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THE DANISH INCINERATOR DIOXIN STUDY. Part 1.

O. H. Manscher*, N. Z. Heidam, J. Vikelsøe, P. Nielsen[1], P. Blinksbjerg[1], H. Madsen[2], L. Pallesen[3] and T. O. Tiernan[4].

National Environmental Research Institute,
Frederiksborgvej 399,
DK-4000 Roskilde,
Denmark.

1) DK-TEKNIK, Gladsaxe Møllevej 15, DK-2860 Søborg, Denmark.
2) IMSOR, Building 321, Technical University of Denmark, DK-2800 Lyngby, Denmark.
3) Statens Seruminstitut, Amager Boulevard 80, DK-2300 S, Denmark.
4) Wright State University, 175 Brehm Laboratory, Dayton, OHIO 45435, U.S.A..

ABSTRACT

During the last two years an extensive series of dioxin measurements has been conducted on Danish municipal and hospital solid waste incinerators. The study was directed toward finding the total annual dioxin emissions from MSWI in Denmark, now estimated to be 3 kg. of dioxines and furanes. This sum is equivalent to 50 g. of 2,3,7,8-TCDD according to the Nordic Equivalents. Measurements were carried out according to a statistical design following a plan of pre-randomized sampling. This procedure allowed causal interpretation of the correlations found between the dioxin emissions and certain operating parameters. The statistical model obtained describes the emissions by variations between incinerators, by variation in time, and by changes in the load, the excess air and the HCl concentration in the flue gas.

KEYWORDS

Chlorinated dibenzo-p-dioxin and dibenzofuran; MSW and Hospital Incinerators; Emission; Operating parameters; Hydrogen Chloride.

INTRODUCTION

This dioxin study (Danmarks Miljøundersøgelser and DK-TEKNIK, 1989) was initiated by a decision in the Danish Parliament in 1985. The Minister of the Environment was called upon to establish a plan of action for dioxin, that came to involve this project concerning measurements on danish municipal solid waste (MSW) incineration plants. The project had three aims. The first was to determine the total annual emission of dioxines from the municipal solid waste incinerators in Denmark. The second was to find correlations between operating conditions and the emissions. The third was to establish the conditions for a program of control measurements on the incinerators.
During this project 350 samples were taken at 10 different municipal solid waste incinerators and at two hospital incinerators. 180 of these samples were analyzed at two laboratories.
This paper is the first of a series describing the experiments and the results obtained.

EXPERIMENTAL

Samples. The samples for the dioxin analysis were taken with an equipment compatible with the Nordic recommendation (Jansson and Bergvall, 1987). The flue gas was extracted isokinetically from the stack, passed through a quartz wool filter placed in a thermostated oven to collect the particulates, then through a watercooled condenser and finally through a XAD-2 filter. The thermostated oven was kept at 120 °C instead of the recommended 160 °C, giving a higher recovery of the field spike. During this project two parallel dioxin samples were taken from nearby places in the stack with a sampling time of generally 1 3/4 hour.

Incinerators. The incinerators were divided into five groups(A-E), according to their construction, plus one group(H) for the hospital incinerators.

Emission. Defined as the total sum of the tetra- to octa-chlorinated dibenzo-p-dioxines and dibenzofuranes.

The operating conditions of the incinerator and some constituents of the flue gas were continuously measured, and every 5 minutes the mean values were recorded in a computer system.

The load. The load was defined as the thermal output of the incinerator and calculated from measurements of the flow of water in the boiler and the temperature difference between the inlet and outlet.

Combustion air flow. Calculated from measurements of the air velocity by a pitot tube and the cross-section of the duct.

Temperatures. They were generally taken from the instrumentation of the plant, but the temperature of the flue gas was measured by DK-TEKNIK with a NiCr/NiAl thermocouple.

CO and CO_2 . Measured by nondispersive infrared (NDIR) in the dried flue gas. For these two parameters the 1 minute means were also recorded.

Excess air. The excess air was described by measurements of the oxygen in dried flue gas with an electrochemical solid phase monitor.

For some constituents of the flue gas only one sample per period were taken:

HCl and SO_2. Determined by taking separate streams of flue gas through bubble flasks, followed by titration. The sampling time was generally one hour within the dioxin sampling period.

Water vapour. The volume of the condensate in the dioxin sampler was measured.

Particulates. The material collected on the quartz wool filter in the dioxin sampler was weighted.

