

## DIOXIN AND PAH IN CHIMNEY SOOT FROM DOMESTIC HEATING APPLIANCES WITH SOLID FUELS

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### Introduction

Dioxins and PAHs in smoke from domestic heating appliances may contribute considerably to the emissions in areas where solid fuels are used. Dioxin emissions reported from combustion tests<sup>1</sup> and soot analysis<sup>2</sup> extend over several orders of magnitude for one type of fuel and combustion equipment. Chimney soot was collected from houses and analyzed for dioxins, PAHs and inorganic components to assess the range of "real world" emissions. From the soot concentrations dioxin and benzo(a)pyrene emissions were estimated taking into account the particle concentration measured during laboratory combustion experiments and the calculated gas-particle partition.

### Materials and methods

Soot samples were collected from 21 houses by a professional chimney sweeper in autumn, when most chimneys are swept in preparation of the winter heating season. The sweeper operated from floor level with mechanical cleaning tools like long stem brushes, while the removed soot was collected by a special vacuum cleaner. The samples represent the total amount of soot after a clean sweep. The amount of soot collected from a chimney may vary from 1 to 15 kg. The samples were collected in the usual vacuum cleaner bags, a new bag being used for each sample. A short questionnaire was filled out with the chimney owner, giving basic information about type of fuel used, type of combustion appliance, time between cleanings etc.

The raw soot samples contained stones, sand, paper, leaves, nutshells, fish bones, plumes etc indicating that debris from the walls and dirt carried by wind and birds makes part of the soot mass in many chimneys. Therefore samples were sieved and the fraction < 2mm was milled and homogenized. Total mass was 0.7 to 13.2 kg per chimney with a fine fraction from 60.2 to 96.5 %. In the fine fraction carbon was analyzed by elemental analysis, sulfur by ICP, chlorine by XRF, PAHs after soxhlet extraction by LRGCMS and PCDD/Fs after acid treatment and extraction by HRGCMS according to the EN-1948 standard parts 2 & 3.

### Results and discussion

Results of the analysis of the soot samples are given in tables 1 and 2. From the masses collected it is clear that wood combustion produces 2 to 3 times more soot in the chimney than coal or oil. Wood soot is richer in carbon with several values over 50% C. Coal and oil normally produce a soot with less carbon and more sulfur and chloride. One case of oil combustion, probably a combination of contaminated fuel and a badly adjusted burner, yielded relatively high amounts of soot, carbon, dioxins and PAHs. The I-TEQ content of soot from both wood and oil combustion extends over 2 orders of magnitude, reflecting the highly variable emissions as found in the literature.

**Table 1. Bulk composition and dioxin concentration in soot samples**

Type of heater	Mass g	Dry matter %	Total S g/kg	Total Cl g/kg	Total C %	PCDD/F ITEQ pg/g
woodstove	2 670	93.0	13.2	4	58.6	207
woodstove	3 050	96.8	35	36.5	32.7	1969
woodstove	4 200	95.6	23.2	13.2	46.2	1346
woodstove	13 200	95.5	32.2	20.1	43.0	2786
woodstove	3 610	96.8	19.2	23.2	47.8	9116
woodstove	2 540	97.3	23.9	9.4	46.3	144
woodstove	7 607	97.8	7.11	4.08	66.9	1350
woodstove	1 948	95.4	27	33.2	25.5	893
open firepl	1 390	96.0	28.9	6.66	18.4	163
open firepl	1 230	98.6	54.1	3.59	22.6	3680
open firepl	3 720	90.9	12.8	17.1	54.4	1229
open firepl	1 713	96.9	12.4	6.74	44.3	590
open firepl	689	95.5	34.4	40.3	18.9	2597
open firepl	1 708	97.7	17.6	3.45	35.8	73
oil	1 771	74.6	104	0.16	1.69	12
oil	2 275	94.2	67.3	0.44	6.20	632
oil	760	97.9	51.4	0.67	17.0	398
oil	2 452	97.0	55.1	4.42	38.6	1429
oil	1 307	94.8	34.2	0.91	1.72	29
coal	2 750	98.0	72	247	11.6	496
coal	2 060	96.6	37.5	365	9.1	276

The woodstove owners who had declared to use paper, waste, waste wood and treated wood as fuel ingredients generally had the highest dioxin concentrations in the soot. These samples also revealed higher sulfur and chloride concentrations and a dominant contribution from PCDDs to the total TEQ, while for clean wood combustion the PCDF contribution was higher. Inversely, from these parameters in our dataset it would be possible to identify the waste burners with high probability. The PAH profiles are dominated by fenantrene, fluoranthene and pyrene. Woodstoves soot contains more lighter PAHs, and this is attributed to increased adsorption of volatile PAHs by the more abundant carbon fraction in this type of soot. PAH concentrations were highest in oil fire soot, but the results cover a range from 1 to 300. One high value is preponderant in the average indicating the same heavy polluter syndrome as for dioxins. From an environmental policy viewpoint, this means that relatively important emission reductions would be achievable by eliminating a limited number of sources with extremely high pollution.

