

Emission Factors and Importance of PCDD/Fs, PCBs, PCNs, PAHs and PM₁₀ from the Domestic Burning of Coal and Wood in the U.K.

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This paper presents emission factors (EFs) derived for a range of persistent organic pollutants (POPs) when coal and wood were subject to controlled burning experiments, designed to simulate domestic burning for space heating. A wide range of POPs were emitted, with emissions from coal being higher than those from wood. Highest EFs were obtained for particulate matter, PM₁₀, (~ 10 g/kg fuel) and polycyclic aromatic hydrocarbons (~ 100 mg/kg fuel for ΣPAHs). For chlorinated compounds, EFs were highest for polychlorinated biphenyls (PCBs), with polychlorinated naphthalenes (PCNs), dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) being less abundant. EFs were on the order of 1000 ng/kg fuel for ΣPCBs, 100s ng/kg fuel for ΣPCNs and 100 ng/kg fuel for ΣPCDD/Fs. The study confirmed that mono- to trichlorinated dibenzofurans, Cl_{1,2,3}DFs, were strong indicators of low temperature combustion processes, such as the domestic burning of coal and wood. It is concluded that numerous PCB and PCN congeners are routinely formed during the combustion of solid fuels. However, their combined emissions from the domestic burning of coal and wood would contribute only a few percent to annual U.K. emission estimates. Emissions of PAHs and PM₁₀ were major contributors to U.K. national emission inventories. Major emissions were found from the domestic burning for Cl_{1,2,3}DFs, while the contribution of PCDD/F-ΣTEQ to total U.K. emissions was minor.

Introduction

Various organic pollutants are released as unwanted byproducts during the incomplete combustion of fuels and waste products. Most notable are the groups of polycyclic aromatic

hydrocarbons (PAHs), and the polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs). Over the past decades, major efforts have been made to reduce emissions of these pollutants. The use of catalytic converters and the introduction of lead-free petrol has resulted in decreasing emissions of PAHs and PCDD/Fs. For PCDD/Fs, abatement measures have mostly focused on stationary sources, such as municipal and medical solid waste incinerators, but also cement kilns etc (e.g. refs 1–3). As a result of these abatement measures, the relative importance of diffusive and/or numerous small-scale sources to the national/regional patterns of emission has increased in recent years. Reliable, quantitative estimates of emissions from diffuse sources are notoriously difficult to obtain. Source inventory estimates of PCB, PCDD/F and PAH emissions to the U.K. atmosphere, for example, give only crude figures for diffuse discharges with large uncertainties attached.

One form of diffuse emission which has attracted attention for PCDD/Fs and PAHs is the domestic burning of coal and wood for residential heating. Recent published U.K. atmosphere emissions inventories have estimated domestic burning to contribute ca. 10% of the PCDD/F-ΣTEQ emissions (2) and between ~30 and 80% (4, 5) of the ΣPAH emission annually. The quantities of these compounds emitted by domestic burning are very uncertain, however, because of the difficulties in measuring them directly, of deriving emission factors (EFs), and the great variability in fuel type/combustion conditions (e.g. ref 1).

Recently, careful analysis of ambient air concentrations has shown that other POPs, such as polychlorinated biphenyls (PCBs) and naphthalenes (PCNs) also have a pyrogenic origin (e.g. ref 6). Indeed, numerous PCN congeners have been identified in waste incinerator fly ash (7). Atmospheric PCB- and PCN-concentrations are generally associated with their past industrial production and use. To our knowledge there are almost no published EFs for either of these groups, making it difficult to estimate the importance of the domestic burning of coal and wood for national emission inventories.

In winter 1998, we conducted a study to assess the role of domestic burning of coal/wood on ambient levels of PCDD/Fs, PCBs and PAHs in the U.K. during the winter (8). Samples were taken concurrently at four sites in northern England to assess the air quality with regards to PCDD/Fs, PCBs and PAHs in urban and rural sites in winter. We estimated that local sources in two villages, where gas was not available for domestic heating, accounted for ~ 25% of the ΣTEQ and ~ 75% of the ΣPAHs in the ambient air at those sites during the winter sampling events (8, 9). The villages were also characterized by a specific atmospheric pattern, with a preponderance of the lower chlorinated PCDFs and many PAHs. These were assumed to stem from the domestic burning of coal and wood. For PCBs, in contrast, the villages did not have a characteristic profile, while ambient concentrations were elevated compared to background concentrations at a semi-rural air monitoring field station. In this study, we made direct measurements of EFs from the burning of house coal and seasoned hardwood in an open fire situation under carefully controlled test conditions for PAHs, PCDD/Fs (i.e., Cl_{1–8}DD-Fs and the 2,3,7,8-substituted congeners), particulate matter (PM₁₀), PCBs and PCNs.

Material and Methods

Controlled Burning Experiments. Suitable fuels, representative of a bituminous housecoal and a seasoned hardwood were chosen and burnt on an open fire operated as closely

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as practicable to the requirements of British Standard (BS) BS3841:Part 1:1994 (10). The burning tests were carried out during the periods April – May 2000 and December 2000. EFs were determined for Cl₁₋₈DD/Fs, the 2,3,7,8-substituted Cl₄₋₈DD/Fs, PCBs, PCNs, PAHs and PM₁₀ particulates.

The following fuels were selected: A 0.4 t sample of a pre-packed bituminous house coal that was considered to be representative of good quality coal used in nonsmokeless areas of the North Midlands and Yorkshire. Seasoned hardwood (mainly beech) was selected to be fairly homogeneous in terms of both log size and shape and to be free of excessive bark. Both fuels were mixed and dried at 30 °C for 48 h in a fan-assisted air-drying oven and allowed to equilibrate with the atmosphere for a further 24 h before use. Representative samples were extracted during the re-bagging process following air-drying. This was carried out by forming a long heap or 'strip' of each fuel. In the case of the house coal, 36 increments (each of 0.5 kg) were taken by scoop from the length of the strip along both sides. The increments were combined and the entire sample reduced and divided in accordance with the requirements of BS1017 Part 1 to provide separate laboratory samples for moisture determination and general analysis (10). In the case of the hardwood logs, forty pieces were randomly selected from the strip, and each one hand-drilled in three locations using a low speed setting and an 8 mm drill-bit in order to produce approximately 500 g wood dust.

Burning Facility and Procedures. Fuels were burnt in an open fire test setting and chimney as described in BS3841: Part 1: 1994 to burn the fuels reproducibly (10). BS3841: Part 2 defines a method of determining the actual gravimetric smoke release rate, relying on an extractive technique drawing a metered sample of flue gases through a filter maintained at 70 °C (11). The latter method was adapted to determine the targeted pollutants. A prescribed volume of dry fuel was ignited in a Fulham Mk.III grate with a standard volume of fuel gas (Figure 1). The radiant output from the fire was measured continuously throughout the test by a quadrant cage radiometer. At a point in the initial burning cycle determined by the radiant output falling back from its peak value to 1.45 kW or 0.75 × peak value (whichever was smaller) the fire was then carefully de-ashed and refuelled with a prescribed volume of fuel, which had been weighed. Immediately following this point, iso-kinetic sampling of flue-gas commenced. The fire was allowed to burn through a second and third radiation peak and on the radiant output reducing to 1.45 kW, the test was terminated, and flue-gas sampling stopped. A single test for gravimetric smoke was deemed to be valid if the ignition time (to 1.15 kW output) was less than 50 min, and if the second radiation peak value lay within the range 1.8–2.3 kW. Replicate tests had to satisfy these criteria plus the mean of their second peak radiant output values ought to lie within the range 1.95–2.15 kW. The test method described in BS3841: Part 1 is intended for coal-based fuels (10). Wood burns on an open fire in a completely different and relatively uncontrolled manner. To achieve an overall test time consistent with that when burning house coal, it was necessary to refuel the fire with wood seven or eight times. From initial sighting tests it was decided that an initial charge of 2.8–3.0 kg of dry wood followed by refuel charges of 1.8–2.0 kg achieved a quick ignition time (to 1.15 kW) and a second peak radiant output of > 1.8 kW thus complying with the primary requirements of BS3841: Part 1 (10).

