Emission of polycylic aromatic hydrocarbons and particulate matter from domestic combustion

Nguyen Thi Kim Oanh(1), L.-B. Reutergårdh(2) and Nghiem Trung Dung(1)
(1) Environmental Engineering Program, School of Environment, Resources and Development, Asian Institute of Technology, PO Box 4, Pathumthani 12120, Thailand
(2) Centre for River Basin Environment Research, GIFU University, 1-1 Yanagido, Gifu Shi, GIFU 501-11, Japan (permanent address: IAER, Stockholm University, S 106 91, Stockholm, Sweden)
Email: kimoanh@ait.ac.th

Abstract

PAHs and particulate matter (PM) emission were monitored for three common fuel-stove systems in Southeast Asia. Smoke samples were taken iso-kinetically from the flue pipe of a hood and analysed for PAHs using HPLC/FLD and UV. On the moisture and ash free basis, the charcoal fuel-stove system produced the least emission factor of 18 PAHs (27 mg/kg charcoal) and 11 genotoxic PAHs (2.6 mg/kg) as well as the least emission rate (11 mg/h) and concentration in the smoke (50 $\mu g/m^3$). As compared to the wood fuel, the coal briquette burning produced lower emission factor of the genotoxic PAHs (12.7 mg/kg vs 15 mg/kg), but higher total 18 PAHs (180 mg/kg vs 126 mg/kg) which mostly consisted of more volatile compounds. The wood fuel high burning rate, however, produced the highest PAHs emission rate (244 mg/h) and concentration (1130 $\mu g/m^3$) which resulted in higher exposure level. Wood fuel burning released the highest PM with the largest amount of adsorbed PAHs. Average daily cooking of a household of 2-3 releases 45 mg of genotoxic PAHs for the wood fuel use, 17.8 mg for coal briquettes and 3.9 mg for charcoal. The exposure to total 11 genotoxic PAHs during the cooking period for the three fuels was 156 $\mu g.h/m^3$, 29 $\mu g.h/m^3$ and 9 $\mu g.h/m^3$, while exposure to benzo(a)pyrene alone was 8100, 1320 and 680 $ng.h/m^3$, respectively.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are principal pollutants from incomplete combustion which are of special interest due to their toxicity, carcinogenicity and ubiquitous presence in the environment (Nicolaou[1], Swartz[2] and McCrillis[3]). Emissions of PAHs vary with fuel-stove combustion systems. The large scale combustion, e.g. industrial with a burning rate of hundreds kg/h, is normally better controlled, more complete and results in lower formation of PAHs than small scale such as domestic cookstoves with burning rate of a few hundred grams to a few kilograms per hour. The emission factor of one PAH, benzo(a)pyrene (B*a*P), from small scale wood stoves, for example, can exceed that from coal, on an energy equivalent basis with a factor of 100 (Smith[4]). Residential wood combustion alone, for example, was estimated to account from >30% of anthropogenic PAHs emission in eastern North America (EPA[5]).

Intensive use of biofuels, for domestic combustion, normally results in high emission factors of PAHs. This is related to the high volatile content of biofuels which commonly leads to higher possibility of incomplete burning. In developing countries, biofuels (wood, agricultural residues, cattle dung, etc.) account for more than 90% of the total fuel consumption in rural areas. Inefficient cookstoves such as tripods or three-stone together with the 'at home' eating habit would result in higher fuel consumption for cooking per capita in developing countries as compared to developed countries and, hence, high emission of incomplete combustion products including PAHs.

