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Polycyclic Aromatic Hydrocarbons in Fine Particulate Matter Emitted from Burning Kerosene, Liquid Petroleum Gas, and Wood Fuels in Household Cookstoves

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Abstract

This study measures polycyclic aromatic hydrocarbon (PAH) compositions in particulate matter emissions from residential cookstoves. A variety of fuel and cookstove combinations are investigated, including: (i) liquid petroleum gas (LPG), (ii) kerosene in a wick stove, (iii) wood (10 and 30% moisture content on a wet basis) in a forced-draft fan stove, and (iv) wood in a natural-draft rocket cookstove. The wood burning in the natural-draft stove had the highest PAH emissions followed by the wood combustion in the forced-draft stove and kerosene burning. LPG combustion has the highest thermal efficiency (~57%) and the lowest PAH emissions per unit fuel energy, resulting in the lowest PAH emissions per useful energy delivered (in the unit of megajoule delivered, MJ_d). Compared with the wood combustion emissions, LPG burning also emits a lower fraction of higher molecular weight PAHs. In rural regions where LPG and kerosene are unavailable or unaffordable, the forced-draft fan stove is expected to be an alternative because its benzo[*a*]pyrene (B[*a*]P) emission factor (5.17–8.24 μg B[*a*]P/MJ_d) and emission rate (0.522–0.583 μg B[*a*]P/min) are similar to those of kerosene burning (5.36 μg B[*a*]P/MJ_d and 0.452 μg B[*a*]P/min). Relatively large PAH emission variability for LPG suggests a need for additional future tests to identify the major factors influencing these combustion emissions. These future tests should also account for different LPG fuel formulations and stove burner types.

Abstract

Introduction

Approximately 2.8 billion people globally rely on domestic burning of solid fuels for daily cooking and heating. Estimates show that exposure to household air pollution caused ~4.3 million premature deaths in 2012,(1) and particulate matter (PM) from residential sources is responsible for 16–30% of the premature deaths due to ambient air pollution.(2, 3) There are also serious concerns over the climate impacts of cookstove emissions.(4, 5) The opportunities for improving public health and reducing environmental impacts through cleaner cookstoves are recognized globally.(6, 7)

Residential combustion of solid fuels is a major source of organic aerosols (OA). Polycyclic aromatic hydrocarbons (PAHs) in the OA are of specific toxicological interest due to their mutagenicity and carcinogenicity.(8, 9) Estimated global emissions of the 16 U.S. Environmental Protection Agency (EPA) priority PAHs (PAH₁₆) reached ~504 Gg in 2007, of which ~60% was ascribed to residential solid fuel combustion.(10) The contribution is much higher in many developing countries such as China, India, and Indonesia. Even in certain industrialized countries, residential wood combustion is also a major source of PAH emissions. For example, in Chile, Finland, and the U.S., PAH₁₆ values from residential wood combustion are 72, 78, and 46% of the national emission totals, respectively.(10) PAHs can undergo long-range transport—for example, they are observed as persistent in the Arctic(11, 12)—and distribute across a variety of environmental media, including indoor and outdoor air, water, food, etc., causing widespread contamination. PAH exposure routes can

vary. In addition to inhalation, exposure routes also include ingestion and dermal contact. Estimates show that residential biomass and fossil fuel combustion sources contribute approximately 54% to the total incremental lifetime cancer risk (ILCR) induced by PAHs following inhalation exposure; the global average ILCR is estimated at 3.1×10^{-5} .(13) Because PAHs produce serious environmental and public health concerns, their sources merit further attention.

In the interest of achieving air quality, climate, and public health benefits, there is potential in promoting cleaner burning residential cooking and heating stoves and fuels for reducing PAHs, PM, and other pollutant emissions. For example, past laboratory studies have shown that, compared with burning uncompressed biomass fuels, burning biomass pellets significantly reduces PAH emissions.(14) Estimates suggest that replacing uncompressed biomass fuels with pellets would result in a 90% reduction in PAH emissions from residential cookstoves in China.(14) Stove design and technology improvements—e.g., forced-draft and gasification—can also lower pollutant emissions.(15–17) It was estimated that, with improved combustion devices and fuels, a 34% reduction in global PAH emissions from the residential sector could be expected.(10)

Despite the importance of introducing cleaner cookstove and fuel platforms for protecting human health and the environment, studies detailing PAH emissions for these relatively efficient fuel and cookstove combinations are limited. Most studies in the literature have focused on emissions for solid fuels such as coal, wood, charcoal, and crop residues burned in traditional or natural-draft cookstoves(18–29) or simulated open biomass burning.(30–33) For example, LPG stoves are commonly discussed as effective alternatives;(34, 35) however, PAH emission measurements for LPG stoves are scant, leading to a gap in knowledge and uncertainty in understanding potential impacts when planning future intervention possibilities. Similar to many air pollutants, PAH emissions from residential combustion sources depend on a variety of factors such as fuel properties, stove type, and fire management practices.(15, 16, 36–39) The aim of the present study is to quantitatively measure individual PAH emissions from a variety of fuel and cookstove systems. A main objective is to observe and quantify how toxic PAH emissions compare when burning LPG, kerosene, and wood in advanced high-efficiency forced-draft and natural-draft cookstoves. Laboratory tests were conducted to optimize experimental control of some of the aforementioned variables and provide a simple initial assessment of cookstove performance while also evaluating energy efficiency and toxic PAH emissions.