Flue Gas Sampling. The flue gas extraction technique for determination of smoke content relies upon the iso-kinetic withdrawal of a portion of the total flue gases throughout the second and third burn cycles. Sampling was maintained during the de-ashing and re-fuelling periods because these operations could contribute significantly to the amounts of

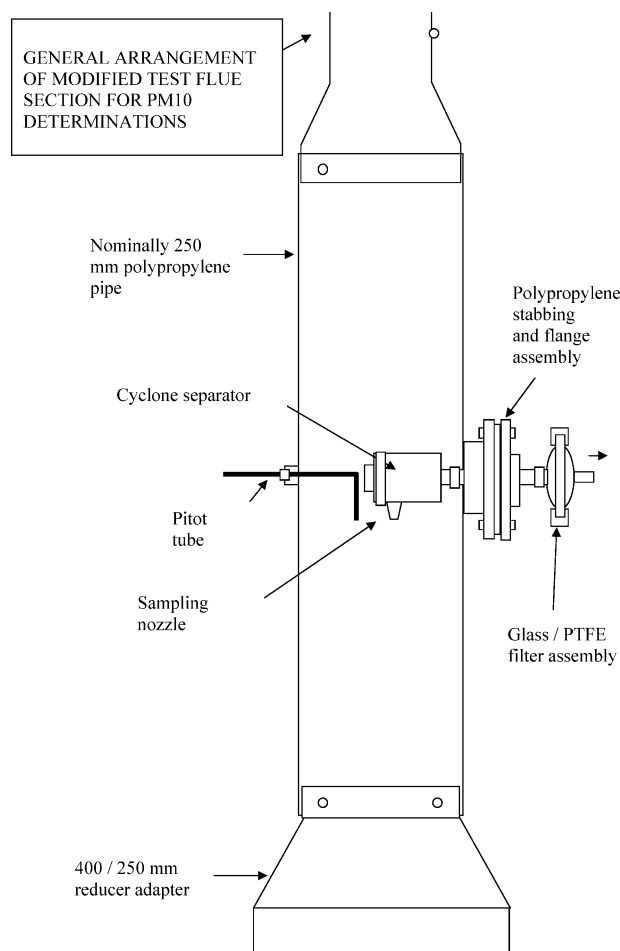


FIGURE 1. Schematic of test flue sampling for organic pollutants and PM₁₀.

specified pollutants (and especially PM₁₀ and trace metals) collected over the entire test period, and these could end up being discharged to atmosphere in a domestic situation. The methods selected for the sampling of the components of interest in the flue gas emissions were as follows: PCDD/Fs, PCBs, PAHs, PCNs – based on European Norm (EN) EN1948–1: 1996 (filter/condenser method); PM₁₀ – based on US EPA Method 201a/202 (12, 13). The filters used were Whatman GF/C grade 90 mm circles. For the sampling and collection of PCDDs, PCDFs and PCBs a set of resin traps were cleaned, and filled with XAD-2 resin. The traps were spiked with 20 ¹³C₁₂-labeled PCDD/Fs, 17 corresponding to the 2, 3, 7, 8-substituted isomers, and 3 to the following isomers: 2, 8-Cl₂DF; 2, 7/8-Cl₂DD; 2, 3, 7-Cl₃DD. In addition, the traps were also spiked with 10 ¹³C₁₂-labeled PCBs (28, 52, 77, 101, 126, 138, 153, 180 and 209) to provide recovery information for the PCB and PCN analysis. All samples were stored at 4 °C pending transportation to the University of Lancaster for analysis. A field blank was run in an identical fashion to the tests, except that the sample probe was left outside the flue test section. For the sampling of PAHs, recovery compounds were supplied by Harwell Scientifics and added to the resin prior to sampling.

Analytical Procedures. PCDD/Fs, PCBs, PCNs. The chlorinated analytes were cleaned-up and analyzed at Lancaster University. The XAD-2 resin and filter were extracted with toluene in a Soxhlet for 18 h, the extract was reduced and ~1 mL of nonane added, the toluene was removed and ~5 mL of hexane added to the remaining nonane. The condensate and washings were back extracted into hexane. The two extracts were combined and digested

TABLE 1. Coal and Hardwood Properties on a Dry Weight Basis

	housecoal	seasoned hardwood
moisture content (after air-drying, %)	2.2	10.8
ash content (%)	3.3	1
volatile matter (%)	36.7	82.5
total sulfur (%)	1.33	0.04
chlorine (%)	0.35	0.04
gross calorific value (kJ/kg)	33,360	18,580

with concentrated H₂SO₄. The reduced extract was eluted through a number of multi-sorbent cleanup columns using 100 mL of hexane. The columns consisted of alternate layers of activated silica, basic silica and acid silica. The 100 mL of hexane were reduced and placed on a GPC column, the first 16 mL of the 1:1 DCM:hexane eluent was discarded and the next 30 mL collected. Separation of the multi-ortho PCBs, coplanar PCBs (# 77, 126, 169) and PCDD/Fs respectively was carried out on a column containing ICN Alumina 1B (ICN Biomedicals GmbH). The following eluents and volumes were used: Fraction A multi-ortho PCBs, 12 mL 7% DCM in hexane; Fraction B coplanar PCBs, 6 mL toluene; Fraction C PCDD/Fs, 30 mL 1:1 DCM:hexane. An injection standard in nonane (³⁷Cl₄-2, 3, 7, 8-Cl₄DD) was added to each of the fractions. Samples for PCN analysis were extracted and cleaned up in an identical manner except that fractions A and B were combined and two injection standards in

dodecane were added (¹²C₁₂ PCB 30 and ¹³C₁₂ PCB 141). Quantification of PCDD/Fs, PCBs and coplanar PCBs was carried out on a Micromass Autospec Ultima high-resolution mass spectrometer operated at a resolution of at least 10,000. Details of the GC columns used and peak identification criteria for PCDD/Fs are given elsewhere (14). Peak identification criteria for the PCBs and PCNs were similar to those in ref 14 and were based on retention times and ion ratios. For coplanar PCB analysis a 30 m DB5-MS column was used (0.25 mm i.d., 0.1 μm film thickness), for multi-ortho PCBs analysis a 60 m DB5-MS column was used (0.25 mm i.d., 0.1 μm film thickness). PCN analysis was performed using a Fisons MD800 GC-MS. Separation was carried out on a CP-Sil8 (Chrompak/Varian, Palo Alto, CA) capillary column (length 50 m, diameter 0.25 mm) using helium as the carrier gas. The detector was operated in electron impact (EI) mode with selected ion monitoring (SIM). Quantification of the PCDD/F and PCBs was achieved by the isotope dilution method using the peak areas of specific ¹³C₁₂-labeled recovery standards and have therefore been recovery corrected. PCN quantification was performed using standards based on a Halowax 1014 technical mixture, the PCN data was not recovery corrected. Tables 2 to 4 contain lists of the compounds quantified. In all cases blank values were subtracted from the data and detection limits, based on the integrated area under the expected peak width for that compound, were applied. A mixture of 7 ¹³C₁₂-labeled PCBs was added to a seventh, unused XAD-2 resin trap to provide an analysis blank. An indication of the amount in the blanks

TABLE 2. Emission Factors of PCDD/Fs from Coal and Hardwood (ng/kg fuel)

