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DIOXIN EMISSION FROM TWO OIL SHALE FIRED POWER PLANTS IN ESTONIA

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It should be noted that the European Dioxin Inventory did not include any measurements of air emission from sources in Estonia. As real dioxin emissions measurements in Estonia were highly needed, dioxin emissions from four oil shale-fired boilers at two power plants (Balti PP and Eesti PP) located in North-East Estonia were measured 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 (now FORCE Technology) was responsible for the measurements, which where conducted in cooperation with the Estonian Environmental Research Centre (EERC) in Tallinn.

All the measured concentrations of dioxins emitted from the two power plants are very low owing to highly efficient combustion of oil shale in the furnaces at very high temperature, effective turbulence and long retention time. The total annual emission of dioxins from oil shale-fired power plants to the air is estimated to be 160 to 300 mg I-TEQ, which is more than ten times below the previous estimations. The total annual emission of dioxins with ashes is considered to be very close to zero, however, due to the periods of unstable combustion conditions, it would be higher, though estimated to be less than 1 g.

Introduction

Oil shale resources occur in many countries, among those three countries (USA, Russia and Brazil) account for 86% of the resource in terms of shale

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oil [1]. The reserves of oil shale in the world are estimated in the amount of 10^{13} t, i.e. they exceed the resources of other solid fuels (coal, lignite and brown coal) all taken together. Two deposits –Estonia deposit and Tapa deposit – have been explored. The reserves of Estonia deposit lying in the area of about 2,000 km² make nearly 5×10^9 t [2].

Until 1998 the concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs) in Estonian oil shale and fly ash were not measured [3, 4]. A discussion with Danish specialists [5, 6] had led to the conclusion that Estonian oil shale power plants may not be the main sources of dioxins at European level, but still major sources in Estonia. It should be noted that the European Dioxin Inventory [3] did not include any measurements of air emission from the sources in Estonia.

Dioxin emissions from four oil shale fired boilers at two power plants located near the town of Narva in Estonia were measured in March 2003. These two power plants produce more than 90% of the power supply in Estonia by combusting more than 10 million tons of oil shale per year, which is around 85% of the total consumption of oil shale in the country. These power plants are the world's largest thermal power stations burning low-grade oil shale.

Emissions of dioxins from oil shale fired plants into the air were measured in Estonia for the first time. The aim of the measurements was to get background data for the estimation of the annual dioxin emission from oil shale power plants in Estonia in order to improve or qualify the estimation based on emissions factors for large coal-fired power stations given in the recent DANCEE Project: Survey of anthropogenic sources of dioxins in the Baltic Region [5, 6].

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Oil Shale

Oil shale is one of the most important mineral resources found in Estonia. By the appearance it resembles brownish, flaky stone. Oil shale contains a significant amount of non-combustible material. Oil shale has a laminated structure, and is soft enough to be scratched with fingernails. Thin oil shale leaves can be lit with a match. This is the reason why oil shale is referred to as "burning rock" in Estonian.

Table 1. **Properties of Crushed Oil Shale [7, 8]**

Parameter	Range	Mean
Heating value, kcal/kg	1,800–2,400	2,000
Moisture, %	11–14	11.4
Organic part, %	28.4–39.2	29.4
Carbonate part, %	29.5–50	45.0
Ash content, %	–	45
Chlorine (dry fuel), %	0.21–0.29	0.22
Sulfur (dry fuel), %	1.7–1.95	

The relatively high content of chlorine in oil shale (0.22%) compared to other fuels, could possibly lead to an increased formation of dioxins. The data on oil shale composition are given in Table 1.

Power Plants

Balti Power Plant was built between 1959 and 1966. It is located 5 km from the town of Narva. The installed capacity of the plant was 1,624 MW of electricity and 505 MW of district heating, but today the available capacity is 1,090 MW, due to shutting down eight of the original 18 boilers TP-17 and two of the eight boilers TP-67.

