DIOXIN EMISSION FROM TWO OIL SHALE FIRED POWER PLANTS IN ESTONIA

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Introduction

In March 2003, dioxin emissions were measured from four oil shale fired boilers at two power plants located near the city of Narva in Estonia. The two power plants produce more than 90 % of the electricity consumption 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.

These measurements of dioxin air emission from oil shale fuelled plants are the first performed in Estonia. 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 /1,2/.

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.

Oil shale

Oil shale is one of the most important mineral products found in Estonia. Its appearance resembles brownish, flaky stone. Oil shale contains significant amount of non-combustible material, i.e. ash. 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. Crushed oil shale and properties

Parameter	**Unit**	**Range**	**Mean**	
Heat 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	
Chloride (dry fuel)	%	0.21 – 0.29	0.22	
Sulfur (dry fuel)	%	0.50 – 0.69	0.52	

The relatively high content of chlorine (0.22 %) compared to other fuels, could possible lead to an increased formation of dioxins.

The power plants

The Balti Power Plant was built between 1959 and 1966. It is located 5 km from the town of Narva. The installed capacity 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 and two respectively, of the originally 18 TP-17 and eight TP-67 boilers.

Figure 1. The Balti Power Plant

The Eesti Power Plant was built between 1969 and 1973. It is located 25 km from the town of Narva. The installed capacity is 1,610 MW of electricity and 77 MW of heat. Eesti PP has fourteen TP-101 boilers in operation, out of the originally 16 boilers.


Figure 2. The Eesti Power Plant

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

Methods and Materials

Emission samplings were 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. In addition, the plant staff collected four ash samples, during the emission sampling. The ash samples were proportional mixtures of bottom ash and fly ash.

The obtained emission samples were analysed according to EN 1948 part 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. Cleanup was done on multicolumn systems involving various kind of treated silica gel, aluminium oxide, carbon-on-fibre or carbon-on-celite. The final extract was reduced to dryness and dissolved in syringe standard.

The ash samples were extracted by means of toluene after degradation and addition of 13C-UL-labeled internal standards. The cleanup 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 2 isotope masses were measured.

Results and Discussion

The main results - expressed as the average of the two samples from each boiler are shown in Table 2. The range for the 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

Parameter	Unit	Balti Power Plant		Eesti Power Plant	
	Boiler type	TP-17	TP-67	TP-101	TP-101
Oil shale burning capacity	t/h	67	115	122	
Steam production	t/h	190	280	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 analysed
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	mg/m^3 (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,d): **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 for the TP-67 boiler at Balti Power Plant, which is close to the EU emission limit value of 0.1 ng I-TEQ/Nm³ for municipal solid waste and hazardous waste incineration. The explanation for the significant 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 for pulverising the oil shale was shut down twice during the sampling period. Obviously, combustion conditions were not optimal and stable, which is also documented by the high CO concentration, which was nearly 50 mg/m³(s,d) when sampling was started, but it decreased to not-detectable-level by the end of the sampling period, as shown in Figure 3. CO concentrations were not detectable at any of the other power plant boilers.

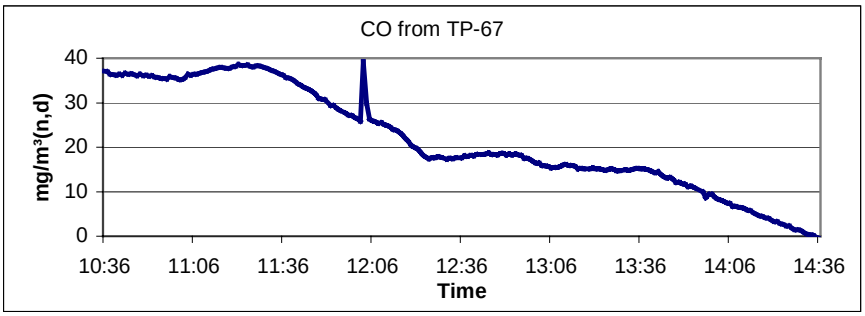

Figure 3. CO emission from boiler TP-67

The 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 is slightly different. It is very clearly seen in the graph for the dioxin congener pattern in Figure 4.

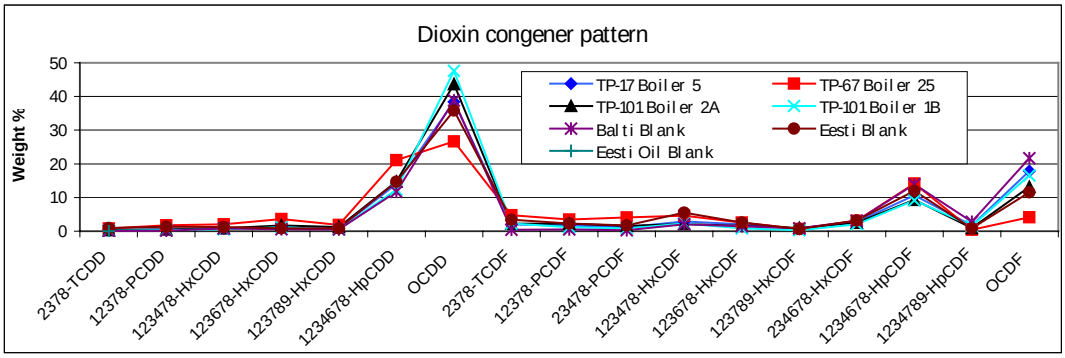

Figure 4. Dioxin congener pattern for all emissions samples and blanks

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

Dioxin in ash

The concentrations of dioxin 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 limit of detection. This strongly indicates a generally very efficient combustion. The low values are in line with the previous findings in the European Dioxin Emission Inventory [4].

The high air emission values of Boiler 25 did not correspond to the low levels in the ash sample from this boiler, which were just as low as 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 from the other boilers. Ash samples taken from around the start of the sampling period would most likely have contained a higher concentration of dioxins.

Total annual dioxin emission

The total emission of dioxins from the two plant sites can be estimated to 160 to 300 mg I-TEQ/year based on the average of the 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 /1/ the emission factor for the shale oil power plants in Estonia was estimated to 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 earlier published national emission estimate of 4.9 g I-TEQ per year from power generation and heating /2/ is too high.

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

Conclusions

All the measured dioxin emission concentrations from the two power plants and the oil plant are very low with exception of one measurement, which was close to the EU emission limit value for MSWI. This high value is most likely due to start up and operational problems, and it may be regarded as representative for periods with less efficient combustion then normal. The very low dioxin emissions are due to the very efficient combustion in the furnaces due to very high temperatures, turbulence and long retention times.

The total annual dioxin emission from the oil shale fired Power Plants to the air is estimated to 160 to 300 mg I-TEQ, which is more then ten times lower than previous estimations.

The total annual dioxin emission with the ashes is considered to be very close to zero, but due to periods with unstable combustion conditions, it could be higher, but estimated less than 1 g.

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