	TEF ^a	mean ^b	housecoal	% blank ^{b,c}	mean	hardwood	% blank ^{b,c}
kg fuel			7.6–7.7			13–16	
MJ			43–45			34–42	
			st.dev. ^d			st.dev. ^d	
2,3,7,8-Cl ₄ DF	0.1	9.3	2.0	nd	0.4	0.1	nd
1,2,3,7,8-Cl ₅ DF	0.05	2.6	0.4	1%	0.2	0.1	7%
2,3,4,7,8-Cl ₅ DF	0.5	1.8	0.4	nd	0.1	0.0	nd
1,2,3,4,7,8-Cl ₆ DF	0.1	0.7	0.2	9%	0.1	0.0	27%
1,2,3,6,7,8-Cl ₆ DF	0.1	0.6	0.1	5%	0.1	0.0	19%
1,2,3,7,8,9-Cl ₆ DF	0.1	nd		nd	0.1		nd
2,3,4,6,7,8-Cl ₆ DF	0.1	0.5	0.1	nd	0.1	0.1	nd
1,2,3,4,6,7,8-Cl ₇ DF	0.01	1.3	0.8	nd	0.3	0.1	nd
1,2,3,4,7,8,9-Cl ₇ DF	0.01	0.3	0.2	12%	0.1	0.0	44%
Cl ₈ DF	1.0e ⁻⁴	1.4	1.2	nd	0.4	0.2	nd
2,3,7,8-Cl ₄ DD	1	0.5	0.0	nd	0.0		nd
1,2,3,7,8-Cl ₅ DD	1	0.4	0.1	nd	0.0		nd
1,2,3,4,7,8-Cl ₆ DD	0.1	0.2	0.0	nd	0.1	0.0	nd
1,2,3,6,7,8-Cl ₆ DD	0.1	0.3	0.2	nd	nd		nd
1,2,3,7,8,9-Cl ₆ DD	0.1	nd		nd	0.1	0.0	nd
1,2,3,4,6,7,8-Cl ₇ DD	0.01	4.1	3.4	43%	1.4	0.9	67%
Cl ₈ DD	1.0e ⁻⁴	33	32	16%	7.3	5.7	39%
Cl ₁ DFs		11000	6930	0%	2100	210	0%
Cl ₂ DFs		4100	340	0%	250	65	1%
Cl ₃ DFs		460	64	0%	28	11	1%
Cl ₄ DFs		140	23	0%	30	17	1%
Cl ₅ DFs		20	2.5	0%	1.5	0.4	2%
Cl ₆ DFs		5.2	1.6	3%	0.7	0.2	10%
Cl ₇ DFs		1.9	1.1	2%	0.6	0.3	4%
Cl ₁ DDs		8.4	4.9	3%	11	4.2	1%
Cl ₂ DDs		180	74	1%	46	20	2%
Cl ₃ DDs		30	1.4	0%	5.9	2.1	1%
Cl ₄ DDs		12	0.7	1%	4.3	0.8	1%
Cl ₅ DDs		3.6	0.3	5%	1.2	0.3	8%
Cl ₆ DDs		3.5	1.5	39%	1.1	0.8	68%
Cl ₇ DDs		7.9	6.4	31%	2.7	1.7	49%
Σ Cl _{1–8} DD/Fs		16000	7400		2500	310	
Σ Cl _{4–8} DD/Fs		230	51		50	25	
Σ TEQ ^a		3.0	0.6		0.2	0.0	

^a van den Berg et al. (16). ^b nd – not detected. ^c Amount in blank as % of amount in corresponding burning trial before back-ground correction. ^d st.dev. – standard deviation (n = 3).

for each compound class has been given in Tables 2 to 5 under the heading % Blanks. This column expresses the amount of an analyte found in the blank as a percentage of the mean amount in the samples before the amount in the blank has been subtracted.

PAHs. PAH analysis was carried out by Harwell Scientifics. GFFs were spiked with 1000 ng each of D₈-naphthalene, D₈-acenaphthylene, D₁₀-acenaphthene, D₁₀-pyrene, D₁₂-benzo[*b*]fluoranthene and D₁₄-dibenzo[*a,h*]anthracene. GFFs and XAD-2 traps and condensate/rinsings fractions were extracted with dichloromethane (DCM). The extracts for each test were combined and evaporated to below 10 mL volume, then made up to 10 mL in a volumetric flask. An aliquot volume of 2 mL was then taken for PAH analysis. After addition of a recovery spike the aliquot was cleaned up by column chromatography, and finally analyzed by GC/MSD (Hewlett-Packard 5970 instrument equipped with a 50 m DB5 0.2 μ m film capillary column operated in SIM) after addition of a syringe standard.

PM₁₀. A proprietary stainless steel in-stack cyclone was used as a classifier, separating PM₁₀ from non-PM₁₀ particles. A Graseby Andersen 90 mm filter holder was located externally to the duct and unheated, therefore maintained at ambient temperature (or slightly higher, as dictated by the flue gas temperature as it passed through the filter). This was clearly not in compliance with US EPA Method 201a but was a necessary expedient in view of the prevailing conditions (12). Whatman GF/C 90 mm filters were used for collection of PM₁₀. The PM₁₀ material collected on the filters and the associated PM₁₀ particles which deposited upstream of the filter during the PM₁₀ tests were recovered and weighed.

Blank levels were in general < 10% of PCDD/F, PAH and PM₁₀ emissions, with higher blank levels for the higher chlorinated PCDDs, some PCB and PCN congeners. Mean recoveries for all samples of the labeled ¹³C₁₂ standards were as follows: PCDD/Fs – 58–76% except for one hepta-furan (52%); PCBs – 68–100% except congener 28 (42%); coplanar PCBs – congener 77–55%; congener 126–28%; congener 169–38%; PCB recoveries for the PCN results – 64 to 123%, except congener 28 (46%).

Representativeness of Fuels and Burning Practice. The vast majority of households burning bituminous coal in the U.K. do so on appliances which are similar in general design to the Fulham Mk.III grate and which are set in openings roughly similar in size to that used for the tests. Combustion air to the undergrate is controlled by means of an adjustable flap or damper and it is unlikely that in the normal course of events the fire would be allowed to burn away with no means of controlling the undergrate air supply and hence the rate of burn. It follows that the concentrations of various pollutants generated during the house coal tests could be viewed as typical of those generated from a household situation, from the equivalent mass of the same fuel charged to an established fire.

Regarding the combustion of wood, the traditional inset open fire is not the most suitable appliance on which to burn wood, although there are a significant proportion of households possessing this type of fire on which wood is burned either by itself, or perhaps more commonly, in admixture with coal. The main influence on differences between the patterns of pollutant emissions from the tests as carried out compared with hardwood burned in a domestic situation on the same appliance type will probably be the moisture content. It is unlikely that seasoned hardwood prepared for domestic consumption would ever be as low in moisture as the wood used in the test work. Therefore, it is reasonable to suggest that certainly PAH, PM₁₀ and possibly PCDD/F, etc. EFs derived from the tests on wood will be lower than those which would be obtained from burning the quality of seasoned hardwood normally charged to a householder's fire.

Results and Discussion

Fuels. The fuel properties highlighted the different natures of coal and wood. Coal had the higher gross calorific value (33 kJ/kg vs 19 for wood), but less volatile matter (37% – wood 83%). Coal had about 10 times more chlorine than wood (0.35 vs 0.04% for wood). These values are within the range typically found for wood (e.g. ref 15). For all EFs on a per weight basis, the burning of coal exhibited much higher emissions than the burning of wood (Tables 2–6). The precision of three independent test runs for both fuels was very satisfactory. Relative standard deviations were < 20% for most PCDD/Fs, PCNs, PAHs and PM₁₀. The determination of EFs for PCBs was less reproducible, which was likely a result of the occurrence of a greater number of PCB congeners in the blanks and the lower concentrations of PCBs in the samples.

Comparison with Published EFs. Cl_{1–8}DD/Fs. To our knowledge, this is the first study reporting all homologue groups of PCDD/Fs in such samples (Table 2). The lower chlorinated DFs dominated the overall emissions from both coal and wood, with EFs decreasing with increasing chlorine number for the PCDFs. EFs were highest for Cl₁DFs (11,000 ng/kg coal – 2,100 ng/kg wood), followed by Cl₂DFs (4,100–250) and Cl₃DFs (460–30). For both fuels, EFs of PCDDs were highest for Cl₂DDs, followed by OCDD and Cl₃DDs.

For Σ Cl_{4–8}DD/Fs, emissions were 230 ng/kg coal and 50 ng/kg wood. Much higher EFs were determined by Chagger et al. for coal (2700 ng/kg), even under good combustion conditions (cited in ref 19), and by Broeker et al. for various coals (60–1800 ng/kg (20)). The EFs for wood were comparable to results from Gullett et al. (15) for wood combustion in fire stoves in the San Francisco Region (10–76 ng/kg wood), but much lower than results reported by Gullett and Touati (21) for forest fires (100 up to 7000 ng/kg wood) and by Broeker et al. for beech wood (500–2400 ng/kg (20)).

