Assessing the magnitude of PM$_{2.5}$ polycyclic aromatic hydrocarbon emissions from residential solid fuel combustion and associated health hazards in South Asia

Madhuri Verma [a],[**], Shamsh Pervez [a],[*], Judith C. Chow [b],[c],[***], Dipanjali Majumdar [d], John G. Watson [b],[c], Yasmeen Fatima Pervez [e], Manas Kanti Deb [a], Kamlesh Shrivas [a], Vikas Kumar Jain [f], Noor A. Khan [g], Papiya Mandal [g], Rajan K. Chakrabarty [h],[****]

[a] School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, 492 010, Chhattisgarh, India
[b] Division of Atmospheric Sciences, Desert Research Institute, Reno, NV, 89512, USA
[c] Institute of Earth and Environment, Chinese Academy of Science, Xian, China
[d] CSIR-National Environmental Engineering Research Institute, Kolkata Zonal Centre, Kolkata, 700107, West Bengal, India
[e] Department of Chemistry, Government Eklavya College, Dondi-Lohara, Balod, CG, India
[f] Department of Chemistry, Government Engineering College, Raipur, CG, 492 015, India
[g] NEERI, Delhi Zonal Centre, A-93/94, Phase 1, Naraina Industrial Area, New Delhi, 110028, India
[h] Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, MO, 63130, USA

ARTICLE INFO

ABSTRACT

In South Asia, combustion of solid fuel for residential heating and cooking is a major emission source of particulate-phase polycyclic aromatic hydrocarbons (p-PAHs), a potent carcinogen for human health. The emission factors (EFs) and source diagnostic ratios of PAHs currently used in regional inventory models have been estimated from controlled laboratory tests, which do not accurately reflect real-world combustion scenarios observed in rural Indian households. Consequently, the health effects associated with p-PAH levels in indoor and ambient air could be severely underestimated and undervalued. We performed a nationwide study across ten different states in the Indian subcontinent to evaluate the EFs and source diagnostic ratios of sixteen U.S. Environmental Protection Agency (EPA) identified high priority p-PAHs emitted from residential solid biomass combustion. Our estimated average annual EFs were 2.4–18.3 fold higher than those reported from previous laboratory-based investigations. Carcinogenic toxicity analysis shows that combustion of dung cake and coal ball, both widely used residential solid fuels, posed the most risk (80% and 59% respectively) in comparison to other PAHs owing to predominant emission of benzo[a]pyrene. Our findings underscore the importance of improved laboratory testing and field validations as crucial steps toward more accurate emission inventories and better assessment of public health impacts.

1. Introduction

A large portion of the population in developing countries depends on unprocessed solid fuels (coal balls, fuel wood, dung cake, and crop residues), with unvented stoves, for household cooking and heating. Emissions of fine particulate matter (<PM$_{2.5}$), trace gases, and polycyclic aromatic hydrocarbons (PAHs) contribute to local and region pollution and adverse health effects (Bond et al., 2004; ; Zhang and Tao, 2009).

PAHs are a class of organic compounds that originate from both petrogenic (e.g. vehicle exhausts, incinerators and power generation plants) and pyrogenic (incomplete combustion of fossil fuel and

Table 1

State wise average Emission Factor and standard deviation of 16 PAH (mg.kg^{-1}) separated by five fuel types; coal balls (CB), fuel wood (FW), dung cakes (DC), crop residues (CR), mixed fuels: dung cakes + fuel wood (MF) during real-world household cooking practices in eleven (11) locations across the ten different States of India.

Fuel type	Sampling locations	PAHs (mg.kg^{-1})																
		Naph	Ace	Anth	Flu	Phe	B[a]A	Flt	Pyr	Chry	B[a]P	D[ah]A	B[b]F	B[k]F	B[ghi]P	I(cd)P	I(cd)F	Σp-PAHs
CB	SLH(CG)	39.0 ± 16.1	7.1 ± 5.0	8.1 ± 5.2	5.9 ± 5.6	10.3 ± 5.7	12.1 ± 11.2	15.3 ± 10.2	4.5 ± 2.9	7.2 ± 3.9	26.02 ± 15.22	10.7 ± 4.7	32.4 ± 25.7	12.0 ± 5.8	9.7 ± 6.8	9.5 ± 6.4	8.4 ± 6.2	218.3 ± 100.4
	JRI(JH)	23.4 ± 6.4	5.9 ± 3.3	12.1 ± 7.1	6.6 ± 2.1	23.3 ± 14.3	20.0 ± 7.2	16.5 ± 9.9	8.6 ± 5.2	11.6 ± 7.4	47.72 ± 23.36	16.6 ± 13.2	49.4 ± 19.9	26.9 ± 10.9	12.4 ± 6.6	22.4 ± 7.7	8.7 ± 4.2	312.1 ± 105.6
	Avg.	28.9 ± 14.0	5.2 ± 3.9	8.1 ± 6.1	5.2 ± 3.9	12.8 ± 12.3	11.9 ± 9.7	13.6 ± 9.3	5.2 ± 4.5	8.1 ± 5.9	31.8 ± 21.6	11.5 ± 9.7	35.1 ± 23.1	16.5 ± 11.3	9.4 ± 6.4	12.9 ± 9.5	6.9 ± 4.9	231.5 ± 114.7
FW	PNBE(BR)	22.1 ± 9.5	9.3 ± 6.2	23.2 ± 6.9	ND	14.0 ± 5.4	ND	22.9 ± 8.1	11.0 ± 8.4	ND	ND	5.6 ± 4.2	ND	ND	4.2 ± 1.6	2.6 ± 1.2	2.9 ± 1.5	134.2 ± 28.1
	JP(RJ)	18.7 ± 7.7	11.4 ± 7.3	18.5 ± 15.9	ND	21.4 ± 17.6	ND	48.9 ± 38.5	15.6 ± 9.3	ND	ND	7.5 ± 3.9	ND	ND	11.0 ± 4.8	7.5 ± 5.3	5.2 ± 2.7	171.7 ± 88.7
	CNB(UP)	36.9 ± 35.9	14.8 ± 5.3	23.1 ± 19.1	ND	16.3 ± 15.3	ND	19.5 ± 8.0	18.9 ± 9.2	ND	ND	12.9 ± 10.5	ND	ND	19.9 ± 15.4	7.9 ± 4.3	4.8 ± 1.2	198.4 ± 113.2
	HYB(TG)	25.7 ± 16.4	9.77 ± 7.5	17.1 ± 10.3	ND	10.4 ± 7.0	ND	35.8 ± 14.8	13.4 ± 9.3	ND	ND	5.8 ± 5.1	ND	ND	15.5 ± 11.2	9.9 ± 7.8	4.6 ± 4.1	159.1 ± 79.7
	FZP(PB)	20.4 ± 13.2	7.4 ± 5.4	9.6 ± 6.8	ND	20.9 ± 15.2	ND	19.2 ± 14.6	10.3 ± 8.5	ND	ND	8.9 ± 4.1	ND	ND	12.018.5	6.4 ± 4.3	5.7 ± 2.8	129.1 ± 73.1
	RE(HR)	41.4 ± 23.9	4.1 ± 5.9	6.6 ± 5.5	ND	12.2 ± 6.1	ND	14.6 ± 9.9	10.2 ± 8.1	ND	ND	5.0 ± 3.9	ND	ND	10.4 ± 7.2	4.2 ± 3.4	4.1 ± 3.3	146.0 ± 90.6
	BBS(OR)	50.8 ± 22.3	10.9 ± 7.6	20.8 ± 15.2	ND	24.7 ± 19.5	ND	20.9 ± 15.8	7.3 ± 3.9	ND	ND	7.1 ± 2.6	ND	ND	18.1 ± 6.8	5.5 ± 1.0	6.1 ± 3.9	211.5 ± 106.5
	R(CG)	26.4 ± 10.4	8.6 ± 4.4	11.4 ± 6.4	ND	16.8 ± 10.8	ND	23.3 ± 8.7	4.1 ± 1.6	ND	ND	6.2 ± 4.6	ND	ND	9.9 ± 3.8	4.7 ± 0.8	2.2 ± 1.4	133.1 ± 36.9
	Avg.	24.5 ± 20.4	6.9 ± 6.3	12.1 ± 12.1	ND	13.1 ± 12.5	ND	19.2 ± 18.8	8.6 ± 8.1	ND	ND	5.8 ± 5.3	ND	ND	10.2 ± 8.9	4.8 ± 4.3	3.5 ± 2.8	108.7 ± 99.5
DC	PNBE(BR)	13.3 ± 9.7	ND	14.7 ± 8.3	ND	1.6 ± 1.3	ND	5.2 ± 5.1	1.6 ± 1.5	ND	52.2 ± 16.1	7.4 ± 3.7	62.6 ± 42.4	3.4 ± 1.6	9.8 ± 3.4	15.2 ± 7.9	10.0 ± 7.5	184.9 ± 70.3
	JP(RJ)	30.3 ± 19.1	ND	18.7 ± 7.9	ND	2.2 ± 0.8	ND	9.7 ± 8.9	0.9 ± 0.5	ND	98.9 ± 50.7	11.9 ± 7.7	64.4 ± 33.6	3.9 ± 1.7	12.7 ± 6.6	30.9 ± 25.6	6.2 ± 2.6	284.1 ± 125.7
	CNB(UP)	18.9 ± 15.3	ND	13.0 ± 7.7	ND	1.8 ± 0.9	ND	5.7 ± 1.6	1.3 ± 1.1	ND	66.3 ± 41.7	13.5 ± 2.1	32.7 ± 21.1	2.1 ± 1.2	6.4 ± 2.7	15.6 ± 2.1	5.6 ± 3.3	180.6 ± 81.7
	HYB(TG)	16.4 ± 9.7	ND	14.1 ± 11.9	ND	1.9 ± 0.9	ND	6.6 ± 3.9	1.6 ± 1.1	ND	81.9 ± 57.5	15.7 ± 9.5	54.9 ± 32.6	2.3 ± 0.3	13.2 ± 8.4	25.0 ± 10.8	15.3 ± 7.3	225.0 ± 107.7
	FZP(PB)	15.7 ± 8.4	ND	25.2 ± 23.3	ND	0.5 ± 0.2	ND	5.6 ± 2.9	1.2 ± 0.5	ND	72.2 ± 38.2	5.5 ± 3.9	22.7 ± 21.0	0.7 ± 0.3	16.9 ± 5.8	19.5 ± 17.4	6.1 ± 5.4	181.9 ± 83.8
	RE(HR)	29.9 ± 22.1	ND	26.9 ± 12.3	ND	2.0 ± 1.5	ND	10.5 ± 7.3	1.2 ± 0.8	ND	111.8 ± 38.2	20.9 ± 12.2	34.3 ± 15.5	1.1 ± 0.6	23.0 ± 20.9	18.4 ± 5.3	11.8 ± 5.4	291.6 ± 121.9
	BBS(OR)	18.8 ± 16.1	ND	22.5 ± 12.5	ND	1.5 ± 0.7	ND	11.6 ± 9.3	1.3 ± 0.5	ND	45.9 ± 27.6	4.9 ± 3.6	21.9 ± 8.3	0.9 ± 0.4	15.1 ± 7.9	16.9 ± 7.7	13.0 ± 8.6	163.1 ± 88.9
	R(CG)	14.8 ± 13.6	ND	11.9 ± 7.2	ND	0.7 ± 0.5	ND	11.8 ± 6.8	1.9 ± 1.4	ND	23.8 ± 9.3	13.4 ± 3.7	30.5 ± 17.1	1.2 ± 0.8	14.4 ± 7.1	19.2 ± 14.8	3.3 ± 0.8	139.1 ± 64.3
	Avg.	15.1 ± 14.6	ND	14.8 ± 12.3	ND	1.2 ± 1.0	ND	6.3 ± 6.2	1.1 ± 0.9	ND	**53.5 ± 43.2**	9.2 ± 7.9	31.9 ± 28.4	1.5 ± 1.5	11.7 ± 9.6	16.5 ± 12.9	6.8 ± 6.4	169.6 ± 144.9
CR (rice straw)	VSKP(AP)[a]	50.2 ± 38.1	9.7 ± 3.3	6.6 ± 3.3	ND	8.1 ± 4.7	6.1 ± 2.3	17.9 ± 6.8	5.8 ± 1.5	41.1 ± 13.8	ND	4.1 ± 2.1	25.2 ± 6.8	ND	2.6 ± 1.2	2.3 ± 1.0	4.1 ± 2.1	227.7 ± 113.4
(rice straw)	WR(MH)[a]	31.2 ± 20.1	2.7 ± 1.4	2.3 ± 1.5	ND	3.5 ± 1.7	3.9 ± 3.9	9.5 ± 5.8	3.1 ± 2.0	29.8 ± 8.1	ND	1.9 ± 1.6	12.3 ± 3.6	ND	1.4 ± 0.3	0.8 ± 0.2	2.4 ± 1.0	132.7 ± 65.9
(turr.stik)	BYT(CG)**	37.9 ± 16.5	7.2 ± 3.1	2.8 ± 1.3	ND	7.2 ± 1.6	5.5 ± 1.9	16.1 ± 8.5	4.7 ± 2.8	44.8 ± 20.5	ND	2.4 ± 1.1	18.7 ± 7.9	ND	2.4 ± 0.7	1.2 ± 0.4	2.8 ± 2.2	187.7 ± 75.9