Poor kitchen ventilation, e.g. lack of chimneys or exhaust, is common in rural areas of developing countries, which results, in many cases, in serious indoor air pollution. In rural houses of developing countries the PAHs level, for example, was found to be in a range 100-10,000 ng/m^3, as compared with 20 ng/m^3 in traffic areas, and 20-100 ng/m^3 in cigarette smoking areas (UNEP[6]). Personal exposure to these toxic air pollutants, thus, may greatly increase. 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 (Mumford[7] and Chang[8]). In order to identify and develop cleaner domestic combustion systems, this study isaimed at providing an initial emission assessment for existing typical fuel-stove systems used in the region. PAHs were selected as the target pollutants due to their toxicity and relatively high emission from domestic sources, and the general lack of PAHs information in the region. Particulate matter (PM) emission and association of PAHs with PM were also assessed.

2 Materials and methods

2.1 Fuel combustion and source sampling

Three fuels commonly used in domestic combustion in the region were selected: charcoal, coal briquettes and wood with the burning conditions given in Table 1. The coal briquettes are composed of 50% fine particles of anthracite coal, 40% peat and 10% clay by weight. The fuel wood was produced from logs of *Eucalyptus globulus* labill, which is a common Eucalyptus species in the region. This fuel wood was burnt openly to resemble a tripod or three-stone-stove, which are commonly applied in rural areas. The burning was conducted with free air supply (free ventilation) resembling domestic combustion conditions, with ignition from the bottom of the fuel bed.

A hood was used to capture the flue gases from the cooking stoves. Sampling was done through a sampling port in the hood pipe. Flue gas samples were taken isokinetically using an Auto5^{TM} of Anderson-Graseby, semi-volatile sampling train (semi-VOST) followed US EPA Modified Method 5 (US EPA[9]). Amberlite resin XAD-2 was used to adsorb PAHs in gas phase. The sampling period covered the whole burning cycle from the moment of stable firing to the end of the burning process, i.e. when visually the burning stopped. All collected samples were sealed properly and wrapped in pre-cleaned aluminum foil and stored frozen at -25°C for a maximum period of one week before analysis.

2.2 Analytical equipment and procedure

The analytical method was developed on the basis of the US EPA method TO-13(12). A High Performance Liquid Chromatography, 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 PAHs analysis (VYDAC 201, TP5 C-18 RP, 0.46x25cm) was used for the separation according to the following conditions at isothermic 30°C and flow rate of 0.8mL/min:

Mobile phase	Solvent composition	Time (minutes)
	50% Acetonitrile/50% Water	0-10
	90% Acetonitrile/10% Water	10-20
	50% Acetonitrile/50% Water	10-55
	50% Acetonitrile/50% Water	60

The equipment was optimised for a mixture of 18 PAHS, including 16 US EPA priority PAHs, coronene and B*e*P. The selected wavelength program of the fluorescence detector is shown in Table 1. An UV detector (HP 1050), working $\lambda =$ 254 nm, was used in parallel to detect fluorescene less sensitive compounds. Due to the lack of fluorescence, acenaphtylene, for example, can be detected only by the UV detector.

Table 2 Excitation and emission wavelength

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

2.3 Sample extraction and clean-up

Samples were extracted by ultrasonification and concentrated by a rotavapor. Sample preparation steps are presented in Figure 1. PAHs in the particulate matter phase and gas-phase were analysed separately to yield two separate sets of data. The used analytical protocol was proved reliable when evaluated with the urban dust Standard Reference Materials, SRM 1649, received as a gift from the National Institute of Standard and Technology, USA (Reutergardh[10]).

3 Results and discussion

All the 18 selected PAHs were detected in the wood fuel smoke (Table 3) including the carcinogens (B*a*A, chrysene, B*h*F, B*k*F, B*a*P, D*ah*A and I*cd*P) and co-carcinogens (fluoranthene, pyrene, B*e*P and B*ghi*P) while only 14 compounds were detected in the smoke from the charcoal and the coal briquette burning, respectively. As anticipated the most volatile PAHs, i.e, those with lower ring numbers (from naphthalene to fluorene) were detected predominantly in the gaseous phase. On contrary, the less volatile heavier PAHs with four or more rings were mostly found adsorbed on particulate matters (Table 3). The emission factor (mass of a pollutant emitted per unit of mass of fuel, on moisture and ash free basis) of individual PAHs, in both gas and particulate matter phase, was the lowest for charcoal. The emission factor of some compounds, such as naphthalene, acenaphthylene, pyrene, benzo(b)fluoranthene and benzo(k)fluoranthene from the coal briquette was higher than from the wood fuel. However, the last four compounds presented in Table 3 with higher ring numbers were not detected in the coal briquettes smoke.

