

Polycyclic Aromatic Hydrocarbon Gaseous Emissions from Household Cooking Devices: A Kenyan Case Study

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Abstract: In developing countries, household energy use is highly variable and complex, yet emissions arising from fuel combustion indoors are typically poorly quantified. Polycyclic aromatic hydrocarbons (PAHs) are emitted during the combustion of organic fuels such as charcoal and biomass. In the present study, multichannel polydimethylsiloxane rubber traps were used for gas-phase PAH sampling and extracted using a low-solvent volume plunger-assisted solvent extraction method. Sixteen US Environmental Protection Agency priority PAHs, primarily in the gas phase, were investigated in indoor air of rural and urban residential homes in coastal Kenya (Mombasa and Taita Taveta Counties) using typical combustion devices of each area. Average gaseous PAH concentrations per household were higher in rural (ranging 0.81–6.09 $\mu\text{g m}^{-3}$) compared to urban (ranging 0–2.59 $\mu\text{g m}^{-3}$) homes, although ambient PAH concentrations were higher in urban environments, likely attributable to traffic contributions. The impact of fuel choice and thereby combustion device on PAH emissions was very clear, with the highest concentrations of PAHs quantified from wood-burning emissions from 3-stone stoves (total PAH averages $46.23 \pm 3.24 \mu\text{g m}^{-3}$ [$n = 6$]). Average benzo[a]pyrene equivalent total concentrations were evaluated for the priority PAHs and ranged from not detected to 43.31, 88.38, 309.61, and 453.88 ng m^{-3} for gas, kerosene, jiko, 3-stone, and improved 3-stone stoves, respectively. *Environ Toxicol Chem* 2020;39:538–547. © 2019 SETAC

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INTRODUCTION

It is well into the twenty-first century, yet an estimated 2.8 billion people in countries with developing economies still rely on solid fuels (dung, coal, crop wastes, wood, charcoal, etc.) and traditional stoves for heating and cooking (International Institute for Applied Systems Analysis 2012; Bonjour et al. 2013). According to recent data, 600 million Africans have limited access to electricity or clean cooking energy and still rely on traditional sources of energy to meet their basic energy needs (World Health Organization 2016; Makonese et al. 2018). As a result, most households in developing countries without access to clean energy provisions use inefficient combustion devices and fuels that have high pollutant emissions, hence significantly increasing the disease burden in these communities. According to the national human activity pattern

survey sponsored by the US Environmental Protection Agency (Klepeis et al. 2001), indoor air quality is an important determinant of health globally because humans spend up to 90% of their time indoors. The recent Global Burden of Disease studies have also estimated that exposure to smoke from household air pollution is responsible for approximately 3.5 million premature deaths worldwide and various health issues such as cancer and cardiovascular diseases (Patelarou and Kelly 2014; Health Effects Institute 2018; Suter et al. 2018).

Household combustion sources generate complex organic aerosols which normally require the use of pollution markers that can serve as surrogates for the numerous coemitted but unmeasured pollutant species. One class of combustion products that has seen a global resurgence of interest in the indoor marker and exposure literature is polycyclic aromatic hydrocarbons (PAHs; Riva et al. 2011; Shen G et al. 2013, 2017; Chen et al. 2016). They are a group of semivolatile organic compounds which contain 2 or more fused benzene rings arranged in different configurations. They are formed from pyrolysis or the incomplete combustion of organic materials and are of specific toxicological interest because of their

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potential mutagenicity and carcinogenicity (Boström et al. 2002; Umbuzeiro et al. 2008). Combustion of fuels of all types, including wood, charcoal, coke, gas, and diesel, is the major anthropogenic activity that produces PAHs, whereas volcanic eruptions and forest fires are the primary natural sources. Total global emissions of the 16 US Environmental Protection Agency priority PAHs (Σ PAH16) were estimated at 504 Gg in 2007, of which more than half (~60%) was ascribed to residential solid fuel combustion (Shen H et al. 2013). Thus, PAHs have remained among the toxic organic pollutants of most concern; and in certain industrialized countries, residential wood combustion is still a major source of PAH emissions. For example, in Finland, Chile, and the United States, Σ PAH16 values from residential wood combustion are 78, 72, and 46% of the national PAH emission totals, respectively (Shen H et al. 2013; Shen et al. 2017). However, recent reviews on the current status of atmospheric PAHs in Africa have indicated that there are few data on the measurement of these organic compounds and their associated health outcomes (Kalisa et al. 2019; Munyeza et al. 2019).

In Kenya, approximately 85% of households still use solid fuels, mainly wood, which is utilized in very poorly ventilated conditions (Lisouza et al. 2011; Rahnama et al. 2017). Several field-testing surveys based on the general performance and usability of biomass cook stoves have been documented in Kenya (Adkins et al. 2010; Pilishvili et al. 2016; Lozier et al. 2016; Tigabu 2017). However, only a few studies in the country have focused on the quantification of PAHs indoors which are attributable to residential biomass burning (Gachanja and Worsfold 1993; Lisouza et al. 2011). Improvements in sampling methods and extraction techniques are still needed to allow for the widespread environmental monitoring of PAHs in air. Denuders are portable sampling devices which have been successfully employed in several atmospheric partitioning studies (Forbes et al. 2012; Forbes and Rohwer 2015). They consist of 2 multichannel polydimethylsiloxane (PDMS) rubber traps in series separated by a quartz fiber filter, where the PDMS serves as an absorbent for gaseous PAHs and the filter collects particle-phase analytes. The PDMS traps employed in the present study have been used in numerous applications such as sugar cane-burning emissions, tunnel air pollution studies, household fire emissions, and underground mining environments (Forbes et al. 2013; Geldenhuys et al. 2015).

The characteristics of indoor PAH pollution in African developing countries such as Kenya are significantly different from those in developed countries because of the traditional cooking methods employed. In addition, Kenya Vision 2030 has identified fuel as one of the infrastructural enablers of its social economic pillar, stating that the availability of sustainable, affordable, and reliable fuels for all citizens is a key factor in the realization of the national development blueprint (Rambo 2013). In this light, more baseline studies on levels of PAHs in both rural and urban Kenya households using different fuel types and cook stoves are needed to better understand exposure levels and to quantify future improvements. Gachanja and Worsfold (1993) analyzed particulate-bound and gaseous PAHs from 2 charcoal stoves generally used in the Kenyan highlands (ceramic-lined

and traditional metal) and concluded that the ceramic stove produced notably lower PAH emissions than the traditional stove. In a related study, Lisouza et al. (2011) characterized and quantified PAH emissions in soot samples collected from traditional thatched rural households of the Western Province of Kenya. Although variance in PAH levels among houses using different biomass fuels such as cow dung, crop residues, or firewood was reported by the authors, there was no comparison of gas-phase PAH concentrations in the breathing zone of urban and rural kitchens based on combustion devices. In addition, levels in ambient air surrounding rural and urban households were not reported in these 2 previous Kenyan studies.