Table 1 (*continued*)

Fuel type	Sampling locations	PAHs (mg·kg⁻¹)																
		Naph	Ace	Flu	Anth	Phe	B[a]A	Flt	Pyr	Chry	B[a]P	D[ah]A	B[b]F	B[k]F	B[ghi]P	I(cd)P	I(cd)F	Σp-PAHs
	Avg.	33.7 ± 25.5	5.3 ± 3.9	ND	3.1 ± 2.9	5.4 ± 3.4	4.4 ± 2.8	12.7 ± 7.5	3.9 ± 2.3	36.2 ± 15.1	ND	2.4 ± 1.8	17.2 ± 7.9	ND	1.9 ± 0.9	1.2 ± 0.9	2.5 ± 1.8	129.9 ± 76.7
MF	PNBE(BR)	25.4 ± 15.2	5.5 ± 6.1	ND	11.8 ± 11.0	21.0 ± 5.5	ND	10.7 ± 2.6	4.3 ± 3.9	9.4 ± 8.2	12.6 ± 7.5	25.5 ± 14.8	7.7 ± 3.8	4.8 ± 1.6	34.8 ± 19.9	10.7 ± 9.9	7.7 ± 5.5	170.9 ± 98.2
	JP(RJ)	37.7 ± 20.9	12.9 ± 6.1	ND	18.2 ± 6.1	24.1 ± 6.6	ND	9.7 ± 3.2	3.6 ± 2.5	11.6 ± 11.0	18.9 ± 7.6	27.6 ± 11.5	6.5 ± 2.7	9.9 ± 4.0	28.1 ± 14.1	13.7 ± 4.6	11.9 ± 4.3	210.2 ± 62.1
	CNB(UP)	38.9 ± 20.9	11.6 ± 4.2	ND	33.0 ± 12.9	26.3 ± 17.9	ND	19.0 ± 4.5	6.9 ± 2.9	11.9 ± 3.7	19.9 ± 10.5	31.4 ± 7.7	14.1 ± 6.5	7.3 ± 4.6	34.5 ± 12.4	25.8 ± 21.7	15.9 ± 3.2	270.1 ± 89.6
	HYB(TG)	27.7 ± 9.4	22.9 ± 15.4	ND	33.6 ± 21.2	12.2 ± 4.2	ND	11.7 ± 6.3	3.9 ± 1.7	13.2 ± 10.0	22.4 ± 10.8	21.8 ± 4.3	8.2 ± 1.7	3.7 ± 1.9	42.8 ± 26.2	13.2 ± 8.1	17.4 ± 11.4	242.4 ± 95.5
	FZP(PB)	46.2 ± 30.6	28.4 ± 16.1	ND	21.4 ± 14.2	6.1 ± 2.6	ND	16.5 ± 11.1	5.3 ± 4.3	10.8 ± 7.7	12.9 ± 6.9	13.8 ± 6.3	7.2 ± 4.8	1.8 ± 0.4	29.6 ± 12.9	18.1 ± 14.6	11.6 ± 7.9	223.5 ± 116.0
	RE(HR)	35.4 ± 22.5	39.8 ± 9.2	ND	32.1 ± 4.9	14.6 ± 5.9	ND	8.9 ± 1.1	5.7 ± 1.3	9.7 ± 5.4	14.1 ± 1.9	32.9 ± 5.2	8.7 ± 2.2	2.3 ± 0.7	30.9 ± 14.4	16.9 ± 11.5	14.2 ± 6.5	251.7 ± 35.9
	BBS(OR)	49.9 ± 28.9	25.6 ± 9.0	ND	23.1 ± 12.3	10.2 ± 2.3	ND	10.3 ± 8.2	5.0 ± 1.7	9.5 ± 3.2	26.9 ± 12.5	23.9 ± 7.8	9.0 ± 5.6	2.4 ± 0.6	47.58 ± 14.91	11.7 ± 7.6	12.7 ± 8.2	257.6 ± 100.1
	R(CG)	37.7 ± 21.0	9.72 ± 6.2	ND	18.7 ± 12.7	9.4 ± 5.6	ND	8.0 ± 3.9	4.8 ± 2.3	8.1 ± 4.9	21.24 ± 10.08	18.3 ± 8.9	6.8 ± 3.9	2.9 ± 0.9	23.9 ± 13.3	10.9 ± 8.0	10.1 ± 8.3	181.9 ± 98.1
	Avg.	31.8 ± 20.9	14.60 ± 13.9	ND	19.6 ± 13.7	12.9 ± 9.9	ND	10.4 ± 6.4	4.3 ± 2.6	8.7 ± 6.6	16.5 ± 9.3	22.1 ± 9.9	7.5 ± 4.4	3.5 ± 3.4	29.7 ± 16.4	11.9 ± 11.5	10.7 ± 7.1	204.2 ± 145.5

[a] ND –not detected.

biomass) sources (Ramdahl and Beecher, 1982; Agency for Toxic Substances and Disease Registry, ATSDR, 1995; Takasuga et al., 2007; Boström et al., 2002; Keyte et al., 2013; Shafy and Mansour, 2016). Assessment of ambient PAHs contributions from unprocessed solid fuels with traditional emission inventories presents a challenge due to variations in reported PAH emissions, spanning over several orders of magnitude (e.g., 1–370 µg of PAHs per kilogram of wood) (Ramdahl and Beecher, 1982). The hydrophobicity nature of PAHs shows great affinity to environmental matrices like soil, water, and air (Senthilkumar et al., 2008). In the atmosphere, low molecular weight (2–4 aromatic ring) PAHs are partitioned in the gases/vapour phase, whereas high molecular weight (5–6 aromatic ring) PAHs present in particulate phase. The International Agency for Research on Cancer (IARC, 2006) reported that high molecular weight PAHs (e.g. benzo(a)pyrene) show potential carcinogenic effects on human health, resulting DNA damage by the formation of adducts in organs (e.g. liver, kidney, lungs) (Vineis and Husgafvel-Pursiainen, 2005; Xue and Warshawsky, 2005). Past studies on indoor and outdoor PAHs have focused on health implications and quantitative analysis of 16 high priority PAHs by the United States Environmental Protection Agency (USEPA) (Yan et al., 2005; Kakareka et al., 2005; Tiwari et al., 2015; USEPA, 2014).

Atmospheric particulate-bound PAHs in India, mainly emitted from solid fuel combustion, have become a matter of concern in recent years (Chakraborty et al., 2014; Ray et al., 2017). EFs of $PM_{2.5}$, temperature-resolved thermal fractions of carbonaceous matter (organic and elemental carbon, OC and EC) along with ionic and elemental species, known as source markers of selected solid fuels at 10 different states in India can be found in Pervez et al. (2018). The present work is the second part of the study on real-world $PM_{2.5}$ emission characterization of household solid fuel combustion in India, emphasizing the thermal and molecular (PAHs) properties of carbonaceous material at 11 locations in 10 different states of India.

The objectives are to: 1) estimate real-world $PM_{2.5}$ particulate PAHs (*p*-PAHs) EFs from solid fuels combustion and 2) evaluate the toxicity levels of different solid fuels. The EFs of sixteen high-priority PAHs in emitted $PM_{2.5}$ were determined. Diagnostic ratios, toxicity levels and annual emission estimates for the five fuel types were calculated.