Methods

Chemicals and Standards

PAH standards were prepared and certified as described in Hays et al.(40) Briefly, both internal and calibration standards (see Table S1) were prepared at the University of Wisconsin, Wisconsin State Laboratory of Hygiene. The internal standard contained: acenaphthene-*d*₁₀, chrysene-*d*₁₂, and dibenzo[*a,h*]anthracene-*d*₁₄ dissolved in a benzene/isopropyl alcohol/hexane (63/32/5 v/v) solvent mixture. Accuracy of the PAH calibration standards was independently verified with a commercially available, certified reference PAH calibration mix dissolved in methylene chloride/benzene (1/1 v/v) (Sigma-Aldrich, St.

Louis, MO). Primary standards ($\pm 1\%$ analytical accuracy) of carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), and propane were used as calibration gases (Airgas Specialty Gas, Durham, NC).

Cookstove Test Facility (CTF)

Emissions testing was performed at the U.S. EPA CTF located in Research Triangle Park, NC. The facility is designed for testing cookstove thermal efficiency and pollutant emissions of a wide variety of fuels and stoves with or without chimneys. More detailed information about the CTF can be found elsewhere.(15, 39) Briefly, emissions were measured and collected from a stainless steel hood connected to a two-stage dilution tunnel system. Negative pressure (2–7 hPa below atmospheric pressure) was maintained throughout the entire system. An induced-draft blower provided filtered dilution air and hood air flows. Real-time measurements of CO, CO₂, CH₄, and total hydrocarbon (THC) gases were obtained at the primary dilution tunnel. For low-emission fuel–cookstove combinations (kerosene, LPG, and the forced-draft biomass stoves), filter-based PM sampling occurred at the primary dilution tunnel. For the higher emission natural-draft stove, PM sampling was conducted using the secondary dilution tunnel.

Fuels and Cookstoves

In the present study, the following fuel and stove combinations were tested: (i) LPG fuel (Peru Solgas/Repsol LPG stove), (ii) kerosene fuel in a wick stove (Butterfly Model 2668), (iii) red oak wood (*Quercus rubra*) fuel in a forced-draft fan-type cookstove (EcoChula-XXL), and (iv) the same wood fuel in a natural-draft rocket-type cookstove (JikoPoa). These two stoves were selected as examples of two different wood stove technologies: natural-draft and forced-draft. Oak is one of the commonly used wood fuels in rural settings. It is noted that there are many other stoves with similar burning techniques and other types of wood fuel that may have different emissions.(26, 41) Wood moisture is one very important factor affecting burning and pollutant emissions;(26, 42) thus, oak fuels with two distinct moisture levels (low, ~10%; high, ~30%) were used in tests. The preparation of wood fuels was described in Jetter et al.(15) Briefly, red oak was cut into the desired size (approximately 2 × 2 cm in cross section and 10 cm in length for the forced-draft fan stove and 35 cm in length for the natural-draft rocket stove) and then air-dried until it reached the desired moisture content. The LPG stove was tested using a blend of 60% w/w propane and 40% w/w butane. Grade 1-K kerosene was used in the kerosene-fueled stove. The six fuel–stove combinations were each tested in triplicate.

Water Boiling Test (WBT) Protocol

The WBT protocol (version 4.2.2) was adopted to test cookstove emissions and determine thermal efficiency.(43) The test protocol includes three phases: cold-start (CS) high-power phase, hot-start (HS) high-power phase, and a low-power simmer phase, in that order. The CS high-power phase begins with the pot and water at ambient temperature. Emissions are sampled from fuel ignition until the water boils. The HS immediately follows the CS with the cookstove hot and the pot and water again at ambient temperature. The low-power phase begins with the cookstove hot and the water temperature maintained at 3 °C below the boiling point for 30 min. Following the WBT protocol, cookstove power, energy efficiency,

and fuel use are determined. Filter sampling and online measurements are conducted for each phase of the WBT protocol.

