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EMISSION OF DIOXINS FROM DANISH WOOD-STOVES

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Abstract

The main purpose of the investigation was to estimate the annual dioxin emission from Danish wood-stoves. 4 stoves of different designs and 3 types of fuel were tested in 2 operating conditions. Sampling was carried out in a dilution tunnel, making reproducible sampling possible. The dioxin emission was found to depend significantly on the type of stove, the type of fuel and the operating conditions. The average emission was 0.18 ng TEQ/Nm^3 (Nordic) in fluegas, or 1.9 ng TEQ/kg fuel. The annual emission in Denmark was estimated to 0.40 g TEQ/year, roughly 100 times lower than the emission from incinerators previously reported.

Introduction

These studies, initiated and funded by the Danish government, represent the final investigations in the Danish Incinerator Dioxin Program. In a preliminary study of different wood-stoves and fuels[1], very high emission of dioxins were found, implying that the annual emission in Denmark of dioxins from this source would be of the same order of magnitude as the emission from incinerators. A follow-up study was subsequently carried out, involving new experiments at another test site at the Danish Technological Institute (DTI), as well as method development and validation studies at the National Environmental Research Institute (NERI)[2]. However, the follow-up study failed to confirm the previously found high emissions. A possible theory for these high values could be carry-over which had occurred at the test site during experiments with extremely high dioxin emission. The present investigation is a complete re-evaluation making use of improved testing, sampling, and analytical methods.

Objectives

The primary goal is to estimate the annual emission of dioxins from wood-stoves in Denmark. Secondary goals are to study the influence of stove design, type of fuel, and operating condition on the dioxin emission. The aim of this is to make a decision ground for reducing the dioxin emission from this source as far as possible, and to make a basis for instructions for users and manufacturers of wood-stoves.

Experimental

The wood-stove experiments were performed at DTI at a special test facility. 4 types of stoves, 3 types of fuels (all pure wood), and 2 operating conditions were investigated.

In the experimental setup, shown in Fig. 1, the stove was connected to a chimney followed by a dilution tunnel system which diluted the total stream of fluegas about 1 to 10. The tunnel was developed by DTI for these experiments, since the preliminary study[1] had shown a poor correspondence between parallel samples taken in the chimney. The low linear velocity in the chimney, 0.1 to 0.3 m/sec, makes isokinetic conditions difficult to obtain, whereas the velocity in the tunnel is constant 3 m/sec. A data logging system registered CO_2, CO, temperatures in chimney and tunnel, draught and flow. Hydrocarbons were measured by FID, chloride sampled in NaOH and analyzed by ion-chromatography.

To minimize carry-over in the system, no experiments with fuels known to be high emitters such as impregnated or painted wood were performed.