2. Methodology

2.1. Field campaign

Household cooking emissions were sampled with minivol $PM_{2.5}$ samplers (Airmetrics, Oregon, USA) at 11 sites across 10 states as shown in Supplemental Fig. S1. Five types of solid fuels were selected to represent common cooking practices of India: coal balls (CB), fuel wood (FW), dung cake (DC), crop residues (CR), mixed fuels (MF, a mixture of coal powder with paddy husk soil (10:2:1 ratios), used in Jharkhand and Chhattisgarh states). Details of the study design, site selection, sampling frequency and duration, transportation and preservation of $PM_{2.5}$ samples, and associated QA/QC have been documented in Pervez et al. (2018). Sampling was conducted twice a day during morning and evening cooking time using five different types of traditional cook stoves for the period of March–June 2017.

2.2. Extraction method

Particulate PAHs were collected on pre-fired (900 °C for 3 h) 47-mm quartz microfiber filters (Whatman QMA) (Chow et al., 1993). One-fourth of the filter was cut into strips and ultrasonically extracted with 50 mL of high-performance liquid chromatography (HPLC) grade dichloromethane (DCM) for 30 min. The extraction procedure was repeated twice to ensure maximum extraction efficiency (Bi et al., 2003; Singh et al., 2013). The extract was evaporated ~5 mL using a rotary evaporator at 30–40 °C prior to a clean-up process. The extract was then loaded on top of the column (10 cm × 1.0 cm id) slurry packed with 5 g
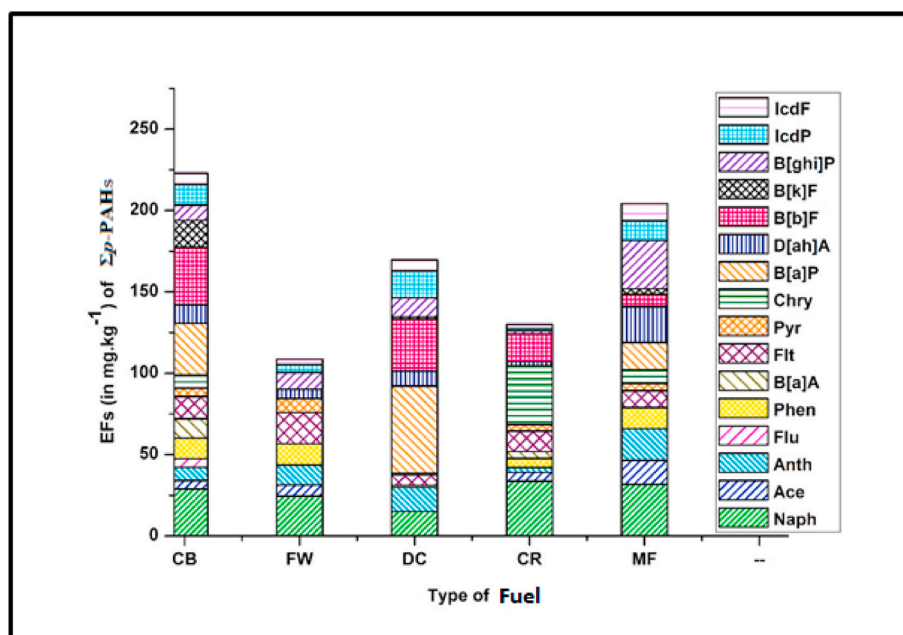
Fig. 1. Averaged Emission Factor (mg.kg^{-1}) of 16 PAHs for burning of coal balls (CB), fuel wood (FW), dung cakes (DC), crop residues (CR), mixed fuels: dung cakes + fuel wood (MF) during real-world household cooking practices in eleven locations across the ten different States of India.

silica gel mesh. The column was eluted with DCM and concentrated to 1 mL under an ultrapure nitrogen gas flow and stored in vials at low temperature (-4 °C) (Singh et al., 2013; Dewangan et al., 2014). The samples were filtered with 0.45 μm polyvinylidene fluoride (PVDF) syringe (Millipore) prior to injection for analysis . Field blank samples were extracted following the same procedure. Recovery of PAHs was determined by spiking blank filter paper with a known concentration standard.

2.3. Gas chromatography –mass spectrometry/mass spectrometry analysis

Particulate PAHs are analysed using an automated GC-MS/MS (GC-Trace 1300; MS- TSQ DUO) equipped with a 30 m long silica capillary column(Thermo Scientific Trace GOLD GC Column, Model TG-5MS) (0.25 mm ID, 5% phenylmethylpolysiloxane stationary phase, 0.25 μm film thickness). Samples were injected (0.1 μl) in split mode (1:10), with the injection port at 290 °C and an initial oven temperature of 150 °C for 2 min. The oven temperature was ramped to 250 °C at 50 °C/min, followed by 10 °C/min ramp rate to 300 °C and held at 300 °C for 7 min. Helium was used as the carrier gas at a 1.0 mL/min flow rate. The total ion chromatograms were analysed qualitatively with the aid of the U.S. National Institute of Science and Technology (NIST) 2.0 mass spectral library after background subtraction. Chromatographic peaks with mass spectral match of 80% or greater were retained, while peaks showing significant abundance but <80% spectral match were noted by their retention times. For quantitative analysis (U.S.EPA 610, 1984), a mixture of 16 PAH standards (1000 μg/L by Supelco, Sigma-Aldrich) was used to identify the relationships between various fuels and air/fuel ratios (Devangen et al. 2014). Sixteen PAHs were identified and quantified including 2 rings: naphthalene (Naph), 3 rings: acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Anth), 4rings: fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chry), 5 rings: benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), 6 rings: benzo[g,h,i]perylene (BghiP), indeno[1,2,3-cd]pyrene (IcdP) and indeno[1,2,3-cd] fluoranthene (IcdF).

2.4. Quality assurance/quality control (QA/QC)

Known concentrations of the standard (EPA 625–16 PAHs mix) were added to 10% of the total samples to determine the recovery ratio. The average recoveries range is 70–80% for total PAHs. Both field and solvent blanks were also analysed to ensure adequate QA/QC. An insignificant amount (<5%) of p-PAHs was found in the field/solvent blanks. The method detection limit (MDL) has been established as three times the standard deviation of concentration of the target species for seven repeat injections of the lowest concentration of the calibration curve.

2.5. Emission factor (EF) and annual emission budget

The method used to calculate PAHs EFs is reported elsewhere (Andreae, and Merlet, 2001; Dhammapala, et al., 2007) and described in Pervez et al. (2018). It is based on the conversion of carbon (C) in the form of carbon dioxide (CO_2) and carbon monoxide (CO), from fuel combustion. The fuel-based EFs can be estimated from in-plume measurements (Moosmuller et al., 2009).

3. Results and discussion

3.1. Emission factors of PAHs

Table 1 summarises state-wise averaged EFs by fuel types for the 16 PAHs. There are some variabilities in fuel quality depending on the regions; type of sampling, stoves, and cooking environment leads to a range of EFs. Among the four most volatilized PAHs (i.e., Naph, Ace, Anth, and Flu) emissions were detected for all five fuel types with the exception of Ace from dung cake (DC) and Flu, from coal balls (CB). Fig. 1 shows that average emissions varied by 1.7 fold among five fuel types. The highest Σp-PAHs was found for coal balls of 244.9 ± 106 mg kg^{-1}, ranging 102–490 mg kg^{-1}, followed by MF 223.4 ± 89 mg kg^{-1}, range 81–448 mg kg^{-1}; DC of 196.1 ± 91.3 mg kg^{-1} (range: 70–384 mg kg^{-1}), CR 137.1 ± 56 mg kg^{-1} (range: 71–305 mg kg^{-1}), and fuel wood (FW) 127.7 ± 62.9 mg kg^{-1} (range: 59–348 mg kg^{-1}). Higher p-PAH EFs for CB might be due to the higher content of unprocessed carbon fraction (Keene, et al., 2006) and the smouldering combustion condition favouring the condensation of PAHs in particulate phase (Jenkins et al.,

Table 2

Comparison of EFs of $\sum$ P-PAHs of 16 USEPA Criteria PAHs, measured for burning of coal balls (CB), fuel wood (FW), dung cakes (DC), crop residues (CR), mixed fuels: dung cakes + fuel woods (MF) with those reported from previous studies. Only reported the EFs of 16 USEPA criteria PAHs for similar types of fuel combustion are included.

Fuel Type	p-PAHs (mg/kg)	study type	References
CB (India)	**239.6 ± 114.7**	**Household combustion –real world**	**present study**
Coal combustion (China)	0.85–214	Residential combustion	Shen et al. (2013)
Coal briquettes and Charcoal	25–100	Domestic combustion	Oanh et al.(1999)
FW	**141.2 ± 84.7**	**Household combustion –real world**	**Present study**
	45.28	test chamber study	Singh et al. (2013)
	43.9 ± 4.3	test chamber study	Gadi et al. (2012)
	24–114	open burning	Keshtkar and Ashbaugh (2007)
Birch Firewood	0.2–16		Hedberg et al. (2002)
	2.3	chamber based study	Venkataraman et al. (2002)
Fireplace/ softwood	79.8		McDonald et al., 2000
Fuelwood (Pine)	6.9		Rogge et al. (1998)
FW	6.4–8.9		Smith, 2000
FW	28	test chamber study	Ramdahl and Beecher (1982)
DC	**181.4 ± 102.9**	**Household combustion –real time**	**present study**
	56.46	test chamber study	Singh et al. (2013)
	59.7 ± 4.4	test chamber study	Gadi et al. (2012)
CR	**163.8 ± 91.1**	**Household combustion –real world**	**present study**
	35.84	test chamber study	Singh et al. (2013)
	35.9 ± 1.9	test chamber study	Gadi et al. (2012)
sugarcane	8.18 ± 3.26	chamber study	Hall et al. (2012)
Wheat straw	62 ± 35	test chamber study	Shen et al. (2013)
	140	test chamber study	Keshtkar and Ashbaugh (2007)
	18.6	open burning	Keshtkar and Ashbaugh (2007)
	240–571	test chamber study	Kakareka and Kukharchyk (2003)
MF	**205.6 ± 90.1**	**Household combustion –real world**	present study

1996). Maximum p-PAHs EFs for each fuel type were found at different location, ranging 266–312 mg kg^{-1} these includes: CB at JRI JH. (312.1 ± 105.6 mg kg^{-1}); for FW at CNB (UP) (174.6 ± 73.1 mg kg^{-1}); for DC at RE (HR) (183.9 ± 53.9 mg kg^{-1}); for CR at VSKP (AP) 83.9 ± 53.9 mg kg^{-1}); and for MF at RE (HR) (266.2 ± 22.4 mg kg^{-1}).