Eesti Power Plant was built between 1969 and 1973. It is located 25 km from the town of Narva. The installed capacity was 1,610 MW of electricity and 77 MW of heat. Fourteen of the installed sixteen boilers TP-101 are in operation.

Three types of boilers of different size at the two plants are designed especially for burning oil shale. Oil shale is crushed to powder, mixed with preheated combustion air, and burned directly in the furnaces. Combustion is operated at about 5–6% O_2, but due to leaks, O_2 concentration will rise to 8–10% after the electrostatic precipitator (ESP). The maximum combustion temperature usually exceeds 1400 °C. Residence time in the high-temperature zone of the boilers in normal operating conditions is in the range of 1–1½ seconds.

Methods and Materials

Emission sampling was performed with a sampling train according to the filter/condenser method described in the CEN standard EN 1948 part 1, Sampling. Two simultaneous samples were taken from each of the four boilers (Table 2). In addition, four ash samples were taken by the plant staff during the emission sampling. The ash samples were proportional mixtures of bottom ash and fly ash.

The obtained emission samples were analyzed according to EN 1948 parts 2 and 3. Quantitative determinations of PCDD/PCDF in various samples according to the isotope dilution method were carried out by means of 2,3,7,8-PCDD/PCDF substituted 13C-UL-labeled internal standards. Before extraction, internal standards were added to the filter. Condensate and rinse were filtered, and this filter was treated together with the sampling filter with hot aqueous acid, and afterwards dried with acetone. Acid, acetone from drying filters, rinsing solution and condensate were combined and extracted with toluene. The filters and XAD-2 tubes were Soxhlet-extracted by toluene. Clean-up was done on multicolumn systems involving various kind of treated silica gel, aluminium oxide, carbon-on-fiber or carbon-on-celite. The final extract was reduced to dryness and dissolved in syringe standard.

Ash samples were extracted with toluene after degradation and addition of 13C-UL-labeled internal standards. The clean-up was done on multicolumn systems (compare above). The final extract was reduced to dryness and dissolved in syringe standard.

The measurements of both sample extracts were carried out by using an HRGC/HRMS combination with HP 5890 series II / VG-AutoSpec on DB 5 and SP2331 capillary columns. For each substance two isotope masses were measured.

Results and Discussion

The main results – expressed as the average of two samples from each boiler – are shown in Table 2. The range for dioxin concentration represents the measured values, without the congeners below the detection limits and the value including the detection limit for these congeners.

Table 2. **Main Results of Dioxin Measurements of Air Emissions**

Item	Balti Power Plant		Eesti Power Plant	
	Boiler type			
	TP-17	TP-67	TP-101	TP-101
Oil shale consumption rate, t/h	67	115	122	122
Steam production, t/h	190	280	320	320
Dioxins (at 10% O_2), pg I-TEQ/m^3 (s,d^*, 10% O_2)	2.9–3.9	80	0.8–1.1	1.2–1.5
Dioxin emission factor, ng I-TEQ/ton oil-shale	17–24	400	2.3–3.0	3.4–4.3
Dioxins in ash, ng I-TEQ/kg dry ash	0.04–0.48	0.0–0.98	0.0–0.58	Not analyzed
Particles in flue gas, mg/m^3 (s,d)	3,400	60	240	400
Flue gas temperature, °C	139	204	195	205
Flue gas flow, m^3/h	614,000	1,033,000	994,000	1,015,000
Flue gas flow, m^3/h (s,d)	375,000	548,000	515,000	517,000
H_2O content (wet gas), %	8.4	8.0	9.9	10.2
O_2 content (dry gas), %	11.3	10.3	7.8	8.5
CO_2 content (dry gas), %	7.9	9.1	11.6	12.0
CO content (dry gas), mg/m^3 (s,d)	< 1.0	26	< 1.0	< 1.0

* *s* refers to the standard conditions 0 °C and 101,3 kPa, and *d* refers to dry gas.