The main objective of the present study was thus to characterize and quantify indoor PAH levels in rural and urban households during the burning of wood, charcoal, kerosene, and liquefied petroleum gas as energy sources for different cook stoves. The application of multichannel PDMS rubber traps for gas-phase PAH sampling with subsequent plunger-assisted solvent extraction (PASE) and gas chromatography-mass spectrometry (GC-MS) analysis is employed for the first time for household combustion emissions in Kenya. Possible influencing factors for PAH levels in indoor environments such as type of dwelling, ventilation, geographical location, fuel used, and type of combustion device used were also explored. The human health risk associated with exposure to PAHs emitted in indoor household environments was assessed by the relative carcinogenic contribution of each individual PAH, calculated using toxic equivalence factors (TEFs). Data from the present study will provide a platform for improved household energy systems to mitigate harmful emissions and thereby reap significant co-benefits, ranging from household-level (such as indoor air quality, health, time savings) to regional (including economic, outdoor air quality) and even global (such as climate change) scales.

MATERIALS AND METHODS

Area of study

Following a survey-based case study on household energy use in various regions of Kenya, a sampling campaign was conducted in the country's coastal region. Two counties in coastal Kenya (Mombasa and Taita Taveta) were identified, each comprising an urban (Voi and Mombasa) and a rural (Taita and Kilifi) area, providing a total of 4 regions (Supplemental Data, Figure S1). In the choice of sampling sites, variability in settlement areas which would lead to different energy consumption behaviors was considered. In urban areas, the choice of sampling sites was based on the level of income, covering both middle- and low-level income earners.

Sampling

Sampling took place during the month of October 2018, and indoor air was monitored at the fuel combustion sites. Samples were taken from 3 households in each of the selected regions, giving a total of 12 sampled households, as detailed in Table 1. Sampling questionnaires were administered at all sampled households.

TABLE 1: Summary of sampling details including location, sampling position, type of fuel, combustion device, and type of dwelling

Sampling location	Sample abbreviation	Type of dwelling ^a	Type of fuel	Combustion device	Sampling position (m)	
					Distance from device	Sampling height
Taita Taveta rural (TTR)						
Household 1	TTR-H1	Brick house	Cyprus firewood	Improved 3-stone	0.24	0.54
Household 2	TTR-H2	Mud house	Wattle, gravellia	3-stone	0.34	0.58
Household 3	TTR-H3	Brick house	Sawdust	Improved 3-stone	0.20	0.51
Taita Taveta urban (TTU)						
Household 1	TTU-H1	Brick house	LPG	Gas stove	0.40	0.86
Household 2	TTU-H2	Brick house	Charcoal	Jiko	0.36	0.45
Household 3	TTU-H3	Brick house	Kerosene	Kerosene stove	0.30	0.46
Mombasa urban (MU)						
Household 1	MU-H1	Brick house	LPG	Gas stove	0.44	1.28
Household 2	MU-H2	Brick house	Charcoal	Jiko	0.22	0.32
Household 3	MU-H3	Brick house	Kerosene	Kerosene stove	0.13	0.43
Kilifi rural (KR)						
Household 1	KR-H1	Outdoor gazebo	Baobab husks	3-stone	0.36	0.32
Household 2	KR-H2	Mud house	Coconut wood	3-stone	0.40	0.51
Household 3	KR-H3	Mud house	Cashew nut tree	3-stone	0.24	0.45

^aMud houses had grass or leaf roofs, whereas brick houses had tiled roofs.
LPG = liquefied petroleum gas.

A PDMS trap coupled to a portable GilAir Plus sampling pump was used to sample combustion emissions using a flow rate of 500 mL min⁻¹ for 10 min. Duplicate samples were taken in every second household in each region. Sampling position, type of fuel, combustion device, and type of dwelling were recorded as summarized in Table 1, with examples shown in Figure 1. Indoor temperatures were measured using a Kestrel 4500 portable weather station. In all charcoal and firewood combustion cases, the sampler location was in the stream of effluent gases. Ambient gas-phase samples and field blanks were also collected in each region. After sampling, traps were sealed with end-caps and wrapped in aluminum foil. Samples and field blanks were then refrigerated (−18 °C) prior to analysis.

Extraction of PAHs

The chemicals and reagents used in the present study are detailed in the Supplemental Data. Sample extraction was based on a PASE method previously developed (Munyeza et al. 2018). In brief, the samples were taken out of the freezer and thawed to room temperature. A 1-μL volume of a 100 ng μL⁻¹ deuterated internal standard mixture was spiked onto the samples before extraction. The traps were plunged 10 times with 1 mL of hexane twice in sequence (thus using a total volume of 2 mL). The extracts were blown down to near dryness under nitrogen, followed by reconstitution of samples in 100 μL of hexane. The amber vials were sealed and refrigerated (−18 °C) until further analysis by GC-MS (refer to the Supplemental Data for the detailed GC-MS procedure).

Characterization and quantification of PAHs

The analysis of gas-phase samples was based on the method previously developed (Munyeza et al. 2018) as described in the

Supplemental Data. The PAHs were identified using retention times, verified by GC (Agilent 6890) connected to an MS (Agilent 5975C) and quantified from peak area responses using the internal standard method. Seven-point matrix-matched analytical curves (concentrations 0.05–1.5 ng μL⁻¹) were used for the quantification of PAHs, where the target PAH analyte peak area ratio to that of the internal standard versus the amount of analyte in nanograms was employed. The internal standard mixture was spiked onto all traps prior to extraction. Losses of PAHs during sample concentration were investigated by analyzing 1 ng μL⁻¹ pure PAH mix standards before and after nitrogen blowdown and reconstitution in n-hexane. Analyte to internal standard ratios between pure standards injected before and after concentration were compared. A 2-tailed *t* test was used to determine the significance of PAH losses in the evaporated samples based on these ratios, and it was concluded that losses were not significant at the 95% confidence interval (*p* > 0.05). Although the relative standard deviations (RSDs) were highest for 2- and 3-ringed PAHs (ranging from 0.2% for acenaphthylene to 19.4% for acenaphthene), no significant losses of PAHs, regardless of their boiling points, were found. This was consistent with a previous study which investigated PAH losses when using nitrogen for sample blowdown (Chang et al. 2001). In addition, vaporization of lighter PAHs was not problematic because an internal standard mixture was added before extraction and concentration, therefore compensating for any losses. Matrix-matched calibration point samples were also blown down to near dryness using pure nitrogen and reconstituted in 100 μL hexane. This step was performed to match the field sample extraction and to correct for the optimized and acceptable recoveries (ranging 76–99%). The limit of detection (LOD) and limit of quantification (LOQ) for each target compound was calculated as 3 times and 10 times the S/N ratio, respectively.



