

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 this study, multi-channel polydimethylsiloxane (PDMS) rubber traps were used for gas phase PAH sampling and were extracted using a low solvent volume plunger-assisted solvent extraction (PASE) method. 16 U.S. 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 from 0.81 to 6.09 $\mu\text{g m}^{-3}$) compared to urban homes (ranging from 0 to 2.59 $\mu\text{g m}^{-3}$), although ambient PAH concentrations were higher in urban environments, likely due 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 of $46.23 \pm 3.24 \mu\text{g m}^{-3}$ (n=6)). Average benzo[a]pyrene equivalent (BaPeq) 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.

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Polycyclic aromatic hydrocarbon emissions from Kenyan homes

Keywords

PAHs; household air pollution; combustion device; clean energy; PASE; GC-MS

1. Introduction

It is well into the 21st 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 (Bonjour et al., 2013, Assessment, 2012). 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 (Makonese et al., 2018, Organization, 2016). 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 U.S Environmental Protection Agency (EPA) (Klepeis et al., 2001), indoor air quality is an important determinant of health globally since humans spend up to 90% of their time indoors. The recent Global Burden of Disease studies have also estimated that the 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 (Health, 2018, Suter et al., 2018, Patelarou and Kelly, 2014).

Household combustion sources generate complex organic aerosols which normally require the use of pollution markers which can serve as surrogates for the numerous co-emitted, 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) (Chen et al., 2016, Shen et al., 2017, Shen et al., 2013a, Riva et al., 2011). PAHs are a group of semi-volatile organic compounds (SVOCs) which contain two or more fused benzene rings arranged in different configurations. PAHs are formed from pyrolysis or the

incomplete combustion of organic materials and are of specific toxicological interest due to their potential mutagenicity and carcinogenicity (Umbuzeiro et al., 2008, Boström et al., 2002). Combustion of fuels of all types including wood, charcoal, coke, gas and diesel is the major anthropogenic activity that produces PAHs, while volcanic eruptions and forest fires are the primary natural sources. Total global emissions of the 16 U.S. Environmental Protection Agency (EPA) 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 et al., 2013b). PAHs have thus 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 U.S., Σ PAH16 values from residential wood combustion are 78, 72, and 46% of the national PAH emission totals, respectively (Shen et al., 2013b, Shen et al., 2017). However, recent reviews on the current status of atmospheric PAHs in Africa have indicated that there is little 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, Rahnema 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, Tigabu, 2017, Pilishvili et al., 2016, Lozier et al., 2016). 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 two multi-channel polydimethylsiloxane (PDMS) rubber traps in series separated by a quartz fibre filter, where the PDMS serves as an absorbent for gaseous PAHs and the filter collects particle phase analytes. The PDMS traps employed in this study have been used in numerous applications such as sugar cane burning emissions, tunnel air pollution studies, household fire emissions and in underground mining environments (Geldenhuijs et al., 2015, Forbes et al., 2013).

The characteristics of indoor PAH pollution in African developing countries such as Kenya are significantly different from developed countries because of the traditional cooking methods employed. Additionally, the Kenya Vision 2030 has identified fuel as one of the infrastructure enablers of its social economic pillar, stating that sustainable, affordable and reliable fuels for all citizens are a key factor in 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) (Gachanja and Worsfold, 1993) analyzed particulate bound and gaseous PAHs from two charcoal stoves generally used in 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) (Lisouza et al., 2011) characterized and quantified PAH emissions in soot samples collected from traditional thatched rural households of Western Province of Kenya. While variance in PAHs 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. Additionally, ambient air surrounding rural and urban households have not been reported in these two previous Kenyan studies.

The main objective of this study was thus to characterize and quantify indoor PAHs levels in rural and urban households during the burning of wood, charcoal, kerosene and LPG as energy sources for different cook stoves. The application of multi-channel PDMS rubber traps for gas phase PAH sampling with subsequent plunger-assisted solvent extraction (PASE) and GC-MS analysis is employed for the first time for household combustion emissions in Kenya. Possible influencing factors for PAHs 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 this 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.

2. Materials and Methods

2.1 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 of an urban (Voi and Mombasa) and a rural area (Taita and Kilifi), providing a total of four regions (**Fig 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.

2.2 Sampling

Sampling took place during the month of October 2018 and indoor air was monitored at the fuel combustion sites. Samples were taken from three 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.

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 **Fig 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 aluminium foil. Samples and field blanks were then refrigerated ($-18 \text{ }^{\circ}\text{C}$) prior to analysis.

Table 1. Summary of sampling details including location, sampling position, type of fuel, combustion device and type of dwelling.