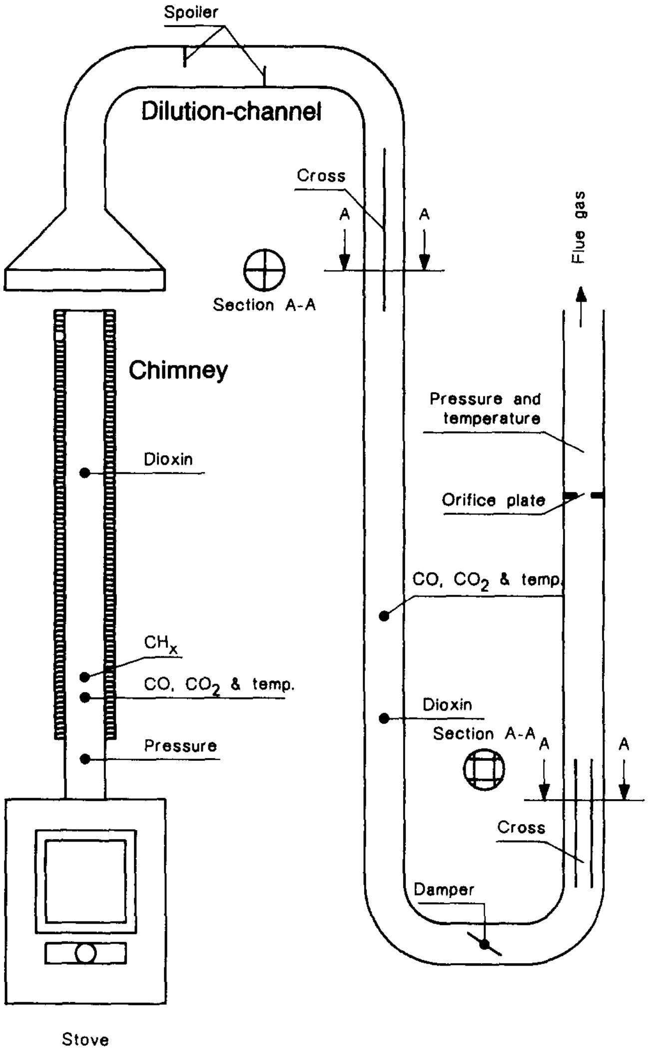

Fig. 1. Experimental setup with dilution tunnel.

Stoves

The stoves were designed for additional heating of single rooms, a widely used practice in Denmark. No. 1 and no. 2 were included in the previous studies[1] and are both widely used in Denmark, no. 3 was an improved version of no. 2. Stove no. 1 to no. 3 are commercial models, whereas stove no. 4 is an experimental prototype designed by DTI. The combustion chambers of all the stoves were lined with refractory bricks or plates 2 to 3 cm thick. The most important technical data for the stoves are summarized in Table 1.

Stove no.	1	2	3	4
Material (iron)	cast	sheet	sheet	sheet
Chamber volume, l	42	42	41	26
Heat output, kW (mean)	6.4	5.6	6.6	5.7
Fuel charge, kg	2.33	2.33	2.31	1.35
Preheating of air	-	-	+	+
2 stage inverted combustion	-	-	-	+

Table 1. Technical data of the stoves.

The experimental stove no. 4 is shown in Fig. 2 in front and left side view. It operates with inverted combustion (downward flame direction) combined with 2 stage combustion and preheating of the combustion air (not shown). The flames are drawn downward through 2 slots in the bottom of the primary combustion chamber, under which 2 secondary combustion chambers are located. The secondary air is supplied through a horizontal perforated distributor tube in the centre. The walls of the primary combustion chamber are heated by the fluegasses.

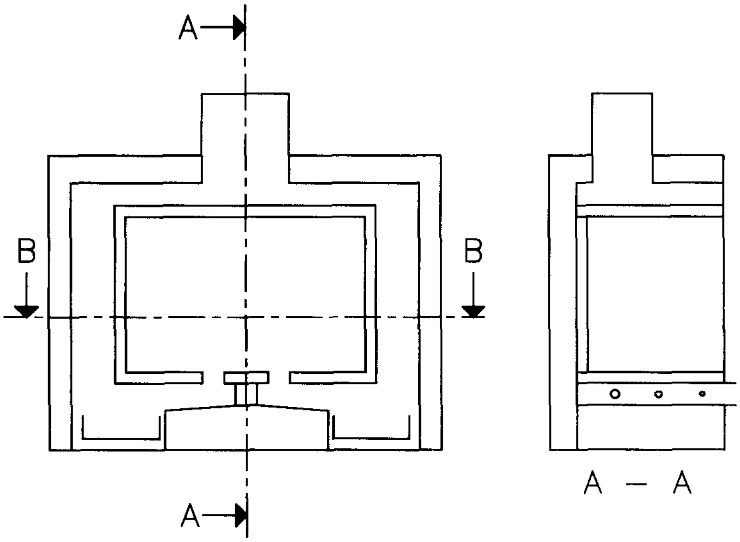

Fig. 2. Experimental prototype stove no. 4 operating with inverted 2-stage combustion.

Fuels

The following fuels were used:

- Beech, reference fuel in the previous study[1]
- Birch, Danish reference fuel
- Spruce, fuel commonly used in Denmark

The wood was harvested in forests near the test site exclusively for this investigation, to be sure that no contamination took place. It was cleaved to pieces about 30 cm long weighing 700 g + - 100 g, and equilibrated in a climate chamber to about 18 % absolute moisture. 4 to 8 kg in 3 to 4 charges were burned during each experiment.
A representative sample of the fuel for each experiment was analyzed for chloride.

Operating conditions

"Optimal" operation is defined as well controlled operation with good combustion efficiency and the emission of CO and hydrocarbons as low as possible.

"Normal" operation is expected to be representative for the use by ordinary people. Flames should be visible, and the combustion rate moderate, corresponding to the heating demand in the house. The CO would be relatively high. The results from this condition were used to estimate the Danish annual emission.