Analytical methods. A spike program was developed for this project, using a penta- and a hepta- ^{13}C labeled furan as field spikes, and a penta- and an octa- ^{13}C labeled furan as laboratory spikes. ^{13}C - labelled dioxines are used in each group as internal standards, and the results are calculated by the internal standard ratio method. The reported values for the dioxin and furan concentrations were corrected for the recovery of the laboratory spike, but not for the recovery of the field spike, as field recovery correction was found to impair precision and fit of data to the statistical model.The dioxin samples were analyzed at two laboratories, the Division of Environmental Chemistry of the National Environmental Research Institute in Denmark and the Wright State University in Ohio, U.S.A.. Further details on the dioxin analyses are given in the article by Vikelsøe and Tiernan (1990).

Statistical methods : The sampling strategy was based on a statistical experimental design. In the design three operating parameters were considered. The objective was to select parameters that could be actively varied by the operators at almost all the incinerators, and parameters that might be directly related to the dioxin emission. The actively manipulated parameters considered were the load, the excess air and the ratio between the underfire and overfire combustion air. A complete factorial design based on these three parameters was the basic unit of the design, which was also used to construct plans for the pre-randomized sampling sequences. Besides these three parameters, a number of other conditions could influence the measured levels. Examples are the time of sampling, the analyzing laboratory, the sampling equipment and the different incinerators. These factors were also considered in the statistical design.
The recorded 5-minutes means were subjected to detailed analysis, and statistics such as the mean, variance and extreme values for the whole period formed the basis for further analysis. As an example, the temperatures were subjected to a principal component analysis in order to reduce the number of parameters.
For the statistical analysis general linear models were applied. By using this model frame the advantages of analysis of variance and regression analysis could be combined. For the calculations the GLM-procedure in SAS(1988) was used. The statistical design ensures a causality for the factors considered in the design, but the analysis can also reveal correlations between emissions and other parameters. Further details on the statistical design are given in Pallesen and Madsen (1990).

RESULTS

It was found that the reported dioxin levels (Table 1), calculated according to the above definition, were greatly influenced by the different incinerators, by the sampling time and by the analyzing laboratory. These block effects explains 73 % of the variance of the data. These results are further discussed in Manscher et al. (1990).

Table 1. Measured mean total dioxin/furan emissions .

Construction group.	Incinerator	Total emission (ng/Nm³)
	Municipal	
A	Reno Syd 1. round	77
A	Reno Syd 2. round	18
A	Århus Nord	23
B	Brøndby	80
C	Kara	473
C	Thyra	428
C	Refa 1. round	37
C	Refa 2. round	39
D	Reno Nord 1. round	391
D	Reno Nord 2. round	171
D	Reno Nord 3. round	47
D	Amager	281
E	Helsingør	117
E	Albertslund	11
	Hospital	
H	Dybendal	2910
H	Hvidovre	3490

Block effects

Incinerators. As expected, a great variation from incinerator to incinerator is seen. The estimated mean emissions range from 10 to 500 ng/m³. The older and smaller incinerators (group E) were expected to have a high emission, but this was not found. The data suggest differences in the emission levels between the groups, however the effect of the sampling period implies that the differences are statistically non-significant. The only group, that is significantly different, is the group of hospital incinerators (group H). For the two incinerators examined in that group an emission level forty times higher than the average municipal waste incinerator were found, based on the amount burned.

Sampling equipment. The analyzed samples were taken evenly from the two parallel samplers. No systematic variation due to the sampling equipment was found, even in the few cases, where significant differences between the particulates collected were seen.

Sampling time. Two of the incinerators were visited twice during the project, and one of the incinerators was visited three times. During each round measurements were taken over a period of 2-3 consecutive days. The day-to-day variation was found to be much less than the period-to-period variation. The latter could be as high as a factor of four.

Analyzing laboratory. The two laboratories reported results, that differed by a factor of two, even though the results from WSU were corrected to the Danish standards using results from the mutual analysis of the two sets of isotope-labelled standards. Since results from the Danish laboratory had a smaller standard deviation than WSU when used in the statistical model calculations, the Danish results were used for the calculation of the total emission levels.

Calculations of the total emission

Based on the emissions in table 1 an average total dioxin/furan emission of 260 ng/m³ at 10 % oxygen was calculated, corresponding to 4 ng/m³ of toxic equivalents. These numbers refers to the emission of an average MSW incinerator operating at its design thermal output with normal excess air and 500 mg/m³ of HCl in the flue gas, and the emission analyzed by the Danish laboratory. It corresponds to a total emission of 1.3 mg/ton of waste burned.

Table 2. Total annual dioxin/furan emissions in Denmark.