Statistically significant variability with p values < 0.05 at 95% confidence interval was found for all individual PAHs across the fuel types and sampling locations based on two-way ANNOVA (SPSS Ver. 16). Among all fuels Σp-PAHs EFs, FW showed the highest variability (59.9–174.6 mg kg^{-1}) across all the locations.

The coefficient of spatial variations (CV) for Σp-PAH EFs across the 11 locations, (by dividing the standard deviation to the corresponding grand mean of locations averaged EFs) varied from 40 to 49% among the five fuel types: 49.3% (FW), 46.5% (DC), 43.2% (CB), 41.1% (CR) and 39.8% (MF) (Röösli et al., 2001).

Table 2 compares the Σp-PAH EFs with previous studies, Σp-PAHs EF for coal balls (CB) (239.6 ± 114.7 mg kg^{-1}) was higher than those reported for residential coal combustion (0.85–214 mg kg^{-1}) by Shen et al.

(2013) in China, and more than two-fold higher than the coal briquettes and charcoal cook stove combustion (25–100 mg kg^{-1}) by Oanh et al. (1999) in Southeast Asia. When compared with test chamber studies, the average Σp-PAH EFs for dung cake (DC) (181.4 ± 102.9 mg kg^{-1}) was 3.2–3.4 fold higher than 59.7 ± 4.4 mg kg^{-1} in Gadi et al. (2012), and 56.46 mg kg^{-1} in Singh et al. (2013). Similarly, Σp-PAH EF for fuel wood (FW) (141.15 ± 84.72 mg kg^{-1}) were 1.6–66.5 fold higher than test chamber studies 45.28 mg kg^{-1} by Singh et al. (2013); 43.9 ± 4.3 mg kg^{-1} by Gadi et al. (2012); 28.0 mg kg^{-1} by Ramdahl and Beecher (1982) and 2.3 mg kg^{-1} by Venkataraman et al. (2002); and However fuel wood combustion by residential cook stove in India are lower than these of residential furnace (2890 mg kg^{-1}) (Kakareka et al., 2005) and hard wood-burning activity (Khalfi et al., 2000). In case of crop residue (CR), EFs (163.8 ± 91.1 mg kg^{-1}) was similar in magnitude to the test chamber study of 140 mg kg^{-1} by Keshtkar and Ashbaugh (2007), but much higher than 62 ± 35 mg kg^{-1} by Shen et al. (2013); 35.9 ± 1.9 mg kg^{-1} by Gadi et al. (2012), 35.84 mg kg^{-1} by Singh et al. (2013) and open burning; 18.6 mg kg^{-1} by Keshtkar and Ashbaugh (2007); 8.18 ± 3.26 mg kg^{-1} (Hall et al., 2012), EFs for coal balls (CB) showed predominance of high molecular weight PAHs (Hp-PAHs) ranging 8–35 mg kg^{-1} with the two highest PAH EFs found for benzo[b]fluoranthene (B [b]F) of 35.1 ± 23.1 mg kg^{-1} and benzo[a]pyrene (B[a]P) of 31.8 ± 21.6 mg kg^{-1} commonly found in coal combustion other elevated PAH EFs exceeding 10 mg kg^{-1} includes B[k]F (16.5 ± 11.3 mg kg^{-1}); Flt (13.6 ± 9.3 mg kg^{-1}); IcdP(12.9 ± 9.5 mg kg^{-1}); B[a]A (11.9 ± 9.7 mg kg^{-1})and D[ah]A (11.5 ± 9.7 mg kg^{-1}). Elevated B[ghi]P (9.4 ± 6.4 mg kg^{-1}) and, Chry (8.1 ± 5.9 mg kg^{-1}) was also found Average EFs of B[a]P for dung cake (DC) 53.5 ± 43.2 mg kg^{-1} was 5.2 fold higher than the test chamber studies (Singh et al., 2013). For fuel wood (FW) higher EFs were found for Naph (24.46 ± 20.38 mg kg^{-1}); Flt (19.2 ± 18.8 mg kg^{-1}); with elevated Phe (13.1 ± 12.5 mg kg^{-1}) and B[ghi]P (10.2 ± 8.9 mg kg^{-1})., whereas elevated EFs for Naph (33.7 ± 25.5 mg kg^{-1}), B[b]F (17.2 ± 7.9 mg kg^{-1}), Flt (12.7 ± 7.5 mg kg^{-1}) were found in crop residue (CR). Mixed fuel (MF) were dominated by Naph (31.8 ± 20.9 mg kg^{-1}), B[ghi]P (29.7 ± 16.4 mg kg^{-1}), D[ah]A (22.1 ± 9.9 mg kg^{-1}) and Anth (19.6 ± 13.7 mg kg^{-1}) different. These variations might be due to the presence of high moisture content, design of cook stoves and burning phase of fuels (Jenkins et al., 1996).

Mass fraction of 2–6 rings PAH to Σp-PAH is given in Fig. 2. Abundance of EFs low (2–3 rings) and high (4–6 rings) PAHs varied by fuel types with a predominance of the 4–6 ring PAHs for all but fuel wood and crop residue. ΣHp-PAHs (4–6 ring) emissions were highest in coal balls (CB) (171.34 ± 96.17 mg kg^{-1}) whereas ΣLp-PAHs (2–3 ring) were predominant in CR (77.9 ± 53.9 mg kg^{-1}) as shown Table S1. Higher emissions of Hp-PAHs were found from the combustion of coal balls (CB), which might be due to the physical adsorption of PAHs in the particulate phase only (Zou, et al., 2003). Fig. 3 shows the highest Hp-PAHs to total PAHs was 72.7% dung cake followed by 67.2% for coal balls and 63.2% for mixed fuel (MF). Combustion efficiency has been reported to significantly impact emission rates of particulate organics (Gupta et al., 1998; Tissari et al., 2019). Pervez et al. (2018), attributed higher emissions of Hp-PAHs for coal balls, dung cake and mixed fuel with modified combustion efficiency of 0.88–0.99.

3.2. Diagnostic ratio

PAHs source diagnostic ratios and binary diagnostic ratios have been used as a tool to categorize and assess the emission sources. These ratios are useful in understanding PAH origins of different environmental media: air (gas + particle phase), water, sediment, soil, as well as biomonitored organisms such as leaves or coniferous needles, and mussels (Tobiszewski, and Namiesnik, 2012). These ratios distinguish PAHs originating from petroleum products, petroleum combustion, and solid fuel (bio- and fossil fuels) combustions. PAH diagnostic ratios also showed intra-source variability as well as inter-source similarity (Galarneau, 2008). EF ratios of eight groups that are commonly found for
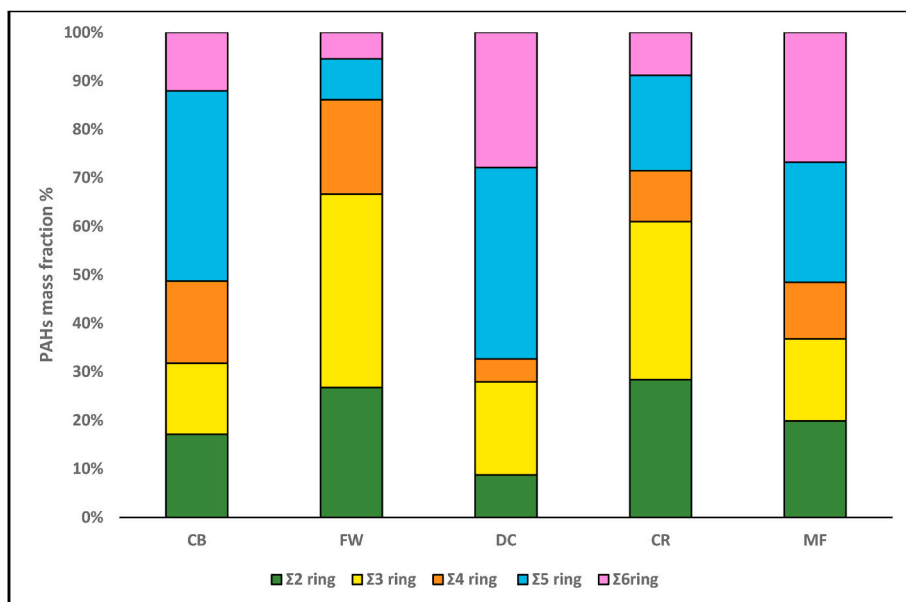
Fig. 2. Average percentage of 2–6 ring PAHs' mass fractions to ΣT*p*-PAHs, as a function of different fuels during real-world household cooking practices in eleven locations across the ten different States of India. 2 rings: naphthalene (Naph), 3 rings: acenaphthene (Ace)+ fluorene (Flu) + phenanthrene (Phe) + anthracene (Anth), 4 rings: fluoranthene (Flt) + pyrene (Pyr) + benz[a]anthracene (BaA) + chrysene (Chry), 5 rings: benzo[b]fluoranthene (BbF) + benzo[k]fluoranthene (BkF) + benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), 6 rings: benzo[g,h,i]perylene (BghiP) + indeno[1,2,3-cd]pyrene (IcdP) + indeno[1,2,3-cd] fluoranthene (IcdF).
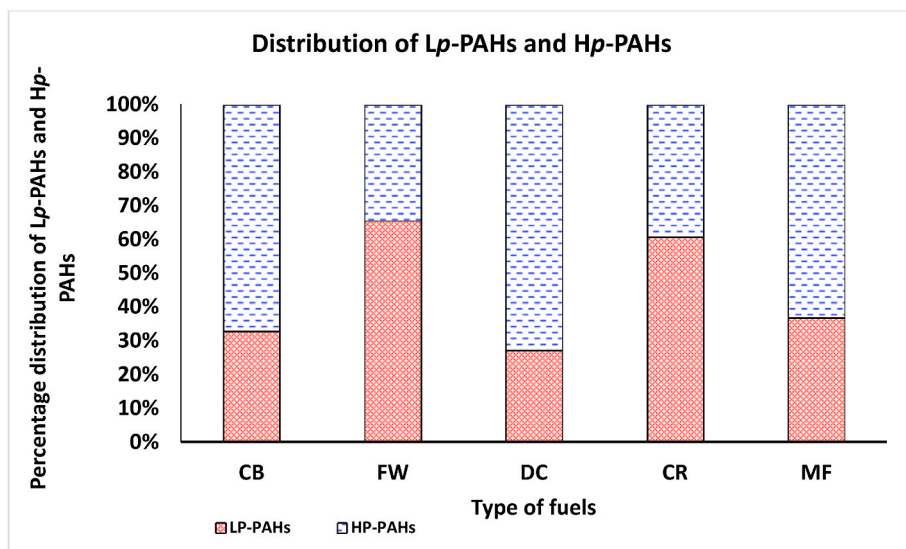
Fig. 3. Averaged Percentage distribution of L*p*-PAHs and H*p*-PAHs in T-PAH EFs for burning of different fuels during real-world household cooking practices in eleven locations across the ten different States of India. L*p*- PAHs (including 2–3 rings PAHs): naphthalene (Naph), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Anth), H*p*-PAHs (including 4–6 rings PAHs): fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (BaA), chrysene(Chry), benzo[b]fluoranthene(BbF),benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP), indeno[1,2,3-cd]pyrene (IcdP) and indeno[1,2,3-cd] fluoranthene (IcdF).