#### Estimation of emission factors

Average emission factors for dioxins and benzo(a)pyrene were derived from soot composition and dust emissions of woodstoves in lab combustion tests. It was assumed that deposited soot is stable and has the same dioxin concentration as the emitted dust. The dust emission is then multiplied by the dioxin soot concentration to obtain the dioxin emission factor.

**Table 2. PCDD - PCDF (pg/g) and PAH (µg/g) in soot samples**

	<b>Woodstove</b>	<b>Wood -open fireplace</b>	<b>Coal</b>	<b>Fuel oil</b>
	8 samples	6 samples	2 samples	5 samples
2,3,7,8-TCDD	195	97	20	30
1,2,3,7,8-PeCDD	634	322	75	134
1,2,3,4,7,8-HxCDD	584	373	74	91
1,2,3,6,7,8-HxCDD	1184	896	210	265
1,2,3,7,8,9-HxCDD	983	698	140	358
1,2,3,4,6,7,8-HpCDD	10266	14207	2150	2297
1,2,3,4,5,6,7,8,-OCDD	21290	35507	4500	4168
2,3,7,8-TCDF	1654	988	325	392
1,2,3,7,8-PeCDF	989	634	220	218
2,3,4,7,8-PeCDF	1536	941	310	332
1,2,3,4,7,8-HxCDF	976	480	215	203
1,2,3,6,7,8-HxCDF	927	466	190	250
2,3,4,6,7,8-HxCDF	1072	412	150	207
1,2,3,7,8,9-HxCDF	77	47	13	18
1,2,3,4,6,7,8-HpCDF	2348	1134	485	1791
1,2,3,4,7,8,9-HpCDF	302	227	50	103
1,2,3,4,6,7,8,9-OCDF	804	1531	255	949
<b>Total pg I-TEQ/g</b>	<b>2227</b>	<b>1388</b>	<b>386</b>	<b>500</b>
naphtalene	8.6	1.5	0.6	1.9
acenaphthylene	11.6	1.2	0.2	2.4
acenaphthene	0.9	0.0	0.0	0.2
fluorene	7.5	1.0	0.3	1.6
fenanthrene	95	17	12	119
anthracene	15	3	2	20
fluoranthene	96	38	56	371
pyrene	87	37	41	286
benz(a)anthracene	31	33	31	167
chrysene	39	46	91	282
benzo(b)fluoranthene	34	62	74	291
benzo(k)fluoranthene	11	16	14	82
benzo(a)pyrene	18	24	7	51
indeno(123cd)pyrene	11	19	15	68
dibenzo(ah)anthracene	2	3	5	20
benzo(ghi)perylene	11	21	15	63
<b>Total 16 PAH</b>	<b>479</b>	<b>323</b>	<b>363</b>	<b>1827</b>

For woodstoves our tests showed an average dust emission of 2.19 grams per kg of fuel. For coal stoves we measured 1.67 g/kg and for oil 0.2 g/kg was assumed. The resulting emission factors are given in table 3.

**Table 3: Average emission factors from soot compared to combustion experiments**

Emission factors: from:	Dioxins in ng TEQ/kg				Benzo(a)pyrene in mg/kg			
	soot	from combustion tests			soot	from combustion tests		
Sources	avg	avg	low	high	avg	avg	low	high
<b>Woodstoves</b>	4.88				0.040			
- wood		24.4	1.97	88.7		1.23	0.1	4.53
- wood + waste		350	3.85	1411		3.85	0.18	4.80
- treated wood		1702				0.329		
<b>Open fireplaces</b>	3.04				0.052			
<b>Coal stoves</b>	0.65	77.1	1.15	282	0.012	0.856	0.27	5.14
<b>Oil heaters</b>	0.10				0.010			

The emission factors obtained in this way are at the low side of the lab tests. For B(a)P this approach leads to emission factors of one order of magnitude lower than those obtained during the combustion experiments, and therefore we conclude that PAHs in the soot deposit are insufficiently stable to estimate emission over a longer period of time.

The assumption that emitted and deposited soot have comparable compositions was based on the calculated distribution between particle and gas phase by Junge's equation. When the average wood soot PCDD/F profile, a measured dust concentration of 100 mg/m<sup>3</sup> and a particle surface of 40 m<sup>2</sup>/g were used, the temperature where 50 % of the TEQ load is in the gas phase is 165 °C. At 100 and 250 °C this fraction is 2.5 % and 97% respectively. In the bottom section of the chimney high temperatures can occur, typically over 200 °C during high rate combustion (up to 500 °C was measured in insulated stainless steel piping), but there is a rapid temperature drop. At the exhaust the temperature generally is below 100 °C, and all dioxins are carried by the particles. Strictly our approach gives reasonable results for chimneys where temperatures remain below 120 °C. Corrections of the estimated emission factors can be applied if the temperature histories of the chimney are known, or on the basis of the soot profiles, which show evidence of evaporation of lower chlorinated congeners, particularly 2,3,7,8-TCDF.

Taking into account the inaccuracy of the method we concluded that real world emissions are of the same order of magnitude as those assumed from lab tests, and not dramatically higher due to unfavorable conditions or stoking habits, as was feared at the start of this project.

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### References

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