EMISSION OF PCDD/F FROM WOODSTOVES IN DENMARK

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Introduction

The emission of PCDD/F from incinerators and industrial sources has drastically decreased in the past decade due to installation of emission abatement systems, to be able to meet the emission limit value. The contribution of smaller sources to atmospheric concentrations of PCDD/F has therefore become more important. A reliable estimation of the contribution from these sources is difficult to obtain, but domestic burning of wood has been identified as one of the most important non-industrial sources. In the Danish Dioxin Air Emission Inventory 1990-2004 /1/ combustion of wood has turned from being an unattended source in 1990 to be the most important source of PCDD/F emission in Denmark. The emission for 2004 was estimated to be 8.5 g I-TEQ, which is around 40 % of the total emission of 22 g I-TEQ. However, the estimation of the total PCDD/F emission from residential wood combustion is quite uncertain, since emissions are greatly influenced by variability in the wood quality and combustion conditions (e.g. chimney draught, combustion air supply, fuel load etc.). Several investigations performed under controlled laboratory conditions have attempted to quantify the emission of PCDD/F from woodstoves and fireplaces /2/. These investigations have found that the emissions of PCDD/F are relatively low when natural wood is used, but it can be very high, if waste or waste wood is burned in wood stoves. Residential burning of waste and waste wood is illegal in Denmark, but it is presumed to be practiced in a certain extent. Waste wood can contain various contaminants, such as pentachlorophenol (PCP), which easily forms very high amount of PCDD/F during combustion.

In the present study the emission of PCDD/F has been directly measured from 12 woodstoves and one boiler, at the actual occurring operating conditions, in 13 Danish residential houses situated in a village in a rural area of Zealand. Normal operating conditions in domestic use of woodstoves is often not as optimal as in laboratory experiments and more realistic and representative emission factors are anticipated by this method.

Materials and Methods

Sampling

Two samples were taken from each of thirteen houses on two successive days. A special dilution system was designed (as seen in the picture), diluting all the flue gas from the chimney with a high amount of ambient air, maintaining a constant flow. In the dilution tunnel the flue gas was cooled down to less than 20 °C at the sampling position. Isokinetic samples were taken from the diluted flue-gas in the dilution tunnel according to European standard EN1948-1, using the filter-condenser method. The all-glass equipment consists of a probe, quarts-wool filter, condenser, XAD-2 filter and a planar glass fibre filter. All samples was taken during complete firing periods, beginning when the wood stove was lighted up in the afternoon and ending late in the evening, when only some glowing charcoal remains in the stove. The total emission of PCDD/Fs was calculated from the measured concentrations and the total volume of diluted flue gas, and it was related directly to the amount of wood burned during the sampling period, giving an emission factor in ng I-TEQ/kg wood. The houses had a variety of common used wood stoves aged from two to app. 20 years,

and one older wood boiler. Six of the houses have steel chimneys and ten houses had brick chimneys. The participating house owners were instructed to operate their wood stove as usual, and they had to report the amount of wood burned during the sampling period. At most of the houses, different sorts of sawed boards was used for lighting the stove and/or as a part of the wood burned, during the sampling periods.

Analysis

The analysis of the 17 PCDD/F congeners having international toxic equivalency factors (I-TEF) was done following a method adapted from European standard EN-1948 2-3 for analysis of the PCDD/Fs in flue-gas. The samples were spiked with eleven $^{13}C_{12}$-labelled PCDD/Fs congeners, and soxhlet extracted for 20 hours with toluene. Clean up was performed by column chromatography using SiO_2/NaOH, SiO_2/H_2SO_4, acidic Al_2O_3, active CAX-21. The analysis of extracts was performed by GC-HRMS.

Results and Discussion

The results are summarized in Table 1, sorted after increasing emission factors.