FIGURE 1: Typical sampling images of different combustion sources in selected household kitchens using (A) a 3-stone stove, (B) a charcoal stove (Jiko), (C) a gas stove, and (D) a kerosene stove.

Statistical analysis

Significance *t* tests were carried out by descriptive statistics using Microsoft Excel, and principal component analysis (PCA) was performed using JMP[®] Pro 14, a statistical software package from SAS Institute.

RESULTS AND DISCUSSION

PAH quantitation

The internal standard method of quantification was employed, and determination coefficients (R^2) for all analytes were >0.912 (Supplemental Data, Table S1). Based on a sampled volume of 5 L, LODs and LOQs were also determined and are given in Supplemental Data, Table S2. The PASE procedure was applied to the analysis of various sets of samples obtained from indoor combustion activities, and typical extracted sample chromatograms are shown in Supplemental Data, Figure S2. Alkanes such as docosane, octadecane, tricosane, and eicosane were also tentatively identified in field samples from the Taita Taveta rural area, as shown in Supplemental Data, Figure S2. However, these analytes were not quantified. No target compounds were detected in any of the field blank samples, which were similarly extracted. No carryover was observed in the analytical and solvent blanks.

Fourteen PAHs out of the initial target 17 PAHs were identified in field samples. The concentrations of gas-phase PAHs found in the traps are presented in Supplemental Data,

Table S3. Gas-phase indoor concentrations were high and varied widely, ranging from 0.12 to 25.92 $\mu\text{g m}^{-3}$. Similar elevated gas-phase concentration ranges, with naphthalene being the most abundant analyte, have been reported in Burundi (Viau et al. 2000) and Japanese kitchens (Ohura et al. 2004). Low-molecular weight PAHs are predominant in the gaseous phase and are known to be less toxic to humans, whereas high-molecular weight PAHs tend to be found in the particulate phase because of their low vapor pressures and are more carcinogenic and/or mutagenic (Dat and Chang 2017). Although considered less toxic, low-molecular weight PAHs exist in higher concentrations and can react with other pollutants such as O_3 and NO_x to form highly toxic nitrated and oxy-PAH compounds and are therefore of importance in risk assessments.

In general, the PAH composition profiles (Figure 2; Supplemental Data, Figure S3) for all of the households showed that lighter PAHs (naphthalene–anthracene) contributed to approximately 85% of gas-phase PAH emissions, which is similar to other biomass combustion profiles in previous studies (Zou et al. 2003; Shen et al. 2011). It has also been reported in the literature that the fraction of PAHs in the vapor phase increases with temperature (Hellén et al. 2017), and in this investigation, indoor temperatures averaged 31 °C (ranging 25–33 °C). Relative humidity values were highly variable because higher values ranging from 71.5 to 93.2% were reported in Mombasa compared to Taita Taveta County, where values ranged from 11.0 to 53.0%. Two specific households in

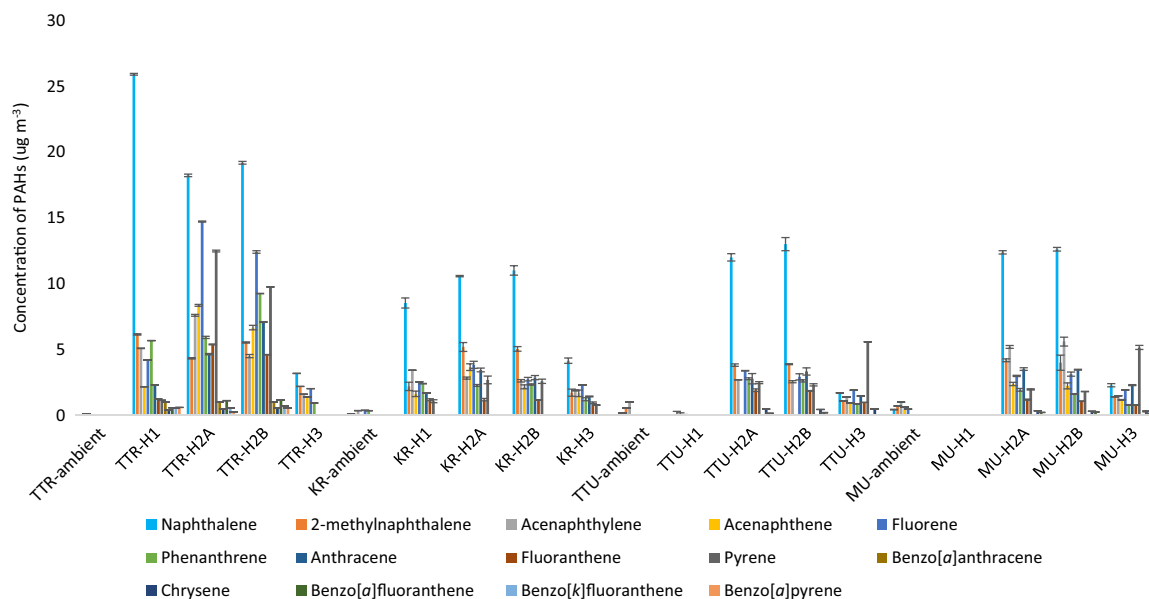


FIGURE 2: Gas-phase polycyclic aromatic hydrocarbon (PAH) concentrations in 12 selected households and ambient backgrounds in urban and rural areas. Error bars show \pm standard deviation, $n = 2$. KR = Kilifi rural; MU = Mombasa urban; TTR = Taita Taveta rural; TTU = Taita Taveta urban.

Taita Taveta rural, TTR-H1 and TTR-H2, exhibited the highest average gaseous-phase PAH concentrations per kitchen, ranging from 4.08 to $6.09 \mu\text{g m}^{-3}$. Duplicate trap samples in every second household per region were comparable and were not statistically significantly different at the 95% confidence interval. However, Taita Taveta rural duplicate samples showed higher trap-to-trap variation, as indicated by the higher %RSDs for specific analytes such as acenaphthylene and benzo[a]pyrene (BaP; Supplemental Data, Table S4). Influencing factors which could have caused marked variations are discussed in the following sections (see *Variation in levels of PAHs with combustion device employed* and *Distribution of PAHs in rural and urban households*). In addition, BaP was only detected in these 2 household samples and ranged from 0.26 to $0.60 \mu\text{g m}^{-3}$. A similar range of 0.24 to $0.97 \mu\text{g m}^{-3}$ for BaP concentration in suspended particulate matter has been reported by Kandpal et al. (1995) during burning of dung cake, wood, coal, and charcoal in India. Higher BaP concentrations of $1.86 \mu\text{g m}^{-3}$ were also reported in the breathing zone of Indian homes in winter, and this observed dissimilarity could be a result of differences in sampling technique or longer sampling times (1 h; Bhargava et al. 2004).

