Research Article

Characterization and Determination of PM$_{2.5}$ Bound Polycyclic Aromatic Hydrocarbons (PAHS) in Indoor and Outdoor Air in Western Sierra Leone

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Abstract

Eleven airborne PM$_{2.5}$ PAH concentrations were characterized in the kitchen, outdoor and living room environments in households that burn wood and charcoal fuels in Western Sierra Leone, during a survey that was conducted in September 2011. The average concentration of total PAHs (Σ_{11}PAHs) was 1279.7 ng/m^3 in kitchen, 41.2 ng/m^3 in outdoor, 19.8 ng/m^3 in living room for households burning wood while those burning charcoal was 96.5 ng/m^3, 13.1 ng/m^3 and 8.9 ng/m^3 in the kitchen, outdoor and living room, respectively. The percentage contribution of higher molecular weight PAHs to Σ_{11}PAHs was about 25% higher compared to medium molecular weight PAHs for either household category in all three locations, with a somewhat different scenario for kitchens with wood stove. The ratio of indoor/outdoor air of Σ_{11}PAHs showed considerable variation among households burning charcoal (p=0.0021; t-test) relative to those burning wood, attributed to non-prolonged equilibrium between the two environments. Benzo(a)pyrene (BaP) equivalency results revealed that BaP and dibenzo(a,h)anthracene were the two most dominant compounds that contributed to more than 90% of the total carcinogenicity in all three environments for households burning wood and charcoal. The results suggest that kitchens, where biomass fuels are burnt continue to be a hazardous place for people of developing countries to spend their time.

Introduction

There is no longer an iota of doubt that smoke emitted from biomass fuels (dung cake, wood, crop residues etc.) is a major source of indoor air pollution and this risk factor has considerable public health undertone [1,2]. The threat of indoor air pollution continues to exist in developing countries where the majority of the people are in rural areas, and evidently in urban areas most people rely on these fuels for domestic cooking. Each day, large numbers of people are exposed to harmful emissions from biomass cooking fires that usually takes place in traditional stoves with low combustion efficiency and without adequate ventilation. Vulnerable to these harmful substances are women who spend most of their time in the cooking area, and young children who often stay close to their mothers around the cooking area. Previous studies have indicated that the levels of indoor air pollution from biomass fuels can be astonishingly high, often higher than ambient air quality standards in some developing countries [3,4]; and can impact the ambient air from indoor residential wood burning [5,6]. Empirical evidence suggests that burning biomass fuels increases the risk of acute respiratory infections, chronic obstructive pulmonary diseases, asthma and tuberculosis, etc. [3,7-11]. Burning biomass fuels in places with limited ventilation releases incombustible by-products such as particulate matter (PM) and polycyclic aromatic hydrocarbons (PAHs).

Fine particulate matter with aerodynamic diameter <2.5 μm (PM$_{2.5}$) is a major component of biomass smoke and one of the largest sources of accumulation mode particles [12]. This size fraction can penetrate deep into the lungs where there is no protective mucus layer that makes it a concern for many researchers. The PAHs are a specific group of compounds that could represent a major class of air contamination. They are widespread products of incomplete combustion of organic materials such as biomass fuels, fossil fuels, waste burning, domestic heating fuels, etc. [13-18]. The PAHs constitute an environmental concern given their persistence (can stay in the environment for long periods of time). Consequently, sixteen PAH compounds have been listed by US EPA as priority pollutants. There are; naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b) fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indeno[1,2,3-c,d]pyrene, dibenzo(a,h)anthracene and benzo(g,h,i)perylene. The PAHs, particularly those with higher molecular weight such as benzo(a)pyrene and dibenzo(a,h)anthracene are known to be human carcinogen and probably carcinogenic to humans, respectively [19]. Although the degree of carcinogenicity and toxicity may vary considerably for priority PAHs, toxic equivalency factors have been determined for all PAH members [20-21] which makes this group of compound a concern to the scientific community.

Several studies have reported concentrations of PAHs in the combustion zone (the kitchen) where the levels are known to be highest [18,22-28] but one that characterize PAHs in the kitchen, outdoor and living room in such an overriding condition in a typical developing country has not been reported to our knowledge. The present report was part of a broader study that investigated the prevalence of acute respiratory infections in women and children potentially caused by

smoke from wood and charcoal stoves in Western Sierra Leone [29]. As evidence of PAHs association with acute respiratory infections ARI prevalence is not yet fully resolved in the wider literature, the results that this paper presents were not reported earlier [29]. Consequently, this study sought to characterize PM$_{2.5}$ bound PAHs in the kitchen, outdoor and living room locations in households burning wood and charcoal fuels so as to reveal the profile distribution. Additionally was to examine the indoor to outdoor air ratio of PAHs to advance the knowledge of the extent of source influence; and estimate the toxicity of PAHs using toxic equivalency factors for the various locations, an approach widely used in health risk assessment.