Sampling location	Sample names abbreviation	*Type of dwelling	Type of fuel	Combustion device	Sampling position (m)	
Taita Taveta Rural (TTR)					Distance from device	Sampling height
Household 1	TTR-H1	Brick house	Cyprus firewood	Improve 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	Improve 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

*Mud houses had grass or leaf roofs whilst brick houses had tiled roofs.



Fig 1. Typical sampling images for different combustion sources in selected household kitchens using a (a) 3-stone stove, (b) charcoal stove (Jiko) (c) gas stove and (d) kerosene stove.

2.3 Extraction of PAHs

The chemicals and reagents used in this study are detailed in the Supplementary Information section. Sample extraction was based on a plunger assisted solvent extraction (PASE) method previously developed (Munyeza et al., 2018). In brief, the samples were taken out of the freezer and thawed to room temperature. A $1 \mu\text{L}$ volume of a $100 \text{ ng } \mu\text{L}^{-1}$ deuterated IS 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 re-constitution of samples in $100 \mu\text{L}$ of hexane. The amber vials were sealed and refrigerated (-18°C) until further analysis by gas chromatography-mass spectrometry (GC-MS) (refer to the Supplementary Information for the detailed GC-MS procedure).

2.4 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 Supplementary Information. PAHs were identified using retention times, verified by gas chromatography (GC, Agilent 6890) connected to a mass spectrometer (MSD, 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 (IS) versus the amount of analyte in ng was employed. The IS mixture was spiked onto all traps prior to extraction. Losses of PAHs during sample concentration were investigated by analyzing 1 ng μL^{-1} pure PAHs mix standards before and after nitrogen blow down and reconstitution in n-hexane. Analyte/IS ratios between pure standards injected before and after concentration were compared. A two-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 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 Acy to 19.4% for Ace), 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). Additionally, vaporization of lighter PAHs was not problematic since an IS 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 re-constituted in 100 μL hexane. This step was performed to match the field sample extraction and to correct for the optimized and acceptable recoveries (ranging from 76% - 99%). The limit of detection (LOD) and limit of quantification (LOQ) for each target compound was calculated as three times the signal to noise (S/N) ratio and as ten times the S/N ratio, respectively.

2.5 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 the SAS[®] Institute Inc. (Cary, North Carolina, USA).

3. Results and discussion

3.1 PAH Quantitation

The internal standard method of quantification was employed and determination coefficients (R^2) for all analytes were above 0.912 (**Table S1**). LODs and LOQs based on a sampled volume of 5 L were also determined and are given in **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 the supplementary information (**Fig S2**). Alkanes such as docosane, octadecane, tricosane, eicosane were also tentatively identified in field samples from the Taita Taveta rural area as shown in **Fig S2**. However, these analytes were not quantified in this study. 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 priority PAHs were identified in field samples. The concentrations of gas-phase PAHs found in the traps are presented in **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 Nap 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 due to 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 (**Fig 2, Fig S3**) for all the households showed that lighter PAHs (Nap - Ant) 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 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 from 25 °C to 33 °C). Relative humidity (RH) values were highly variable, as higher RH values ranging from 71.5% to 93.2% were reported in Mombasa compared to Taita Taveta county where RH values ranged from 11.0% to 53%. Two specific

households in Taita Taveta Rural, TTR-H1 and TTR-H2 exhibited the highest average gaseous phase PAH concentrations per kitchen, ranging from 4.08-6.09 $\mu\text{g m}^{-3}$. Duplicate trap samples in every second household per region were comparable and were not statistically significantly different at 95% confidence interval. However, TTR duplicate samples showed higher trap to trap variation as indicated by the higher %RSDs for specific analytes such as Acy and BaP (**Table S4**). Influencing factors which could have caused marked variations are discussed in sections 3.2 and 3.3. Additionally, BaP was only detected in these two household samples and ranged from 0.26-0.60 $\mu\text{g m}^{-3}$. A similar range of 0.24-0.97 $\mu\text{g m}^{-3}$ for BaP concentration in suspended particulate matter has been reported by Kandpal *et al.* (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).