fossil fuel and biomass combustion emissions includes: Anth/(Anth + Phe), Flt/Pyr, Flt/(Flt + Pyr), B[a]P/IcdP, B[a]P/B[ghi]P, I(cd)P/B[ghi]P, I(cd)P/(I(cd)P + B[ghi]P) and B[a]A/(B[a]A + Chry) emissions (Rajput et al., 2011; De La Torre-Roche et al., 2009; Bari et al., 2010; Hays et al., 2005; Jenkins et al., 1996) all compare with past studies for five fuel types in Table 3.

3.2.1. Simple source diagnostic ratio

The ratios of Flt/Pyr, Bap/IcdP, Bap/BghiP, and IcdP/BghiP were used to identify the fossil and biomass fuel burning sources. This study reported 10 fold difference in Flt/Pyr ratios 1.09–9.66 ranging from 1.09 to 3.54 for MF; 1.22–6.19 for FW; 2.78–3.69 for CB; 3.35–9.66 for DC; and 3.12–3.66 for CR. Similarly Bap/BghiP, ratios were ranged between 0.88 and 9.88 with 2.17–3.18 for CB; 2.35–6.19 for DC; 0.88–2.46 (MF), 0.43–9.88 (3.13–4.14 (CB); 1.73–9.88 (DC); 0.43–0.99 (MF)]. Ratios IcdP/BghiP are less variable from 0.32 to 2.68 with 1.00–1.95 (CB); 0.32–0.71 (FW); 1.31–2.68 (DC); 0.52–0.64 (CR); 0.35–1.58 (MF) respectively. Diagnostic ratios of post and present studies are given in Table 3.

3.2.2. Binary diagnostic ratios

The EFs ratios of Anth/(Anth + Phe) of <0.1 and >0.1 are used to infere petrogenic and pyrogenic sources respectively (Pies et al., 2008). This study yield high Anth/(Anth + Phe) EFs ratios of 0.36–0.80 with lower ratios for crop residue 0.36 ± 0.09 and coal balls: 0.36 ± 0.17; 0.43 ± 0.21 for fuel wood; and highest 0.89 ± 0.10 for dung cake;; 0.56 ± 0.18 for mixed fuel suggesting less efficient combustion in the presence of insufficient oxygen. Ratios of Flt/(Flt + Pyr), have been used to indicate for many sources: <0.5 for gasoline engine (Fang et al., 2004); >0.5 for diesel engine) (Rogge et al., 1993; Mandalakis et al., 2004), >0.50 coal combustion (Yunker, et al., 2002), >0.60 wood combustion) (Dvorska, et al., 2011)), and in the range of 0.45–0.53 rice straw burning (Jenkins et al., 1996), and 0.49–0.55 biomass burning (Wiriya, et al., 2016). As expected, ratios of Flt/(Flt + Pyr) in all five fuel types exceeded 0.5 consistent with those found in chamber studies (Hays et al., 2005; Jenkins et al., 1996). However, these ratios are lower for the open burning studies; 0.4–0.5 for fossil fuel combustions, 0.43 ± 0.04 for wood burning and 0.49 ± 0.03 for crop residue burning (Rajput et al., 2011).

Table 3

Averaged values of source diagnostic ratios (mean ± standard deviation) of p-PAHs for emissions resulting from burning of coal balls (CB), fuel wood (FW), dung cakes (DC), crop residues (CR), mixed fuels: dung cakes + fuel woods (MF) during household cooking practices in eleven locations across the 10 different states of India and comparison with those reported for other industrial and domestic combustions.

sources	Study type	Anth/ (Anth + Phe)	Flt/Pyr	Flt/(Flt + Pyr)	B[a]P/I (cd)P	B[a]P/ BghiP	I(cd)P/B [ghi]P	I(cd)P/(I (cd)P + B [ghi]P)	B[a]A/(B[a] A + Chry)	Reference
Coal balls	Real-world household combustion	0.36 ± 0.17	2.63 ± 1.90	0.68 ± 0.17	2.47 ± 1.08	3.40 ± 1.34	1.37 ± 0.60	0.57 ± 0.09	0.56 ± 0.18	Present study
Fossil- & bio-fuels		0.14 ± 0.04	0.90 ± 0.09	0.47 ± 0.03	0.70 ± 0.54	0.74 ± 0.54	1.07 ± 0.23	0.51 ± 0.06	–	Rajput et al. (2011)
Coal combustion		–	–		–	–	–	–	0.2–0.35	Akyüz and Cabuk (2010)
Fossil fuel combustion		–	–	0.4–0.5	–	–	–	–	–	De La Torre-Roche et al. (2009)
Coal combustion		–	–	1.0–1.4	–	–	–	–	–	Lee et al. (1995)
Fuel wood	real world household combustion	0.43 ± 0.21	2.22 ± 1.89	0.65 ± 0.15	–	–	0.48 ± 0.32	0.31 ± 0.11	–	present study
Wood-fuel	Chamber based	0.18 ± 0.03	0.75 ± 0.12	0.43 ± 0.04	–	–	–	–	–	Bari et al. (2010)
Grass, wood combustion		–	–	>0.5	–	–	–	–	–	De La Torre-Roche et al. (2009)
Wood burning		–	–		–	–	–	–	0.79	Dickhut et al. (2000)
Dung cake	real world household combustion	0.89 ± 0.10	5.80 ± 4.56	0.83 ± 0.10	3.25 ± 2.88	4.56 ± 4.44	1.40 ± 1.27	0.55 ± 0.15		Present study
Crop residues	real world household combustion	0.36 ± 0.09	3.22 ± 0.95	0.76 ± 0.05	–	–	0.64 ± 0.30	0.38 ± 0.09	0.11 ± 0.05	Present study
Paddy-residue	Test chamber study	0.17 ± 0.01	0.97 ± 0.21	0.49 ± 0.05	1.63 ± 0.45	2.20 ± 0.20	1.43 ± 0.51	0.58 ± 0.09	–	Hays et al., (2005); Jenkins et al., (1996)
Wheat-residue	Test chamber study	0.21 ± 0.01	1.05 ± 0.08	0.51 ± 0.02	1.22 ± 0.66	1.43 ± 0.37	1.28 ± 0.39	0.55 ± 0.08	–	Hays et al., (2005); Jenkins et al., (1996)
Wheat-residue	Open biomass burning	0.10 ± 0.05	0.97 ± 0.13	0.49 ± 0.03	0.34 ± 0.09	0.27 ± 0.15	0.80 ± 0.27	0.43 ± 0.08	–	Rajput et al. (2011)
Paddy-residue	Open biomass burning	0.15 ± 0.03	0.84 ± 0.04	0.46 ± 0.01	0.64 ± 0.16	0.64 ± 0.21	0.98 ± 0.13	0.49 ± 0.03		Rajput et al. (2011)
MF	real world household combustion	0.56 ± 0.18	2.44 ± 1.55	0.69 ± 0.11	1.37 ± 0.95	0.56 ± 0.27	0.40 ± 0.56	0.27 ± 0.14	–	Present study
Vehicle emission		–	–	–	–	–	–	–	>0.35	Akyüz and Cabuk (2010)
		–	–	–	–	–	–	–	0.53	Dickhut et al. (2000)

Ratios of B[a]A/(B[a]A + Chry) in the range of 0.2–0.35 infer coal combustion (Akyüz and Cabuk, 2010) and higher (0.79) for wood burning (Dickhut et al., 2000). Ratios of B[a]A/Chry found in coal balls (0.56 ± 0.18) and crop residue (0.11 ± 0.05) were ~2-fold higher than those reported Akyüz and Cabuk (2010) for a chamber-based study. These values are helpful in differentiating the emissions of fossil fuels and solid biomass combustion applied in this study. .

Moreover, I(cd)P/(I(cd)P + B[ghi]P) ratio was also used to distinguish the fossil fuel from biomass combustion emissions. This study yield ratio >0.5 for coal balls and dung cake and <0.5 for the other three fuels.

It should be noted that these source diagnostic ratios, determined by the respective PAH's concentrations in the emissions plume does not necessarily represent the same p-PAH sources in air. These ratios change with vapour/particle partitioning of PAH compounds in the atmosphere via dispersion and aging (Zhang, et al., 2005). The Measured diagnostic ratios of Anth/Phe, BaA/Chry, BbF/BkF, and Flt/Pyr in this study showed significant variation compared to those reported for outdoor air (Fang et al., 2004; Bourotte et al., 2005; Ravindra et al., 2008). This indicates that these diagnostic ratios should be used with caution for source identification.

3.3. Toxicity assessment

The PAHs are toxic upon chronic human exposure through inhalation of combustion fumes that lead to health hazards. The toxicity of the solid fuels are assessed based on the individual PAH emission, potential inhalation exposure integrated life time cancer risk (ILCR), and non-cancer hazard potential. Similar methodology has been used in previous studies to assess human health impact from air toxics (Mukherjee et al., 2012, 2014; Srivastava and Som, 2007).