Online Measurements and Filter-Based Sampling

Gaseous CO, CO₂, THC, and CH₄ are measured continuously using infrared and flame ionization detector analyzers (models 200, 300-HFID and 300M-HFID, California Analytical; Orange, CA) and recorded every five seconds.⁽¹⁵⁾ Gas analyzers are calibrated with zero and span checks before and after testing each day. Potential bias due to losses in the sample transfer line is monitored by injecting the calibration gases both at the point of sampling and at the inlet of the gas analyzers. Particles with aerodynamic diameter 2.5 μm (PM_{2.5}) are sampled isokinetically on quartz-fiber (Qf) and polytetrafluoroethylene (PTFE, Tf) membrane filters positioned in parallel downstream of PM_{2.5} cyclones (University Research Glassware; Chapel Hill, NC). A second quartz filter (Qb) is placed downstream of the PTFE filter to estimate the positive artifact due to gas-phase adsorption of semivolatile organics. All quartz filters were analyzed for PAHs. Only filter-based PAHs are considered in the present study. Background concentrations of CO, CO₂, CH₄, and THC were measured with all real-time instruments for at least 10 min before and after each test and were subtracted from measured test concentrations to correct emissions results. PM_{2.5} mass was measured gravimetrically with a microbalance (MC5, Sartorius, Germany). Filters were stored in a freezer at <0 °C prior to PAH analysis.

PAH Analysis and Quality Control

Due to its sensitivity, thermal extraction gas-chromatography–mass spectrometry (TEx-GC–MS) was utilized to identify and quantify the individual PAHs in the sampled cookstove emissions (Gerstel TDSA2/TDS/Agilent 6890/5973 MS system). The TEx-GC–MS equipment and methodology were described extensively elsewhere.⁽⁴⁴⁾ Briefly, a 0.4 cm² Qf punch (or three punches for artifact filters and low-emission samples from LPG) was carefully placed inside a prebaked (550 °C) glass tube and spiked (1 μL) with an internal standard mixture containing deuterated PAH compounds. Following automated tube insertion into the oven unit, the sample was heated to 325 °C at a rate of 50 °C/min and held for 11 min; 50 mL/min of He flowed over the sample. Desorbate was directed to a cryogenically cooled programmable temperature vaporization inlet (−85 °C) operating in splitless mode. The GC inlet was rapidly heated (720 °C/min) to 325 °C. The sample was chromatographed on an ultralow-bleed capillary column (DB-5, 30 m × 0.25 mm I.D. × 0.25 μm film thickness) with helium as the carrier gas (1 mL/min). The GC oven was temperature-programmed as follows: 65 °C for 10 min ramped to 325 °C at a rate of 10 °C/min and held for 15 min. Chromatographed compounds were detected using an Agilent 5973 MS detector operating in selected ion monitoring mode.

The internal standard method and a multilevel, linear ($R^2 > 0.9$) calibration was used (0.1–1 ng) for PAH quantification. A midlevel calibration check was performed daily prior to sample analysis and was used as a continuing calibration in cases where measured and fixed concentrations were not within 20%. These daily checks were within 20% for most targets even when replicated over several months. TEx-GC–MS detection limits for the PAH targets are also provided in Table S1. PAHs below their detection limit were reported as “ND”.

Midlevel check recoveries for PAHs were within $105 \pm 33\%$, on average. The sum of all 25 PAHs is defined as PAH₂₅. Retention time shifts were negligible (<1%) throughout the analysis. Target analyte validation was achieved using the retention times and isotopic fragment ratios exceeding a 3/1 signal/noise ratio. Carryover tests were performed by reheating the TEx sample/apparatus immediately following the initial extraction and then examining the GC–MS chromatogram for the presence of target compounds,(45) which indicated an extraction efficiency of >98%. Naphthalene was the only PAH detected (0.16 ± 0.11 ng) above its method detection limit (0.02 ng) in the blank filters.

Data Analysis

Positive Adsorption Artifact and Correction

For the cookstove sources and sampling conditions used presently, a positive adsorption artifact (the adsorption of gas-phase organic matter on the Qf) has typically dominated the PM sampling error.(46, 47) Individual particle-phase PAH concentrations reported here are corrected for the artifact using the quartz filter behind the PTFE filter method, defined as $Q_f - Q_b$. This method has normally provided an upper limit estimate of adsorbed organics on Qf.(46, 48) Additionally, a parameter (F_a) defined as Q_b/Q_f is used to quantitatively estimate the fraction of positive adsorption artifact for each PAH.