Materials and Methods

Study location and sample collection

The study was conducted in fifteen small settlements spanning from Kent to Lower Allen Town in Western Sierra Leone during a survey that has been described elsewhere [29]. Households with wood stoves were identified in the Western rural area, while those with charcoal stoves were in the peri-urban area. As similar socio-cultural and demographic settings (household variables, such as, kitchen type, ventilation condition etc.) are quite identical for most of these communities, detailed information has been described earlier [27]. Briefly households in the rural area burn wood in simple stove arranged in tripod in kitchens separated from the main house, but households in the peri-urban area burn charcoal in the locally made stove in kitchens that are not separated from the house. Every kitchen has a main door and window that are normally opened during cooking activities. Eight households with wood stove and seven with charcoal stove were monitored for particulate PAHs in the three locations, namely: kitchen, outdoor and living room.

A Sibata ATPS-20H dual impactor (Sibata Scientific Technology Limited) was used to collect PM$_{2.5}$ and PM$_{2.5-10}$ PAHs on a 20 and 10 mm diameter Teflon-coated glass fiber filters at a flow rate of 1.5 l/min across the three locations. Gravimetric measurement of PM$_{2.5}$ and PM$_{2.5-10}$ were not made due to the unavailability of sensitive mass balance in Sierra Leone. Airborne particulate samples were concurrently collected during the day for 12-hrs in the kitchen and outdoor locations, but 24-hr sample collection was done in the living room in every household that was sampled. The difference in the sampling frame was due to the non-assurance by the participating households in securing the sampling devices in the kitchen and outdoor locations, respectively. Samples were collected at a height of 1 m above ground in all three locations to simulate the respirable height. A distance of 1.5 m away from the cooking stove in the kitchen location was chosen so as to reflect a reasonable distance of PAH exposure. Outdoor monitoring was made 4-5 m from the kitchen environment. Immediately after sampling each day, filters were wrapped in aluminum foil and refrigerated before transported to Japan for chemical analysis.

Analytical and QA/QC procedures for PAH determination

Samples collected for PM$_{2.5}$ were processed and analyzed for PAHs in view of the increasing importance of PM$_{2.5}$ for exposure assessment. Hence, results of PM$_{2.5}$ PAHs are reported. Description of the analytical procedure employed in the extraction, separation and analysis of PAHs has been described elsewhere [27,30,31]. In brief, a mixture of benzene/ethanol in the ratio 3:1 was used to extract PAHs from PM$_{2.5}$ filters in an ultrasonic bath that lasted for 50 minutes in two cycles. After centrifugation at 3000 rpm for 10 minutes, the extracts were filtered, and the filtrates were transferred to a rotary evaporating flask

into which 100 µl of dimethyl sulfoxide was added for preservation. This was evaporated to about 1 ml using rotary evaporator (BUCHI R-210/R-215 Switzerland), in a water bath at a temperature of 55°C and pressure of 180 Torr. The final volume was adjusted to 1 ml by adding 900 µl of acetonitrile and the sample solution was injected into an HPLC system. The separation and identification of 11 out of the 16 EPA priority PAHs was enhanced by HPLC system (HP 1100: Agilent Technologies) that was fitted with fluorescence detector supported by diode array detector. A guard column (30 × 4.6 mm, 5 µm) for clean-up and an analytical column of PAHs (125 × 4.6 mm, 5 µm) were C$_{18}$ EnviroSep-PP (Phenomenex). The 11 PAHs quantified were based on their elution order as follows: phenanthrene [PHE], anthracene [ANT], fluoranthene [FLT], pyrene [PYR], benzo(a)anthracene [BaA], chrysene [CHY], benzo(b)fluoranthene [BbF], benzo(k)fluoranthene [BkF], benzo(a)pyrene [BaP], dibenzo(a,h)anthracene [DBA] and benzo(g,h,i)pyrelene [BgP].

Analysis of field blanks were done to assure laboratory quality control and the results were corrected for trace levels of PHE and PYR. Recovery analysis was done by reconstituting and taking three PAHs surrogates namely: benzo(a)pyrene-d$_{12}$ phenanthrene-d$_{10}$, pyrene-d$_{10}$ through the extraction process to examine method performance. The recoveries ranged between 83% and 97% largely in agreement with the wider literature [23,27]. The concentration of each PAH was calculated from peak areas by comparison with the calibration standard peak area. A four-point calibration curve of different concentrations in the range of 0.005 µg/ml to 0.5 µg/ml. This calibration solution was prepared by diluting the standard solution with a range of individual concentrations (containing 99.9 µg/ml to 200.2 µg/ml). This was done to determine the linearity of responses and the average coefficient of determination of individual PAH was >0.98. The limits of detection (LOD) for individual PAHs, defined as triple standard deviation of peak area of a dilute standard solution ranged from 0.001 ng/ml (CHY) to 0.04 ng/ml (DBA). Similarly, the limits of quantification (LOQ) was determined as ten times the standard deviation of the peak area of the same diluted standard solution and the values ranged from 0.01 ng/ml (CHY) to 0.42 ng/ml (DBA).