PCBs. As a general trend, EFs decreased with increasing degree of chlorination (Table 3), similar to the pattern observed for the PCDFs (see above). However, Cl₃Bs had much lower EFs than Cl₄Bs (900 vs 7200 ng/kg fuel for coal and 76 vs 410 ng/kg fuel for wood, respectively). For the higher chlorinated PCBs, EFs decreased with increasing degree of chlorination. Major PCBs emitted from both coal and wood were #49 and #41/64 (>3,000 ng/kg coal; >100 ng/kg wood). Other congeners showed lower EFs, by 1–2 orders of magnitude. EFs for coplanar PCBs #77, #126 and #169 were also determined, and decreased from #77 (4 Cl) to #169 (6 Cl). Data on PCB emissions from combustion is scarce. Gullett et al. (15) determined EFs for PCBs in wood fuels – their values exceed our measurements by about an order of magnitude. We cannot explain the differences, which probably reflect the inherent variability in different fuels, procedures and analytical methods. Part of the discrepancy might be that the measurements by Gullett et al. (15) may indeed represent 'worst-case' scenarios with unusually dry fuel and high burn rates (22).

PCNs. A wide range of PCN congeners was detected in the test runs (Table 4). Similar to the EFs for PCDFs and PCBs, higher EFs were determined for the lower chlorinated congeners. Cl₃Ns and Cl₄Ns showed highest EFs (around 300 and 50 ng/kg fuel for coal and wood, respectively) with much lower EFs for the higher chlorinated congeners. PCN #24 dominated with an EF of 120 ng/kg (coal) and 32 ng/kg (wood). EFs for PCNs (total 680 and 120 ng/kg for coal and wood, respectively) were lower than those determined for PCBs (8,900 and 600 ng/kg). We believe these are the first published measurements of EFs for PCNs, so no comparison is possible.

TABLE 3. Emission Factors of PCBs from Coal and Hardwood (ng/kg fuel)

	TEF ^a	mean ^b	housecoal	% blank ^c	mean ^b	hardwood	% blank ^c
kg fuel			7.6–7.7			13–16	
MJ			43–45			34–42	
			st.dev. ^d			st.dev. ^d	
17/18		nd			18		96%
22		240	150	20%	8.3	7.0	78%
28/31		660	340	28%	61	32	68%
41/64		3100	1200	1%	110	95	33%
44		170	110	24%	16		137%
49		3400	3900	9%	180	200	18%
52		120	65	31%	19	13	60%
60/56		97	10	21%	31	11	32%
61/74		67	23	19%	31	16	24%
70		160	41	14%	38	15	28%
77	1.0e ⁻⁴	21	10	11%	2.7	0.8	30%
87/115		46	53	33%	7.3	2.9	43%
95		72	58	28%	15	5.3	43%
99		33	33	27%	7.0	2.7	37%
101/90		100	95	26%	14	5.7	47%
105	1.0e ⁻⁴	40	47	29%	5.3	2.2	44%
110		88	110	38%	13	8.1	48%
114	5.0e ⁻⁴	2.3	2.5	24%	0.3	0.1	42%
118	1.0e ⁻⁴	96	120	27%	8.5	2.9	48%
123	1.0e ⁻⁴	6.6	5.7	0%	1.2	0.3	0%
126	0.1	1.8	1.0	4%	0.2	0.0	14%
141		18	16	23%	0.6	0.4	83%
149		51	49	34%	9.1	3.7	48%
151		16	14	33%	nd		115%
153/132		110	97	23%	18	6.3	40%
156	5.0e ⁻⁴	13	13	23%	0.9	0.3	57%
157	5.0e ⁻⁴	2.5	2.7	28%	0.2	0.1	53%
158		12	11	0%	4.4	3.3	0%
167	1.0e ⁻⁵	5.2	5.6	21%	0.4	0.2	52%
169	0.01	0.2	0.1	3%	0.1	0.0	27%
170/190		17	13	19%	1.2	0.3	56%
174		13	8.6	23%	2.8	0.9	38%
180		31	20	19%	nd		491%
183		8.4	5.3	26%	1.6	0.4	44%
187		17	10	23%	3.6	0.7	38%
189	1.0e ⁻⁴	0.9	0.5	25%	nd		
194		3.9	2.6	0%	1.3	0.4	0%
199		1.1	0.5	21%	0.4	0.1	25%
203		7.1	2.6	19%	2.2	1.1	29%
ΣCl ₃ Bs		900	490		76	39	
ΣCl ₄ Bs		7200	5100		410	250	
ΣCl ₅ Bs		490	5200		72	250	
ΣCl ₆ Bs		230	210		33	26	
ΣCl ₇ Bs		87	56		9.2	15	
ΣCl ₈ Bs		12	5.5		3.8	3.4	
ΣPCBs		8800	6600		630	439	
Σ TEQ ^a		0.20	0.10		0.020	0.003	

^a van den Berg et al. (16). ^b nd – not detected. ^c Amount in blank as % of amount in corresponding burning trial before back-ground correction. ^d st.dev. – standard deviation (*n* = 3).

Helm and Bidleman (6) suggested that PCNs #44, #29, #54, and the more toxic #66 and #67 could indicate combustion sources, based on the comparison of air profiles from suburban and industrial locations in Toronto, Canada. There are disparities between the congeners quantified here and in the Toronto study. We cannot comment on congeners 29, 44 and 54, for example. However, congeners 66/67 do have elevated EFs relative to the other Cl₆Ns and may therefore be indicative of combustion. It should be kept in mind that our study only focused on the burning of coal and wood. It is assumed that in a major urban-industrial conurbation like Toronto, many different emission and combustion sources are present. Indeed it would be surprising if a 'wood' or 'coal'-based signal was dominant in a major city.

PAHs and PM₁₀. EFs for PAHs were dominated by the lighter weight phenanthrene, naphthalene and acenaphthylene (17–22 mg/kg coal, 6–8 mg/kg wood), followed by fluorene, pyrene, fluoranthene and anthracene (ca. 15 mg/

kg coal, 3 mg/kg wood) and decreased further with increasing molecular weight (Table 5). These EFs were rather high compared to those determined by Oanh et al. (23) and Wenborn et al. (5) for coal: Oanh et al. (23) determined EFs < 3 mg/kg for fluorene and higher molecular weight PAHs, while Wenborn et al. (5) reported EFs of, in general < 7 mg/kg, with the exception of 16 mg/kg for fluorene. Similar patterns and EFs were determined for the burning of hardwood in fireplaces by McDonald et al. (24) with ca. 3–4 mg/kg for fluorene, pyrene, fluoranthene and anthracene, while Wenborn et al. (5) reported 6–8 mg/kg for these PAHs.

The PM₁₀ EFs were 40 and 8 g/kg for coal and wood, respectively (see Table 6). The value for wood compares well to that determined by Gullett et al. (15) for different woods in a fireplace (3–17 g/kg) and the range of 1–28 g/kg shown for woods burned in different appliances in the U.S. (25). Oanh et al. (23) reported a range of 7–51 g/kg for wood and coals burned in fuelstove systems typical for southeast Asia.

TABLE 4. Emission Factors of PCNs from Coal and Hardwood (ng/kg fuel)

