Emission of Polycyclic Aromatic Hydrocarbons and Particulate Matter from Domestic Combustion of Selected Fuels

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Polycyclic aromatic hydrocarbons (PAH) and particulate matter (PM) emission were monitored for three common fuel-stove systems in Southeast Asia, namely, Eucalyptus wood sticks open burning, charcoal stove, and coal briquette stove. Smoke samples were taken isokinetically from the flue pipe of a hood and analyzed for PAH using HPLC/FLD and UV. Wood fuel burning produced the highest emission of 18 PAH and 11 genotoxic PAH in terms of the emission factor on energy basis (mg/MJ), emission rate, and pollutant concentration in smoke, while the charcoal produced the least. On a fuel-weight basis, wood fuel produced almost the same emission factor of the total of 18 PAH (110 mg/kg) as coal briquettes but twice as much as genotoxic PAH, 13.4 vs 6.5 mg/kg. The wood fuel high burning rate, however, resulted in the highest total 18 PAH emission rate (208 mg/h) and concentration (957 μg/m^3), leading to a high exposure to toxic pollutants. The PM emission factor in milligrams per kilogram of fuel was 51, 36, and 7 for the wood, charcoal, and coal briquettes, respectively. The largest fraction of PAH in PM was found for wood fuel burning smoke. The average daily cooking of a household of 2–3 releases 40 mg of genotoxic PAH from wood fuel, 9 mg from coal briquettes, and 3.3 mg from charcoal burning. The charcoal fuel stove was identified as the cleanest system, not taking into account the pollutant emission during charcoal production.

Introduction

The polycyclic aromatic hydrocarbons (PAH), sometimes called polynuclearic aromatics (PNA), are the principal pollutants from incomplete combustion, which are of special interest due to their toxicity, carcinogenicity, and ubiquitous presence in the environment (*1–3*). Emissions of PAH vary with combustion systems. The large-scale combustion, e.g., industrial with a burning rate of hundreds kilograms per hour, is normally better controlled, more complete, and results in lower formation of PAH than small-scale combustion such as domestic cookstoves with a burning rate of a few hundred grams to a few kilograms per hour. For example, the emission factor of benzo[*a*]pyrene (B*a*P), a well-established carcinogenic PAH from small-scale wood stoves can exceed that from coal on an energy equivalent basis with a factor of 100 (*4*). Residential wood combustion alone, for example, was estimated to account for >30% of anthropogenic PAH emission in eastern North America (*5*).

Intensive use of biofuels, for domestic combustion, normally results in high emission factors of PAH. This is related to the high volatile content of biofuels, which commonly leads to a higher possibility of incomplete burning. On a global basis, it is estimated that about 50% of the world households use biofuels for daily cooking and/or heating. With the current economic trend, it is likely that the vast majority of those presently using biofuels will continue to rely on the fuels in short and medium terms (*6*). In developing countries, biofuel (wood, agricultural residues, cattle dung, etc.) use accounts for more than 90% of the total fuel consumption in rural areas (*4, 7*) of which fuelwood is by far the most popular, i.e., over 90% of rural population uses fuelwood for cooking (*8, 9*). Fuelwood is normally burned in simple tripods or three-stone stoves with an efficiency as low as 8–12% (*9*) or traditional domestic cookstoves with an efficiency of 10–15% (*10*). A wide range of traditional and improved cookstoves, such as portable metal and ceramic cookstoves, fixed chula, are also in use, which have efficiencies in the range of 25–30% (*7, 8, 11*). The efficiency of these cookstoves is, however, much lower than that of modern energy used in urban areas and in developed countries, e.g., a kerosene cookstove has an efficiency of 50%, and a LPG cookstove of >60%, and a biogas stove of 55% (*7, 11*).

The low efficiency of cookstoves together with the "at home" eating habit does result in higher fuel consumption per capita for cooking in developing countries as compared to developed countries, which subsequently leads to high emission of products of incomplete combustion including PAH.