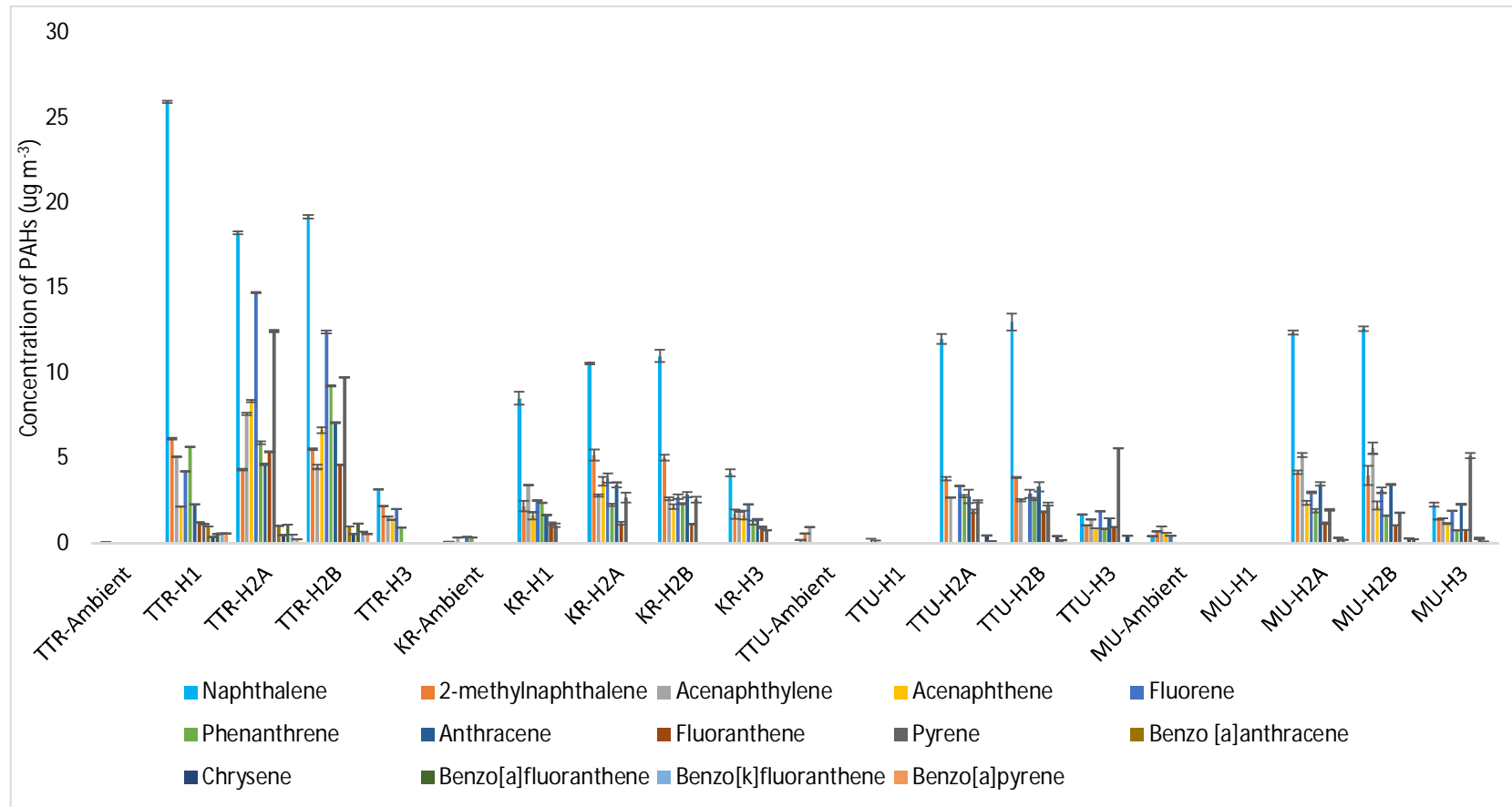


Fig 2 Gas phase PAH concentrations in 12 selected households and ambient backgrounds in urban and rural areas. Error bars show \pm standard deviation, $n=2$.

3.2 Variation in levels of PAHs with combustion device employed

Since 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 et al., 2013a). This is because dirty fuels may burn relatively clean in efficient improved 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, Orasche et al., 2013). A variety of fuel and cook stove combinations which were investigated in this 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 this study, an improved 3-stone cook stove referred to a built-in or constructed structure in which firewood is placed (see **Fig S4**). Generally, traditional wood stoves are expected to produce higher emissions due to under-ventilated conditions.

As illustrated in **Fig S5**, wood combustion in the traditional and improved 3-stone stoves contributed to the highest (35% and 26%) PAH concentration 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 LPG cook stove, PAH concentrations were all below method detection limits except for Nap, 2-mNap and Acy which were detected but were lower than the quantification limits. Consequently, total PAH concentrations for the LPG stove in this study were considered as not statistically significant from zero.

Overall target analyte profiles for each combustion device are illustrated in **Fig 3**. The profiles revealed that the concentrations of Nap that were found in 3-stone and charcoal stoves were approximately three orders of magnitude greater than concentrations of other analytes. Although the 3-stone profile had higher Nap, Flu and Pyr 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. When the characterization of performance and

emissions from charcoal stoves was investigated in a previous study in USA (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 this 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 8–20% are mostly employed by charcoal producers in sub-Saharan Africa, meaning 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 this study.