Variation in levels of PAHs with combustion device employed

Because emission performance often varies dramatically with fuel type and stove design, previous studies have recommended evaluation of various PAH concentrations based on the fuel–stove combination (Shen G et al. 2013). This is because dirty fuels may burn relatively clean in improved-efficiency stoves and, conversely, clean fuels may also produce more pollutants under substandard combustion conditions. A number of studies have investigated and compared emissions

from wood combustion based on different stoves or heating appliances in laboratory-controlled conditions (Orasche et al. 2012, 2013). A variety of fuel and cook stove combinations which were investigated in the present study are summarized in Table 1. Cook stoves are commonly called “improved” if they are more efficient, visually emit less emissions, or are safer than the traditional cook stoves or 3-stone fires. In the present study, an improved 3-stone cook stove refers to a built-in or constructed structure in which firewood is placed (see Supplemental Data, Figure S4). Generally, traditional wood stoves are expected to produce higher emissions because of their underventilated conditions.

As illustrated in Supplemental Data, Figure S5, wood combustion in the traditional and improved 3-stone stoves contributed to the highest (35 and 26%) PAH concentrations, followed by charcoal burning using the jiko stove (26%). Kerosene burning produced relatively lower (13%) PAH emissions compared to the traditional combustion devices, and gas stoves produced no quantifiable PAH emissions. A similar pattern was observed in the PAH concentration profiles of wood, charcoal, kerosene, and gas stoves in rural homes of Tanzania (Titcombe and Simcik 2011). For the liquefied petroleum gas cook stove, PAH concentrations were all below method detection limits except for naphthalene, 2-methylnaphthalene (2-mNap), and acenaphthylene, which were detected but lower than the quantification limits. Consequently, total PAH concentrations for the liquefied petroleum gas stove in the present study were considered as not statistically significantly different from zero.

Overall target analyte profiles for each combustion device are illustrated in Figure 3. The profiles revealed that the concentrations of naphthalene that were found in 3-stone and charcoal stoves were approximately 3 orders of magnitude greater than concentrations of other analytes. Although the

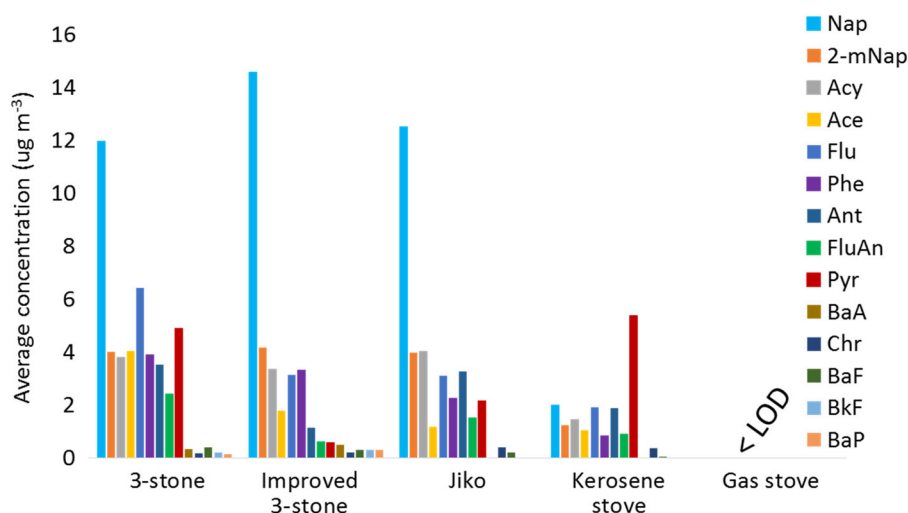


FIGURE 3: Average polycyclic aromatic hydrocarbon concentrations for various combustion devices. Ace = acenaphthene; Acy = acenaphthylene; Ant = anthracene; BaA = benzo[*a*]anthracene; BaF = benzo[*a*]fluoranthene; BaP = benzo[*a*]pyrene; BkF = benzo[*k*]fluoranthene; Chr = chrysene; Flu = fluorene; FluAn = fluoranthene; LOD = limit of detection; 2-mNap = 2-methylnaphthalene; Nap = naphthalene; Phe = phenanthrene; Pyr = pyrene.

3-stone profile had higher naphthalene, fluorene, and pyrene concentrations, overall levels of PAHs were similar to charcoal burning using jiko stoves. However, high-molecular weight emissions were lower from the jiko compared to the 3-stone stoves. When the characterization of performance and emissions from charcoal stoves was investigated in a previous study in the United States (Jetter and Kariher 2009), large amounts of smoke were produced during a cold start compared to a hot start. For this reason, these devices are typically ignited outdoors and are taken inside only when the charcoal is hot and stops smoking. In the present study, the jiko was started on the veranda or with open doors to avoid too much smoke. Traditional earth kilns with low wood-to-charcoal conversion efficiencies of 8 to 20% are mostly employed by charcoal producers in sub-Saharan Africa, meaning that large quantities of wood are used per unit of charcoal produced (Lambe et al. 2015). This inefficient production of charcoal could also be the reason for the relatively higher PAH emissions reported from the jiko combustion devices in the present study.

The improved 3-stone cook stove did not demonstrate a significant advantage over the traditional 3-stone because gas-phase analytes were still present at high concentrations, which was likely attributable to the types and quality of fuels which were used. A 2-tailed *t* test confirmed that levels of PAHs from these 2 combustion devices were not significantly different at the 95% confidence interval ($p > 0.05$). Although high concentrations were quantified from improved 3-stone cook stoves, a marked decrease in the emission of the heavier 4- to 5-ring PAHs was observed with these devices, which is promising because heavier PAHs are known to be more toxic (see Supplemental Data, Figure S6). For example, when the woman tending the fire was interviewed, it was reported that the cypress firewood which was used in household TTR-H1 (for improved 3-stone) was not dry, resulting in poor combustion and leading to high PAH concentrations and choking smoke in

the kitchen. However, when dry sawdust was used with another improved 3-stone stove in TTR-H3, lower PAH emissions were found compared to those in TTR-H1. These findings are consistent with those of a previous study, which showed that, apart from type of combustion device, particle concentration of smoke and associated PAH concentration also depend on the wood moisture content and burning period involved (Chomanee et al. 2009). In addition to the type of fuel influencing the evaluation of cook stoves, differences in ventilation sources could have contributed to PAH variation because most rural households had no chimneys but a small door and a window (see pictures in Supplemental Data, Figure S7).