Poor kitchen ventilation, i.e., lack of properly designed and installed chimneys or exhaust, is common in rural areas of developing countries. This together with the low-efficiency cookstoves and large amount of biofuels used results, in many cases, in serious indoor air pollution (*6*). For example, high concentrations of CO, NO$_2$, PM, and B*a*P were found indoors with the highest values at standing breathing level in the kitchen when dung cake, fuelwood, and coal were burning. The B*a*P associated with PM, in particular, was 0.97, 0.61, 0.35, and 0.24 μg/m^3 when the dung cake, wood, coal, and charcoal burned, respectively (*7, 11*). In rural houses of developing countries, the PAH level was found to be in the range 100–10000 ng/m^3, compared to 20 ng/m^3 in traffic areas and 20–100 ng/m^3 in cigarette smoking areas (*12*). Personal exposure to these toxic air pollutants, thus, may greatly increase due to the high emission from domestic cooking. It has been found that the high lung cancer mortality in a rural area of China is related to the use of smoky coal in domestic combustion (*13, 14*). A large portion of the world population, mainly in the rural areas of developing countries, and primarily house-bound women and children may be adversely affected by the toxic emissions. In recognition of the need to identify and develop cleaner domestic combustion systems, this study aimed at providing an initial assessment of emission from various existing typical fuel-stove systems used in the region. PAH were selected as the target pollutants due to their carcinogenicity, mutagenicity,

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TABLE 1. Summary of Fuels, Stoves, and Source Sampling Conditions

types	ash (%)	gross heat value (MJ/kg)	moisture (%)	amount (g)	stove	time, (min)	vol (m³)[a]	isokinetic, (%)[d]	temp of sampled gas (°C)	collected PM (mg)
charcoal (Mangrove)	3	31[b]	5.1	1204	Thai bucket	162	4.591	95	75	66.1
				1004.5	charcoal	146	4.002	92	78	51.1
				943	stove	155	4.513	96	69	24.6
				2557		373	9.819	98	46	42.8
				2473		379	9.78	92	53	68.1
				2499.5		355	9.262	95	49	91
wood (Eucalyptus chip)	0.5	19.7[b]	10.2	1918	Open burning	57	1.567	100	150	81.4
				3268.5	in pile	109	2.69	89	169	251.9
				3390.5		132	2.794	74	125	114.7
coal briquettes (from Vietnam)	39	23[c]	3.5	1208	Vietnamese	300	7.112	97	57	8.7
				1206.5	cylindrical coal	270	6.591	98	64	10
				1211.5	briquette stove	241	6.932	98	64	6.2

[a] Volume of dry gas at 25 °C and 760 mmHg. [b] Values for charcoal and hardwood are from ref 4. [c] Computed from gross heat of anthracile coal particles, 23 MJ/kg,[15] and peat, 19−27 MJ/kg.[4] [d] Percentage of isokinetic sampling rate.

and relatively high emission factors from domestic burning sources and the general lack of information on the pollutants in the region. Particulate matter (PM) emission and the association of PAH with PM were also assessed.

Materials and Methods

Fuel Combustion and Source Sampling. Three fuels commonly used in domestic combustion in the region were selected, charcoal, coal briquettes, and wood, with the characteristics and burning conditions given in Table 1. Charcoal was purchased from a local market in Pathumtahni, Thailand. It was produced from mangrove, the prime fuel wood used for charcoal making in the country and Southeast Asia (16). The charcoal was burned in a so-called Thai double-skinned bucket, which is an insulated charcoal stove with a metallic outer cover and ceramic liner. The stove has a grate and ash insulating layer. Efficiency of this type of stove is 25−30% (8). The stove is 35 cm in height with an opening outer diameter of 30 cm and an inner diameter of 25 cm.

The coal briquettes were brought from Vietnam. They are composed of 50% fine particles of anthracite coal, 40% peat, and 10% clay by weight. The coal briquettes were burned in a Vietnamese double-skinned cylindrical cookstove with a metallic outer cover and a ceramic liner. The stove is 25 cm in height and 20 cm in outer and 15 cm in inner diameter. It is similar to the Thai cookstove except for the grate, which is made of two metal bars separating the briquette burning zone and the ash insulating layer. The efficiency of this cookstove was not determined but is expected to be in the same range as the Thai cookstove.

The fuel wood was sticks (20−25 cm long, 4−5 cm thick) produced from logs, free from bark, of *Eucalyptus globulus* labill, which is a common Eucalyptus species in the region. This fuel wood was burnt openly on a ceramic support 35 cm in height. The average burning rate was 1.78 kg/h, which is within the typical range of the wood fuel burning rate for single-family domestic cooking of 0.5−6 kg/h (10).