IUPAC No.	REP ^a	mean	housecoal	% blank ^{b,c}	mean	hardwood	% blank ^{b,c}
kg fuel			8.1–8.3			13–14	
MJ			49–52			40–42	
			st.dev. ^d			st.dev. ^d	
19		40	3.0	nd	7.2	2.8	nd
24		120	9.3	nd	32	5.6	nd
15		43	14	nd	5.5	1.7	nd
16		46	20	nd	7.6	1.5	nd
17/25		86	15	8%	5.8	4.6	60%
23		20	19	75%	0.0	0.0	321%
42		5.2	0.6	22%	1.7	0.6	28%
33/34/37		45	5.4	16%	12	3.8	42%
47		16	1.9	21%	2.7	0.6	42%
36/35		79	2.0	6%	16	8.0	20%
28/29/43		29	10	12%	6.9	1.6	27%
27/30		21	2.2	2%	1.5	0.8	10%
35		29	8.1	10%	5.9	1.6	27%
38/40		31	22	54%	1.7	2.2	132%
46		24	11	48%	4.4	3.9	94%
52/60		5.5	0.2	21%	1.0	0.4	33%
58		1.1	0.2	16%	0.4	0.4	73%
61		3.3	1.2	14%	0.4	0.3	41%
50		4.8	2.4	18%	0.4	0.4	34%
51		1.4	0.2	19%	0.0	0.0	751%
57		3.2	1.5	nd	0.2	0.2	nd
62		3.8	0.5	nd	0.4	0.3	nd
53		3.1	0.6	nd	0.5	0.3	nd
59		6.3	1.5	nd	0.8	0.8	nd
66/67	1.3e ⁻³	4.7	0.7	nd	0.4	0.1	nd
64/68	7.5e ⁻⁵	1.2	0.4	nd	0.0	0.0	nd
69	2.0e ⁻³	1.1	1.0	nd	0.6	0.5	nd
71/72		1.1	0.6	nd	1.1	0.1	nd
63		0.0	0.0	nd	0.0	0.0	nd
65		0.0	0.0	nd	0.0	0.0	nd
73	1.0e ⁻³	1.0	0.3	11%	0.4	0.4	9%
74		1.2	0.2	nd	0.1	0.2	nd
75		5.4	3.6	nd	0.0	0.0	nd
ΣCl ₃ Ns		360	44		58	15	
ΣCl ₄ Ns		280	52		52	15	
ΣCl ₅ Ns		32	5.5		4.1	0.7	
ΣCl ₆ Ns		8.1	2.1		2.1	0.7	
ΣCl ₇ Ns		2.1	0.5		0.5	0.6	
Cl ₈ N		5.4	3.6		nd		
ΣCl ₃₋₈ Ns		680	89		120	25	
ΣREP-TEQ ^a		0.009	0.003		0.002	0.002	

^a Relative potencies from Blankenship et al. (17); for 66/67 and 64/68 a 50:50 mix was assumed; REP for 69 as cited in Blankenship et al. (17).

^b Amount in blank as % of amount in corresponding burning trial before back-ground correction. ^c nd – not detected. ^d st.dev. – standard deviation ($n = 3$).

In an earlier study, Wenborn et al. (5) reported 8 g/kg wood and 10 g/kg coal.

The PAH- and PM₁₀-EFs reported here for the combustion of hardwood were comparable to those determined in several other studies. However, the EFs determined for coal were in general much higher than literature values. Interestingly, the EFs determined in this study were very reproducible (Table 5). Nevertheless, we caution against the unquestioned use of the EFs determined here for PAHs and PM₁₀ for coal.

Toxic Equivalents. PCDD/F-TEQ. Sum of toxic equivalents (ΣTEQ) were calculated for PCDD/Fs and PCBs with the WHO toxic equivalency factors (TEFs) for humans/mammals as reported by van den Berg et al. (16). PCDD/F-TEQs were 3.0 and 0.21 ng ΣTEQ/ng fuel for coal and wood, respectively. These TEQs match almost exactly those determined by Wenborn et al. (5) for coal (3.0) and wood (0.24) in a similar study. These EFs were much lower than those determined for coal (100–110 ng ΣTEQ/kg) by Chagger et al. (cited in 19). For the different woods used by Gullett et al. (15), EFs ranged from 0.25 (oak) to 2.4 (artificial logs) ng ΣTEQ/kg fuel. In this study, highest EFs were determined for 2,3,7,8-TCDF and the highest chlorinated DDs. This was not

observed by Gullett et al. (15), who determined the highest EF for OCDF. Major contributors to the ΣTEQ in this study were 2,3,4,7,8-Cl₅DF and 2,3,7,8-Cl₄DF for both coal and wood.

PCB-TEQ. For PCBs, the ΣTEQ was 0.2 and 0.02 ng/kg fuel for coal and wood burning, respectively. These ΣTEQs were almost exclusively dominated by PCB 126 in both cases. Gullett et al. (15) determined much lower ΣTEQs for the emissions from oak, namely 0.0014 ng ΣTEQ/kg fuel. However, in their study PCB 126 was not detected, possibly explaining the discrepancy between the results.

PCN-TEQ. There are no consensus TEFs for PCNs yet agreed. For PCNs, the main toxic mechanism is their ability to bind to the Ah receptor. Relative potencies (REPs) derived from individual experiments with in vitro assays have been reported by Blankenship et al. (17) and Kannan et al. (26). These were used to calculate ΣREP-TEQs for wood and coal emissions (Table 4). ΣREP-TEQs for PCNs were 0.009 and 0.002 ng/kg fuel for coal and wood, respectively, or were lower by about a factor of 10 relative to PCB-TEQs. Similar ΣREP-TEQs were obtained using the induction TEFs by Kannan et al. (26).

TABLE 5. Emission Factors for PAHs from Coal and Hardwood (mg/kg fuel)

	IEF ^a	mean	housecoal	% blank ^b	mean	hardwood	% blank ^b
kg fuel			7.2–7.7			15–16	
MJ			44–52			36–41	
			st.dev. ^c			st.dev. ^c	
Naphthalene	1e ⁻⁸	19	5.20	1.4%	8.2	2.20	1.6%
Acenaphthylene		17	1.90	0.1%	6.6	1.30	0.2%
Acenaphthene		4.9	0.24	0.6%	0.6	0.15	2.2%
Fluorene		15	2.10	0.2%	2.8	0.50	0.6%
Phenanthrene		21	2.30	0.4%	6.8	1.30	0.7%
Anthracene		14	0.95	0.3%	1.7	0.36	1.2%
2-Methyl phenanthrene		12	1.10	0.2%	1.0	0.23	1.2%
2-Methyl anthracene		12	1.10	0.1%	0.3	0.06	1.6%
1-Methyl anthracene		10	1.10	0.1%	0.4	0.11	0.9%
1-Methyl phenanthrene		7.9	0.41	0.3%	0.7	0.15	1.4%
9-Methyl anthracene		2.7	0.38	0.1%	0.1	0.02	2.4%
4,5-Methylene phenanthrene		7.6	0.51	0.2%	1.1	0.25	0.5%
Fluoranthene	1e ⁻⁸	14	1.50	0.3%	3.5	0.60	0.6%
Pyrene		15	1.00	0.3%	3.2	0.55	0.6%
Retene		9.8	0.71	0.2%	0.2	0.14	3.9%
Benzo[c]phenanthrene		2.0	0.06	0.4%	0.3	0.06	1.3%
Benz[a]anthracene	1e ⁻⁵	10	0.38	0.2%	0.8	0.19	1.1%
Chrysene	1e ⁻⁴	7.0	0.39	0.4%	0.7	0.16	1.8%
Cyclopenta[c,d]pyrene		5.9	0.48	0.2%	1.0	0.24	0.6%
Benzo[b]naph[2,1-d]thiophene		2.2	0.04	0.2%	0.0	0.00	9.2%
5-Methyl Chrysene		0.1	0.03	0.8%	0.0	0.00	9.1%
Benzo[b]fluoranthene		5.1	1.05	0.2%	0.3	0.08	1.8%
Benzo[j]fluoranthene		4.1	1.01	0.3%	0.4	0.12	1.7%
Benzo[k]fluoranthene	1e ⁻³	2.3	0.15	0.4%	0.2	0.06	2.0%
Benzo[e]pyrene		6.9	0.26	0.3%	0.4	0.09	2.6%
Benzo[a]pyrene	1e ⁻⁴	8.0	0.07	0.2%	0.6	0.14	1.2%
Indeno[1,2,3-cd]pyrene	1e ⁻⁴	4.5	0.30	0.2%	0.4	0.10	0.9%
Dibenzo[ah,ac]anthracene		1.3	0.03	0.0%	0.1	0.02	0.5%
Benzo[g,h,i]perylene	1e ⁻⁸	7.8	0.53	0.2%	0.3	0.08	2.0%
Anthanthrene		1.9	0.01	0.0%	0.1	0.05	0.2%
Dibenzo[a,e]pyrene		1.2	0.09	0.1%	0.04	0.01	0.7%
Dibenzo[a,i]pyrene		0.7	0.03	0.1%	0.02	0.01	1.2%
Dibenzo[a,h]pyrene		0.5	0.02	0.1%	0.01	0.00	5.8%
ΣPAHS		250	25		43	9	
ΣInduction-TEQ ^a		4.4e ⁻³			0.4e ⁻³		

^a Geometric mean of the in vitro TCDD-Induction Equivalency Factors from Bosveld et al. (18). ^b Amount in blank as % of amount in corresponding burning trial before back-ground correction. ^c st.dev. – standard deviation ($n = 3$).