Emission Factors and Efficiency

PAH emission factors are calculated using the TEx–GC–MS-measured concentrations in samples, dilution ratio, sampling flow volumes, and burned fuel mass. For quality control purposes, emissions factors are also calculated using the carbon mass balance method that is typically used for field-based emissions measurement studies.(31, 32, 36, 38, 49) PAH mass emission factors are presented per unit fuel mass ($\mu\text{g/kg}$), fuel energy ($\mu\text{g/MJ}$), useful energy delivered ($\mu\text{g/MJ}_d$), as an emission rate ($\mu\text{g/min}$), and as a specific emission rate ($\mu\text{g/min/L}$) for the low-power simmer phase.(15) Modified combustion efficiency (MCE) defined as the molar ratio of $\text{CO}_2/(\text{CO}_2 + \text{CO})$ is used as a proxy of combustion conditions. Thermal efficiency (TE) is calculated as the ratio of useful energy (energy absorbed from the water heating and evaporation during the test) divided by fuel energy. Statistical analysis is performed using SPSS (Statistical Package for the Social Sciences, IBM Corporation) with $\alpha = 0.05$. Nonparametric tests are used for correlation analysis and difference comparisons.

Results and Discussion

Artifact Correction

Sampling artifacts for organic carbon (OC) and semivolatile organic compounds including PAHs are widely recognized and examined for ambient air samples; however, the specific organic species in cookstove emissions contributing to this artifact are unknown presently. High vapor pressure (VP), low molecular weight (MW) PAHs are present at higher concentrations in the cookstove emissions, are more likely to be gaseous, and thus contribute to the adsorption artifact. TEx–GC–MS analysis of Qb shows higher concentrations of acenaphthylene (152 amu), phenanthrene and anthracene (178 amu), and fluoranthene and pyrene (202 amu), in that order. Although, for certain compounds such as 1-methylchrysene,

perylene, and dibenzo[*a,h*]anthracene ($p > 0.05$), the correlations are not significant, likely due to their low or nondetectable levels on the Qb. For most PAHs, the concentrations measured on Qb and Qf correlate positively ($r = 0.60$ – 0.91 , $p < 0.001$, Table S1).

As expected, higher VP, lower MW PAHs contribute substantially to the artifact, as evidenced by F_a values (Figure 1). The calculated F_a value for naphthalene is less than those of the other semivolatile PAHs despite its high vapor pressure. Possibly, naphthalene adsorbs more readily to PM_{2.5} than quartz material because $Q_f \gg Q_b$ in this case. Perhaps its volatility subjects naphthalene to loss during sample handling and analysis without particles present, introducing a low bias in F_a . Pooled F_a values correlate negatively ($r = -0.631$, $p < 0.05$) with PAH MW (Figure S1) and positively with vapor pressure (VP) ($r = 0.539$, $p < 0.05$) (Figure S2). F_a values decrease as PAH concentrations increase (Figure S2) and stabilize at $\sim 20\%$ with PAH concentrations $> 50 \text{ ng/m}^3$ on the Qf. A similar trend was observed in literature for organic carbon (OC) with F_a gradually decreasing from > 0.8 to 0.2 with increasing OC concentration.(48, 50) This change in F_a is explained partly by the gradual saturation of vacant adsorption sites on the filter as PAH concentrations rise.(48, 50) Adsorption of gases onto particles collected on Qf may also effectively reduce F_a . This effect is especially pronounced as filter loads increase. Additional factors affecting gas absorption/adsorption (such as temperature and exhaust relative humidity, among others) are not significant. Results from the stepwise linear regression model identified MW or vapor pressure (MW is usually correlated positively with vapor pressure) as the most significant influencing factor affecting the F_a , and the inclusion of other factors did not increase the explanation of variance in the F_a value. Finally, F_a was $< 5\%$ for PAHs with MW $> 252 \text{ amu}$, showing that these PAHs are predominantly in the particle phase.

Emission Factor Calculations

Artifact-corrected results are used to calculate PAH emission factors. A strong linear relationship is observed between PAH emission factors calculated using the diluted emission capture and carbon mass balance methods ($m = 1.1$, $r = 0.999$, $p < 0.05$) (Figure S3). The relative difference between calculation methods ranges from 0.7 to 20% with a median difference of 8.5% . Typically, field studies that apply the carbon mass balance method for determining emission factors use only CO and CO₂, and this study affirms the acceptability of ignoring the particle-phase and volatile carbon species. For example, ignoring particle-phase carbon leads to a median difference of approximately 0.04% (0.02% – 0.26% as an interquartile range). If only CO and CO₂ measurements are used in the calculation (with PM carbon and gaseous total hydrocarbons unaccounted for), a relative median difference of approximately 0.54% (0.35% – 1.0%) is observed in emission factors, showing that the volatile and particle-phase carbon species are minor relative to the CO₂ and CO emissions. These observed differences are slight compared with the uncertainty in pollutant emission factors due to different fuel and stove properties and the various burning conditions. The diluted emission capture method is applied to emissions from this point forward.