Although kerosene is normally associated with alternative cleaner cooking energies in urban areas, our data showed that kerosene cook stoves still result in pronounced household pollution. This could have been caused by the kerosene grade (quality) or the old-fashioned kerosene stoves, which are inefficient. As illustrated in Figure 3, PAHs from the kerosene stoves were generally present at lower concentrations, $< 2.00 \mu\text{g m}^{-3}$, for all analytes except for pyrene. The dominance of pyrene from kerosene combustion was also reported in a previous study, which suggested that PAH emissions from kerosene could be reduced by switching to biokerosene (Andrade-Eiroa et al. 2010). A growing body of evidence suggests that kerosene use in households may pose greater risk than previously assumed because many of the traditional kerosene cooking devices are still inefficient (Lam et al. 2012; Lam 2014; Shen et al. 2017). Biomonitoring studies of PAH exposure in women using kerosene stoves showed that kerosene smoke is potentially more toxic than biomass smoke (Adetona et al. 2013; Alexander et al. 2017). In the present study, when subjects were interviewed on the negative aspects of kerosene, they complained about the choking smell of kerosene smoke and subsequent headaches. This could be attributable to the fact that kerosene is a similar petroleum distillate to diesel

(Miele and Checkley 2017), which might also explain the elevated pyrene concentrations in the present study.

Distribution of PAHs in rural and urban households

Efforts to characterize differences between urban and rural atmospheric PAH pollution in Africa have largely been hindered by a paucity of sampling data. As illustrated in Figure 4A, PAHs showed a strong rural to urban gradient, with maximum concentration in rural homes. Although Kilifi rural homes were more ventilated, with some households cooking outdoors on open fires, most rural kitchens had poor ventilation in general. Rural Kilifi kitchens had poorly structured roofing made from coconut palm fronds, and thus the roofs had many holes and were well ventilated. In addition, they had openings in the walls which served as windows (see Supplemental Data, Figure S8). Lack of properly designed and installed chimneys or exhaust was evident in Taita Taveta rural households, yet urban kitchens were typically more ventilated (see Supplemental Data, Figures S7 and S8). This coupled with the low-efficiency cook stoves and a large amount of firewood used could have attributed to the higher concentrations in rural compared to urban homes. In addition, the detection of naphthalene, fluorene, phenanthrene, and acenaphthene as main PAHs from wood combustion is clearly seen as values doubled from urban to rural households. Elevated PAH levels were also found in rural homes of Burundi (average of $43 \mu\text{g m}^{-3}$ for 12 PAHs; Viau et al. 2000), Vietnam (total of $957 \mu\text{g m}^{-3}$ for 18 Σ PAHs; Kim Oanh et al. 1999), and Thailand (total of $366 \mu\text{g m}^{-3}$ for 17 Σ PAHs) when firewood, sawdust briquettes, or kerosene were used in domestic cook stoves. However, lower total concentrations, in the nanograms per cubic meter range, have been reported in other African indoor environments (Munyeza

et al. 2019), for instance, in Sierra Leone, where total concentrations ranged from 1.38 to 4282 ng m^{-3} , which could have been a result of only the particle phase being measured.

With regard to ambient variations, the pattern illustrated in Figure 4B suggests that the general outdoor air quality with respect to gas-phase PAHs was better in rural areas. The highest ambient PAH concentrations were reported in Mombasa urban area, which is a result of traffic in the area because Mombasa is known as a busy port city. In addition, there is higher population density in urban areas compared to rural areas, where homes are more widely spread out, resulting in greater dilution of pollutants from household activities. The choice of combustion device used in urban and rural areas was based on the cost of the device; its availability, energy requirements, and fuel consumption rates; as well as cultural issues. Three-stone and improved 3-stone devices were only used in rural areas; and based on the questionnaire results, these were preferred because they are cheap and easily available. Subjects in rural areas also gave cultural reasons for using the 3-stone devices, mentioning that they were inherited from their parents and that it makes local foods such as *ugali* taste better. Kerosene, liquefied petroleum gas, and charcoal stoves were mainly distributed in urban areas because they are easily available, easier to use, and more affordable for urban residents compared to those in rural areas.

Toxicity assessment of gaseous PAHs

Investigation of PAH concentrations indoors can be considered incomplete if the carcinogenic potency of individual PAHs is not assessed. To evaluate the human health risk connected with exposure to PAHs emitted at each sampling site, the relative carcinogenic contribution of each individual PAH based on BaP (BaP equivalent [BaP_{eq}]) was calculated for the indoor

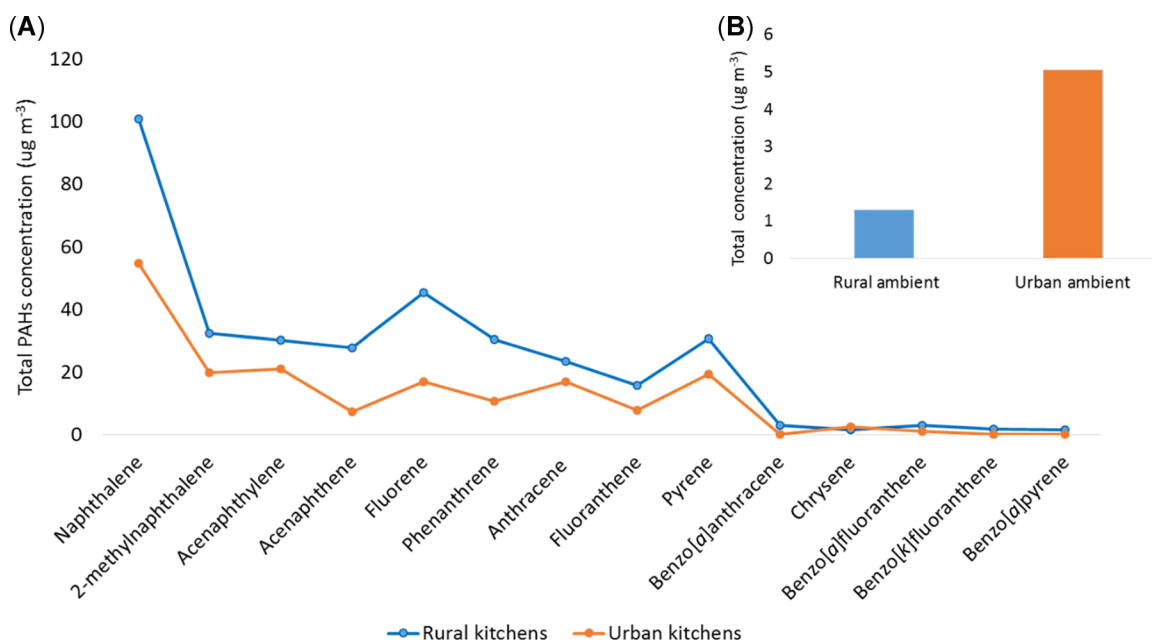


FIGURE 4: Comparison of total polycyclic aromatic hydrocarbon (PAH) concentrations in (A) rural and urban kitchens ($n = 12$), and (B) rural and urban ambient environments.