Data analysis

The Σ_{11}PAHs notation represents the total concentration of 11 PAHs. In identifying marker(s) of exposure of PAHs in the different locations, Pearson correlation matrix for every pair of PAH and Σ_{11}PAHs was conducted with the supposition that two or more components may correlate either due to a common source or origin. Due to the uniform distance and same volume of air sampled between the kitchen and outdoor locations for the different households, indoor to outdoor (I/O) air ratio was estimated for each fuel category. The kitchen was regarded as 'indoor' in this context. As humans are exposed to a mixture of PAHs, Pairwise correlation analyses were carried between the kitchen and outdoor Σ_{11}PAHs to reinforcement the I/O relationship between the two environments. The toxicity of PAHs was explained by BaP equivalent (BaP$_{eq}$) concentrations. This approach integrates the absolute concentrations of PAHs in the mixture and the carcinogenic potential of individual PAH estimated by adopting toxic equivalence factors (TEFs) proposed by [21]. The sum of BaP$_{eq}$ concentration represents the total carcinogenicity of PAHs in the mixture.

Results

The PM$_{2.5}$ Σ_{11}PAHs values ranged from 403.8-3433.5 ng/m³ in kitchen; 20.8-87.6 ng/m³ in outdoor; and 11.5-37.5 ng/m³, in the living

room. The average values were 1279.7 ng/m³, 41.2 ng/m³ and 19.8 ng/m³ in the kitchen, outdoor and the living room, respectively. Taking into account results for households using charcoal, PM$_{2.5}$ Σ_{11}PAHs ranged from 13.3-278.7 ng/m³ mean 96.5 ng/m³; from 9.2-25.4 ng/m³ mean 13.1 ng/m³; and from 5.1-18.3 ng/m³ mean 8.9 ng/m³ in the kitchen, outdoor and living room locations, respectively. The profiles of individual PAH in the three locations for households using wood and charcoal are presented in Figures 1 and 2, respectively. The figures for both types of fuel showed that PAHs in the kitchen are more dominant than the other two environments. All of the individual PM$_{2.5}$ PAHs concentrations in outdoor and living room are within the same order of magnitude, but most in the kitchen are an order of magnitude higher for households burning wood. Most PM$_{2.5}$ PAHs measured in kitchens for households using charcoal have concentrations that are one order of magnitude higher than the other two environments.

The pattern of PM$_{2.5}$ PAH dominance to Σ_{11}PAHs in households using wood appears to be the same with a distribution of around 57% in the three locations, respectively. It was observed that PYR, BaP, DBA and FLT were more dominant in the kitchens; DBA, BaP, PHE and FLT were in outdoor and BaP, PHE, FLT and DBA in the living rooms. A similar pattern of dominance was observed in households using charcoal with a distribution of about 66% in the various environments. The study revealed that DBA, BgP, BaP and BbF were found to be more present in the kitchens; DBA, FLT, BgP and PHE were in outdoor and DBA, BgP, FLT and BaP in the living rooms. The percentage contribution of the medium molecular weight (MMW) and higher molecular weight (HMW) to Σ_{11}PAH is presented in Table 1. It was observed that HMW PAHs were more dominant relative to MMW PAHs in all three locations.

From the Pearson correlation analyses in Tables 2 and 3, it was revealed that MMW PAHs (FLT, PYR, BaA and CHY) and HMW PAHs (BbF, BkF, BaP, DBA and BgP) strongly correlated with each other and Σ_{11}PAHs with few exceptions in the kitchen location for households burning either wood or charcoal. The pattern of correlation as revealed in Tables 4 and 5 in the outdoor location for households burning either wood or charcoal appeared to be similar with few exceptions. The HMW PAHs tend to be strongly correlated with each other and Σ_{11}PAHs with few exceptions as lower molecular weight (LMW) PAHs (PHE and ANT) and MMW PAHs showed weak or no correlation among each other and Σ_{11}PAHs especially in households burning charcoal. In the living room of households burning wood, there was no clear pattern of relationship among individual PAH and Σ_{11}PAHs as observed in Table 6; but a strong correlation among HMW PAH and Σ_{11}PAHs was exhibited, with BaA and CHY as members of the MMW PAHs showed similar trend to those of HMW PAH as illustrated in Table 7. Quite obvious was the non-correlation of PHE with Σ_{11}PAHs for the different locations except in the kitchen for households burning wood. This observation could imply that exposure to PHE should be characterized independently. Even though HMW PAHs should be considered strong markers of overall exposure to PAHs in the various locations (kitchens, outdoor and living rooms) for either household, MMW PAHs in the kitchen location could also be considered indicators of overall PAH exposure.