Thermal Efficiency and the Effects of Start Phase and Fuel Moisture Content

TEs can vary with the CS and HS phase, depending on stove materials and design and test protocols, among other factors.(15, 16) Generally, the LPG cookstove exhibits the highest

TE (~57%) followed by the kerosene stove (~42%), the wood combustion in the forced-draft woodstove (31%), and the natural-draft woodstove (25%). The TE difference among these cookstoves is significant ($p < 0.001$) (Figure S4-a). However, the figure shows the negligible influence on the TE ($p < 0.05$) due to the start phase and fuel moisture content variables. The forced-draft stove MCEs of 99.5 ± 0.1 and $98.7 \pm 0.5\%$ for low and high-moisture fuels and the natural-draft wood stove MCEs of 97.8 ± 0.3 and $97.5 \pm 0.2\%$ for the low and high-moisture fuels, respectively, show no significant difference (Figure S5). In the low-power simmer phase, MCEs (97.0 ± 0.1 vs $96.7 \pm 0.5\%$) are also similar (Table S2).

PAH₂₅

The start phase at high power does not significantly affect PAH₂₅ on a fuel mass basis nor on a useful energy basis (Figure S4-b). Therefore, from this point forward, results from the CS and HS phases are averaged and treated as one high-power phase.

Table 1 provides the wide range of PAH₂₅ emission factors for different fuel–stove combinations. Emission factors for individual stoves and fuels are given in Table S2. The wood combustion in the natural-draft cookstove shows the highest emissions. LPG shows the lowest emissions; however, due to high emission variability, the PAH₂₅ values among the LPG, kerosene, and wood combustion in the forced-draft fan stove are not significantly different. PAH₂₅ values produced using low- and high-moisture wood fuels also show no significant difference. This result is applicable to values calculated on a per fuel mass basis, per fuel energy basis, and on a specific emission rate basis ($\mu\text{g}/\text{min}/\text{L}$ water) (Figure S6). The influence of fuel moisture content is complicated and often treated as nonlinear. (42, 51, 52) Despite the significantly different TE values among stoves, stoves with high TEs do not necessarily produce low PAH emissions in the present study. In fact, there is no significant correlation between TE and PAH₂₅ emission ($p > 0.05$) currently. TE depends mainly on heat transfer efficiency and less so on MCE, to which the PAH₂₅ emission correlates inversely ($p < 0.001$).

For the low-power phase, PAH₂₅ emission factors are expressed on a fuel mass basis (Table S2), a fuel energy basis, and as a specific emission rate (μg PAH/min/L water) (Table 1). Emissions on a useful energy basis are not evaluated because the useful energy delivered to the cooking pot is difficult to measure in the low-power phase. Considering emissions per unit fuel energy, burning high-moisture wood in the natural-draft cookstove shows the highest emissions ($117 \pm 19 \mu\text{g}/\text{MJ}$), whereas LPG shows relatively low emissions ($16.4 \pm 5.9 \mu\text{g}/\text{MJ}$) on average. A similar result is revealed when using the specific emission rate. Though the difference was statistically not significant due to high test variability and perhaps the relatively small sample size, the obvious general trend for the low-power phase is the same as that in the high-power phase.

PAH₁₆

The 16 U.S. EPA priority PAHs are commonly reported in emissions studies; therefore, we also account for the emissions of PAH₁₆ (Table 1) and compare with literature results. For the PAH₁₆ emission, the highest emissions are found for the wood combustion in the natural-draft cookstoves, followed by the kerosene burning, the wood combustion in the

forced-draft cookstove and LPG, in that order. Differences among the latter three stove–fuel combinations are statistically not significant.

Particulate PAH emission factors measured in the present study were compared to other studies in literature in the measurement units of PAHs mass per fuel mass (mg/kg) because many past studies reported emissions on fuel weight basis. In a past study,(21) $\text{PAH}_{16} = 2.98 \text{ mg/kg}$ in PM emissions from kerosene burned in a wick stove, agreeing with the 2.15 mg/kg on average in the present study. Literature-based PAH emissions from wood combustion are mainly for traditional or improved natural-draft cookstoves. The PAH_{16} emissions from the combustion of wood logs in natural-draft stoves ranged from 0.39 to 43 mg/kg with an overall average and geometric mean of 3.10 and 2.08 mg/kg, respectively. (20–23, 25–27, 29) Results for the wood combustion in the natural-draft stove in the present study fall within this range, although the average value in this study is as high as 13.5 mg/kg during the high-power phase. The PAH_{16} emissions for the wood combustion in the forced-draft stove (0.407 mg/kg during the high-power phase) are a factor of ~ 7.8 lower than the calculated overall mean from the literature for wood combustion in natural-draft stoves. A recent study on the mutagenicity and pollutant emissions from cookstoves reported PAH_{16} in PM emissions of 27.8, 13.5, and 2.06 mg/kg for wood combustions in a three-stone fire, a natural-draft stove, and a forced-draft stove, respectively.(53)

Despite a notable difference in fuel and stove types, the burning experiments in these literature studies are conducted by either bringing a known amount of water to the boiling point and simmering(29) or burning known amounts of fuels (fuel amounts were usually estimated in trial tests to ensure that enough fuel was used to boil the water to its boiling point)(20–28) and sampling with(18, 19, 23–29, 36) or without a fire startup phase.(20–22) Different sampling methods and laboratory PAH analysis methods were also used. These experimental differences can affect the reported emission factors. However, the general trend is clear: PAH emissions for wood combustion in natural-draft stoves are consistently higher than that for wood combustion in forced-draft stoves, and much lower emissions can be expected with the use of cleaner fuels such as LPG.