TABLE 6. Emission Factors of PM₁₀ from Coal and Hardwood

	mean	housecoal	mean % blank	mean	hardwood	mean % blank
kg fuel		7.1–7.3			14–16	
MJ		44–46			32–41	
(g/kg)		st.dev. ^a			st.dev. ^a	
PM ₁₀	40	3.9		7.9	0.7	

^a st.dev. – standard deviation ($n = 3$).

PAH-TEQ. In a similar study using in vitro assays for the toxic action of PAHs, Bosveld et al. (18) determined and summarized induction equivalency factors for a range of PAH, these are included in Table 5. These induction ΣTEQs were 4400 and 410 ng/kg fuel for coal and wood, respectively and hence much higher than any of the ΣTEQs calculated above. In both cases, the main contributor to the induction ΣTEQ was benzo[k]fluoranthene, with ca. 50% of the total. It should be pointed out that PAHs are much more prone to degradation reactions than any of the other compound groups.

Formation of Chlorinated Congeners. A 'worst-case scenario' for the formation of chlorinated aromatic compounds from combustion systems would combine the following features: i) poor gas-phase mixing; ii) low combustion temperatures; iii) oxygen starving conditions; iv) high particulate matter loading; v) particulate matter-bound copper; vi) presence of HCl and/or chlorine; and vii) significant gas-phase residence time in the 250–700 °C

temperature range (27). It was suggested that the formation of PCDDs proceeds generally via cyclization of halogenated basic molecules (i.e. chlorophenols); the formation of PCDFs via the halogenation of aromatic intermediate and final products (28). These reactions are obviously not limited to chlorinated dioxins and furans. Under poor combustion conditions, Wikström et al. (28) observed a clear shift of the PCDD/F homologue group profile toward the lower chlorinated PCDDs and PCDFs. These 'sooting' conditions had a higher C:Cl ratio present in the flame (due to more soot). This could be the reason for the observed preponderance of the lowest chlorinated congeners for most chlorinated organic pollutants in our burning trials. Similarly, Yasuhara et al. (29) observed that lower chlorinated PCDFs dominated over PCDDs in combustion products under low combustion temperatures (~ 600 °C). The same conditions also resulted in elevated PCB concentrations. These studies support the hypothesis that the formation of PCDFs and PCBs (and likely PCNs) is enhanced during low-temperature oxygen-poor combustions.

The formation of PCDDs, especially Cl₇₋₈DDs, on the other hand, seems to depend more on the presence of chlorinated phenols in the fuel and flame (e.g. ref 29). The observed increase in EF for the highest chlorinated PCDDs could be explained by this extra formation pathway, namely through the condensation of chlorinated phenols.

Comparison of EFs for Chlorinated Compounds. The same samples were analyzed for 4 different groups of

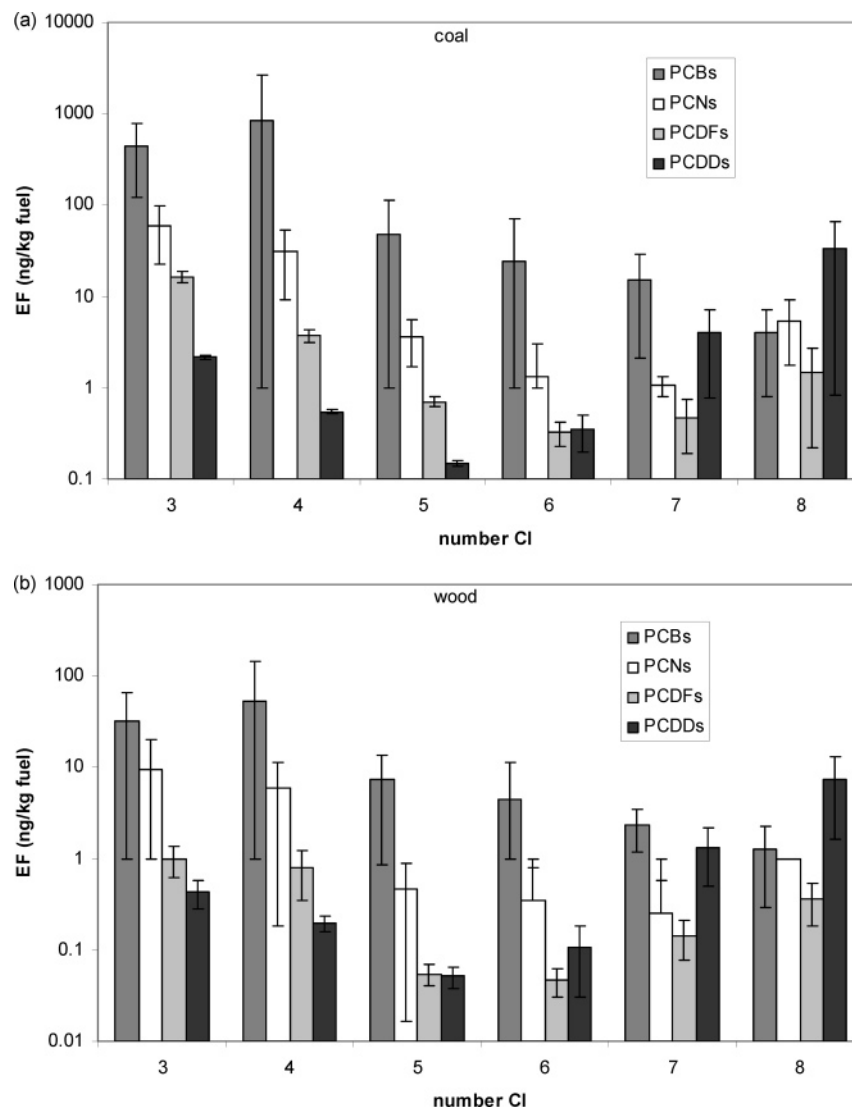


FIGURE 2. Normalized Emission Factors for PCBs, PCNs, PCDFs and PCDDs from the domestic burning of (a) coal and (b) hardwood (ng/kg fuel) (For PCBs and PCNs – average concentration for all congeners with same number of chlorines, for PCDDs and PCDFs – homologue group concentration divided by its theoretical number of congeners).

chlorinated organic pollutants (i.e. PCDDs, PCDFs, PCBs and PCNs). This enabled a comparison of the emissions for tri- to octachlorinated congeners from coal and wood. To achieve this (homologue groups were analyzed for PCDDs and PCDFs, but selected congeners for PCBs and PCNs), EFs were normalized to obtain a mean EF per congener for a given number of chlorines and compound groups (Figure 2). The same trends were apparent for congeners with three to five chlorines for coal and wood – EF for PCBs > PCNs > PCDFs > PCDDs. For the congeners with six chlorines, PCBs > PCNs > PCDFs ~ PCDDs, while PCDDs displayed higher EFs than PCNs and PCDFs with seven chlorines. For the octa-chlorinated compounds, PCDD > PCBs ~ PCNs ~ PCDF.

The EFs for PCDD/Fs suggest that congeners with one or two chlorines were the most abundant (The low EF for Cl₁DDs could be a result of the analytical method used here). Decreasing EFs with increasing degree of chlorination were also seen for the PCBs, although Cl₃Bs had lower EFs than Cl₄Bs. However, the variation within a given homologue group was large for the PCBs. For PCNs, EFs decreased from Cl₃Ns to Cl₇Ns, with an apparent increase for Cl₈N (Figure 3). The variability within a given degree of chlorination was much smaller than for PCBs. These results suggest that for PCDFs and PCNs, the magnitude of the EF depended mostly on the

total number of chlorines, and seemed independent of the molecular conformation. The results for PCBs were noticeably less reproducible for any given degree of chlorination. This might be partially because PCBs were the only nonplanar molecules considered here. In summary, it is suggested that domestic burning releases (i) mostly lower chlorinated congeners and of those (ii) more PCBs than PCNs, PCDDs or PCDFs. However, these emissions seem more important for PCDD/Fs but less important for PCBs and PCNs in the context of the U.K.'s national emission inventory (see below).