The values are generally very low, except the data for the boiler TP-67 at Balti Power Plant, that are close to the EU emission limiting value of 100 µg I-TEQ/Nm³ for municipal solid waste and hazardous waste incineration. This significantly higher emission is most likely due to operational problems. The boiler had just been started a few hours before the measurement started, and one of the four hammer mills pulverizing oil shale was shut down twice during the sampling period. Obviously, combustion conditions were not optimal and stable, which is also documented by high concentration of CO, which was nearly 50 mg/m³(s,d) when sampling was started, but it decreased to a not-detectable-level by the end of the sampling period, as shown in Fig. 1. CO concentrations were not detectable at any of the other power plant boilers.

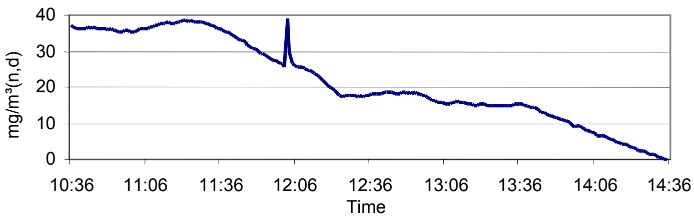

Fig. 1. CO emission from the boiler TP-67

Low values are in the same range as the blanks, and the dioxin pattern for all samples and blanks are nearly identical, except the ones for the TP-67 boiler, which are slightly different. It is very clearly seen in the graph for the dioxin congener pattern in Fig. 2.

For the TP-67 boiler, the proportion of OCDD and OCDF are remarkably lower and that of 1,2,3,4,6,7,8-HpCDD higher than in the case of other samples. This indicates that this particular boiler operated in different combustion conditions during the sampling time. This sample is therefore considered to represent start-up situations or periods of other unusual combustion conditions.

Dioxins in Ash

The concentrations of dioxins in the ash samples from the power plants were mostly below the detection limit. Only one congener in one of the samples was slightly above the detection limit. This strongly indicates a generally highly efficient combustion. The low values are in line with the previous findings in the European Dioxin Emission Inventory [3].

High values of emission from boiler No. 25 into the air did not correspond to their low levels in the ash sample from this boiler, which were just as low as in the other ash samples. The staff sampled it, and most likely they did it by the end or after the sampling period. At this time the combustion was stabilised, CO was not detectable, and dioxin concentration could have decreased to the same low level as found in the case of other boilers.