The burning of all three fuels was conducted with a free air supply through an opening or a width gap of the hood (Figure 1). With the opening width adjusted to around 10 cm, the flame was above the opening and shielded from the wind. During the burning the lower watch door was also closed. The ignition was done from the fuel bed bottom. The coal briquettes were burning without stoking, which is a common cooking practice using this fuel. For charcoal and wood burning the fuels were stoked on the top, along the periphery of the fuel bed with minimum disturbance to the existing fire, just 2 times during each burning batch. This was done, when necessary, to keep the firing periods long
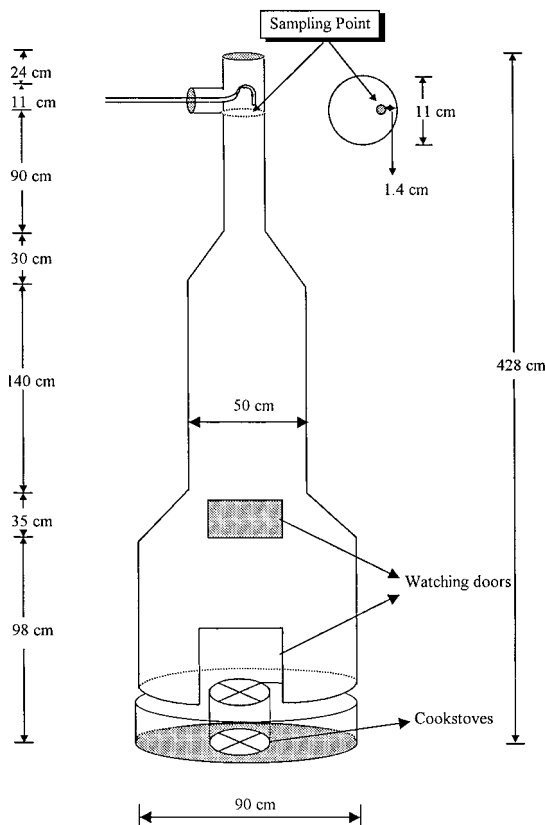

FIGURE 1. Hood and sampling port.

enough to collect the desired sample volumes. The ignition period of the fuels was on the order of 2−5 min. Small wood chips and paper were used to start the fire for charcoal and coal briquettes. Wood fuel was ignited fast with some paper, and the fire was sustainable after less than 2 min.

A hood, thermally insulated, was constructed to capture the flue gases from the cooking stoves (Figure 1). Sampling was done through a port in the hood flue pipe. To ensure a uniform flow of the flue gas and representative sampling of PM, the port was located at a distance 8 times that of the flue pipe diameter downstream and 2 times that of the diameter upstream from disturbances, respectively (17), as shown in Figure 1. The small stack diameter (11 cm, Figure 1) could accommodate only one traverse point with the position determined by the U.S. EPA Method 1 (18). The sampling probe nozzle was thus fixed, and the sampling port was closed

using metal-lining insulated material to minimize disturbances of gas flow. During the sampling the filter box and the sampling probe were heated at around 125 °C.

The sampling period covered the whole burning cycle from the moment of stable firing (fuel had been ignited) to the end of the burning process, i.e., when visually the char burning stopped. The fire induction period (first 2−5 min) was excluded from sampling since different supplementary fuels were used to start fire. When sampling stopped, the ash and any possible unburned fuel was extinguished by the airtight method and cooled, and its weight recorded. This weight was subtracted from the initial fuel weight to obtain the weight of the burned fuel on an ash-free basis. The ash content of the fuels was determined separately and used to obtain the actual weight of the burned fuels, which was used for the calculation of emission factors. The related information is given in Table 1.

The samples were taken isokinetically using an Anderson-Graseby Auto5 semivolatile sampling train (semi-VOST) and followed the U.S. EPA Modified Method 5 (*17*). The train consisted of four impingers followed the XAD-2 trap. The first impinger was the condensate knockout. The second impinger, of the standard Greenburg−Smith design, contained 100 mL of distilled and deionized water. Both the third and fourth impimgers were of the modified Greenburg-Smith type. The former was empty, while the latter contained 350 g of activated silica gel. A sorbent trap containing 30 g of Amberlite resin (XAD-2) was used to adsorb gaseous PAH. Before use the resin (and the glass wool) was Soxhlet extracted by methylene chloride for 24 h at approximately four cycles per hour and dried by pure nitrogen gas stream. A pretest and post-test leak-check of the sampling train were performed for each sample.

The flue gas flow rate was measured by the integrated manometer in the Auto5 train, and the isokinetic sampling rate was maintained automatically by the device. Sampling was done at a height of around 4 m above the fire level (Figure 1). The flue gas velocity at the sampling point was 6−8 m/s. Considering the configuration of the hood, the upward flow along the largest cylinder above the stoves was estimated to 0.7−1 m/s and the average residence time of flue gas in the hood was around 2−3 s before sampling. No spillage of the smoke or flame blow-away was observed.

