.d.	n.d.
Decachlorbiphenyl	<0.13	<0.012	<0.040	<0.018
Sum: Tri + Decachlorobiphenyl	9.0	8.6	2.4	1.1
2,4,4'-Trichlorbiphenyl	0.16	0.15	0.039	0.014
2,2',5,5'-Tetrachlorbiphenyl	0.52	0.48	0.13	0.041
2,2'4,5,5'-Pentachlorbiphenyl	0.82	0.83	0.18	0.071
2,2'4,4'5,5'-Hexachlorbiphenyl	0.37	0.33	0.12	0.065
2,2'3,4,4',5'-Hexachlorbiphenyl	0.39	0.42	0.14	0.090
2,2'3,4,4',5,5'-Heptachlorbiphenyl	0.077	0.067	0.041	0.029
3,3'4,4'-Tetrachlorbiphenyl	<0.026	<0.019	<0.010	<0.010
3,3'4,4',5-Pentachlorbiphenyl	<0.026	<0.023	<0.008	<0.013
3,3'4,4'5,5'-Hexachlorbiphenyl	<0.016	<0.007	<0.006	<0.006

Notes: 1. * analyzed by Landesumweltamt Nordrhein – Westfalen laboratory 31. 03. 1998.
2. n.d. – not detected.

Estonian thermal power plants are the world largest thermal power plants burning low-grade local oil shale. During the European Dioxin Project the concentration of dioxins was determined at Baltic Power Plant in oil shale (EOIL 1 and 1B) and fly ash (EOIL 2 and 2B) taken from electrostatic precipitators (Tables 2 and 3).

The concentration of the most congeners was below the detection limit of the method. Based on the two fly ash analyses, it was concluded that the power plants are probably not the major sources of dioxins [9].

The PCDD/Fs were slightly more concentrated in the fly ash samples. The values obtained were near the lower end of the range measured for dioxins in the filter dust samples taken from German plants combusting hard coal and brown coal (0.3–21.0 ng I-TEQ/kg) [9]. It should be noted that the European Dioxin Inventory did not include any measurements of air emission from the sources in Estonia, and that the estimation of the emission based on fly ash analysis can be very inaccurate, especially in the case of very unusual processes like oil shale burning.

Data on dioxin emission factors for oil shale combustion are not available in the literature [10]. In expert estimates of PCDD/F and PCB emissions made in some European countries, emission factors used to calculate dioxin emission at stationary fuel combustion are given in Table 4. Kakareka *et al.* [10] data on dioxin factors for oil shale are the same as those for coal combustion.

Table 4. **PCDD/F Emission Factors at Stationary Fuel Combustion, µg TEQ/t [10]**

Fuel	Power generation	Industrial & municipal	Residential
Fuel oil and other liquid fuels	0.2	0.2	0.2
Coal	0.2	1	2.5
Peat	0.2	1	2.5
Firewood	0.2	1	5
Oil shale	0.2	1	2.5

As in Estonia actual data on PCDD/Fs emissions are needed, dioxin was measured in air emission from one oil shale processing plant and four oil shale-fired boilers at two power plants located near the town of Narva, Estonia, on March 3–8, 2003.

Danish Cooperation for Environment in Eastern Europe (DANCEE) sponsored the project: "Dioxin emission from oil shale-fired power plants in Estonia" and dk-TEKNIK ENERGY & ENVIRONMENT was responsible for the measurements, which where conducted in cooperation with the Estonian Environmental Research Centre [11].

Conclusion

Based on the analyses of PCDD/Fs and PCBs in oil shale and fly ash it was concluded that the power plants are probably not the major sources of dioxins in Estonia. The results of the European Dioxin Emission Inventory Project have been discussed with the experts [12], and it has been estimated that the oil shale power plants are not the main sources at the European level, but may still be the major ones in Estonia. Therefore, for the further research on dioxins in Estonia, it is very important to elucidate the significance of this source.

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Presented by A. Raukas
Received March 23, 2004