Smith[4] reported emission of 16 PAHs (similar to the PAHs monitored in this study excluding BeP and coronene) and methyl-, phenyl-napththalenes in a range of 47-250 mg/kg for different wood stoves, which were shown to vary with combustion conditions. The total 18 PAHs for wood fuel burning in this study (126 mg/kg) is within the range. However, the compounds monitored in the two studies are not strictly the same, which may weaken the comparison. The obtained emission factors for the wood fuel are in general less than the US EPA data (US EPA[11]) for catalytic, non-catalytic (improved) and conventional residential wood stoves/space heaters. For example, BaP, one of the most well-established carcinogenic PAHs, has emission factor of 2-3 mg/kg from the US EPA data as compared to 0.78 mg/kg in this study. The obtained BaP value, however, falls in the lower range of emission from wood fuel burning in domestic stoves, 0.7 mg/kg to 6.5 mg/kg (Smith[4]). The obtained BaP emission factor for charcoal, 0.19 mg/kg, which was higher than the value presented by Smith[4] of 0.3 µg/kg. For coal briquettes the average emission factor of B*a*P is 0.52 mg/kg.

Association of some PAHs (BaP, pyrene, anthracene) with soot particles retards PAHs photodegradation and during the atmospheric residence of several days to several weeks (Nicolaou[1]) PAHs can undergo long transport with the particles and become widespread in the environment. The large amount of PAHs found on PM (6.4 mg/kg) and the high PM emission from wood fuel burning (57 mg/kg, Table 2) are, thus, of concern not only because of the immediate indoor exposure but also the outdoor exposure. The ratio between B*a*P associated with PM and PM, for example, was highest for wood fuel burning, 10.5 mg/g, lower for coal briquettes, 0.2 mg/kg, and was not detected in charcoal. The ratio obtained for wood fuel is higher than values quoted by Smith[4], for biofuel smoke, 0.18-0.52 mg/g and for wood fuel burning in residential stoves, 0.5 mg/g.

PM emission from tropical wood burnt in small open stoves reported by Smith[4], 6.4-8.9 g/kg, is more than 100 times higher than the obtained PM emission factor. The high sampling port location (around 4 m) used in our experiment, preventing large settleable PM from being collected, should be the primary reason for the lower PM data. However, as PAHs are mainly attached on submicron size particles (Kiss[12]) the total PAHs and B*a*P, in particular, on PM would not be significantly affected by this factor. Low PM data lead to the mentioned high B*a*P/PM ratio in this study.

The high rate of wood fuel burning (1.8 kg/h) resulted in the high emission rate of 18 PAHs, 244 mg/h, as compared with that of coal briquette burning (Table 2). Concentration of 18 PAHs and genotoxic PAHs in the flue gases are ranking in the same order, highest for wood burning (1130 and 104 µg/m^3) followed by coal briquette (140 and 9.7 µg/m^3) and the lowest for charcoal burning (50 and 4.5 µg/m^3). Figure 2 presents the concentration of individual PAHs in the smoke from the three fuel-stove systems.