House no.		3	12	4	2	9	13	6	5	8	11	1	7	10
Stove age, years		> 15	> 6	2	< 5	2	7	7	3	18	> 10	6	< 5	< 5
Kg wood burned in sampling period	Sample a	21,5	7,0	11,3	5,6	6,6	6,2	12,5	10,5	5,2	7,8	13,9	6,2	11,1
	Sample b	13,3	8,6	14,7	6,6	6,1	9,5	15,5	10,8	7,3	9,6	2,9	8,7	17,3
Emission ng I-TEQ/kg wood	Sample a	0,1	0,4	0,3	1,3	n.a.	2,7	3,1	9,8	7,7	6,4	40	51	52
	Sample b	0,05	0,3	1,0	0,8	1,2	0,03	0,5	2,5	12	18	46	72	140
Average 1, ng I-TEQ/kg wood		0,1	0,4	0,6	1,1	1,2	1,4	1,8	6	10	12	43	61	96
Average 2, ng I-TEQ/kg wood		18												
Average 3, ng I-TEQ/kg wood		3,5										67		
n.a.= not analysed because of interference														

Table 1. PCDD/F emission factors per kilo wood burned for each measurement

The averages 1, 2 and 3 is the average of the two measurement on each house, the average of all the samples, and the average for uncontaminated wood and contaminated wood respectively.

The individual results are shown graphically in Figure 1.

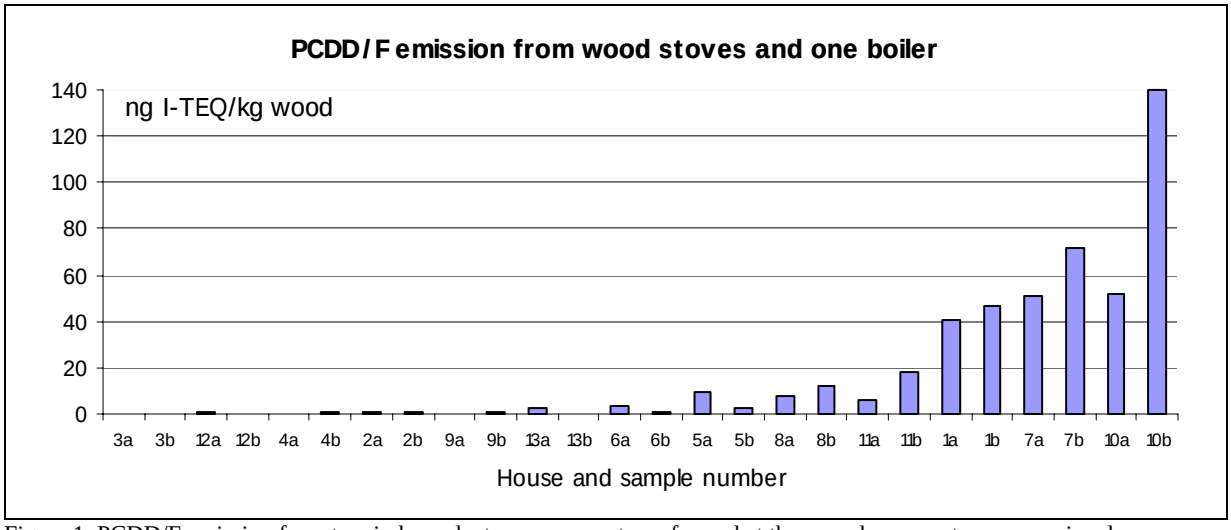

Figure 1. PCDD/F emission from two independent measurements performed at the same house on two successive days.

The variations in the measured emissions are extremely high. The highest measured emission factor was 140 ng I-TEQ/kg woods, which is 4,700 times greater than the smallest of 0.03 ng I-TEQ/kg wood. The emission does not seem to have any correlation to either stove age, type of chimney or amount of wood burned.

Variations in the PCDD/F emission can be explained by differences in stove type and model, the individual firing technique and the kind and quality of the wood used, but it can not explain the three largest emissions from house 1, 7 and 10. The use of waste wood, especially if treated with PCP, could be the explanation, but as treatment of wood with PCP cannot be seen on the wood, it is not possible to verify, without making analysis of PCP in the wood. Actually some of the houses with the highest emission factors reported that some waste wood, but without painting was burned. A memory effect due to soot depositions in the stove and the chimney is also possible, and consequently higher PCDD/F emissions could be measured, even though no treated wood was burned during the sampling period, if it has been used previously.