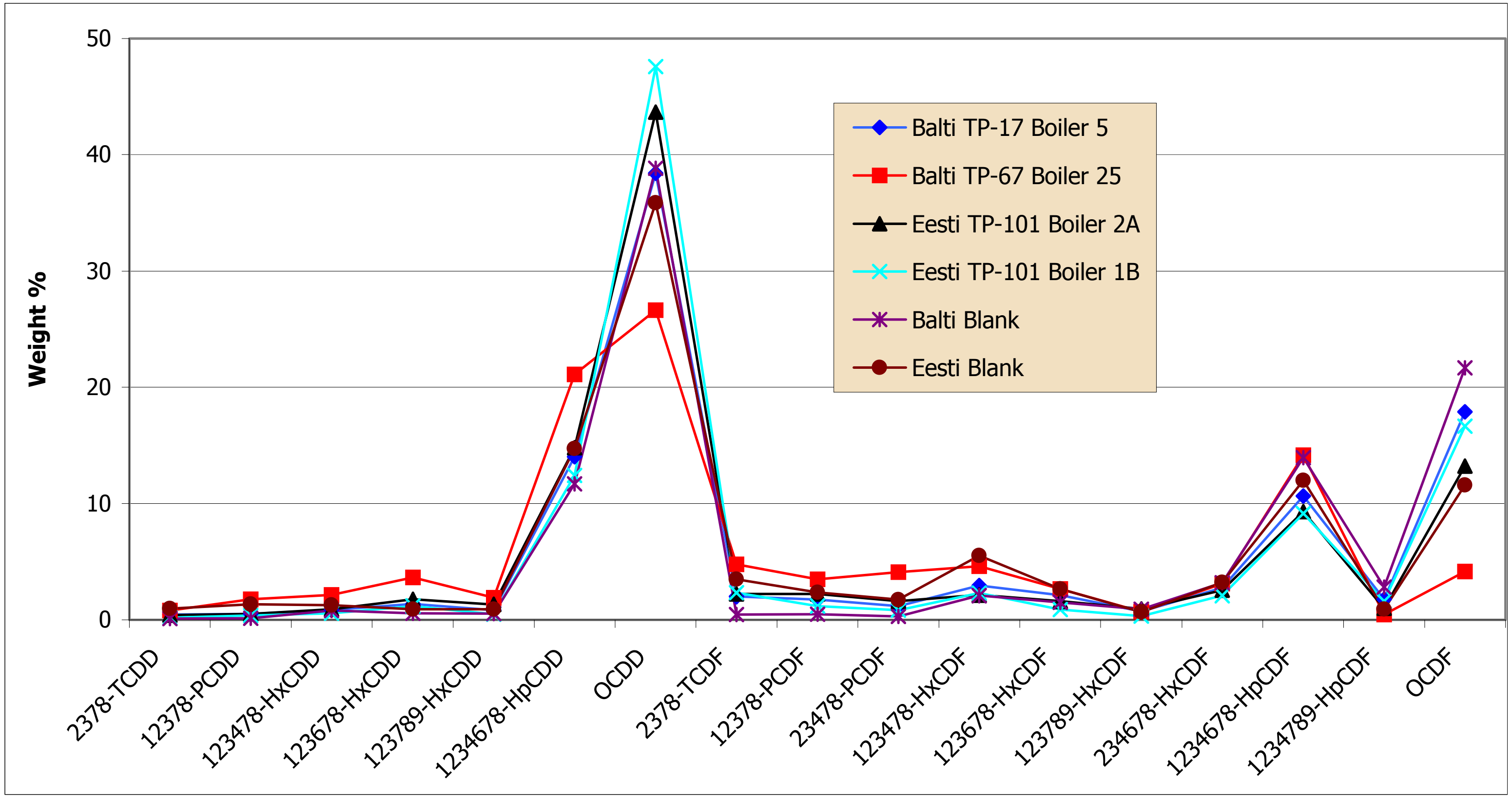

Fig. 2. Dioxin congener pattern for all emission samples and blanks

Ash samples taken at the start of the sampling period would most likely contain a higher amount of dioxins.

Total Annual Dioxin Emission

The total emission of dioxins from the two plant sites can be estimated to be 160 to 300 mg I-TEQ yearly, basing on the average of three lower emission values and the assumption that all boilers in total have one day a month with start-up or operational problems and a higher emission as found for the TP-67 boiler. The calculation is also based on a total yearly consumption of oil shale at 10 Mt for the two power plants.

In the previous publication [5] the emission factor for shale oil power plants in Estonia was estimated to be 300 ng I-TEQ/ton oil. This corresponds to 3 g I-TEQ per year, or ten times higher emission than our results. These low values from shale oil plants indicate also that the national emission estimate of 4.9 g I-TEQ per year from power generation and heating [6] published earlier is too high.

The total annual dioxin emission with ashes is, basing on the measurement, considered to be very close to zero. During start-ups and other periods with unstable combustion conditions, dioxin concentrations in ashes could be higher, and some dioxin emissions with the ash must be expected, but the total amount is supposed to be low, less than 1 g/year, which should be compared with the large amount of ashes of about 4.5 Mt. Most of the ash is dumped in huge ash landfills.

Conclusions

- All the measured concentrations of dioxins from the two power plants are very low as combustion in the furnaces is very efficient owing to very high temperature, effective turbulence and long retention time.
- The total annual dioxin emission from the oil shale-fired power plants into the air is estimated to be160 to 300 mg I-TEQ, which is more than ten times lower than the previous estimations.
- The total annual dioxin emission with ashes is considered to be very close to zero, but due to the periods of unstable combustion conditions, it would be higher, though estimated to be less than 1 g.

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