The conditions were obtained by setting the air-intakes to appropriate positions found in previous testing of the stoves according to Danish and Swedish standards. The "normal" condition was characterized by a low air intake.

Experimental procedure

Two experiments were performed a day, each comprising a full combustion cycle of at least 3 hours duration. The stove was lit with 75 % the nominal charge of fuel. When the charge was approaching burnout, i.e. flames no longer were visible, the charcoal layer was levelled, and a next full nominal charge filled in. At least 3 charges were burned in each experiment.

Experimental plan

An experimental plan was devised, comprising all combinations of stoves, fuels and operating conditions, making a total of 24 experiments. To avoid bias and systematic errors, the plan was carried out in a pre-randomized sequence. The extraction and cleanup of the dioxin samples were done in a second pre-randomized sequence, and the GC/MS performed in a third pre-randomized sequence. During analysis, the identity of the individual samples was unknown to the analysts.

Analytical Methods

The dioxin samples were taken by DTI isokinetically in the dilution tunnel according to the Nordic recommended method[3]. Quartzwool filters thermostated to 160 °C were used. A volume of 4 to 6 m^3 diluted fluegas was sampled during a whole combustion experiment, corresponding to 0.4 to 0.6 m^3 or 0.2 to 0.3 Nm^3 (20 % CO_2) undiluted fluegas. The dilution factor of the tunnel was calculated on basis of the CO_2 concentrations.

The dioxin analysis were performed by NERI. The samples were extracted by refluxing 24 hours in toluene using water-removing equipment[4]. The clean-up of the high tar samples was performed according to a procedure found in the method development study[2] using 30 g of silica and 4 g of basic alumina for 0.25 Nm^3 fluegas, omitting carbon clean-up. The samples were diluted 1 to 4 before GC/MS, which were performed on a SE-54 column as group-specific analysis. Laboratory spikes were used for recovery correction for congener groups individually, the spike mix containing 1 carbon-labelled isomer in each congener group.

Validation of the tunnel-sampling in combination with the modified analytical method was done by comparison with the method used in the preliminary study[2]. Stored samples from the previous study as well as new samples taken in chimney and dilution tunnel were analyzed with both methods. No statistical significant difference between the dioxin levels of the methods were found, e.g. the very high levels of the previous study could be reproduced by the new method. To check the general dioxin level in the study, some of the samples were analyzed by RIVM, Bilthoven, The Netherlands. The results from RIVM were on the same level as the NERI results.

Results and statistics

The predominant congener group from all the experiments of the present study was TCDF. The distribution profile of the congener groups are shown in Fig. 4 as average percent of total PCDD + PCDF. Fig. 4 includes average distribution profile from PCP-impregnated wood and pure beechwood results of the previous study[1]. It is evident that the group distribution of the present study differs sharply from that of the previous study.

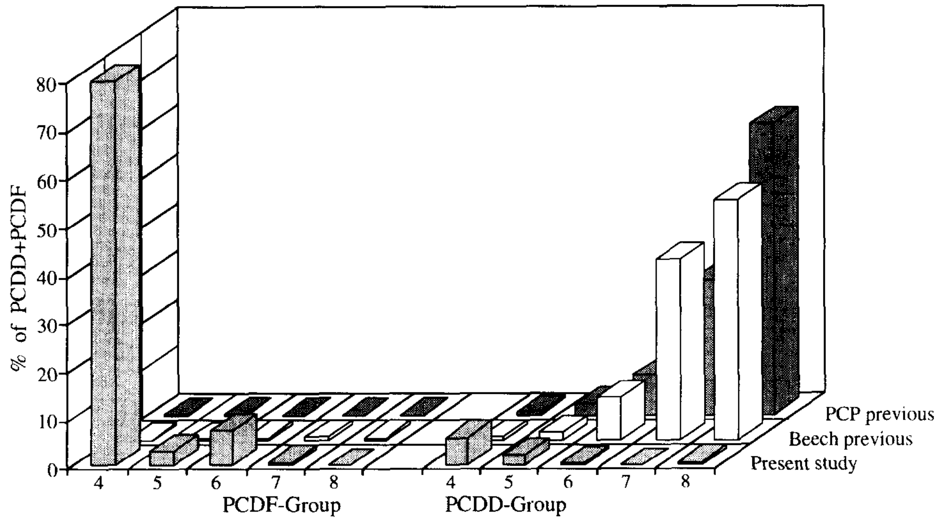

Fig. 3. Congener group distribution profile. Present study (average of all experiments) compared with previous study (average of beech wood and average of PCP-impregnated wood).