3.3.1. Exposure assessment

The potential inhalation exposure (E_i in mg/kg/day for an individual PAH species 'i') for a person engaged in cooking using solid fuel can be calculated as follows

$$E = C_i \times IR_a \times ED/BW_a \qquad (1)$$

Where C_i is the average concentration of the PAH specie 'i' in combustion plume in mg/m³; IR_a is the inhalation rate for an adult (0.83 m³/h); ED is the exposure duration (2 h/day) and BW_a is average body weight for Indian adult (60 kg) (ICMR, 2010).

3.3.2. ILCR and non-cancer Hazard assessment

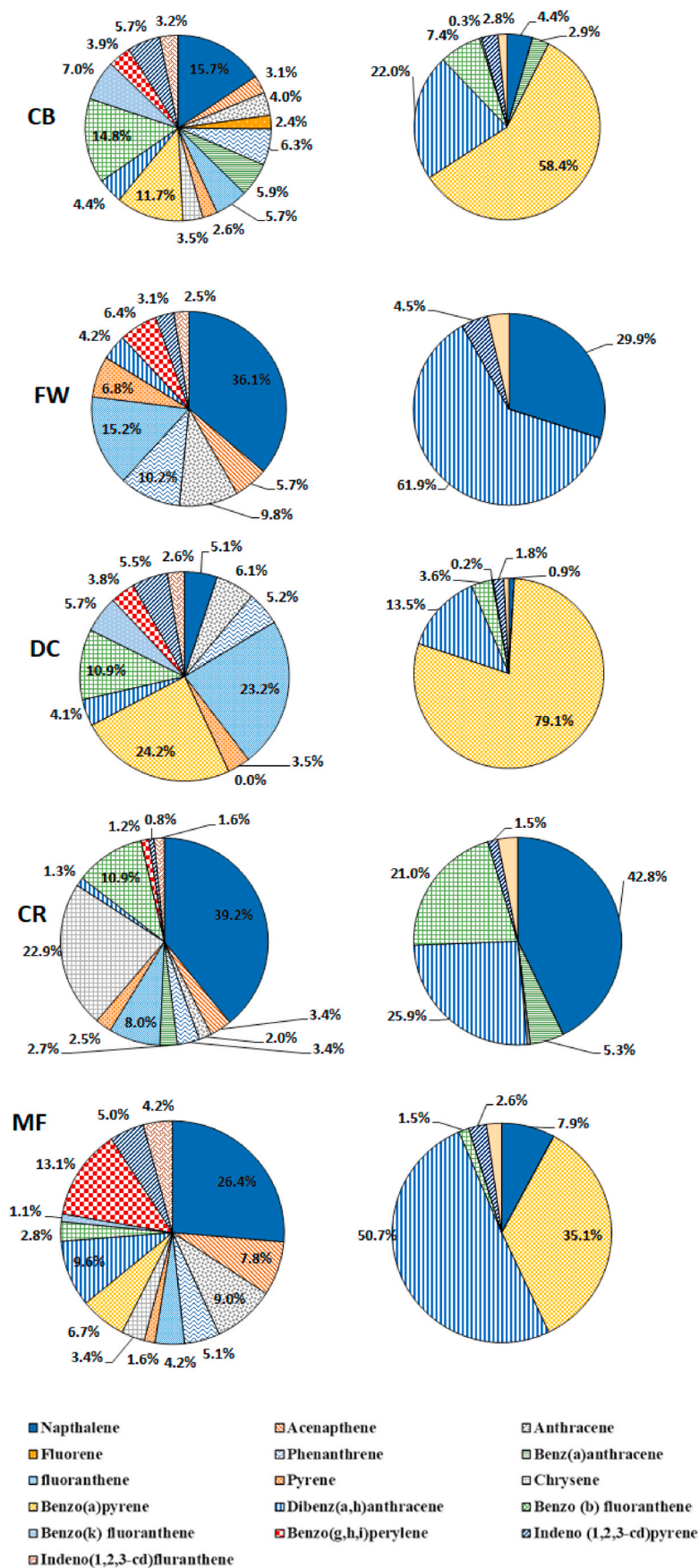The integrated life time cancer risk or ILCR for PAHs species esti-

Fig. 4. Percent contribution of individual PAH to: (a) total *p*-PAH emissions (b) total carcinogenic risk due to combustion of solid fuel.

Table 4
Ranking the fuel as per the toxicity.

Solid fuel	Rank	p-PAH Emission compared to FW	toxicity compared to FW	most toxic p-PAH species
Fuel wood	1	1	1	Dibenzo(a,h) anthracene
Crop residue	2	3	2	Naphthalene
Dung Cake	3	1	5	Benzo (a)pyrene
Mixed fuel	4	19	52	Dibenzo(a,h) anthracene
Coal ball	5	25	76	Benzo (a)pyrene

Toxicity scale:1 - least toxic; 5 - most toxic.

Table 5
Annual emission estimates of p-PAHs from household solid fuel burning emission in India.

PAHs	Fuel type			
(M.yr^{-1})	Coal balls	Fuel wood	Dung cake	Crop residues
Naph	1.5 ± 0.9	2251.2 ± 1954.4	341.2 ± 333.4	552.1 ± 401.1
Ace	3.1 ± 2.2	712.3 ± 640.1		93.1 ± 69.1
Anth	5.2 ± 2.5	1125.0 ± 1100.6	340.5 ± 276.2	51.0 ± 48.1
Flu	2.7 ± 2.3	–		
Phen	6.9 ± 6.5	1216.2 ± 1161.31	30.3 ± 21.5	90.2 ± 64.1
B[a]A	6.8 ± 5.1	–		65.3 ± 49.0
Flt	7.3 ± 4.8	1782.11 ± 1653.0	137.8 ± 135.0	215.3 ± 132.2
Chry	3.3 ± 3.1	802.1 ± 801.0	19.0 ± 15.2	67.3 ± 40.4
Pyr	5.2 ± 3.1	–		627.4 ± 264.7
B[a]P	18.0 ± 12.3	–	1214.7 ± 975.1	
D[ah]A	6.1 ± 5.0	491.1 ± 483.5	218.7 ± 181.0	40.4 ± 31.3
B[b]F	18.5 ± 4.7	–	717.7 ± 640.0	291.1 ± 144.5
B[k]F	8.9 ± 5.7	–	32.7 ± 28.36	1061.1 ± 502.5
B[ghi]P	4.6 ± 4.2	860.1 ± 815.7	265.7 ± 223.1	32.1 ± 20.9
IcdP	6.9 ± 3.3	516.4 ± 491.2	369.7 ± 291.0	20.3 ± 9.2
IcdF	3.9 ± 3.8	300.3 ± 292.7	154.7 ± 145.1	41.1 ± 25.2
[a]Σp-PAHs	0.1 ± 0.01	10.0 ± 5.8	3.8 ± 2.1	3.2 ± 0.2

[a] whereas indicate the value of Σp-PAHs in Gg.yr^{-1}; Mega gram per year abbreviated as M.yr^{-1}.

mated as

$$ILCR_i = C_i \times UR_i \tag{2}$$

where UR_i is the inhalation unit risk of the PAH species 'i'.

The non-cancer health hazard from exposure to HAPs has been estimated as hazard quotient, (HQ),

$$HQ = C_i / RfC_i \tag{3}$$

where RfC_i is the chronic inhalation reference concentration for PAHs species 'i', below which adverse health effects are not likely to occur (RAIS, 2020).

The cumulative non-cancer health hazard from exposure to all estimated PAHs is expressed as the hazard index (HI):

$$HI = \sum_i HQ \tag{4}$$

The chronic inhalation reference concentration and unit risk values for individual compounds have been adapted from the US EPA, The Risk Assessment Information System (RAIS, 2020). The supporting data has been given in Tables S2–S4.

The non-cancer hazard index has been found <1.0 for all cooking fuels, indicating no harmful exposure from solid fuel fumes. However, 7

of the 16 measured PAHs (i.e., B[a]A, Chry, B[a]P, D[ah]A, B[b]F, B[k]F, IcdP) are known as probable/possible carcinogens (Nisbet and LaGoy, 1992; Jia et al., 2011; Ramírez et al., 2011; IARC, 2019). Fig. 4 compares the relative percentage concentrations of individual 16 PAHs to total-PAHs and compares of 8 PAHs to carcinogenic toxicity, for five fuel types. B[a]P was the major contributor to PAHs carcinogenic toxicity risks for dung cake (79%), coal balls (58%), and mixed fuel (35%), Fig. 4 (b), In contrast, it contributed 24%, 12%, and 7% of the total of p-PAHs Fig. 4(a), for the respective fuels. Dibenz(a,h)anthracene was the second largest contributor to PAH carcinogenic risks with 62% for fuel wood and 51% for mixed fuel; corresponding to 4% and 10% PAHs emission from respective fuels. Carcinogenic contribution for naphthalene (Naph) was also high and accounted for 44% in crop residues and 31% in fuel wood, corresponding to 39% and 36% of the total PAHs, from respective fuels. Table 4 shows emissions and toxicity rankings compared to the fuel wood (FW). The cancer risk from p-PAH in fuel wood (1.4×10^{-6}) marginally higher than the acceptable risk of one in a million. The cancer risks for coal balls and mixed fuels were higher than other fuels.

3.4. Annual PAHs emission estimates

The biomass fuel consumption data for Indian states were obtained based on a survey of Indian government agencies (TERI. 2015) as reported by Pervez et al. (2018). Annual emissions were calculated using the method by Dhammpala et al. (2007). Without contribution for mixed fuel combustion, total PAHs emissions from household solid fuel-burning were 17.1 ± 8.1 Gg yr^{-1}, accounting for 0.82% of the total PM$_{2.5}$ emissions (2.00 Tg yr^{-1}) from household solid fuel-burning activity in India. Table 5 showed 10 ± 5.8 Gg yr^{-1} for fuel wood, 3.8 ± 2.1 Gg yr^{-1} (DC), 3.2 ± 0.1 Gg yr^{-1} for crop residue, 0.1 ± 0.1 Gg yr^{-1} for coal balls.