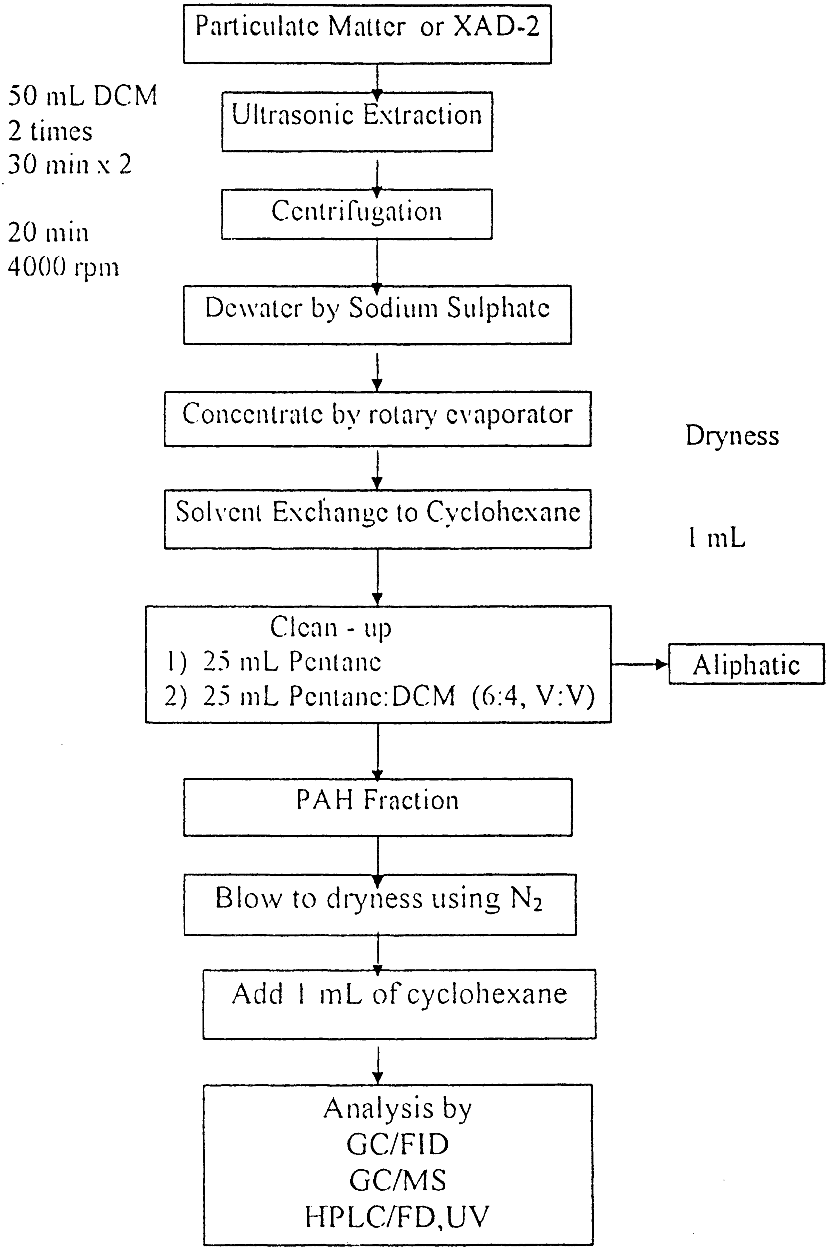

Figure 1: Sample Preparation Procedures.

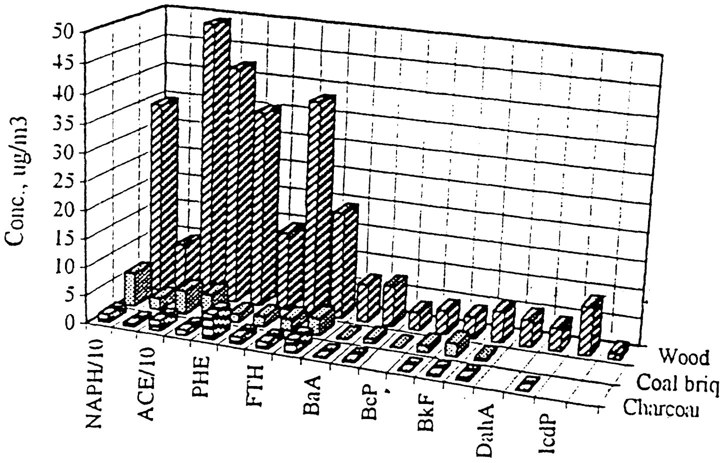

Figure 2 Concentration of PAHs in smoke from wood, coal briquettes and charcoal burning (order of PAHs is followed Table 2; NAPH, ACY and ACE are presented with 10 times reduction).