The I/O ratio for individual PM$_{2.5}$ PAH and Σ_{11}PAHs for households using wood and charcoal is presented in Table 8. Mean I/O ratio were elevated in households using wood relative to charcoal. The spread of I/O ratio for PM$_{2.5}$ PAH and Σ_{11}PAHs for the households was largely variable with respect to the mean values. Low concentrations of outdoor PAHs and elevated levels of kitchen PAHs may have resulted in the

observed variation among the I/O ratios especially BaA; suggesting that emission and production rate of some PAHs is not uniform for the two locations among the households that were sampled. The majority of the ratio for either household exceeded the baseline value of three. The I/O ratio for ANT, FLT, PYR, CHY, DBA, and Σ_{11}PAHs were significantly elevated in households using wood than those using charcoal, but even though other compounds did not show significant difference at 95% CI, their absolute differences are not negligible between households using wood and charcoal. The I/O ratio for Σ_{11}PAHs for households using wood and charcoal has an average coefficient of variation of 0.47 and 1.07, respectively; a measure of the variability of data relative to its mean. The pairwise correlation coefficient between the kitchen and outdoor Σ_{11}PAHs for households burning wood was r=0.66; p=0.077 and r=-0.26; p=0.546 for households burning charcoal.

The toxicity equivalency factors (TEFs) estimated for PM$_{2.5}$ bound Σ_{11}PAHs for households using wood and charcoal in the three locations are summarized in Table 9. BaP and DBA were the dominant contributors to the total BaPeq. BaP accounted for 47%, 52% and 34%; while DBA contributed 46%, 39%, and 58% to the total BaPeq in the kitchen, living room and outdoor, respectively for households using wood. In the same way for households using charcoal, BaP contributed 45%, 21% and 25%; but DBA accounted for 53%, 72% and 66% to total BaPeq in the kitchen, living room and outdoor locations, respectively. BaP and DBA accounted for 93%, 91%, and 92% to total BaPeq in kitchen, living room and outdoor for households using wood; but the two compounds made up 98%, 93% and 91% of the total BaPeq in households using charcoal.

Discussion

Eleven out of the sixteen US EPA priority PAHs were characterized in the kitchen, outdoor and living room environments. The concentrations of PAH was highest in the kitchen than in outdoor and living room, respectively, and this observation could not be considered weird taking into account the cooking activities (source strength) and the type of biomass fuels that are used in kitchens where no proper ventilation system exists. Individual PAH concentration in kitchens with wood stoves are significantly elevated than those using charcoal by over an order of magnitude, suggesting further that wood stoves or wood burning devices are big emitter of PAHs, firmly consistent with previous studies [22,27,32]. Studies have shown that PAHs are highest in a similar environment where an indoor source (cooking or space heating or environmental tobacco smoke) dominate [33,34]. The level of PM$_{2.5}$ bound Σ_{11}PAHs observed in this study is lower in the kitchen environment than previous studies [22,24,27,32], but higher than the ambient levels measured in Europe and America [33,35]; even though the number of investigated PAHs vary. Different factors, such as ventilation rate, kitchen type and space, measurement duration, measurement activity etc. could all account for varied PAH concentrations among the studies.

Although the DBA level recorded in the kitchens with wood stoves in this study was lower than a previous study [18]; it was observed to be a common contaminant in the different locations for households burning either wood or charcoal. This observation is an indication that BDA may have a common origin or source in rural areas. Characteristically, many homes cook two times a day; usually daytime, and the significant variation of Σ_{11}PAHs concentrations in kitchens using either wood or charcoal is suggesting that there were both extended and limited cooking periods carried out in the kitchen location coupled with the possibility of air exchange differences among
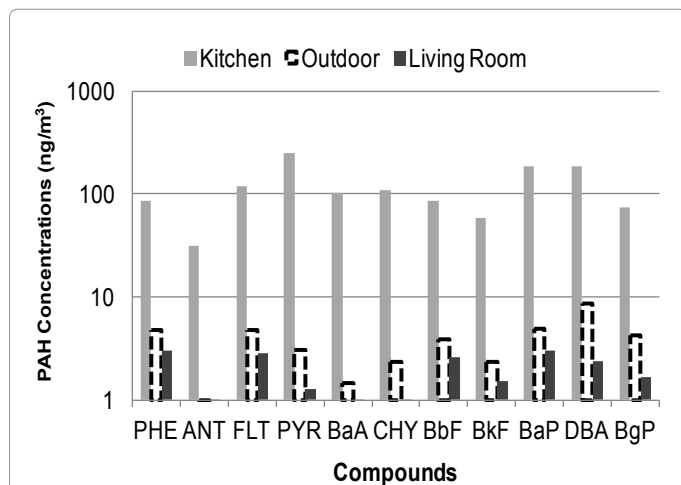
Figure 1: Profile of 11 individual PAH measured in the kitchen, outdoor and living room environment in households using wood, n=8.
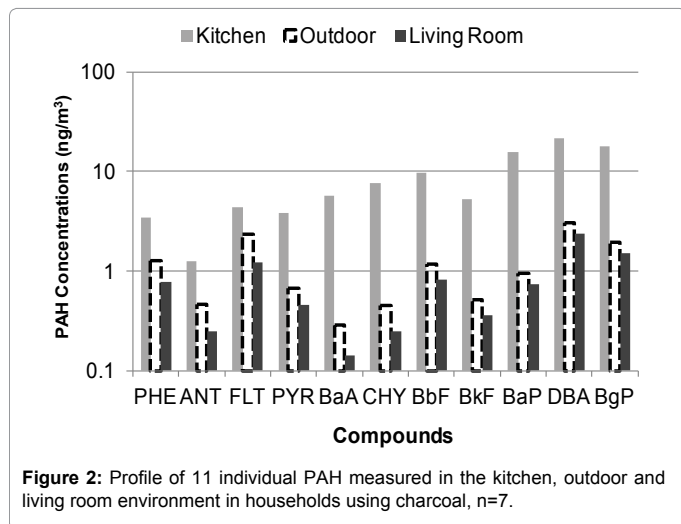