The emission from several of the other houses is too small to be seen in the figure, but they can be seen in Figure 2, where the three houses with the highest emission have been removed.

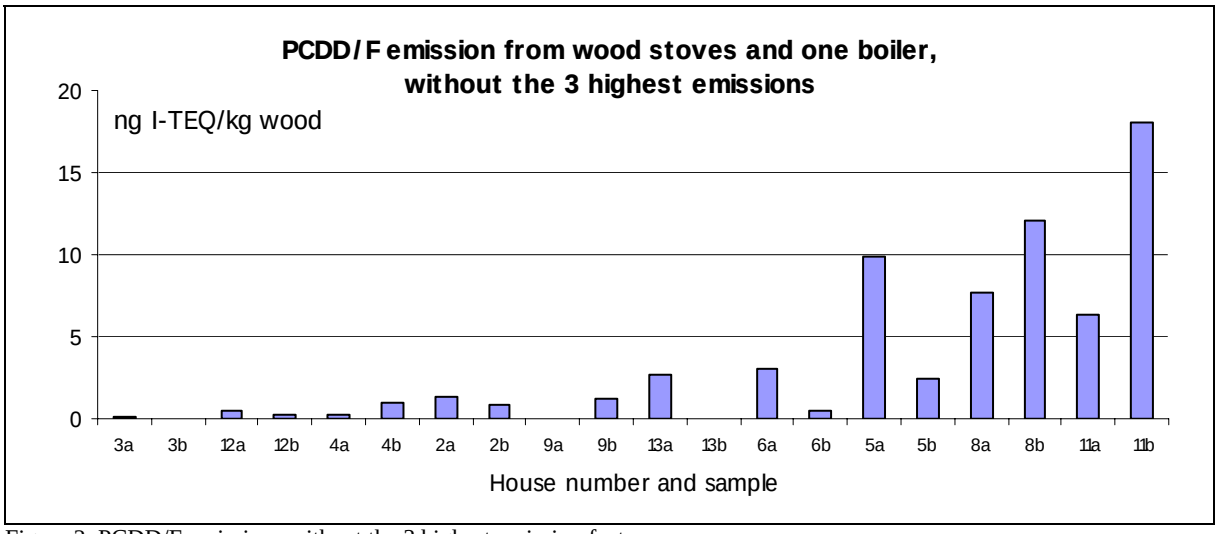

Figure 2. PCDD/F emissions without the 3 highest emission factors.

The emission factors for households heating and cooking with biomass from the UNEP toolkit is compared to the average measured emission factors in table 1.

Emission to air	UNEP toolkit Household heating and cooking with biomass		Average measured emission factors
	ng TEQ/GJ	ng TEQ/kg	ng TEQ/kg
Contaminated wood/biomass fired stoves	1.500	22	67
Virgin wood/biomass fired stoves	100	1.5	3.5
Mixed wood	-	-	18

Table 2. Measurements compared to UNEP Toolkit emission factors for wood fired stoves for household heating

Measuring in the same village and some of the same houses in the winter 2003/04 reported in /4/ showed variations from 0.3 to 18 ng I-TEQ/kg wood, with a median of 4 ng I-TEQ /kg. Variations from 0.6 to 5.3 ng I-TEQ /kg are reported by Schleicher et al. in 2001 /4/. These data is considerable higher than the UNEP emission factor of 1.5 ng I-TEQ/kg for combustion of virgin wood in stoves. In the Danish Dioxin Air Emission Inventory 1990-2004 /1/, an average emission factor of 7.2 ng TEQ/kg for old and new wood stoves and boilers, was used

for the calculation of the 2004 emission, which is less than the half of the average emission factor of 18 ng TEQ/kg found in this study.

Conclusion

The measurements clearly demonstrate, that a reliable estimation of the emission factor for domestic wood burning sources is very difficult to obtain. The emission seems to depend very much on the firing behaviour and the potential use of contaminated wood, e.g. treatment with the colourless PCB treated, which cannot be seen afterwards. The real average emission factor for e.g. the Danish emission of dioxin from wood stoves and boilers could be considerable higher, than the emissions factors found in e.g. the UNEP toolkit.

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