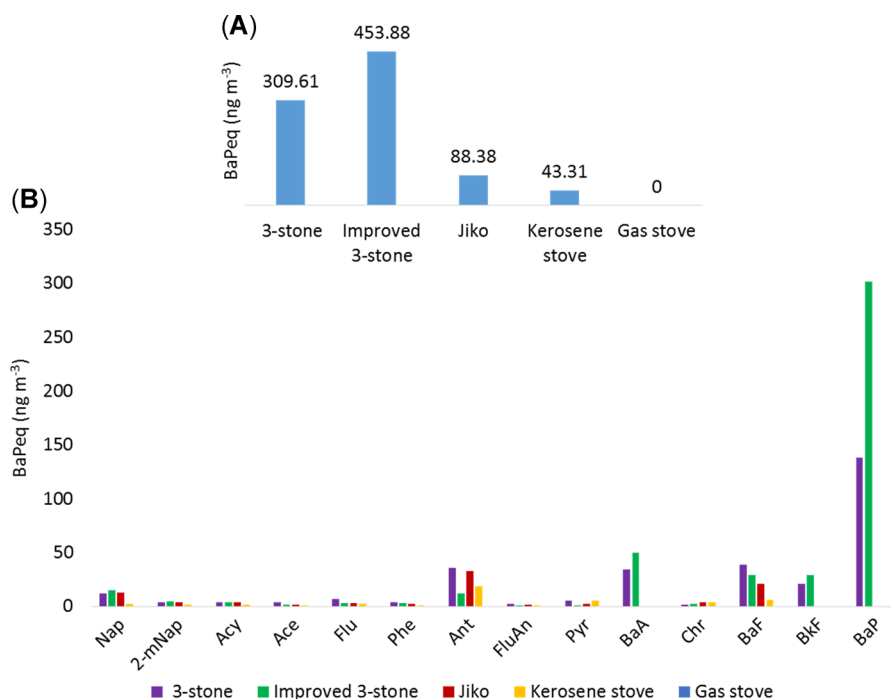


FIGURE 5: Comparison of benzo[a]pyrene equivalent (BaPeq) total concentrations. (A) Total average BaPeq concentrations from different combustion devices, and (B) the relative toxicity contribution of each individual polycyclic aromatic hydrocarbon. Ace = acenaphthene; Acy = acenaphthylene; Ant = anthracene; BaA = benzo[a]anthracene; BaF = benzo[a]fluoranthene; BkF = benzo[k]fluoranthene; Chr = chrysene; Flu = fluorene; FluAn = fluoranthene; 2-mNap = 2-methylnaphthalene; Nap = naphthalene; Phe = phenanthrene; Pyr = pyrene.

PAH concentrations using TEFs proposed by Nisbet and LaGoy (1992). Based on the proposed TEF values, BaPeq or toxic equivalence quotient values for each household are shown in Supplemental Data, Figure S9. The TEF values were applied to the different combustion devices used in the present study, and the relative toxicity contribution of each individual PAH in the PAH profile is given in Figure 5. The BaPeq total concentrations which were examined for the priority PAHs were 0 (not detected), 43.31, 88.38, 309.61, and 453.88 ng m⁻³ for gas, kerosene, jiko, 3-stone, and improved 3-stone stoves, respectively. A similar trend was observed in Tanzania, where BaPeq total concentrations of 0 for liquefied petroleum gas, 8 ng m⁻³ for kerosene/charcoal mix, 44 ng m⁻³ for charcoal, and 767 ng m⁻³ for open wood fire were obtained (Titcombe and Simcik 2011). Although low-molecular weight PAHs like naphthalene, 2-mNap, acenaphthylene, and acenaphthene mostly contributed to total indoor PAH concentrations, total BaPeq values were mainly influenced by the heavier benzo[a]anthracene (BaA), benzo[a]fluoranthene (BaF), benzo[k]fluoranthene (BkF), and BaP (Figure 5B), attributable to their higher TEFs.

PCA

We performed PCA on the results given in Supplemental Data, Table S3, using mean centered data and correlation-based variance. Although PCA is often used for modeling purposes, in the present study it was strictly used to identify potential differences between our samples; PCA plots were used to visualize the interdependence between data sets, and 2 different plots were

employed, namely score plots (Supplemental Data, Figure S10a) and loading plots (Supplemental Data, Figure S10b). It was observed that the first principal component accounted for 61.1% of the explained variance between samples, whereas the second principle component accounted for 30.1%. The scores plot illustrated that good grouping of samples was only observed with respect to ambient (orange ellipsoid, samples 1, 6, 11, and 16) and liquefied petroleum gas (green ellipsoid, samples 12 and 17) combustion samples. A biplot (Supplemental Data, Figure S11) was used to further illustrate that the increased concentrations of BaA accounted for the variation of samples MU-H2A (18) and MU-H2B (19). As mentioned previously (*PAH quantitation*), it was also observed that the samples from the first 2 houses in Taita Taveta rural area (TTR-H1 and TTR-H2A + TTR-H2B) were very different from all of the other samples. The rest of the combustion devices and sampling sites did not show any substantial grouping patterns because they were irregularly distributed on the plot. The loading plot clearly illustrated the PAHs which were responsible for the intersample variations. The loading plot illustrated that the increased concentrations of naphthalene, 2m-Nap, phenanthrene, acenaphthene, anthracene, fluoranthene, and BaF accounted for the variation of TTR-H1 and TTR-H2A + TTR-H2B.

CONCLUSIONS AND RECOMMENDATIONS

For rural communities, the present study has shown that the use of wood-burning 3-stone combustion devices exposes people indoors to the highest number of carcinogenic gaseous PAHs (total average of 46.23 $\mu\text{g m}^{-3}$). Exposure to PAHs could

cause great health risks, especially for poorly ventilated households. Charcoal combustion using jiko stoves contributed to the highest PAH emissions in urban areas, although lower amounts of high-molecular weight compounds were quantified. Kerosene stoves showed an approximately 50% reduction in PAH emissions compared to jiko, 3-stone, and improved 3-stone stoves. No PAHs were detected from the gas stoves, which shows that liquefied petroleum gas combustion for cooking purposes is a step in the right direction toward use of clean fuel for the near elimination of household PAH pollution. The present results suggest that the use of clean energy sources in combination with more efficient combustion devices could reduce global PAH emissions from the residential sector.