Figure 2: Profile of 11 individual PAH measured in the kitchen, outdoor and living room environment in households using charcoal, n=7.

the contribution of MMW and HMW PAHs appeared to be the same in the kitchen environment for households using wood stove contrary to an earlier report [27]. We presume that during the non-burning period, HMW PAHs could persist much longer without degradation in such environment. Moreover, the contribution of HMW PAHs in outdoor and living room locations for households using either wood or charcoal appeared to be higher than MMW PAHs.

One of the main features of the various kitchens was they were naturally ventilated due to the presence of an open window and door giving rise to the possibility of air movement between the kitchen and outdoor. Hence, determining the I/O ratio is useful to indicate whether the existence of PAH indoors is the result of an indoor source or the infiltration of outdoor air. The indoor sources of PAHs were present indoors (kitchen) and was presumed to be by far the most important source of outdoor PAHs [40-41]. Furthermore, it has been suggested that the I/O ratio above three is an indication that PAHs are produced in an indoor environment where combustion source exists [41-42]. This benchmark depicting source influence of individual PM$_{2.5}$ PAH and Σ_{11}PAHs was exceeded in almost all of the households using either wood or charcoal. Without a doubt, PAHs in the kitchens would have affected the outdoor levels, and a similar observation was made earlier [33] despite variation in the study design. The lower average coefficient of variation of the I/O ratio for Σ_{11}PAHs in households using wood relative to charcoal could probably be due to prolonged equilibrium between the two environments. This presumption could be further explained by considering the fact that burning wood logs disperses prolonged smoke from the kitchen by ventilation through open doors and windows even after a meal is cooked. On the contrary, however, the higher average coefficient of variation for the I/O ratio for Σ_{11}PAHs in households using charcoal relative to those using wood is an indication of non-prolonged equilibrium between the two environments, in view of the fact that charcoal emits less smoke coupled with extinguishing charcoal fires immediately after every cooking activity.

From the results of pairwise correlation analyses, there was a good reason to believe that Σ_{11}PAHs concentrations in kitchens with wood stoves would have affected outdoor Σ_{11}PAHs levels. However, this trend was not observed for kitchens with charcoal stoves. This observed pattern of association between the two environments could tend to support the argument in the preceding sentences of prolonged and non-prolonged equilibria. It is reasonable to suggest that since outdoor Σ_{11}PAHs were probably driven from the kitchen in households burning wood, the kitchen overall PAHs concentration could be used as an indicator for ambient exposure. However, such advancement would need further investigation given the small sample size of this study. The economic burden to buy charcoal could explain the reason why burning lumps of charcoal are immediately put off after every cooking activity in the kitchen, thereby reducing the possibility of prolonged dispersion of smoke. It is worth noting that that there was no air exchange measurement made between the kitchen and outdoor locations due to logistics difficulty, a factor that would have informed the readers of the air exchange rate between the kitchen and outdoor environment.

the kitchens. For example, the kitchen with wood stove with the highest Σ_{11}PAHs relative to the others was explained to be having extended burning activities a day prior to sampling.

The profile of PAH dominance FLT, PYR, BaP and DBA is consistent with results reported for wood and charcoal burning stoves with slight variation in the order being described [36-37]. Similar profile (FLT PYR, BaP, and BgP) have been reported for incense burning in Taiwan in the burning area [38], an indication that the emission pattern of PAHs could have intersource similarity [39]. From Table 1, it was revealed that the contribution of MMW PAHs and HMW PAHs was similar for households using wood and differs greatly for those in households using charcoal in the kitchen environment. It is interesting to note that

Location	Households using wood		Households using charcoal	
	MMW (%)	HMW (%)	MMW (%)	HMW (%)
Kitchen	45.1	45.7	21.0	72.0
Outdoor	26.8	56.1	30.7	58.5
Living room	26.3	57.8	23.3	64.4

MMW PAHs=FLT, PYR, BaA and CHY
HMW PAHs=BbF, BkF, BaP, DBA and BgP

Table 1: Percentage contribution of medium molecular weight (MMW) and higher molecular weight (HMW) PM$_{2.5}$ PAHs in kitchen, outdoor and living room locations.