4. Conclusion

The evaluation of emission factors, based on the real-world sampling of domestic cooking emissions for 10 Indian states, shows the highest PAH emissions in coal balls and lowest in fuel wood. All of the five most commonly used solid fuels have shown 4–6 fold higher emissions than those of measured in open burning or laboratory test chamber studies. Large variations were found in cooking characteristics, air supplies, and moisture content in the flaming and smouldering phases of combustion. Naphthalene, fluorene, anthracene, phenanthrene, fluoranthene, dibenzo[ah] anthracene, and benzo [ghi] perylene, were estimated at significant levels in emission plumes. Emission factors of mixed fuel (MF) showed the lowest variability (39.8%) with the highest variability (49.3%), found in fuel wood (FW), attributing to the moisture content. High EF variabilities were also found for dung cake (46.5%), coal balls (43.2%) and crop residues (41.1%). Diagnostic ratios of IcdP/(IcdP + BghiP) > 0.5 were found to be associated to be with coal ball fuel emission, whereas ratios of Flt/(Flt + Pyr) > 0.5 were linked to crop residue burning. Higher carcinogenic risk toxicity order was found for coal ball > mixed fuel > dung cake > crop residue > fuel wood. High variabilities associated with PAHs EFs from household solid fuel combustion activities across the selected regions address the need to assess PAHs emissions from different types of burning activities in real-world situations and on a regional scale to evaluate nation-wide emission estimates.

Credit author statement

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apr.2021.101142.

References

Akyüz, M., Cabuk, H., 2010. Gas–particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey. Sci. Total Environ. 408 (22), 5550–5558.

Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. Glob. Biogeochem. Cycles 15 (4), 955–966.

ATSDR, 1995. Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAHs). United States Department of Health and Human Services, Public Health Service, Atlanta, GA. http://www.atdsr.cdc.gov/toxpro.les/phs69.

Bi, X.H., Sheng, G., Peng, P., Chen, Y., Zhang, Z., Fu, J., et al., 2003. Distribution of particulate- and vapor-phase n-alkanes and polycyclic aromatic hydrocarbons in urban atmosphere of Guangzhou, China. Atmos. Environ. 37, 289–298.

Bond, T.C., Streets, D.G., Yarber, K.F., et al., 2004. A technology-based global inventory of black and organic carbon emission from combustion. J. Geophys. Res. 109, D14203. https://doi.org/10.1029/2003JD003697.

Boström, C.E., Gerde, P., Hanberg, A., Jernström, B., Johansson, C., Kyrklund, T., Rannug, A., Törnqvist, M., Victorin, K., Westerholm, R., 2002. Cancer Risk Assessment, Indicators, and Guidelines for Polycyclic Aromatic Hydrocarbons in the Ambient Air. Environ. Health Perspect. 110, 451–488.

Bourotte, C., Forti, M.C., Taniguchi, S., Caruso, M., Lotufo, P.A., 2005. A wintertime study of PAHs in fine and coarse aerosols in Sao Paulo City, Brazil. Atmos. Environ. 39, 3799–3811.

Bari, M.A., Baumbach, G., Brodbeck, J., Struschka, M., 2010. Characterisation of particulates and carcinogenic polycyclic aromatic hydrocarbons in wintertime wood-fired heating in residential areas. Atmos. Environ. https://doi.org/10.1016/j.atmosenv.2010.11.053.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Fraz1er, C.A., Purcell, R.G., 1993. The dri thermal/optical reflectance carbon analysis System: description, evaluation and applications in U.S. Air quality studies. Atmos. Environ. 27A. 8, 1185–1201.

Chakraborty, D., Mondal, N.K., Datta, J.K., 2014. Indoor pollution from solid biomass fuel and rural health damage: a micro-environmental study in rural area of Burdwan, West Bengal. Int. J. Sustain. Built Environ. 3 (2), 262–271. https://doi.org/10.1016/j.ijsbe.2014.11.002.

De La Torre-Roche, R.J., Lee, W.Y., Campos-Díaz, S.I., 2009. Soil-borne polycyclic aromatic hydrocarbons in El Paso, Texas: analysis of a potential problem in the United States/Mexico border region. J. Hazard. Mater. 163, 946–958.

Dewangan, S., Pervez, S., Chakrabarty, R., Zielinska, B., 2014. Uncharted sources of particle bound polycyclic aromatic hydrocarbons from South Asia: Religious/ritual burning practices. Atmos. Pollut. Res. 5 (0), 283–291.

Dhammapala, R., Claiborn, C., Jimenez, J., Corkil, J., Gullett, B., Simpson, C., Paulsen, M., 2007. Emission factors of PAHs, methoxyphenols, levoglucosan, elemental carbon and organic carbon from simulated wheat and Kentucky bluegrass stubble burns. Atoms. Environ. 41 (12), 2660–2669.

Dickhut, R.M., Canuel, E.M., Gustafson, K.E., Liu, K., Arzayus, K.M., Walker, S.E., Edgecombe, G., Gaylor, M.O., Macdonald, E.H., 2000. Automotive sources of carcinogenic polycyclic aromatic hydrocarbons associated with particulate matter in the Chesapeake Bay Region. Environ. Sci. Technol. 34, 4635–4640.

Dvorska, A, Lammel, G, Klanova, J., 2011. Use of diagnostic ratios for studying source apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central Europe. Atoms. Environ. 45, 420–427.

Fang, G.C., Chang, C.N., Wu, Y.S., Fu, P.P.C., Yang, I.L., Chen, M.H., 2004. Characterization, identification of ambient air and road dust polycyclic aromatic hydrocarbons in central Taiwan, Taichung. Sci. Total Environ. 327, 135–146.

Gadi, R., Singh, D.P., Mandal, T.K., Saud, T., Saxena, M., 2012. Emission estimates of particulate PAH from biomass fuels used in Delhi, India. Human Ecol. Risk Assess. 18 (4), 871–887.

Galarneau, E, 2008. Source specificity and atmospheric processing of airborne PAHs: implications for source apportionment. Atmos. Environ. 42, 8139–8149.

Gupta, S., Saksena, S., Shankar, V.R., et al., 1998. Emission factors and thermal efficiencies of cooking biofuels from five countries. Biomass Bioenergy 14, 547–559.

Hedberg, E., Kristensson, A., Ohlsson, M., Johansson, C., et al., 2002. Chemical and physical characterization of emissions from birch wood combustion in a wood stove. Atmos. Environ. 36, 4823–4837.

Hall, D., Wu, Y.C., Stormer, J., Engling, G., Capeto, K, Wang, J., Brown, S, Li, H.W, Yu, K. M., 2012. PAHs, carbonyls, VOCs and $PM_{2.5}$ emission factors for pre-harvest burning of Florida sugarcane. Atmos. Environ. 55, 164–172.

Hays, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullett, B. K. al, 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. Atmos. Environ. 39, 6747–6764.

International Agency for Research on Cancer, 2006. Polycyclic Aromatic Hydrocarbons, IARC Monogaraph 92, Lyone, France. http://monographs.iarc.fr/ENG/Meetings/92-pahs.pdf.

IARC, 2019. Agents Classified by the IARC Monographs, vols. 1–124. International Agency for Research on Cancer, Lyon. Available at: https://monographs.iarc.fr/listof-classifications.

Jenkins, B.M., Jones, A.D., Turn, S.Q., et al., 1996. Emission factors for polycyclic aromatic hydrocarbons from biomass burning. Environ. Sci. Technol. 30, 2462–2469.

Jia, Y., Stone, D., Wang, W., Schrlau, J., Tao, S., Simonich, S.L.M., 2011. Estimated reduction in cancer risk due to PAH exposures if source measures during the 2008 Beijing olympics were sustained. Environ. Health Perspect. 119, 815–820. https://doi.org/10.1289/ehp.1003100.

Khalfi, A., Trouve, G., Delobel, R., et al., 2000. Correlation of CO and PAH emissions during laboratory-scale incineration of wood waste furnitures. J. Anal Applied Pyrolysis 56, 243–262.

Kakareka, S.V., Kukharchyk, T.I., 2003. PAH emission from the open burning of agricultural debris. Sci. Total Environ. 308, 257–261.

Kakareka, S.V., Kukharchyk, T.I., Khomich, V.S., 2005. Study of PAH emission from solid fuels combustion in residential furnances. Environ. Pollut. 133, 383–387.

Keene, W.C., Lobert, R.M., Crutzen, P.J., Maben, J.R., Scharffe, D.H., Landmann, T., Hely, C., Brain, C., 2006. Emissions of major gaseous and particulate species during experimental burns of southern African biomass. J. Geophys. Res. 111 https://doi.org/10.1029/2005JD006319.

Keshtkar, H., Ashbaugh, L.L., 2007. Size distribution of polycyclic aromatic hydrocarbon particulate emission factors from agricultural burning. Atmos. Environ. 41, 2729–2739.

Keyte, I.J., Roy, M., Harrison, R.M., Lammel, G., 2013. Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons – a review. Chem. Soc. Rev. 42, 9333–9391.

Lee, W.J., Wang, Y.F., Lin, T.C., Chen, Y.Y., Lin, W.C., Ku, C.C., Cheng, J.T., 1995. PAH characteristics in the ambient air of traffic-source. Sci. Total Environ. 159, 185–200.

McDonald, J.D., Zielinska, B., Fujita, E.M., et al., 2000. Fine particle and gaseous emission rates from residential wood combustion. Environ. Sci. Technol. 34, 2080–2091.

Majumdar, D., Ray, S., Chakraborty, S., Rao, P.S., et al., 2014. Emission, speciation, and evaluation of impacts of non-methane volatile organic compounds from open dump site. J. Air Waste Manag. Assoc. 64 (7), 834–845. https://doi.org/10.1080/10962247.2013.873747.

Mandalakis, M., Gustafsson, Ö., Reddy, C.M., Xu, Li, 2004. Radiocarbon Apportionment of Fossil versus Biofuel Combustion Sources of Polycyclic Aromatic Hydrocarbons in the Stockholm Metropolitan Area. Environ. Sci. Technol. 38 (20), 5344–5349.

Moosmuller, H., Chakrabarty, R.K., Arnott, W.P., 2009. Aerosol light absorption and its measurement: a review. J. Quant. Spectrosc. Radiat. Transf. 110 (11), 844–878.

Mukherjee, A.K., Mukhopadhaya, K., Sen, S., 2012. Variability of BTEX in residential indoor air of Kolkata metropolitan city. Indoor Built Environ. 21 (3), 374–380. https://doi.org/10.1177/1420326X11409465.

Nisbet, I.C.T., LaGoy, P.K., 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Regul. Toxicol. Pharmacol. 16, 290–300.