Before sampling, all the parts of the train to be in contact with the flue gas were cleaned properly and rinsed with methylene chloride twice. Sample recovery was done according to the U.S. EPA Modified Method 5. All PM attached to the probe nozzle, line, and other parts to the front half of the filter holder, inclusively, was removed and placed in one container. These parts were rinsed with methylene chloride, and rinsate was also placed in the container. The contents of this container were extracted together with filter paper to produce PAH in the PM fraction. The rinsate of all parts from the second half of the filter holder up to the second impinger was placed in another container, which later was extracted together with XAD-2 to give the PAH in vapor. The contents of the condensate knock out and the second impinger were kept separately. The extracts from these impingers were also added to the XAD-2 extract to form the PAH in the gas phase. Field blanks of filters and washing methylene chloride were used to check for possible contamination.

The particulate matter and gas-phase samples were stored separately. All collected samples were sealed properly and wrapped in precleaned aluminum foil and stored frozen at −25 °C for a maximum period of 1 week before analysis. Determination of the moisture and particulate matter content of flue gas was made followed U.S. EPA Methods 4 and 5, respectively (*18*).

Reagents and Materials. All reagents were of chromatographic grade, from J. T. Baker Co., except for anhydrous sodium sulfate (analytical grade) and silica gel (chromatograhic grade), 60−230 mesh, which were purchased from Merck Co. All reagents were tested with procedural blanks for possible contamination.

Analytical Equipment and Procedure. The analytical method was developed on the basis of U.S. EPA Method TO-13 (*19*). A high-performance liquid chromatograph, HP 1050, with an autosampler, a quaternary pump, and a programmable fluorescence detector (FLD, 1046A, ASEP-12) was used for the analysis. A reversed-phase column (with guard column) from Hewlett-Packard Co. and specified for PAH analysis (VYDAC 201 TP5 C-18 RP, 0.46×25 cm) was used for the separation according to the following conditions at 30 °C and a flow rate of 0.8 mL/min:

TABLE 2. Excitation and Emission Wavelengths

time (min)	excitation (nm)	emission (nm)
0.00	280	320
16.00	260	320
18.50	250	368
20.00	240	460
21.50	240	370
24.00	265	400
26.50	290	450
28.50	295	405
36.50	300	500
39.00	302	445

mobile phase:	solvent composition	time (min)
	50% acetonitrile/50% water	0−10
	gradient	10−20
	90% acetonitrile/10% water	20−55
	gradient	55−60
	50% acetonitrile/50% water	60

The equipment was optimized for a mixture of 18 PAH, including 16 U.S. EPA priority PAH plus coronene and B*e*P. The selected wavelength program of the fluorescence detector is shown in Table 2. A UV detector (HP 1050), working $\lambda = 254$ nm, was used in parallel to detect fluorescence less-sensitive compounds. Due to the lack of fluorescence, acenaphthylene, for example, can be detected only by the UV detector.

A external standard of all 18 PAH in a mixture was used for quantitative analyses. A good linear correlation between the compound concentrations and peak height or peak areas was found with most of the R^2 values in the range 0.98−0.99 for all 18 PAH compounds. The minimum detectable quantity of the method was determined (higher than 3 times of the noise level), and the results are presented in Table 3. The quantification limits were taken as 10 times of the noise level.

Sample Extraction and Cleanup. The samples were extracted by ultrasonification using an ultrasonic bath of Branson, 3200 specification. A RE 120 Büchi, Switzerland, rotavapor was used for concentration. A hand-packed column was prepared following the procedure given in TO-13 (*19*) and used for sample cleanup. Sample preparation steps are presented in Figure 2.

The collected particulate matter samples were analyzed separately to yield PAH in the PM phase. The condensable part of the gas-phase PAH, collected in the condensate knock-out, and the contents of the second iminger were combined and extracted twice each time by an equal volume of dichloromethane. The extract was then combined with the other parts (XAD-2 and washing), and the combination was extracted by ultrasonification to yield the gas-phase PAH.