The free ventilation used in the experiment resulted in dilution of the flue gas with the surrounding air. A rough assessment of the exposure to the toxic compounds was made assuming that the diluted sampled smokes have approximately the same pollutant concentration as the air accumulated in the kitchens that are not equipped with a flue pipe. Supposing the daily cooking fuel consumption of a household of 2-3 is 3 kg of wood (approximately 50 MJ) or 1.4 kg of coal briquettes (2 pieces) or 1.5 kg of charcoal the total genotoxic PAHs emitted from cooking would be 45 mg, or 17.8 mg or 3.9 mg, respectively. With approximate cooking time of 1.5 hours for the wood fuel, 3 hours for the coal briquettes and 2 hours for the charcoal the exposure level to genotoxic PAHs would be 156 μg.h/m3 (1.5 h x 104 μg/m^3), 29 μg.h/m^3 and 9 μg.h/m^3, respectively. The exposure to B*a*P alone during the cooking period for wood fuel, coal briquettes and charcoal combustion is 8100, 1320 and 680 ng.h/m^3 respectively. If the China occupational proposed standard of 150 ng/m^3 (Smith[4]) is used, the exposure during a working day (8 hours) would be 1200 ng.h/m^3 which is much less than the exposure due to cooking with wood fuel and lower than exposure due to coal briquettes.

4 Conclusions

Among the three tested fuel-stove systems the charcoal burning produced the least PAHs. Though wood fuel produced less emission factor of 18 PAHs than coal briquettes its PAHs emission rate and concentration in the smoke were the highest, which are alarming. 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 PAHs indoors, but result in increased ambient air levels. Improvement of domestic cookstoves, which

Emission factor of individual PAHs, mg/kg fuel																	E. factor, mg/kg		E. rate, mg/h	
ACY	ACE	FLU	PHE	ANT	FTH	PYR	BaA	CHRY	BeP	BbF	BkF	BaP	DahA	BghiP	IcdP	COR	Total*	Gen.*	Total*	Gen.*
12	60	5.4	5	2.02	4.5	2.2	0.46	0.39	0.06	0.21	0.34	0.18	nd	nd	0.56	nq	120	8.9	234	13.3
nd	nd	nq	0.026	0.04	1.05	0.57	0.46	0.6	0.39	0.39	0.15	0.6	0.68	0.56	0.7	0.16	6.4	6.1	10	9.8
12	60	5.4	5	2.1	5.5	2.7	0.92	0.99	0.45	0.6	0.5	0.78	0.68	0.56	1.3	0.16	126	15	244	23
26	54	5.4	1.8	2.3	2.6	3.8	0.27	1.1	nq	1.5	2.9	0.52	nd	nd	nd	nd	180	12.7	27	1.9
nd	nq	nq	0.001	5.E-04	0.01	0.01	0.003	nd	0.01	nq	nq	0.002	nd	nd	nd	nd	0.03	0.04	0.01	0.01
26	54	5.4	1.8	2.3	2.6	3.08	0.27	1.1	0.01	1.5	2.9	0.52	nd	nd	nd	nd	180	12.7	27	1.9
2.9	10.4	0.53	2.6	0.67	0.62	1.35	0.09	0.11	nd	nd	0.17	0.19	nd	nd	nd	nd	27	2.5	10.6	0.94
nd	0.01	3.E-04	0.005	2.E-04	0.03	0.02	0.004	0.001	nd	0.03	5.E-04	nd	nd	0.002	nd	nd	0.01	0.08	0.05	0.04
2.9	10.4	0.53	2.6	0.67	0.65	1.4	0.09	0.11	nd	0.03	0.18	0.19	nd	0.002	nd	nd	27	2.6	11	0.98