Although large variations in PAH emissions were observed between households, the main contributor to indoor PAH profiles in the selected 12 households was naphthalene. However, the contribution of naphthalene to BaP_{eq} concentrations was insignificant, and only heavier analytes such as anthracene, BaA, BaF, BkF, and BaP displayed high concentrations that are equivalent to toxic levels. The estimated BaP_{eq} concentrations indicated that people living in traditional houses in rural areas are exposed to high doses of gaseous PAHs from indoor air pollution generated by poorly ventilated burning of wood. While the use of cleaner energy sources such as liquefied petroleum gas and electric stoves is awaited in remote areas, simple measures should be implemented to adequately vent the smoke outside of the houses. This would lower immediate exposure to high concentrations of toxic PAHs indoors. These kitchen ventilation improvements together with household energy transitions can play a significant role in improving human welfare through reductions in the global burden of disease and environmental impacts. Therefore, it is vital to engage the community and educate them on steps they can take toward clean cooking.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.4648.

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Data Availability Statement—Data, associated metadata, and calculation tools are available from the corresponding author (patricia.forbes@up.ac.za).

REFERENCES

Adetona O, Li Z, Sjödin A, Romanoff LC, Aguilar-Villalobos M, Needham LL, Hall DB, Cassidy BE, Naeher LP. 2013. Biomonitoring of polycyclic

- aromatic hydrocarbon exposure in pregnant women in Trujillo, Peru—Comparison of different fuel types used for cooking. *Environ Int* 53:1–8.
- Adkins E, Tyler E, Wang J, Siriri D, Modi V. 2010. Field testing and survey evaluation of household biomass cookstoves in rural sub-Saharan Africa. *Energy Sustain Dev* 14:172–185.
- Alexander D, Northcross A, Wilson N, Dutta A, Pandya R, Ibigbami T, Adu D, Olamijulo J, Morhason-Bello O, Karrison T. 2017. Randomized controlled ethanol cookstove intervention and blood pressure in pregnant Nigerian women. *Am J Respir Crit Care Med* 195:1629–1639.
- Andrade-Eiroa A, Leroy V, Dagaut P, Bedjanian Y. 2010. Determination of polycyclic aromatic hydrocarbons in kerosene and bio-kerosene soot. *Chemosphere* 78:1342–1349.
- Bhargava A, Khanna R, Bhargava S, Kumar S. 2004. Exposure risk to carcinogenic PAHs in indoor-air during biomass combustion whilst cooking in rural India. *Atmos Environ* 38:4761–4767.
- Bonjour S, Adair-Rohani H, Wolf J, Bruce NG, Mehta S, Prüss-Ustün A, Lahiff M, Rehfuess EA, Mishra V, Smith KR. 2013. Solid fuel use for household cooking: Country and regional estimates for 1980–2010. *Environ Health Perspect* 121:784–790.
- Boström CE, 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.
- Chang F-H, Lin T-C, Chao H-R, Chao M-R. 2001. A study on losses of PAHs during sample concentration for chromatographic analysis: Evaporation with a stream of nitrogen. *Int J Environ Anal Chem* 80:13–26.
- Chen Y, Shen G, Huang Y, Zhang Y, Han Y, Wang R, Shen H, Su S, Lin N, Zhu D. 2016. Household air pollution and personal exposure risk of polycyclic aromatic hydrocarbons among rural residents in Shanxi, China. *Indoor Air* 26:246–258.
- Chomanee J, Tekasakul S, Tekasakul P, Furuuchi M, Otani Y. 2009. Effects of moisture content and burning period on concentration of smoke particles and particle-bound polycyclic aromatic hydrocarbons from rubber wood combustion. *Aerosol Air Qual Res* 9:404–411.
- Dat N-D, Chang MB. 2017. Review on characteristics of PAHs in atmosphere, anthropogenic sources and control technologies. *Sci Total Environ* 609:682–693.
- Forbes PB, Karg EW, Geldenhuys G-L, Nsibandé SA, Zimmermann R, Rohwer ER. 2013. Characterisation of atmospheric semi-volatile organic compounds. *Clean Air J* 23:3–6.
- Forbes PB, Karg EW, Zimmermann R, Rohwer ER. 2012. The use of multi-channel silicone rubber traps as denuders for polycyclic aromatic hydrocarbons. *Anal Chim Acta* 730:71–79.
- Forbes PB, Rohwer ER. 2015. Denuders. *Compr Anal Chem* 70:155–181.
- Gachanja A, Worsfold P. 1993. Monitoring of polycyclic aromatic hydrocarbon emissions from biomass combustion in Kenya using liquid chromatography with fluorescence detection. *Sci Total Environ* 138:77–89.
- Geldenhuys G, Rohwer E, Naudé Y, Forbes P. 2015. Monitoring of atmospheric gaseous and particulate polycyclic aromatic hydrocarbons in South African platinum mines utilising portable denuder sampling with analysis by thermal desorption-comprehensive gas chromatography-mass spectrometry. *J Chromatogr A* 1380:17–28.
- Health Effects Institute. 2018. State of global air. [cited 2018 August 7]. Available from: <https://www.stateofglobalair.org/>
- Hellén H, Kangas L, Kousa A, Vestenius M, Teinilä K, Karppinen A, Kukkonen J, Niemi JV. 2017. Evaluation of the impact of wood combustion on benzo[a]pyrene (BaP) concentrations; ambient measurements and dispersion modeling in Helsinki, Finland. *Atmos Chem Phys* 17:3475–3487.
- International Institute for Applied Systems Analysis. 2012. *Global Energy Assessment—Toward a Sustainable Future*. Cambridge University Press, Cambridge, UK.
- Jetter JJ, Karher P. 2009. Solid-fuel household cook stoves: Characterization of performance and emissions. *Biomass Bioenergy* 33:294–305.
- Kalisa E, Archer S, Nagato E, Bizuru E, Lee K, Tang N, Pointing S, Hayakawa K, Lacap-Bugler D. 2019. Chemical and biological components of urban aerosols in Africa: Current status and knowledge gaps. *Int J Environ Res Public Health* 16:941.
- Kandpal J, Maheshwari R, Kandpal TC. 1995. Indoor air pollution from combustion of wood and dung cake and their processed fuels in domestic cookstoves. *Energy Convers Manag* 36:1073–1079.