Individual PAH Profiles

Individual PAH emission factor data are presented in Table S2 and Figure S7. How PAH distributions vary across the different stoves is an interesting feature of the data. For example, the natural-draft stove emits more high molecular weight PAHs, while the LPG stove generally emits lower and intermediate volatility PAHs. This emissions pattern is readily observed in the normalized compositional profiles (Figure S8). The mass fraction of PAHs with 5 rings comprises roughly 50% of the total PAH emissions from the wood combustion in the natural-draft cookstove, whereas these compounds comprise only 10–20% of the PAHs in burning kerosene and LPG and $\sim 40\%$ in the wood combustion emissions from the forced-draft stove. Distinct composition profiles would presumably affect the potential toxicity of particles from different fuel–stove combustion emissions.

Low-power phase PAH emission profiles are slightly different from high-power phase PAH emissions. Generally, all stoves operating at low power emit higher PAH concentrations over the MW range of 202 to 228 amu, and heavier PAHs tend to be emitted from the natural- and

forced-draft cookstoves burning wood (Figures S9 and S10). The LPG stove PAH emission contributions are isolated to intermediate volatility PAHs, similar to the high-power phase observations for this fuel and stove. The mass fractions of PAHs with 4 and 5 rings are 84 ± 2 and $3.7 \pm 2.3\%$ in the LPG emissions, respectively. Those fractions are 73 ± 6 and $19 \pm 5\%$ in emissions from burning the low-moisture wood in the natural-draft cookstove.

Relationships among PAHs, CO, and PM_{2.5}

The PAH₂₅ correlates positively to coemitted CO ($r = 0.896$, $p < 0.001$ in the high-power phase and $r = 0.736$, $p = 0.003$ in the low-power phase) and PM_{2.5} ($r = 0.598$, $p < 0.001$ in the high-power phase and $r = 0.807$, $p < 0.001$ in the low-power phase).

The mass proportion of the PAH₂₅ in PM_{2.5} varies among fuel–stove combinations and burning phases (Table S3). The difference between the high- and low-power phases for most fuel–stove combinations is not significant except for the wood combustion in the natural-draft woodstove, in which significantly lower PAH₂₅/PM_{2.5} ratios (1.23 – 1.28 $\mu\text{g}/\text{mg}$) are observed in the low-power phase compared with those observed in the high-power phase (5.73 – 7.59 $\mu\text{g}/\text{mg}$). Relatively high mass fractions were observed for kerosene burning in both the high- and low-power phases (10.1 ± 3.3 and 9.15 ± 5.44 $\mu\text{g}/\text{mg}$, respectively), followed by the wood combustion in the natural-draft stove during the high-power operation (7.41 ± 1.20 and 6.66 ± 2.94 $\mu\text{g}/\text{mg}$ for low- and high-moisture woods) and LPG combustion (5.34 ± 4.29 and 10.6 ± 2.6 $\mu\text{g}/\text{mg}$ in the high- and low-power phases, respectively). The lowest PAH₂₅/PM_{2.5} fractions are found in the wood combustion in the forced-draft stoves (1.13 ± 0.63 and 1.41 ± 0.88 $\mu\text{g}/\text{mg}$ in high- and low-moisture wood combustion during the high-power phase and 2.81 ± 1.85 $\mu\text{g}/\text{mg}$ in the low-power phase of dry wood combustion). A relatively high PAH₂₅/PM ratio in kerosene combustion compared with that in wood combustion had also been reported previously. For example, in another laboratory study,(20, 21) the particulate PAHs (16 priority PAHs and benzo[*a*]pyrene) emission per unit mass of PM for kerosene burning in a wick stove was ~ 10.0 $\mu\text{g}/\text{mg}$ (close to the result in the present study), which is much higher than the particulate PAH emissions per unit mass of PM for wood burning, ranging from 0.08 to 1.64 $\mu\text{g}/\text{mg}$. Though the mass proportion of PAH₂₅ in PM_{2.5} is relatively high for kerosene and LPG compared with that for the wood combustion in natural-draft cookstoves, it is necessary to note that the absolute emissions were lower for the former two fuel–stove combinations, as discussed above.