Influence of Chlorine Content on Formation of PCDD/Fs, PCBs and PCNs. This study was not designed to elucidate the role of chlorine content on the amount of chlorinated compounds formed during the burning trials. However, within the limited scope of two different samples, the following observations can be drawn. The chlorine content of coal was ~ 9 times that of wood (Table 1), while emissions of non-chlorinated PAHs were higher by a factor of 4–6 (see later) for coal. The following ratios (coal:wood) were determined for the emissions of the different chlorinated compounds: 14 for PCBs, 6 for PCNs, 7 for PCDFs, 4 for PCDDs.

Formation of Chlorinated PAHs. The simultaneous determination of PAHs and the chlorinated compounds enables a comparison of the emissions of the chlorinated versus the 'native' PAHs.

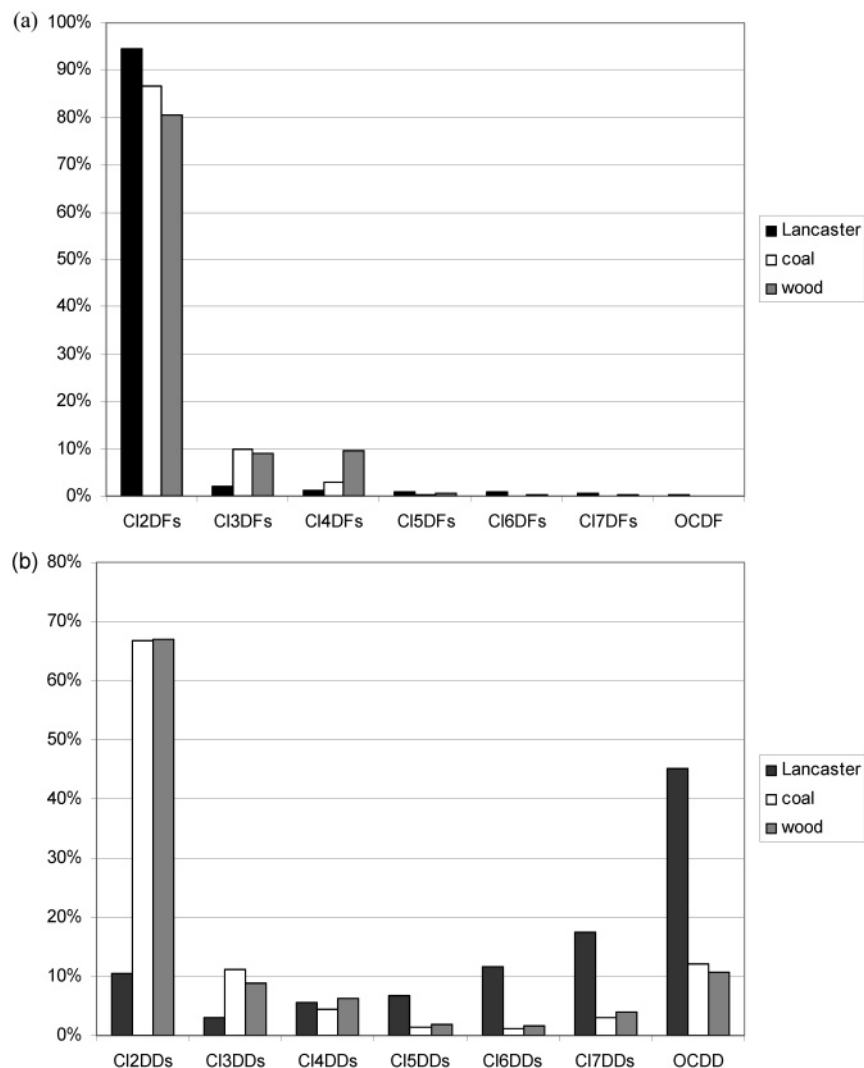


FIGURE 3. Comparison of homologue group profiles in ambient air at Lancaster and emission profiles from coal and wood for (a) PCDFs and (b) PCDDs.

Naphthalenes. A minute fraction of naphthalene (EF 10–20 mg/kg) was detected as Σ PCNs (100–700 ng/kg).

Biphenyls. In a study by MacDonald et al. (24), EFs of biphenyl were comparable to that of fluorene for different woods burned. In our case, this would result in EF for biphenyl of ~ 3 mg/kg fuel, with Σ PCBs being detected at 600–9000 ng/kg fuel. These results suggest that a multitude of chlorinated PAHs was formed in the burning trials (of which we only analyzed PCNs and PCBs), but that the purely chlorinated compounds only account for ppms of the parent PAHs.

Comparison with Ambient Air Profiles. EFs are used in emission estimates to calculate emissions from well-studied processes, such as the domestic burning of coal and wood. This study was designed to assess the impact of domestic burning on ambient concentrations of these different organic pollutants. Ambient air profiles of PCDDs, PCDFs, PCBs and PCNs can therefore usefully be compared to those obtained in the controlled burning trials. For the purpose of these comparisons, ambient air measurements from Hazelrigg, Lancaster University's field station were chosen. These measurements can be considered representative of semi-rural northern England, an area where domestic burning of coal and wood is still widely practiced in the winter months. Furthermore, the fuels were selected to represent coal and wood typically used in northern English households. As an added advantage, ambient air samples and the EFs were

analyzed in the same laboratory under similar conditions.

For PCDDs and PCDFs, ambient concentrations from Lohmann et al. (30) were chosen, in which 37 air samples were analyzed for $\text{Cl}_{2-8}\text{DD}/\text{Fs}$, representing the autumn/winter of 1997. The mean ambient air profile of PCDFs was dominated by Cl_2DFs (> 95%), with minor contributions by the other homologue groups (Figure 3). Cl_2DFs were also the main homologue group in the EFs for wood and coal (> 80%). However, Cl_3DFs and Cl_4DFs contributed ca. 10% each to the EFs, a profile that is not mirrored in the ambient air profile.

While the profile for PCDFs was relatively close for ambient air and EFs, a much greater contrast was evident for PCDDs. The EFs were dominated by Cl_2DDs (> 65%), with 10% contributions of Cl_3DDs and OCDD (Figure 3). However, the mean ambient air profile was dominated by the highest chlorinated congeners: OCDD (> 40%), Cl_7DDs (> 15%) and Cl_6DDs (> 10%). These comparisons suggest that the domestic burning of coal and wood did not dominate the ambient air profiles of PCDDs and PCDFs during the measurement campaign.

For PCBs, the mean results of a long-term study by Lee and Jones (31) were chosen. The ambient air profile for PCBs was dominated by Cl_3Bs ($\sim 40\%$) with decreasing contributions with increasing degree of chlorination for the other PCBs (Figure 4). The EF profile, on the other hand, was dominated by the Cl_4Bs (70–80%). Again, this suggests that