- Kim Oanh NT, Bætz Reutergårdh L, Dung NT. 1999. Emission of polycyclic aromatic hydrocarbons and particulate matter from domestic combustion of selected fuels. *Environ Sci Technol* 33:2703–2709.
- Klepeis NE, Nelson WC, Ott WR, Robinson JP, Tsang AM, Switzer P, Behar JV, Hern SC, Engelmann WH. 2001. The National Human Activity Pattern Survey (NHAPS): A resource for assessing exposure to environmental pollutants. *J Expo Sci Environ Epidemiol* 11:231–252.
- Lam NL. 2014. Residential use of kerosene in low-and middle-income countries: Pollutant emissions, markers of pollution, drivers and impacts. PhD thesis. University of California, Berkeley, CA, USA.
- Lam NL, Smith KR, Gauthier A, Bates MN. 2012. Kerosene: A review of household uses and their hazards in low- and middle-income countries. *J Toxicol Environ Health B* 15:396–432.
- Lambe F, Jürisoo M, Wanjiu H, Senyagwa J. 2015. Bringing clean, safe, affordable cooking energy to households across Africa: An agenda for action. Stockholm Environment Institute, Stockholm, Sweden.
- Lisouza FA, Owuor OP, Lalah JO. 2011. Variation in indoor levels of polycyclic aromatic hydrocarbons from burning various biomass types in the traditional grass-roofed households in western Kenya. *Environ Pollut* 159:1810–1815.
- Lozier MJ, Sircar K, Christensen B, Pillarisetti A, Pennise D, Bruce N, Stanistreet D, Naeher L, Pilishvili T, Farrar JL. 2016. Use of temperature sensors to determine exclusivity of improved stove use and associated household air pollution reductions in Kenya. *Environ Sci Technol* 50:4564–4571.
- Makonese T, Ifegbesan AP, Rampedi IT. 2018. Household cooking fuel use patterns and determinants across southern Africa: Evidence from the demographic and health survey data. *Energy & Environment* 29:29–48.
- Miele CH, Checkley W. 2017. Clean fuels to reduce household air pollution and improve health. Still hoping to answer why and how. *Am J Respir Crit Care Med* 195:1552–1554.
- Munyeza CF, Dikale O, Rohwer ER, Forbes PB. 2018. Development and optimization of a plunger assisted solvent extraction method for polycyclic aromatic hydrocarbons sampled onto multi-channel silicone rubber traps. *J Chromatogr A* 1555:20–29.
- Munyeza CF, Rohwer ER, Forbes PB. 2019. A review of monitoring of air-borne polycyclic aromatic hydrocarbons: An African perspective. *Trends Environ Anal Chem* 24:e00070.
- Nisbet IC, Lagoy PK. 1992. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul Toxicol Pharmacol* 16:290–300.
- Ohura T, Amagai T, Fusaya M, Matsushita H. 2004. Polycyclic aromatic hydrocarbons in indoor and outdoor environments and factors affecting their concentrations. *Environ Sci Technol* 38:77–83.
- Orasche J, Schnelle-Kreis J, Schön C, Hartmann H, Ruppert H, Arteaga-Salas JM, Zimmermann R. 2013. Comparison of emissions from wood combustion. Part 2: Impact of combustion conditions on emission factors and characteristics of particle-bound organic species and polycyclic aromatic hydrocarbon (PAH)-related toxicological potential. *Energy Fuels* 27:1482–1491.
- Orasche J, Seidel T, Hartmann H, Schnelle-Kreis J, Chow JC, Ruppert H, Zimmermann R. 2012. Comparison of emissions from wood combustion. Part 1: Emission factors and characteristics from different small-scale residential heating appliances considering particulate matter and polycyclic aromatic hydrocarbon (PAH)-related toxicological potential of particle-bound organic species. *Energy Fuels* 26:6695–6704.
- Patelarou E, Kelly FJ. 2014. Indoor exposure and adverse birth outcomes related to fetal growth, miscarriage and prematurity—A systematic review. *Int J Environ Res Public Health* 11:5904–5933.
- Pilishvili T, Loo JD, Schrag S, Stanistreet D, Christensen B, Yip F, Nyagol R, Quick R, Sage M, Bruce N. 2016. Effectiveness of six improved cookstoves in reducing household air pollution and their acceptability in rural western Kenya. *PLoS One* 11:e0165529.
- Rahnema A, Sanchez F, Giordano P. 2017. Alternative cooking fuels in Kenya: How can household decision-making be impacted? Working paper 1177-E. IESE Business School, Barcelona, Spain.
- Rambo CM. 2013. Renewable energy project financing risks in developing countries: Options for Kenya towards the realization of vision 2030. *Int J Bus Financ Manage* 1:1–10.
- Riva G, Pedretti EF, Toscano G, Duca D, Pizzi A. 2011. Determination of polycyclic aromatic hydrocarbons in domestic pellet stove emissions. *Biomass Bioenergy* 35:4261–4267.
- Shen G, Preston W, Ebersviller SM, Williams C, Faircloth JW, Jetter JJ, Hays MD. 2017. Polycyclic aromatic hydrocarbons in fine particulate matter emitted from burning kerosene, liquid petroleum gas, and wood fuels in household cookstoves. *Energy Fuels* 31:3081–3090.
- Shen G, Tao S, Chen Y, Zhang Y, Wei S, Xue M, Wang B, Wang R, Lu Y, Li W. 2013. Emission characteristics for polycyclic aromatic hydrocarbons from solid fuels burned in domestic stoves in rural China. *Environ Sci Technol* 47:14485–14494.
- Shen G, Wang W, Yang Y, Ding J, Xue M, Min Y, Zhu C, Shen H, Li W, Wang B. 2011. Emissions of PAHs from indoor crop residue burning in a typical rural stove: Emission factors, size distributions, and gas-particle partitioning. *Environ Sci Technol* 45:1206–1212.
- Shen H, Huang Y, Wang R, Zhu D, Li W, Shen G, Wang B, Zhang Y, Chen Y, Lu Y. 2013. Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. *Environ Sci Technol* 47:6415–6424.
- Suter MK, Karr CJ, John-Stewart GC, Gómez LA, Moraa H, Nyatika D, Wamalwa D, Paulsen M, Simpson CD, Ghodsian N. 2018. Implications of combined exposure to household air pollution and HIV on neuro-cognition in children. *Int J Environ Res Public Health* 15:163.
- Tigabu A. 2017. Factors associated with sustained use of improved solid fuel cookstoves: A case study from Kenya. *Energy Sustain Dev* 41:81–87.
- Titcombe ME, Simcik M. 2011. Personal and indoor exposure to PM 2.5 and polycyclic aromatic hydrocarbons in the southern highlands of Tanzania: A pilot-scale study. *Environ Monit Assess* 180:461–476.
- Umbuzeiro GA, Franco A, Martins MH, Kummrow F, Carvalho L, Schmeiser HH, Leykauf J, Stiborova M, Claxton LD. 2008. Mutagenicity and DNA adduct formation of PAH, nitro-PAH, and oxy-PAH fractions of atmospheric particulate matter from São Paulo, Brazil. *Mutat Res* 652:72–80.
- Viau C, Hakizimana G, Bouchard M. 2000. Indoor exposure to polycyclic aromatic hydrocarbons and carbon monoxide in traditional houses in Burundi. *Int Arch Occup Environ Health* 73:331–338.
- World Health Organization. 2016. Ambient air pollution: A global assessment of exposure and burden of disease. Geneva, Switzerland.
- Zou LY, Zhang W, Atkison S. 2003. The characterisation of polycyclic aromatic hydrocarbons emissions from burning of different firewood species in Australia. *Environ Pollut* 124:283–289.