PAH Emissions and Tier-Rated Performance

ISO International Workshop Agreement (IWA) 11:2012 guidelines(54) are provided for rating cookstoves and fuels (tiers 1–4, with tier 4 representing the best-performing stoves) using emitted pollutants CO and PM_{2.5} as indicators. Pollutant emission factor scales are specified on a useful energy basis for the high-power phase and per specific emission rate in the low-power phase. Figure 2a considers CO emissions, showing for the high-power phase that all stoves tested are sub-tier 4. However, the story changes for PM_{2.5} (Figure 2b). While wood combustion in the natural-draft cookstove is sub-tier 1, the forced-draft fan stove is sub-tier 3 or 4 when burning low-moisture wood, while kerosene and LPG stoves are sub-tier 4.

To our knowledge, individual pollutants other than CO and PM_{2.5} have not yet been examined relative to the ISO cookstoves tier-rated system. For the first time, Figure 2 allows us to visualize the cookstove performance in subtiers while considering B[a]P emissions. B[a]P is selected due to its carcinogenicity.(8, 9) This exercise is meant to provide a novel perspective on the potential toxic effect of the stove emissions. Irrespective of the CO emissions tier of the natural-draft stove, the relatively high B[a]P emissions suggests the natural draft stove represents a higher potential exposure risk similar to PM_{2.5}. Also at high power, the kerosene burning and wood combustion in the forced-draft stoves emit B[a]P in similar quantities despite being tiered differently with regard to PM_{2.5}, suggesting different resolving power between PM_{2.5} and B[a]P pollutants.

For the low-power phase, all the stoves tested are sub-tier 4 for CO emissions (Figure 3a). However, the PM_{2.5} emissions ratings show the kerosene and LPG stoves in sub-tier 4 and the wood cookstoves in sub-tiers 2 and 3, Figure 3b. The wood and kerosene stoves represent a potentially similar B[a]P exposure risk. Ultimately, when rating stoves, it may be important to consider the concentration strength of individual chemical pollutants, especially those with high toxic potentials.

Implications and Limitations

Comparing emissions per useful energy delivered ($\mu\text{g}/\text{MJ}_d$) is one way to estimate the extent to which adoption of cleaner fuels and cookstoves potentially reduces emissions. Because the effect of fuel moisture content on PAH emissions for these particular experiments is not significant, results for low- and high-moisture fuels were averaged for this next analysis. High-power test phase data are used because the useful thermal energy delivered is accurately known. Using B[a]P emissions as the example (409 ± 150 , 6.70 ± 4.64 , 5.36 ± 2.26 , and $0.841 \pm 1.456 \mu\text{g}/\text{MJ}_d$ for wood combustion in the natural-draft cookstove, wood burning in the forced-draft fan cookstove, kerosene, and LPG, respectively), an approximate 85% reduction in emissions of B[a]P is expected when adopting LPG instead of kerosene in wick stoves or wood in forced-draft stoves. Reductions greater than 95% may also be expected if kerosene, LPG, and wood combustion in the forced-draft fan stove were used instead of burning wood in the natural-draft cookstoves.

Emission rate is commonly used to evaluate potential indoor air quality impacts and consequent exposure risk and health impacts of cookstove emissions.(8, 15, 55) The WHO sets emission rate targets (ERTs) for PM_{2.5} and CO for vented and unvented stoves. For instance, the ERT and intermediate ERT for PM_{2.5}, for which 100 and 60% of homes meet the Annual Quality Guideline (AQG) of $35 \mu\text{g}/\text{m}^3$, are 0.23 and 1.75 mg/min for unvented cookstoves and 0.80 and 7.15 mg/min for vented cookstoves, respectively. ERTs may be used as a basis for fuel and stove device selection.(8, 55) Again, B[a]P from the high-power phase is the current focus. The average emission rates of B[a]P for wood combustion in the natural-draft rocket stove, wood combustion in the forced-draft fan stove, the kerosene burning, and the LPG burning were 26.8 ± 11.6 , 0.552 ± 0.396 , 0.452 ± 0.196 , and $0.0426 \pm 0.0722 \mu\text{g}/\text{min}$, respectively. Therefore, the use of LPG or wood in the forced-draft stoves would reduce nearly 98% of indoor B[a]P compared with the use of wood in the natural-draft stove. If LPG is used instead of wood in the forced-draft fan stove or kerosene, indoor

B[a]P concentrations will decrease markedly by ~90%. The use of wood in the forced-draft fan stove has indoor PAH emissions comparable to those for kerosene burning in the wick stove.