Pies, C., Hoffman, B., Petrowsky, J., Yang, Y., Ternes, T.A., Hofmann, T., 2008. Characterization and source identification of polycyclic aromatic hydrocarbons (PAHs) in river bank soils. Chemosphere 72, 1594–1601.

Oanh, N.T.K., Lars, B.R., Nghiem, T.D., 1999. Emission of polycyclic aromatic hydrocarbons and particulate matter from domestic combustion of selected fuels. Environ. Sci. Technol. 33 (16), 2703–2709.

Pervez, S., Verma, M., Tiwari, S., Chakrabarty, R.K., Watson, J.G., Chow, J.C., Paniker, A. S., Deb, M.K., Siddiqui, M.N., Pervez, Y.F., 2018. Household solid fuel burning emission characterization and activity levels in India. Sci. Total Environ. 654, 493–504.

Rajput, P., Sarin, M.M., Rengarajan, R., Singh, D., 2011. Atmospheric polycyclic aromatic hydrocarbons (PAHs) from post-harvest biomass burning emissions in the Indo-Gangetic Plain: isomer ratios and temporal trends. Atmos. Environ. 45, 6732–6740.

Ramdahl, T., Beecher, G., 1982. Combustion of wood in residential sector in small-air tight wood-stove. Anal. Chim. Acta 144, 83–91.

Rogge, W.F., Hildemann, L.N., Mazurek, M.A., et al., 1998. Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces. Environ. Sci. Technol. 32, 13–22.

Ramírez, N., Cuadras, A., Rovira, E., Marcé, R.M., Borrull, F., 2011. Risk Assessment Related to Atmospheric Polycyclic Aromatic Hydrocarbons in Gas and Particle Phases near Industrial Sites. Environ. Health Perspect. 119, 1110–1116.

Ravindra, K., Sokhi, R., Grieken, R.V., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42, 2895–2921.

ICMR, 2010. Development of an Atlas of Cancer in India, A project of national Cancer Registry Programme. (n.d.). Retrieved from http://www.ncrpindia.org/Cancer_Atlas_India/map.

RAIS, 2020. (The risk assessment information System) chemical toxicity value. USEPA. https://rais.ornl.gov/tools/rais_chemical_risk_guide.html. (Accessed December 2020). Last accessed.

Ray, D., Chatterjee, A., Majumdar, D., Ghosh, S.K., Raha, S., 2017. Polycyclic aromatic hydrocarbons over a tropical urban and a high altitude Himalayan Station in India: temporal variation and source apportionment. Atmos. Res. 197, 331–341. https://doi.org/10.1016/j.atmosres.2017.07.010.

Smith, K.R., 2000. Indoor air pollution implicated in alarming health problems. In: Indoor Air Pollution-Energy and Health for the Poor. Newsletter published by World Bank, Washington, DC, USA, p. 1.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol. 5.Natural gas home appliances. Environ. Sci. Technol. 27 (13), 2736–2744.

Srivastava, A., Som, D., 2007. Hazardous air pollutants in industrial area of Mumbai - India. Chemosphere 69 (3), 458–468. https://doi.org/10.1016/j.chemosphere.2007.04.050. Epub 2007 Jun 4. PMID: 17544479.

Röösli, M., Theis, G., Künzli, N., Staehelin, J., Mathys, P., Oglesby, L., 2001. Temporal 602 and spatial variation of the chemical composition of PM10 at urban and rural sites in the 603 Basel area, Switzerland. Atoms. Environ. 35 (21), 3701–3713.

Senthilkumar, K., Sajwan, K.S., Richardson, J., Kannan, K., 2008. Contamination profiles of heavy metals, organochlorine pesticides, polycyclic aromatic hydrocarbons, and alkylphenols in sediment and oyster collected from marsh/estuarine Savannah GA USA. Mar. Pollut. Bull. 56, 136–149.

Shen, G., Xue, M., Wei, S., Chen, Y., Wang, B., Wang, R., Lv, Y., Shen, H., Li, W., Zhang, Y., Huang, Y., Wei, W., Zhao, Q., Li, B., Wu, H., Tao, S., 2013. The influence of fuel moisture, charge size, burning rate and air ventilation conditions on emissions of PM, OC, EC, parent PAHs, and their derivatives from residential wood combustion. J. Environ. Sci. 25 (9), 1808–1816.

Singh, D.P., Gadi, R., Mandal, T.K., Saud, T., Saxena, M., Sharma, S.K., 2013. Emissions estimates of PAH from biomass fuels used in rural sector of Indo-Gangetic Plains of India. Atmos. Environ. 68, 120–126 (2013).

Shafy, H.I.A., Mansour, M.S.M., 2016. A review on polycyclic aromatic hydrocarbons: source, environmental impact, effect on human health and remediation. Egypt. J. Petrol. 25, 107–123.

Takasuga, T., Umetsu, N., Makino, T., Tsubota, K., Sajwan, K.S., Senthilkumar, K., 2007. Role of temperature and hydrochloric acid on the formation of chlorinated hydrocarbons and polycyclic aromatic hydrocarbons during combustion of paraffin powder, polymers, and newspaper. Arch. Environ. Contam. Toxicol. 53, 8–21.

Tata Energy Research Institute (TERI), 2015. Household energy demand, TERI Energy and Environment Data Diary and Yearbook 2014-15. The Energy and Resources Institute (TERI), New Delhi, India.

Tissari, J., Väätäinen, S., Leskinen, J., Savolahti, M., Lamberg, H., Kortelaine, M., Karvosenoja, N., Sippula, O., 2019. Fine Particle Emissions from Sauna Stoves: Effects of Combustion Appliance and Fuel, and Implications for the Finnish Emission Inventory.

USEPA, 2014. Technical Factsheet on Polycyclic Aromatic Hydrocarbons (PAHs).

Tiwari, M, Sahu, S.K, Pandit, G.G., 2015. Inhalation risk assessment of PAH exposure due to combustion aerosols generated from household fuels. Aeros. Air Qual. Res. 15, 582–590.

Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110–119.

USEPA, 1984. Method 610; Polynuclear Aromatic Hydrocarbons. United States Environmental protection Agency, USA.

Venkataraman, C., Negi, G., Sardar, S.B., et al., 2002. Size distribution of polycyclic aromatic hydrocarbons in aerosol emissions from biofuel combustion. J. Aerosol Sci. 33, 503–518.

Vineis, P., Husgafvel-Pursiainen, K., 2005. Air pollution and cancer: biomarker studies in human populations. Carcinogenesis 26 (11), 1846–1855.

Wiriya, W., Chantara, S., Sillapapiromsuk, S., Lin, N.H., 2016. Emission profiles of PM$_{10}$-bound polycyclic aromatic hydrocarbons from biomass burning determined in chamber for assessment of air pollutants from open burning relationship to air-mass movement. Aero. Air Qual. Res. 16 (11), 2716–2727.

Xue, W, Warshawsky, D, 2005. Metabolic activation of polycyclic and heterocyclic aromatic hydrocarbons and DNA damage: A review. Toxicol. Appl. Pharmacol. 206 (1), 73–93. https://doi.org/10.1016/j.taap.2004.11.006.

Yan, B, Abrajano, TA, Bopp, RF, Chaky, DA, Benedict, L, Chillrud, SN, 2005. Molecular tracers of saturated and polycyclic aromatic hydrocarbon inputs into Central Park Lake, New York City. Environ. Sci. Technol. 39, 7012–7019.

Yunker, M.B. Macdonald, R.W., Vingarzan, R., Mitchel, R.H., Goyette, D., Sylvestre, S, 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Organic Geochemistry 33, 489–515.

Zhang, Y., Tao, S., 2009. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. Atmos. Environ. 43 (4), 812–819.

Zhang, X.L., Tao, S., Liu, W.X., Yang, Y., Zuo, Q., Liu, Z., 2005. Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: A multimedia approach. Environ. Sci. Technol. 39, 9109–9114.

Zou, L.Y., Zhang, W., Atkinson, S., 2003. The characterization of polycyclic aromatic hydrocarbons emissions from burning of different firewood species in Australia. Environ. Pollut. 124, 283–289.

Brumsack, H., Heinrichs, H., Lange, H., 1984. West German coal power plants as sources of potentially toxic emissions. Environ. Technol. Lett. 5, 7–22.

Benner, B.A., Wise, S.A., Currie, L.A., Klouda, G.A., Klinedinst, D.B., Zweidinger, R.B., Stevens, R.K., Lewis, C.W., 1995. Distinguishing the contributions of residential wood combustion and mobile source emissions using relative concentrations of dimethylphenanthrene isomers. Environ. Technol. Lett. 29, 2382–2389.

Bruce, N., Perez-Padilla, R., Albalak, R., 2000. Indoor air pollution in developing countries: a major environmental and public health challenge. Bull. World Health Organis. 78, 1078–1092.

Bhargava, A., Khanna, R.N., Bhargava, S.K., 2004. Exposure risk to carcinogenic PAHs in indoor-air during biomass combustion whilst cooking in rural India. Atmos. Environ. 38, 4761–4767.

Chen, S.C., Liao, C.M., 2006. Health risk assessment on human exposed to environmental polycyclic aromatic hydrocarbons pollution sources. Sci. Total Environ. 366, 112–123.

Dasch, J.M., 1982. Particulate and gaseous emissions from wood burning fireplaces. Environ. Sci. Technol. 16, 639–645.

Ezzati, M., Lopez, A.D., Vander Hoorn, S., et al., 2002. Selected major risk factors and global and regional burden of disease. Lancet 360, 1347–1360.

Gibbs, G.W., 1985. Mortality of aluminium reduction plant workers, 1950 through 1977. J. Occup. Med. Toxicol. 27, 761–770.

He, X., Chen, W., Liu, Z., Chapman, R.S., 1991. An epidemiological study of lung cancer in Xuan Wei County, China: current progress. Case-control study on lung cancer and cooking fuel. Environ. Health Perspect. 94, 9–13.

IARC (International Agency for Research on Cancer), 1987. IARC Monograph of carcinogenic risk to humans, Suppl 7, Overall evaluation of carcinogenicity. An updating of IARC monograph 1 (42), 321–324.

Mastral, A.M., Callen, M.S., 2000. A review on polycyclic aromatic hydrocarbon (PAH) emission from energy generation. Environ. Sci. Technol. 34, 3051–3057.