	Waste burned t/year	Emiss. fact. mg/t	Total sum kg/y	Toxicity eqv.(Nordic) g/y
MSW incinerators	1,706,000	1.3	2.2	34
Hospital "	17,000	53.	0.9	14
Total	1,723,000		3.1	48

The toxicity equivalents are calculated according to Manscher and Madsen (1990), using a factor of 1.5 % of the total sum. In spite of the fact that the hospital incinerators only burn 1 % of the waste, they contribute 30 % of the total dioxin/furan emissions.

Operating parameters

The operating parameters have a great influence on the emission of an individual incinerator. When they are taken into account simultaneously with the block effects, 92 % of the variance is explained.

The equation describing these influences is

$$Log_e(emission) = \mu(\ ) + 2.53*RLD + 0.23*O_2 + 0.19*log_e(HCl) \quad (1)$$

where emission is the expected measurement of the total sum of tetra- to octa-chlorinated dioxines and furans per Nm^3 at 10 % oxygen; $\mu(\ )$ is a constant accounting for the block effects of the particular incinerator, the time of sampling and the analyzing laboratory; RLD is the relative load deviation from the design load; O_2 is the difference of the oxygen percentage from a nominal value of 11 % in the dry flue gas, and HCl is the content of hydrogen chloride in the flue gas measured as mg/m^3. These results are further discussed in Nielsen et al. (1990) and Vikelsøe et al. (1990).
The calculated variations in emissions are shown in table 3. Due to the proportionality between the total amount of dioxines and furanes and the toxic equivalents, the changes in emissions are valid for both.

Table 3. Dependence of emissions on operating parameters.

Parameter	Low	Normal	High
Load, %	80	100	120
Relative emission	60	100	166
Oxygen %	9	11	13
Relative emission	64	100	157
HCl, mg/m^3	100	500	1000
Relative emission	73	100	114

The load. The variation of the load gives a very significant contribution to the variation of the dioxin emissions of an individual incinerator. The coefficient to the RLD in (1) is 2.53 ± 0.23, which means that an increase in the load of 10 % increases the emissions by 25 %.

Excess air. The excess air has a significant influence on the emission. The coefficient to the O_2 in (1) is 0.23 ± 0.03, which means that an increase of the excess air from 11 to 12 % oxygen will increase the emissions by 25 %. This model is valid between 9 and 13 % of oxygen. Based on the parabolic relation between oxygen and carbon monoxide, a similar relation between oxygen and dioxin with a minimum could be expected. In the dataset there is only one observation where a low oxygen is related to a high carbon monoxide, and indeed a very high dioxin concentration was found, but this single observation cannot be used as a basis for a conclusion.

Air distribution. The ratio between the underfire and overfire combustion air was shown to be not significant for the dioxin emissions. This result is in accordance with the general assumption that the dioxines in the flue gas are formed in the colder parts of the incinerator, e.g. in the boiler.

Correlations

Hydrogen chloride. For models that, in addition to the block effects, contain the parameters of load and excess air, it is found that among the rest of the parameters considered, only the hydrogen chloride becomes significant. The coefficient to the $log_e(HCl)$ in (1) is 0.19 ± 0.03, which corresponds to a 14 % increase in the dioxin emissions when the HCl emission is doubled. This relation is valid in the range of 100 to 1000 mg/m^3 of HCl. With the HCl included in the model, the percentage of variation explained rises from 92 to 93. The small magnitude of this effect probably accounts for why it has not been previously observed.

CO and temperatures. These parameters do not appear in the model, even though they correlate with the emissions. The explanation is that these parameters are affected by changes in the operating parameters, and therefore do not in themselves add any explanatory power to the model.

Carbon in flyash. Another component that was expected to influence the emissions, was the carbon in the flyash. This was examined, and no correlation was found.

Special results

Start-up. During start-up high values of CO and low temperatures are found. In this project 14 samples taken during 5 start-ups were analyzed, and the emissions were greater by a factor of 5 during the first 1-2 hours, and are nearly normal thereafter. With modern incinerators that operate continuously for long periods, this is not important, and the contribution from start-up was not included in the calculation of the total emissions.

Sewage sludge. One incinerator that regularly dries and burns sewage sludge was examined. There was a slight increase in the emissions during the burning of the sewage sludge, but it was not statistically significant.

CONCLUSIONS AND FUTURE RESEARCH

During this project we have reached a good statistical description of the changes of the dioxin/furan emissions with respect to incinerator operating conditions.It is shown, that the dioxin emissions can be reduced by operating with less excess air and by avoiding to overload the incinerators. The chemical and physical factors that affect dioxin emissions have not been investigated in this study. Also deserving further investigation are the effects of incinerator construction design parameters.

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