The analytical protocol used proved reliable when evaluated against the urban dust standard reference materials,

TABLE 3. Emission Factors (mg/kg fuel) of Individual PAHs from Domestic Combustion of Charcoal, Coal Briquettes, and Wood[a]

fuel (burning rate)	phase	NAPH	ACY	ACE	FLU	PHE	ANT	FTH	PYR	BaA	CHRY	BeP	BbF	BkF	BaP	DahA	BghiP	IcdP	COR	PM mg/kg	BaP/PM[c] (mg/g)
									emission factor of individual PAHs, mg/kg fuel												
wood (1.78 kg/h)	total	39.1	11.03	35.5	4.83	4.46	1.83	4.94	2.44	0.817	0.883	0.406	0.539	0.448	0.693	0.602	0.501	1.13	0.048	51	10.5
	vapor	39.1	11.03	35.5	4.83	4.43	1.81	4	1.93	0.406	0.348	0.06	0.194	0.308	0.156	nd	nd	0.51	nq		
	%[b]	100	100	100	100	99.5	98.5	81.02	79.3	49.7	39.5	14.7	36.1	69.5	22.5	0	0	45.1	0		
coal briquette (0.27 kg/h)	total	44.5	14.6	30.5	3.05	1.041	1.289	1.005	2.18	0.108	0.6	0.0047	0.58	1.68	0.303	nd	nd	nd	nd	7	0.18
	vapor	44.5	14.6	30.5	3.05	1.04	1.288	1	2.17	0.107	0.6	0	0.58	1.68	0.302	nd	nd	nd	nd		
	%[b]	100	100	100	100	99.96	99.8	99.6	99.7	98.7	100	0	100	100	99.6						
charcoal (0.44 kg/h)	total	7.48	1.79	9.64	0.493	2.408	0.628	0.606	1.25	0.062	0.105	nd	0.017	0.863[c]	0.172[c]	nd	0.0028	nd	nd	36	0
	vapor	7.48	1.79	9.63	0.492	2.404	0.622	0.582	1.23	0.058	0.104	nd	nd	0.009[d]	0.172	nd	nd	nd	nd		
	%[b]	100	100	99.95	99.97	99.81	99.1	95.96	98.4	94.01	99.01	nd	0	0	100	nd	0	nd	nd		

[a] Names of compounds with minimum detectable quantity and detector in parentheses. NAPH: Naphthalene (MDQ-UV = 0.41 ng). ACY: Acenaphthylene (UV-0.22 ng). ACE: Acenaphthene (UV-0.35 ng). FLU: Fluorene (FLD-0.005 ng). PHE: Phenanthrene (FLD-0.013 ng). ANT: Anthracene (FLD-0.008 ng). FTH: Fluoranthene (FLD-0.015 ng). PYR: Pyrene (FLD-0.032 ng). BaA: Benzo(g)anthracene (FLD-0.014 ng). CHRY: Chrysene (FLD-0.019 ng). BeP: Benzo[e]pyrene (UV-0.066 ng). BbF: Benzo[b]fluoranthene (UV-0.038 ng). BkF: Benzo[k]fluoranthene (FLD-0.012 ng). BaP: Benzo[a]pyrene (FLD-0.02 ng). COR: Coronene (FLD-0.72 ng). DahA: Dibenzo(a,h)anthracene (FLD-0.02 ng). BghiP: Benzo[g,h,i]perylene (FLD-0.02 ng). IcdP: Indeno[1,2,3-c,d]pyrene (UV-0.15 ng). nd: not detected (<3 times of noise level). nq: not quantified (<10 times of noise level). [b] PAH in vapor phase in percentage of total PAH detected on both particulate matter and in vapor phase. [c] Detected only in vapor phase of one sample, reported values are not averaged. [d] BkF on particulate matter. [e] Ratio between BaP associated with PM and PM.
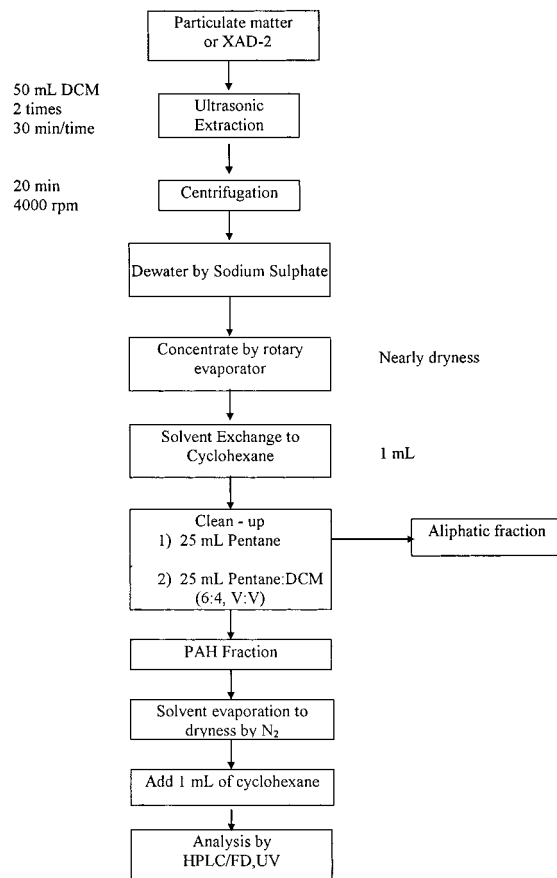

FIGURE 2. Sample preparation procedure.