	PHE	ANT	FLT	PYR	BaA	CHY	BbF	BkF	BaP	DBA	BgP	∑PAHs
PHE	1.000											
ANT	**0.993**	1.000										
FLT	**0.883**	**0.919**	1.000									
PYR	**0.888**	**0.928**	**0.988**	1.000								
BaA	**0.828**	**0.880**	**0.946**	**0.978**	1.000							
CHY	**0.855**	**0.904**	**0.966**	**0.988**	**0.995**	1.000						
BbF	**0.815**	**0.860**	**0.883**	**0.930**	**0.975**	**0.962**	1.000					
BkF	0.789	**0.849**	**0.933**	**0.968**	**0.988**	**0.986**	**0.942**	1.000				
BaP	0.790	**0.847**	**0.916**	**0.952**	**0.964**	**0.965**	**0.901**	**0.990**	1.000			
DBA	**0.820**	**0.873**	**0.899**	**0.935**	**0.956**	**0.964**	**0.922**	**0.974**	**0.978**	1.000		
BgP	0.699	0.766	**0.830**	**0.883**	**0.931**	**0.924**	**0.880**	**0.965**	**0.973**	**0.962**	1.000	
∑$_{11}$PAHs	**0.885**	**0.929**	**0.970**	**0.993**	**0.988**	**0.995**	**0.949**	**0.982**	**0.971**	**0.968**	**0.921**	1.000

Values in bold represent strong correlation.
Table 2: Pearson correlation matrix among individual PM$_{2.5}$ PAHs and ∑$_{11}$PAHs in kitchens of households burning wood.

	PHE	ANT	FLT	PYR	BaA	CHY	BbF	BkF	BaP	DBA	BgP	∑PAHs
PHE	1.000											
ANT	0.598	1.000										
FLT	0.550	**0.875**	1.000									
PYR	0.141	0.784	0.631	1.000								
BaA	0.469	**0.957**	**0.888**	**0.801**	1.000							
CHY	0.494	**0.979**	**0.865**	**0.826**	**0.991**	1.000						
BbF	0.566	**0.843**	**0.947**	0.629	**0.909**	**0.863**	1.000					
BkF	0.487	**0.835**	**0.934**	0.678	**0.920**	**0.872**	**0.994**	1.000				
BaP	0.562	**0.850**	**0.946**	0.599	**0.917**	**0.871**	**0.995**	**0.988**	1.000			
DBA	0.514	**0.806**	**0.951**	0.576	**0.877**	**0.822**	**0.990**	**0.985**	**0.991**	1.000		
BgP	0.689	**0.838**	0.711	0.382	0.698	0.745	0.581	0.530	0.618	0.569	1.000	
∑$_{11}$PAHs	0.611	**0.931**	**0.960**	0.654	**0.951**	**0.929**	**0.972**	**0.959**	**0.980**	**0.961**	0.743	1.000

Values in bold represent strong correlation.
Table 3: Pearson correlation matrix among individual PM$_{2.5}$ PAHs and ∑$_{11}$PAHs in kitchens of households burning charcoal.

	PHE	ANT	FLT	PYR	BaA	CHY	BbF	BkF	BaP	DBA	BgP	∑PAHs
PHE	1.000											
ANT	0.501	1.000										
FLT	0.576	0.476	1.000									
PYR	0.417	**0.918**	0.660	1.000								
BaA	0.126	**0.839**	0.561	**0.916**	1.000							
CHY	0.148	**0.870**	0.543	**0.935**	**0.992**	1.000						
BbF	0.001	**0.834**	0.172	0.749	**0.828**	**0.871**	1.000					
BkF	0.035	**0.837**	0.264	0.759	**0.866**	**0.898**	**0.986**	1.000				
BaP	0.049	**0.868**	0.333	**0.849**	**0.931**	**0.956**	**0.973**	**0.979**	1.000			
DBA	-0.131	0.724	0.013	0.626	0.729	0.781	**0.974**	**0.946**	**0.919**	1.000		
BgP	-0.053	0.746	0.007	0.591	0.675	0.728	**0.967**	**0.942**	**0.894**	**0.968**	1.000	
∑$_{11}$PAH	0.210	**0.928**	0.417	**0.894**	**0.921**	**0.954**	**0.959**	**0.968**	**0.984**	0.887	**0.875**	1.000

Values in bold represent strong correlation.
Table 4: Pearson correlation matrix among individual PM$_{2.5}$ PAHs and ∑$_{11}$PAHs in outdoor of households burning wood.

	PHE	ANT	FLT	PYR	BaA	CHY	BbF	BkF	BaP	DBA	BgP	∑PAHs
PHE	1.000											
ANT	**0.938**	1.000										
FLT	0.471	0.617	1.000									
PYR	0.849	**0.800**	0.727	1.000								
BaA	-0.22	-0.18	-0.03	0.054	1.000							
CHY	0.199	0.107	0.130	0.347	0.336	1.000						
BbF	0.100	-0.01	0.187	0.359	0.414	**0.958**	1.000					
BkF	-0.042	-0.14	0.085	0.218	0.500	**0.940**	**0.985**	1.000				
BaP	0.205	0.072	0.105	0.395	0.448	**0.975**	**0.978**	**0.961**	1.000			
DBA	0.036	-0.13	-0.01	0.218	0.367	**0.903**	**0.958**	**0.959**	**0.945**	1.000		
BgP	-0.159	-0.29	-0.16	0.045	0.499	**0.901**	**0.931**	**0.969**	**0.927**	**0.947**	1.000	
∑$_{11}$PAH	0.303	0.171	0.221	0.504	0.418	**0.956**	**0.972**	**0.937**	**0.988**	**0.932**	**0.873**	1.000

Values in bold represent strong correlation.
Table 5: Pearson correlation matrix among individual PM$_{2.5}$ PAHs and ∑$_{11}$PAHs in outdoor of households burning charcoal.