The quantified emission reductions for other wood types may be different from the results for oak wood studied here, but nevertheless, emission reductions would be expected when replacing natural-draft stoves by forced-draft stoves, and there would be a more significant reduction with the use of clean fuels such as LPG. This study shows that the LPG stove has the lowest PAH, CO, and PM_{2.5} emissions. Kerosene emissions of PM_{2.5}, CO, and targeted PAHs are lower than those measured for wood burning in a natural-draft cookstove but higher than LPG. Hazardous pollutant emissions and their associations with adverse health outcomes in households using kerosene for cooking and lighting are well-documented.(8, 56, 57) These sources would benefit from further investigation such as that provided here. In certain regions where LPG and kerosene are unavailable or unaffordable for local residents, our study results suggest that a high-efficiency, forced-draft biomass cookstove burning wood may effectively reduce emissions and consequently improve air quality and human health.(4) Of course, the use of chimneys further reduces indoor pollution.(8)

Only particle-phase PAHs were analyzed in this study despite the fact that gas-phase PAH emissions are also substantial and vary with fuel-cookstove types and burning conditions. (20–22, 42) This potentially limits comparing these PAH emission factors to other studies and partially constrains emissions inventory development. An effective intervention may require the examination of a larger number of fuels and cookstove devices than the current investigation. For example, multiple burner designs are commercially available for LPG stoves and likely affect pollutant emissions. Despite the present study being laboratory controlled, relatively large uncertainties in PAH emissions are observed. The coefficient of variation in PAH emissions per useful energy delivered in the high-power phase ranged from 15% in the kerosene combustion to nearly 100% in the LPG combustion. Future laboratory studies are needed to better understand contributions to this wide potential range of PAH emissions. Finally, the demand for further comparisons between laboratory and field studies is substantial. Such information will help clarify the uncertainties associated with cookstove and fuel performance during actual use and will help to evaluate impacts on air quality and human health by promoting use-appropriate fuels and cookstoves.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

F_a values (percent of measured concentration in gas-phase filter to that in the corresponding particle-phase filter) for individual PAH compounds. Data are reported as means and standard errors.

Figure 2.

Figure 2. B[a]P vs CO (a) or PM_{2.5} (b) emissions per useful energy delivered to water during the high-power test phase. Sub-tier levels per ISO IWA 11:2012.

Figure 3.

B[a]P emissions vs CO (a) or $\text{PM}_{2.5}$ (b) emissions per liter of water per minute during the low-power simmer system. Sub-tier levels per ISO IWA 11:2012

Table 1.**PAH₂₅, PAH₁₆, and B[a]P Emission Factors for Tested Fuel–Stove Combinations^a**

Fuel-stove combination	High power					
	Fuel energy basis			Useful energy basis		
	PAHs	PAH16	B[a]P	PAHs	PAH16	B[a]P
	µg/MJ	µg/MJ	µg/MJ	mg/MJ _d	mg/MJ _d	µg/MJ _d
LPG	20.0±19.6	19.2±18.7	0.466±0.793	0.036±0.036	0.034±0.034	0.842±1.44
kerosene	53.5±9.2	50.0±8.4	2.25±0.95	0.128±0.020	0.119±0.018	5.36±2.26
LMW-FD	17.9±12.9	15.9±11.0	1.64±1.64	0.058±0.038	0.050±0.033	5.17±4.91
HMW-FD	31.4±17.3	27.5±15.5	2.48±1.24	0.102±0.059	0.089±0.053	8.07±4.26
LMW-ND	890±250	803±230	109±31	3.54±0.83	3.19±0.77	433±108
HMW-ND	756±352	686±323	95.7±45.9	3.09±1.44	2.80±1.32	391±187
Fuel-stove combination	Low power					
	Fuel energy basis			Per liter water per time		
	PAHs	PAH16	B[a]P	PAHs	PAH16	B[a]P
	µg/MJ	µg/MJ	µg/MJ	µg/min/l	µg/min/l	µg/min/l
LPG	16.0±5.7	15.8±5.9	0.075±0.053	0.713±0.234	0.705±0.240	0.003±0.002
kerosene	45.2±34.4	42.2±33.9	1.02±0.48	1.39±0.94	1.30±0.94	0.035±0.020
LMW-FD	54.8±25.4	49.4±22.6	5.86±3.38	2.11±1.44	1.90±1.29	0.230±0.183
LMW-ND	61.5±22.0	57.7±21.1	2.35±0.63	2.45±0.73	2.29±0.70	0.094±0.020
HMW-ND	115±18	105±19	10.1±2.0	4.74±0.86	4.37±0.91	0.418±0.071

^a Including (i) LPG stove, (ii) kerosene stove, (iii) low moisture wood in the forced-draft cookstove (LMW-FD), (iv) high-moisture wood in the forced-draft stove (HMW-FD), (v) low-moisture wood in the natural-draft stove (LMW-ND), and (vi) high-moisture wood in the natural-draft stove (HMW-ND) operating in high- and low-power phases, ± standard deviation. In the low-power phase, the combination HMW-FD was not tested.