SRM 1649, received as a gift from the National Institute of Standard and Technology.

Results and Discussion

All of the 18 selected PAH were detected in the wood fuel smoke (Table 3), including the carcinogens (BaA, chrysene, BbF, BkF, BaP, DahA and IcdP) and co-carcinogens (fluoranthene, pyrene, BeP and BghiP), while only 14 compounds were detected in the smoke from the charcoal and the coal briquette burning.

The emission factors of the total 18 PAH on a fuel-weight basis (mg/kg) were almost the same for both coal briquette and wood fuel burning, 110 mg/kg. On an energy basis (mg/MJ), however, the average emission factor of wood burning, 5.6 mg/MJ, is higher than that of coal briquettes, 4.4 mg/MJ, but the ranges of values are overlapped (Table 4). The lowest emission factors were found for charcoal burning on both a fuel weight basis, 24.7 mg/kg, and an energy basis, 0.8 mg/MJ. The first three more volatile and noncarcinogenic PAHs (naphthalene, acenaphthylene, and acenaphthene) contributed largely to the obtained emission factors, i.e., 90, 86, and 19 mg/kg for coal briquettes, wood fuel, and charcoal, respectively. If only the genotoxic PAHs, i.e., the carcinogenic and co-carcinorgenic, are taken into account, the emission factor ranking order was from the wood fuel, 13.4 mg/kg (6.7−18.3 mg/kg), to the coal briquettes, 6.5 mg/kg (1.2−9.3 mg/kg), and finally to the charcoal, 2.2 mg/kg (1.1−3.2 mg/kg).

The PAH emission of the three tested systems was found to correspond to the fuel's volatile content, which may be due to the fact that a complete combustion of fuels with a high volatile content is more difficult to achieve (4). In fact, the volatile content on a moisture-free basis of hardwood is around 80% (4) and of typical charcoal in Thailand (21 ± 4)%

TABLE 4. Summary of Emission Data of Total 18 PAH and Genotoxic PAH

fuel	parameter	emission factor (mg/kg)		emission factor (mg/MJ)		emission rate (mg/h)		conc (μg/m³)	
		total	Gen.[a]	total	Gen.[a]	total	Gen.[a]	total	Gen.[a]
wood	average	110.2	13.4	5.6	0.68	208	23	957	104
	range	43−192	6.7−18.3	2.2−9.7	0.34−0.93	66−386	13.5−28.2	295−1790	62.3−125
	vapor/total (%)	95	59						
coal briquetts	average	101.5	6.5	4.4	0.28	26.4	1.7	136	8.7
	range	33−191	1.2−9.3	1.4−8.3	0.05−0.4	10.1−47.6	0.35−2.4	52−247	1.8−12.2
	vapor/total (%)	99.9	99.7						
charcoal	average	24.7	2.2	0.8	0.071	10.2	0.97	45.4	4.5
	range	15−35	1.1−3.2	0.47−1.14	0.035−0.103	6−14.6	0.43−1.3	25.1−68.6	1.8−6.1
	vapor/total (%)	99.6	96.8						

[a] Note: Gen[a]—Genotoxic PAH include 11 carcinogenic and co-carcinogenic PAH, from fluoranthene to indeno[1,2,3-c,d]pyrene.

(20). For the coal briquettes, the estimated volatile content based on the briquette composition would give a value of 42% not including the volatile content of the clay, i.e., only the volatile content of peat of 65% and anthracite coal of 32% (4) are accounted for.

As anticipated, the most volatile PAH, i.e., those with 2−3 ring numbers (from naphthalene to anthracene), were detected predominantly in the gaseous phase, >98−99%, of emission from all three fuel-stove systems.