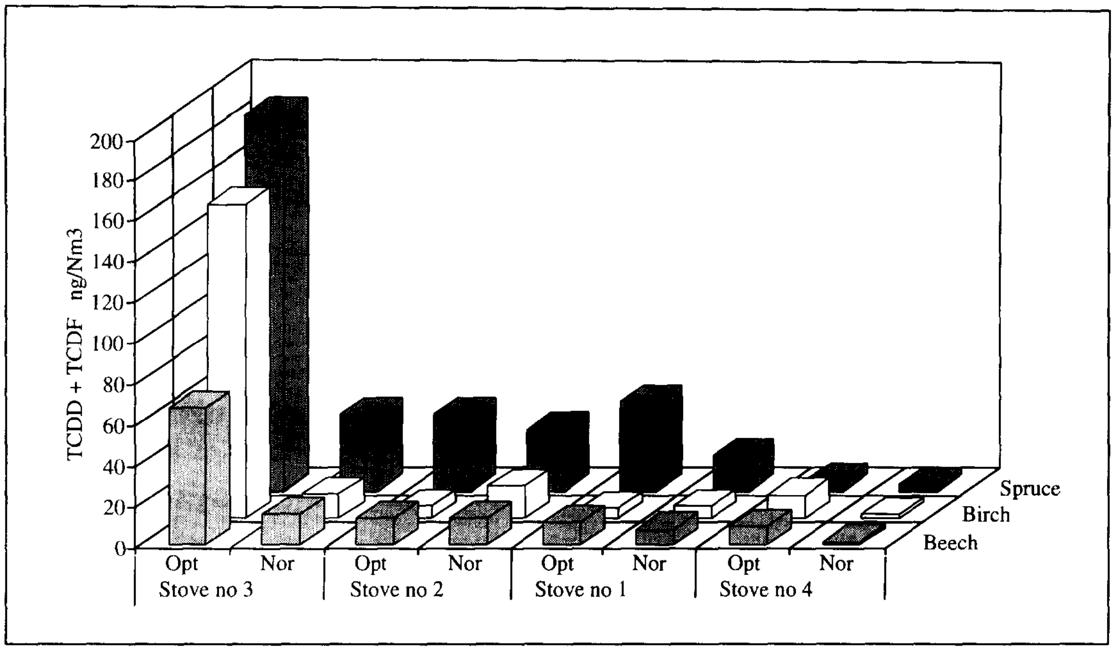

Fig. 4 Dioxin emission in fluegas from wood-stoves. Results from all experiments.