	PHE	ANT	FLT	PYR	BaA	CHY	BbF	BkF	BaP	DBA	BgP	∑PAHs
PHE	1.000											
ANT	-0.237	1.000										
FLT	-0.610	0.429	1.000									
PYR	0.460	-0.06	-0.18	1.000								
BaA	-0.083	0.261	0.700	0.290	1.000							
CHY	0.361	-0.39	-0.17	-0.44	-0.07	1.000						
BbF	-0.402	0.672	**0.810**	-0.33	0.521	0.035	1.000					
BkF	-0.491	0.673	**0.866**	-0.28	0.575	-0.09	**0.986**	1.000				
BaP	-0.504	0.649	**0.900**	-0.11	0.554	-0.35	**0.880**	**0.929**	1.000			
DBA	-0.148	-0.32	0.494	-0.06	0.202	0.067	0.282	0.305	0.459	1.000		
BgP	-0.629	0.583	**0.819**	-0.29	0.338	-0.32	**0.866**	**0.910**	**0.949**	0.473	1.000	
∑$_{11}$PAH	-0.372	0.549	**0.893**	-0.11	0.614	-0.16	**0.916**	**0.940**	**0.970**	0.552	**0.909**	1.000

Values in bold represent strong correlation.
Table 6: Pearson correlation matrix among individual PM$_{2.5}$ PAHs and ∑$_{11}$PAHs in the living rooms of households burning wood.

	PHE	ANT	FLT	PYR	BaA	CHY	BbF	BkF	BaP	DBA	BgP	∑PAHs
PHE	1.000											
ANT	0.257	1.000										
FLT	**0.897**	0.075	1.000									
PYR	0.220	**0.964**	0.037	1.000								
BaA	-0.376	0.772	-0.44	0.741	1.000							
CHY	-0.269	**0.844**	-0.34	**0.810**	**0.979**	1.000						
BbF	-0.439	0.745	-0.48	0.744	**0.973**	**0.971**	1.000					
BkF	-0.410	0.760	-0.44	0.754	**0.966**	**0.967**	**0.997**	1.000				
BaP	-0.370	0.797	-0.48	0.770	**0.978**	**0.983**	**0.977**	**0.967**	1.000			
DBA	-0.409	0.742	-0.46	0.751	**0.959**	**0.930**	**0.975**	**0.980**	**0.941**	1.000		
BgP	-0.389	0.701	-0.39	0.674	**0.884**	**0.879**	**0.937**	**0.957**	**0.882**	**0.953**	1.000	
∑$_{11}$PAH	-0.188	**0.883**	-0.26	**0.865**	**0.950**	**0.967**	**0.959**	**0.970**	**0.947**	**0.962**	**0.937**	1.000

Values in bold represent strong correlation.
Table 7: Pearson correlation matrix among individual PM$_{2.5}$ PAHs and ∑$_{11}$PAHs in the living rooms of households burning charcoal.

Compounds	Households using wood		Households using charcoal		p-value
	Range	*Mean*	*Range*	*Mean*	
PHE	1.8-84.8	23.2	0.7-21.0	6.4	0.066
ANT	7.7-82.5	31.2	1.2-5.9	2.7	**0.008**
FLT	5.7-87.1	27.8	0.9-4.0	1.9	**0.015**
PYR	19.7-181.6	89.1	1.7-11.7	6.4	**0.003**
BaA	20.1-720.0	198.1	0.2-332.0	105.4	0.191
CHY	15.5-144.4	83.6	0.8-91.5	28.8	**0.029**
BbF	8.6-82.9	33.9	1.0-56.5	18.2	0.140
BkF	11.3-124.2	42.7	0.6-65.5	27.1	0.238
BaP	14.1-173.8	71.1	1.2-196.2	55.2	0.335
DBA	11.9-64.8	28.1	1.2-25.3	8.8	**0.012**
BgP	10.4-51.8	23.2	1.1-28.8	17.4	0.289
∑$_{11}$PAHs	13.5-48.9	31.5	1.4-27.6	8.8	**0.002**

p-values in bold are significant at 95% CI.
Table 8: Indoor to outdoor (I/O) ratio of individual PAH and ∑$_{11}$PAHs indicating the range and mean values.