In the smoke from wood fuel burning, the gaseous PAH reduced considerably with the increase of ring numbers (Table 3) with DahA, BghiP, and COR detected only in the particulate matter phase. The PAH in PM was 5% of the total 18 PAH (in both phases), which is in the same range found by a study on emission of 19 PAH (the 18 PAH minus coronene plus methylnaphthalene and perylene) from open burning of forest wood in a wind tunnel, i.e., 7.6% out of 25.8 mg/kg of fir slash and 3.3% out of 31.7 mg/kg of pine slash (21).

For coal briquette and charcoal burning the PAH fraction associated with PM was small, i.e., 0.1% and 0.4% of the total of 18 PAH, respectively (Table 4). For individual PAH, the fraction also increased with the increase in the ring numbers and some PAH, i.e., BeP, BbF, and BghiP, were detected only in the PM phase at low levels (Table 3). A higher fraction of the genotoxic PAH, which are of four or more ring numbers, was found on PM, e.g., 41% for wood burning, 3.2% for charcoal burning, and 0.3% for coal briquette burning.

The temperature of the sampled flue gas ranged from 46 to 169 °C (Table 1) depending on the type of fuels burned. This was the temperature measured at the sampling port level, i.e., after the flue gas was mixed with air entering through the opening at the bottom of the hood (Figure 1) and raised to the port level. The average residence time of the flue gas in the hood was around 2−3 s, as mentioned earlier. The wood fuel burning was characterized by the highest sampled gas temperature, >125 °C, while the temperature of the sampled gas from burning coal briquettes and charcoal was lower, 46−78 °C. This may suggest that the PAH in wood burning smoke would have a higher gaseous-phase fraction compared to the other two fuels. The obtained results of the PAH-phase partitioning in Tables 3 and 4, however, showed the lowest fraction of PAH, especially those with ≥4 rings, in the gas phase of wood fuel smoke. The short residence time of flue gas in the hood before being sampled may not be sufficient for the phase equilibrium to be established (21). In addition, the amount of PM emitted as well as the sorption characteristics may also result in the differences in the PAH fraction on the particles of the fuels.

In fact, the fraction in PM of both the total of 18 PAH and the genotoxic PAH for the three fuels was found to correspond to the PM emission factor. The wood burning produced the highest PM emission (51 mg/kg) and highest amount of PAH

in PM, while the coal briquette burning produced the lowestPM (7 mg/kg) and lowest PAH in PM phase. The ratio between BaP in PM and PM or the BaP concentration in PM, for example, was also highest for wood fuel, 10.5 mg/g, second highest for coal briquettes, 0.18 mg/g, and zero for charcoal. This ratio depends on both BaP and PM emission and was found in a wide range in the literature. The study of fir and pine slash burning in a wind tunnel (21) reported a high emission factor of PM, i.e., 5.9 and 3.9 g/kg, respectively, while the emission factor of BaP in PM was low for both fuels, 12.5 μg/kg of fuel. Therefore, the resulting concentration of BaP in PM, 1.9−4.2 mg/kg, is 3 orders lower than the obtained value in this study, though the BaP emission factors (in both phases) were only 2−4 times lower than that of this study. The ratio obtained in this study is more compatible with that reported for wood and root fuels burning in metal stoves using the chamber method, 0.7−2.1 mg/g (10) and the ratio reported for wood fuel burning in residential stoves, 0.5 mg/g (4).

For charcoal burning, BaP (and also BkF) was detected only in the gas phase of one sample with a large volume (>9 m³), though there were three samples (out of six samples) having a volume >9 m³. No abnormal burning or sampling conditions in the batch experiment were reported, and the values presented in Table 3 are from this sample alone and not averaged. It was higher than a reported emission factor of charcoal of 0.3 μg/kg (4). For coal briquettes, the average emission factor of BaP is 0.303 mg/kg. No emission data was found in the literature for domestic combustion of similar coal briquettes.

Previous studies (4) on emission of 16 U.S. EPA priority PAH plus methyl- and phenylnaphththalenes reported a range of 47−250 mg/kg for different wood stoves and 6−300 mg/kg for fireplaces, which were shown to vary with combustion conditions. The total of 18 PAH emission for wood fuel burning found in this study (110 mg/kg) is within the range. Compared to the reported EPA data (22), emission factors for the first eight lower ring number PAH for wood burning presented in Table 3 are comparable with those from catalytic and noncatalytic stoves but less than those from conventional stoves. Larger discrepancies are found for heavier PAH (from BaA onward in Table 3), e.g., BaP has an emission factor of 2−3 mg/kg from the U.S. EPA data as compared to 0.693 mg/kg (0.38−0.98 mg/kg) obtained in this study. The latter, however, falls in the lower range of emission from wood fuel burning in domestic stoves, 0.7−6.5 mg/kg, and is close to the average BaP emission from fireplaces of 1 mg/kg (4). The BaP emission factors from the fir and pine slash (21) were 0.163 and 0.387 mg/kg, respectively, i.e., lower than the level obtained in this study. The emission factors of the total of 18 PAH as well as BaP obtained for fuel wood by the present study is, thus, considered to be in the range reported by other studies.