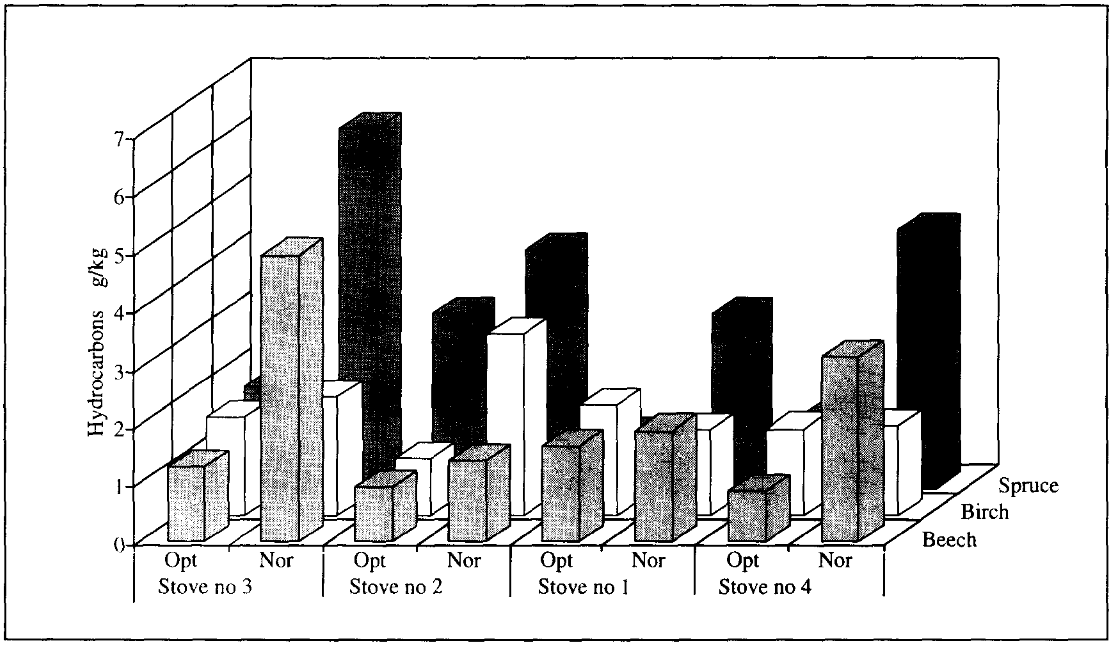

Fig. 5. Total hydrocarbon emission in fluegas from wood-stoves. Results from all experiments.

The dioxin emission from all the experiments are shown in Fig. 4, the emission of total hydrocarbons in Fig. 5. It is clearly seen that large differences between emissions from the experiments exist, the results ranging from 1.5 to 184 ng/Nm^3. Furthermore, the pattern in Fig. 4 looks very different from the pattern in Fig. 5.

A statistical analysis was performed by the Danish Prognosis Information (DPI), based on general linear models. The following statistical model involving active (direct controllable) parameters was found:

$$\log(\text{DIOXIN}) = \mu(\text{STOVE}) + \mu(\text{FUEL}) + \mu(\text{OPERATION}(\text{STOVE})) + \varepsilon$$

That is, the dioxin emission depends significantly upon type of stove, the type of fuel, and the operating conditions. However, the influence of operation depends upon the type of stove. ε is combined model and analytical error.

- The statistical analysis shows that highly significant differences between stoves, between fuels, and between optimal and normal operation for each stove exist.
- The standard deviation of the error ε in the present study is only the half of the error in the preliminary study.
- There is no interference between STOVE and FUEL, i.e. the influence of FUEL is the same for all combinations of stove and operation.
- Stove no. 4 has significantly lower emission than the others, and stove no. 1 has lower emission than stove no. 2 and no. 3.
- The emissions from birch and beech are not significantly different, but they are significantly lower than the emission from spruce (average 42 % of spruce).
- The "optimal" operation leads, somewhat surprising, to significant higher emission for stove no. 3 and no. 4 (average 230 % of emission from "normal" operation), but not for the others.

The tendency in most of these results can be recognized retrospectively in Fig. 4.

The statistical analysis was extended to include passive parameters, such as temperatures, draught, heat-output, CO, HCl and total hydrocarbons (THC) in fluegas, chloride in fuel etc. Surprisingly, the introduction of passive parameters did not lead to a significantly better model. In particular, no significant correlation between dioxin emission and HCl in fluegas was found. However, there was a weak, but not significant correlation with the chloride in the fuel (Fig. 6). Another interesting result was that no significant correlation with hydrocarbons existed. This is understandable from a comparison of Fig. 4 and Fig. 5.

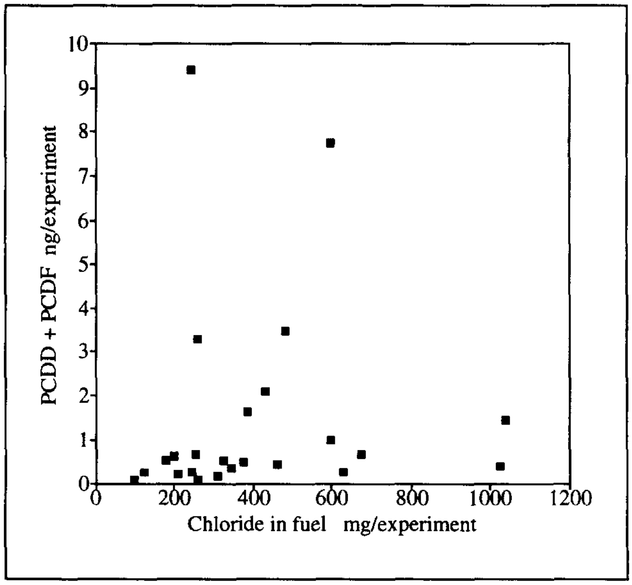

Fig. 6. Dioxin in fluegas versus chloride in fuel.
No significant correlation was found.

Finally, if all active parameters were neglected, a highly significant positive correlation between dioxin emission and heat-output emerged.