Location	Households using wood		Households using charcoal	
	Range (ng/m^3)	Mean (ng/m^3)	Range(ng/m^3)	Mean (ng/m^3)
Kitchen	143.5-919.4	395.5	4.1-138.4	39.2
Outdoor	3.4-30.1	14.3	1.5-9.7	4.2
Living Room	1.6-12.9	5.9	1.1-8.4	3.2

Table 9: Benzo(a)pyrene equivalency (BaPeq) concentrations forPM$_{2.5}$ ∑$_{11}$PAHs in the kitchen, outdoor and living room locations.

The mean PM$_{2.5}$ Σ_{11}PAH concentrations in the three locations (kitchen, living room and outdoor) in households using wood and charcoal reduced when their contribution to the total BaPeq was considered. The obvious reason for this observation was PAHs with low toxicity factors, such as; PHE, FLT, PYR, BgP etc. that dominated in indoor and outdoor air obviously played a minor role in the total BaPeq. Although BaP is widely regarded as a surrogate compound for PAH mixture in air, results from this study suggest that DBA, known to have a TEF of 5 at low dose and close to 1 at high dose [43] could play a significant role in assessing PAHs toxicity and health risk. This underlines the importance of DBA in future health risk assessment because people spend most of their time in these environments. But the toxicity estimate measured by the BaPeq concentrations in this study in all of the three locations is not negligible since the threshold of 1 ng/m^3 suggested by WHO for inhaled air was exceeded. The mean BaPeq concentration in the current study is lower than two previous studies conducted during cooking in kitchens with wood and charcoal stoves in Sierra Leone; 616 ng/m^3 and 58 ng/m^3 [27]; and in Tanzania; 391 ng/m^3 and 92 ng/m^3 [32] but higher than the levels reported for children's exposure in outdoor air in New York 0.45 ng/m^3 [43].

Since the toxicity dose by inhalation of PAHs is cumulative over time, the BaPeq estimate by all indication could be considered worrisome in the three locations, thus sounding an alarm bell to local stakeholders' to consider intervention programmes aimed at reducing the risk associated with exposure to biomass fuels especially in the kitchen. The indicator species (PM$_{2.5}$) has been widely implicated to different health endpoints ranging from lung cancer, cardiovascular diseases, respiratory diseases etc. in a recent review on the health effects of wood smoke [44]. The chemical composition of PAHs on PM$_{2.5}$ could explain the carcinogenic activity of this size fraction [45,46], and a greater part of the anthropogenic combustion related PAHs are responsible for the known hazardous hydrocarbons [47]. Chronic daily exposure to carcinogenic PAHs could impact several disease conditions as previously explained [23], given that samples were collected in the breathing zone.

This study supports the growing body of evidence that rural areas of developing countries where biomass fuels are burnt continues to be an important source of airborne PAHs. Therefore, in an effort to mitigate the exposure problems related to biomass fuels particularly in the kitchen, deeper thought should now be taken. The key to this should include promoting the use of improved stoves with chimneys and provide adequate ventilation in kitchens in rural Sierra Leone given the overwhelming evidence of reduced emission of indoor air pollutants. Such approach is against the backdrop that the transition to cleaner fuels is not quite feasible in the near future in rural environments in Sierra Leone. Yet, improved stoves with chimney would offer the diversion of smoke emitted from the kitchen to outdoor or community environment, a measure that would not achieve risk tradeoff between the two environments. Such action would be seen as a step to reduce the high exposure levels in the kitchen. Additionally, since charcoal emits less amount of smoke (less PAH emission), even though the levels emitted in this study are considered unsafe for humans, efforts should be made to improve the efficiency and heating conditions of the existing charcoal stove. Measures should include improving the stove design and the conditions often used to produce charcoal. Therefore, charcoal production facilities should be localized in areas where measures are taken to increase the burning efficiency and not entirely left in the hands of ordinary men or women whose methods of charcoal production continue to emit significant levels of indoor air pollutants. This action would improve combustion characteristics thereby reducing air pollution exposure. We should point out that the benefit to upgrading the current quality of charcoal does not take into consideration the wider implication of managing the forest ecosystem.

Conclusion

This study characterized PM$_{2.5}$ PAHs in the kitchen, outdoor and living room in households that burn wood and charcoal. PAH concentrations decrease in the order; kitchen to outdoor to the living room in households that use either wood or charcoal. A mixture of medium molecular weight PAHs (PYR and FLT) and higher molecular weight PAHs (BaP and DBA) were dominant in kitchens burning wood. Higher molecular weight PAHs (DBA, BgP, BaP and BbF) were dominant in kitchens burning charcoal. Though PAH profile slightly differs in the kitchen, they appeared to be similar in outdoor and living room in households using wood and charcoal fuels. The I/O ratio for Σ_{11}PAHs showed higher variability for households using charcoal relative to those using wood. The BaP equivalency results revealed high a potential health risk in the kitchen than outdoor and living rooms, respectively. The DBA played an important role in the total carcinogenic potential of PAHs. This study has re-echoed the widely held view that kitchens of developing countries remain a hazardous environment as long as people continue to use biomass fuels.

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