The comparison is, however, relative. First of all, it is weakened by the discrepancy in the monitored compounds. Second, the emission of PAH is a function of many fuel, stove, and burning parameters, which are different in different studies. The wood fuel used in this study was dry (10% moisture), made in small pieces from the easy-to-burn Eucalyptus log, which contained no bark and was burned in the controlled experimental conditions.

The obtained PM emission was low compared to those reported for tropical wood fuel burned in small open stoves (4), 6.4−8.9 g/kg. Many factors may contribute to the obtained low PM emission including the easy-to-burn selected wood fuel and the controlled burning conditions in this study. The high sampling port (around 4 m, Figure 1) may exclude certain large settleable PM as some were seen to deposit on the hood floor. However, PAH in PM emitted from combustion are preferably sorbed on submicron, usually soot, particles due to their large specific surface (23). The 18 PAH and BaP, in particular, in PM are, therefore, not expected to be significantly affected by the exclusion of large settleable particles from the collected PM samples. In fact the concentration of BaP in PM obtained in this study is comparable to the concentration of BaP in respirable PM (RPM) obtained in the study for wood and root fuels burning in metal stoves (10), 4.4−17.9 mg/g.

The emission factor is a good basis to compare pollutant emission from combustion of different fuels. However, to assess the harmful effects of emission, the emission rate (mg/h) and concentration of pollutants in smoke (μg/m^3) should be of more interest since they are directly related to duration and levels of exposure. The high rate of wood fuel burning (1.78 kg/h) resulted in a high emission rate of 18 PAH, 208 mg/h, as compared to coal briquette burning, 26.4 mg/h, and charcoal, 10.2 mg/h (Table 4). Concentrations of the total 18 PAH and genotoxic PAH in the flue gas are ranking in the same order, highest for wood burning (957 and 104 μg/m^3) followed by coal briquette (136 and 8.7 μg/m^3) and the lowest for charcoal burning (45.4 and 4.5 μg/m^3).

Of the three tested fuel-stove systems, charcoal burning produced the lowest emission of the total of 18 PAH and genotoxic PAH in terms of emission factors, emission rate, and concentration in the smoke. However, it worth mentioning that a significant quantity of PAH, one of the principal products of incomplete combustion (PIC), is released during charcoal production. In Thailand, mangrove charcoal is commonly produced in simple brick beehive kilns ranging from medium to large size (16), which must release a large amount of the pollutants into the environment. However, the population exposed to this release is much less than that to the emission from daily domestic cooking. Besides, technologies are available to reduce the emission from charcoal production. Use of the charcoal fuel-stove system to reduce indoor air pollution from cooking is thus recommended, though it involves a higher fuel cost than the other two fuels.

Supposing a household of 2−3 uses 3 kg of wood fuel or 1.4 kg of coal briquettes (2 cakes) or 1.5 kg of charcoal for daily cooking the genotoxic PAH emitted is 40 mg from the wood fuel, 9 mg from coal briquettes, and 3.3 mg from charcoal. If the ventilation in the kitchen is limited, the resulting high concentration of the pollutants in the smoke and the prolonged cooking time, 1.5 h for the wood, 3 h for coal briquettes, and 2 h for charcoal, will lead to a significant exposure to these toxic compounds.

It is believed that there is no "threshold" or "safe" level for the genotoxic compounds; hence, exposure to these PAH at any level provides the risk of genotoxic effects. Although to give an overview picture of PAH emission from domestic combustion more fuel stoves in the region have to be tested with various combustion parameters, the obtained results indicate high levels of exposure resulted from cooking, especially for wood fuel. Presently, fuel switching to electricity or LPG is generally not affordable for the poor in developing countries. A proper kitchen design with an enclosed chamber for cooking devices and a flue pipe to vent the smoke outside would reduce immediate exposure to high levels of toxic PAH indoors. Improvement of domestic cookstoves, which provide more complete or cleaner burning of the fuels, is essential to reduce the total pollutant load into the environment.

Acknowledgments

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