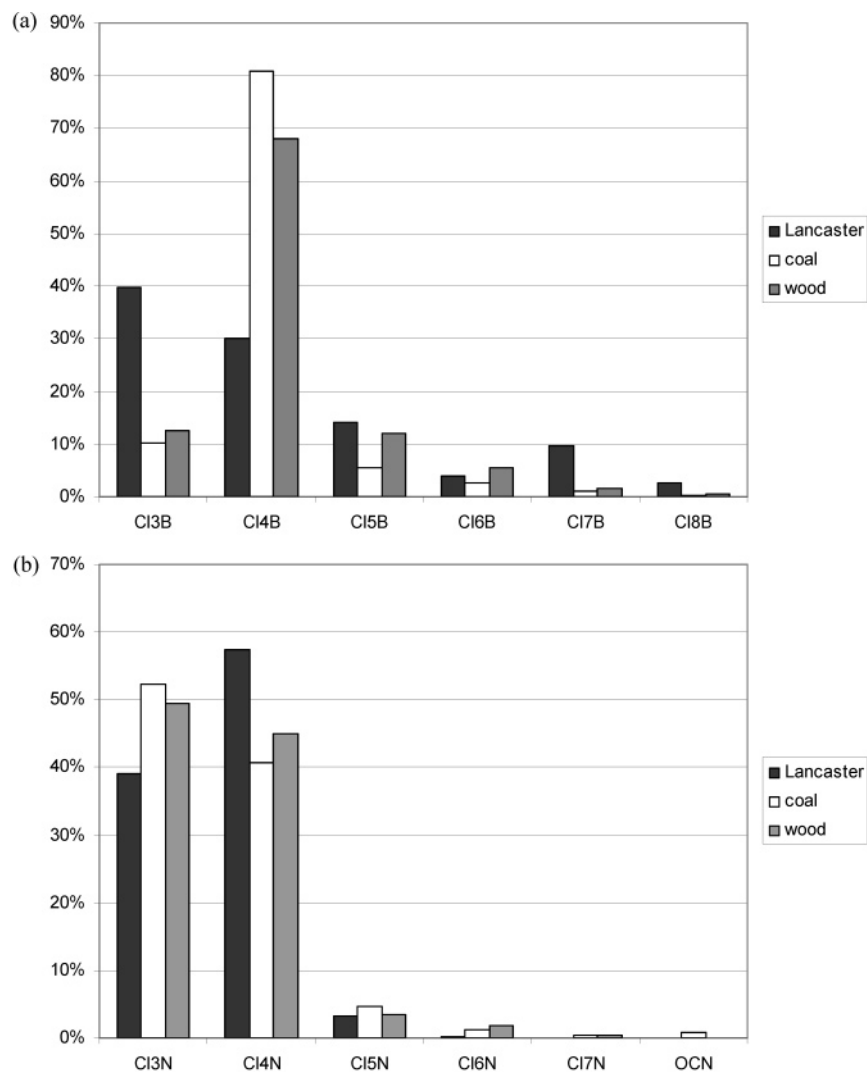


FIGURE 4. Comparison of homologue group profiles in ambient air at Lancaster and emission profiles from coal and wood for (a) PCBs and (b) PCNs.

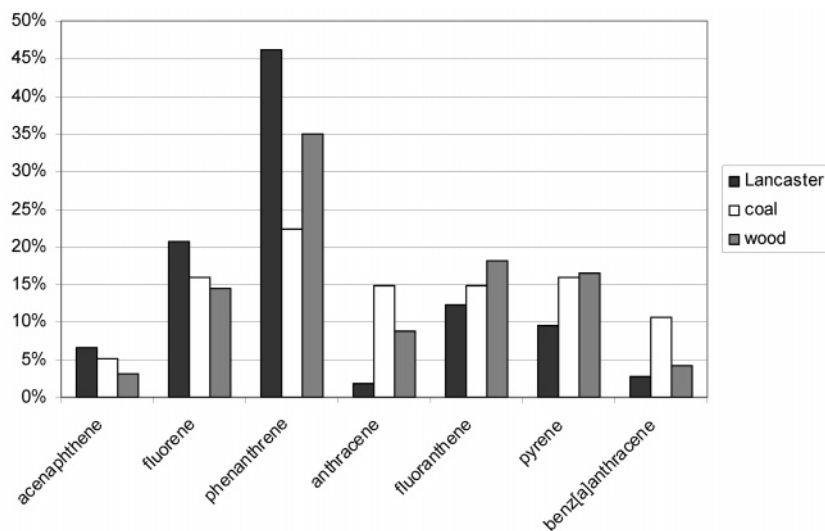


FIGURE 5. Comparison of compound profiles in ambient air at Lancaster and emission profiles from coal and wood for PAHs.

any emission-derived PCBs were not strongly influencing ambient air concentration at the site.

For PCNs, ambient air concentrations by Lee et al. (32) were chosen (Figure 4). In this case there is a remarkable similarity between the ambient air profile and those from

the EF. Major contributors were Cl₃Ns and Cl₄Ns in all cases. This similarity does not necessarily imply that the ambient PCNs were combustion-derived, though. It could also be the result of similar product distributions obtained during the industrial formulation of PCNs and burning emissions.

TABLE 7. Estimated Inputs from the Domestic Burning of Coal and Wood to the U.K. Atmosphere and Potential Contribution to the National Inventory

	Est total emissions		U.K. NAEI ^c for 1998	% due to domestic burning	other estimates
	coal	wood			
amount (t/a)	2.40E+06	7.21E+05			
ΣPAHs (t/a) ^a	420	31	2685	17%	90% (5)
BaP (t/a) ^a	3.7	0.9	13	36%	
ΣPCBs (kg/a)	21	0.5	2840	0.1%	
ΣCl ₄₋₈ DD/Fs (g/a)	555	36	40100	1%	
ΣTEQ (g/a) ^b	7.2	0.1	401	2%	12% (2)
ΣPCNs (kg/a)	1.6	0.09	284	1%	
PM ₁₀ (kt/a)	25	5.7	210	15%	

^a EF for coal and PM₁₀ from ref 5. ^b van den Berg et al., ref 16. ^c Ref 33.

For PAHs, the mean results of a long-term study by Lee and Jones (31) were chosen for comparison (Figure 5). Ambient profiles were dominated by phenanthrene (> 45%) and fluorene (> 20%). The EF profile for wood was similarly dominated by phenanthrene (35%). The EF profile for coal, on the other hand, had fairly similar contributions of fluorene, phenanthrene, anthracene and pyrene (Figure 5). This comparison indicated a potential for a sizable contribution of wood burning emission on the ambient air profile in Lancaster, but not for coal burning. It should be stressed that both the emission profile and the EF apply only to the burning of pure materials. It has been shown that the addition of household waste results in increased EFs of chlorinated compounds such as PCDD/Fs (e.g. refs 20 and 33).

National Importance of Domestic Burning. Table 7 uses the EFs measured in this study to calculate the national emissions from domestic coal and wood burning, assuming they are representative for the country as a whole (only for PAHs and PM₁₀, EF for coal were used from Wenborn et al. (5)). These emissions are based on national domestic coal and wood consumptions of ca. 2.4 and 0.7 million tonnes per year in the late 1990s, respectively. It should be noted, however, that recent trends in the U.K. show a shift from bituminous to smokeless fuel, which would likely result in lower emissions. National atmospheric emissions inventories (NAEI (34)) compiled for PAHs, PCBs and PCDD/Fs in the U.K. are also shown in Table 7, and the potential contributions of domestic coal/wood burning are highlighted. As expected, their importance differs substantially between compound groups.

PAHs, Benzo[a]pyrene (BaP), PM₁₀. NAEI estimates suggest emissions of 2,700 t/a for the 16 US-EPA PAHs (34). Residential combustion accounts for ca. 500 t/a (~ 20%), which is close to our estimate (17%) in Table 7. For BaP alone, the NAEI estimates annual emissions of 13 t, of which ca. 30% were due to residential combustion (34), again in good agreement with the estimates from this study of 36% (Table 7). Estimates for emissions of PM₁₀ derive ~ 30 kt/a, of which ca. 15% stem from the domestic burning of coal and wood. The domestic burning of coal and wood is clearly a major contributor to total PAH and PM₁₀ emissions and the biggest single emitter of BaP.

PCBs, PCNs. NAEI (34) estimated annual emissions for PCBs on the order of 3,000 kg/a for 1997–8. The emissions due to the domestic burning of coal and wood (ca. 21 and 0.5 kg/a, respectively) are minute in comparison. There are no annual emission estimates available for PCNs. However, a crude estimate can be obtained by scaling the annual emission of PCBs to PCN using the ratio of their global production (total PCN production of ~ 150,000t, or ca. 10% of total PCBs (35)). This would indicate annual emission for the U.K. on the order of 300 kg/a. The emissions derived from the domestic burning of coal and wood combined would only add ~ 2 kg/a. This calculation suggests that for these

industrially produced high volume chemicals, volatilisation of the industrial formulations still dominates ambient air concentrations.

PCDD/Fs, ΣTEQ. For PCDD/Fs-ΣTEQ, NAEI estimates annual emissions of ~ 400 g TEQ for 1998, of which ca. 20% were from domestic burning (34). This is in-line with 52 g TEQ from domestic burning of solid fuels, or ca. 16% (8%–24%) of the emission inventory for 1996 as detailed by Alcock et al. (2). However, use of the EF determined in this study puts the total emission from the domestic burning of coal and wood at ca. 7 g TEQ/a, or just 2% of total emissions.

Acknowledgments

We are grateful to the U.K. Department of the Environment, Food and Rural Affairs for financial support. This is publication number 0241 from the Research Center for Ocean Margins (RCOM).

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Received for review August 11, 2004. Revised manuscript received November 26, 2004. Accepted November 30, 2004.

ES0487451