n detectable quantity and detector in parentheses

ACY: Acenaphthylene (UV-0.35 ng)
ACE: Acenaphthene (UV-0.22 ng)
FTH: Fluoranthene (FLD-0.015 ng)
PHE: Phenanthrene (FLD-0.013 ng)
ANT: Anthracene(FLD-0.008 ng)
BeP: Benzo[e]pyrene (UV-0.066 ng)
BaA: Benzo[a]anthracene (FLD-0.014 ng)
CHRY: Chrysene (FLD-0.019 ng)
COR: Coronene (FLD-0.72 ng)
BkF: Benzo[k]fluoranthene (FLD-0.012 ng)
BaP: Benzo[a]pyrene (FLD-0.02 ng)
)
BghiP: Benzo[g,h,i]perylene (FLD-0.062 ng)
IcdP: Indeno[1,2,3-c,d]pyrene (UV-0.15 ng)
nd: not detected
nq: not quantified
actor

eported for the mass of fuel on the moisture and ash free basis.

Table 3 Emission factors (mg/kg fuel) of individual PAHs from domestic combustion of charcoal, coal briquettes and wood.

provide more complete or cleaner burning of the fuels, is essential to reduce the total pollutant load into the environment.

Acknowledgement

This study was financed by the Swedish Agency for Research Cooperation with Developing Countries of the Swedish Development Cooperation Agency (SAREC/Sida) through the Asian Regional Research Program on Energy, Environment and Climate of the Asian Institute of Technology.

References

(1) Nikolaou, K., Maselet, P. and Mouvier, G. *The science of the total environment*, 1984, **32**, 103-132.

(2) Swartz, R.C., Schults, D.W., Ozretich, R.J., Lamberson, J.O., Cole, F.A., DeWitt, T.H., Redmond, M.S., and Ferraro, S. *Environmental toxicology and chemistry*, 1995, **14**, 1977-1987.

(3) McCrillis, R.C., Watts, R.R. and Warren, S.H. *J. air and wastes*, 1992, **42**, 691-694.

(4) Smith, K.R. *Biofuels, air pollution and health – a global review*, Plenum Press, New York and London, 1987.

(5) US EPA, Deposition of air pollutants to the Great Lakes, First report to Congress, EPA453/R93-055, 1994.

(6) United Nation Environmental Program, *Urban air pollution*, UNEP/GEMS Environment Library No. 4, 1991.

(7) Mumford, J.L., Chapman, R.S., Harris, D.B., He, X.Z., Cao, S.R., Xian, Y.L. and Li, X.M. *Environm. Internat.*, 1989, **15**, 315-320.

(8) Chang, J.C., Wise, S.A., Cao, S.R. and Mumford, J.L. *Environm. Sci. Technol.*, 1992, **26**, 999-1004.

(9) EPA Modified Method 5 (Method 0010) Sampling Train, Revision 0, US EPA, September 1986.

(10) Reutergårdh, L.-B., Kim Oanh, Dung, N.T., Zhang, Y.-H., Yao, W.-X., Ho, P.N., Viet, P.H., Huy, D.Q. and co-workers (1998), Results of inter-laboratory calibration using SRM-1649, Manuscript.

(11) http://www.epa.gov/ttn/chief/ap42etc.html#LE, Locating and estimating (L&E) documents, Draft L&E documents, Polycylic aromatic hydrocarbons, February 1996.

(12) Kiss, G., Zita, V.-P., Hlaway, J. and Harris, J. *Quarterly J. of Hungarian Meteorological Service,* 1996, **100**, 135-142.