To avoid the uncertainty in estimating the volume of flue gas emitted from stoves, the statistical analysis was repeated using the dioxin emission per kg of fuel. A second statistical model was found, and this compared well with first model based on fluegas concentrations, as all the main conclusions was the same. However, the influence of fuel was more significant and pronounced in the second model, as the birch and beech emitted on the average only 34 % of spruce.

The tox-equivalents were estimated assuming the same isomer distribution in each group as previously found for MSW-incineration[5]. In this way it was found that the toxicity could be expressed in Nordic equivalents as about 1.5 % of PCDD + PCDF, the same percentage as found for incineration[5,6].

Annual emission in Denmark

The weighted average fluegas concentration from the Danish wood stoves was estimated to 12 ng/Nm^3 PCDD + PCDF, corresponding to **0.18 ng/Nm^3 TEQ Nord.**

The weighted average dioxin production based un fuel weight was estimated to 126 ng/kg PCDD + PCDF, corresponding to **1.9 ng/kg TEQ Nord.**

The annual emission from Danish wood-stoves was computed, using emission per kg of fuel, and the amounts of the various fuels sold, to **0.40 g/year TEQ Nord.** This is roughly 100 times lower than the annual emission from incinerators estimated in the Danish incinerator study[5,6].

An estimate of the uncertainty on the annual emission is roughly 60 %.

Discussion

In the previous study[1], the average emission for pure beech wood was about 10000 ng/Nm3 TCDD + TCDF, and the average for PCP-impregnated wood about 65000 ng/Nm3 TCDD + TCDF. A very likely explanation for this high emission for pure wood in the previous study is indicated in Fig. 3. It can be seen that the group-profile from the pure wood and the PCP impregnated wood of that study are very similar, HpCDD and OCDD being dominant. They are very different from the average profile of the present study, where TCDD is the main product. This strongly suggests that carry-over has been responsible, probably via soot deposited in the chimney.

In the present study, the influence of stove design and operation has been demonstrated.

- The group distribution profile dominated by TCDF is very different from the much more even profile of MSW incineration. This suggests that another formation mechanism operates, probably in the flame zone.
- The stove no. 1 and no. 2 are of very similar design, and they do not have significantly different dioxin emissions.

- A common feature of no. 3 and no. 4 is air-preheating, and both show significant difference between "normal" and "optimal" operation. The explanation of the higher emission in the "optimal" operation is not evident, as the increased air intake results in a higher heat-output, a higher fluegas temperature, a lower flame temperature and a higher oxygen concentration. The preheating of air results in higher temperatures, but this is also the case in "normal" operation. It may even be that the higher hydrocarbon concentration in the "normal" condition creates a reducing atmosphere, which suppresses chlorination and hence dioxin formation.
- Stove no. 4 operating using inverted 2-stage combustion has the lowest dioxin emission of the stoves. The reason for this is not clear, since the result is not mirrored in the physical or chemical parameters (e.g. temperatures, CO and hydrocarbons). Somehow it must be inherent in this combustion principle.

Conclusion

The results from the present study indicate that the dioxin emission from wood-stoves burning pure wood is a comparatively minor source. This can be reduced even further by improvements in the stove design and operation, and by making precautions that only pure wood is used for fuel.

Acknowledgements

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References

1 DEPA. Emissions from fireplaces and stoves. Copenhagen, Denmark: Danish Environmental Protection Agency, 1990. (DEPA Environmental Report no. 149).

2 Vikelsøe J, Cederberg T, Madsen H, Hansen K, Grove A. Emissions from Danish household stoves. Presented at the 11th International Symposium on Chlorinated Dioxins and Related Compounds, Research Triangle Park, North Carolina, USA, September 1991.

3 Jansson B, Bergvall G. Recommended methodology for measurements of PCDD and PCDF in the Nordic countries. *Waste Management & Research* 1987;5: 251-7.

4 Lamparski LL, Nestrick TJ. Novel extraction device for the determination of chlorinated dibenzo-p-dioxins and dibenzofurans in matrices containing water. *Chemosphere* 1989;19: 27-31.

5 DEPA. Dioxin emission from waste incineration plants. Copenhagen, Denmark: Danish Environmental Protection Agency, 1989. (DEPA Environmental Report no. 117).

6 Manscher OH, Heidam NZ, Vikelsøe J, Nielsen P, Blinksbjerg P, Madsen H, Pallesen L, Tiernan TO. The Danish incinerator study. Part 1. *Chemosphere* 1990;20: 1779-1784.