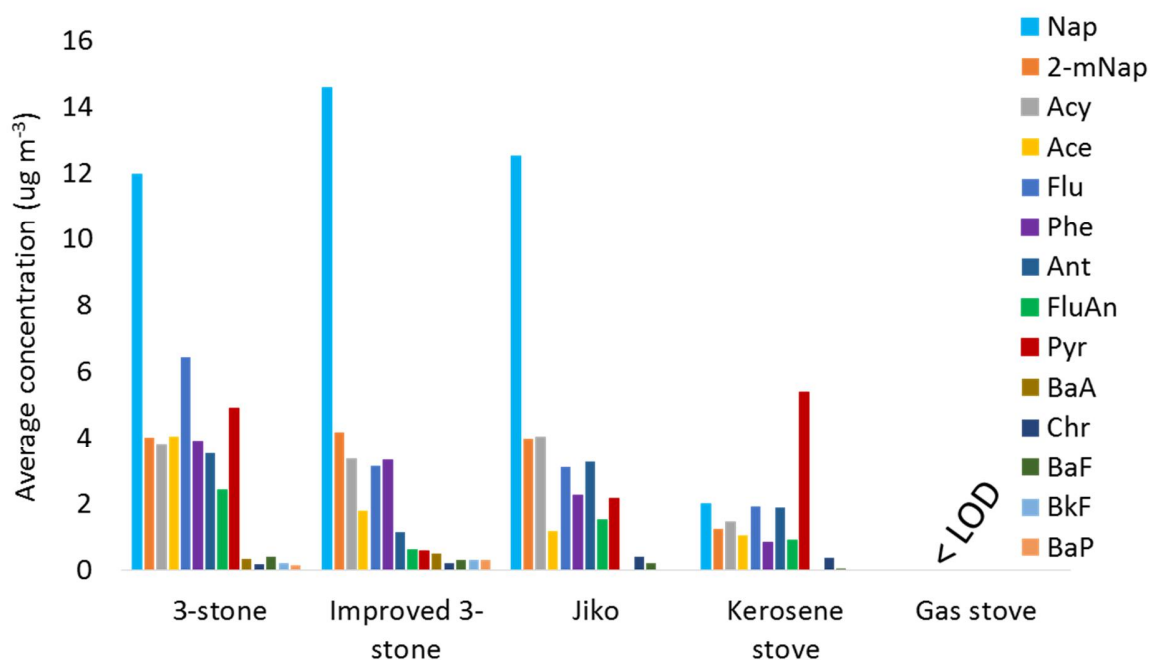


Fig 3 Average PAH concentrations for various combustion devices. Ace = acenaphthene; Acy = acenaphthylene; Ant = anthracene; BaA = benzo[*a*]anthracene; BaF = benzo[*a*]fluoranthene; BaP = benzo[*a*]pyrene; BkF = benzo[*k*]fluoranthene; Chr = chrysene; Flu = fluorene; FluAn = fluoranthene; LOD = limit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

The improved 3-stone cook stove did not demonstrate much significant advantages over the traditional 3-stone since gas-phase analytes were still present at high concentrations, which was

likely due to the types and quality of fuels which were used. A two-tailed t-test confirmed that levels of PAHs from these two combustion devices were not significantly different at 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 4-5 ring PAHs was observed with these devices, which is promising since heavier PAHs are known to be more toxic (see **Fig S6**). For example, when the woman tending the fire was interviewed, it was reported that the cyprus firewood which was used in household TTR-H1 (for improved 3-stone) was not dry, therefore resulting in poor combustion leading to high PAH concentrations and choking smoke in the kitchen. However, when dry sawdust was used with another improved 3-stone in TTR-H3, lower PAH emissions were found compared to those in TTR-H1. These findings are consistent with 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 also contributed to PAH variation since most rural households had no chimneys but a small door and a window (see pictures in **Fig 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 **Fig 3**, PAHs from the kerosene stoves were generally present at lower concentrations $< 2.00 \mu\text{g m}^{-3}$ for all analytes except for Pyr. The dominance of Pyr from kerosene combustion was also reported in a previous study which suggested that PAHs emissions from kerosene could be reduced by switching to bio-kerosene (Andrade-Eiroa et al., 2010). A growing body of evidence suggests that kerosene use in households may pose greater risk than previously assumed since many of the traditional kerosene cooking devices are still inefficient (Lam, 2014, Shen et al., 2017, Lam et al., 2012). 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 our study, when subjects were interviewed on negative aspects of kerosene, they complained about the choking smell of kerosene smoke and subsequent headaches. This could be

due to the fact that kerosene is a similar petroleum distillate to diesel (Miele and Checkley, 2017), which might also explain the elevated Pyr concentrations in this work.

3.3 Distribution of PAHs in rural and urban households

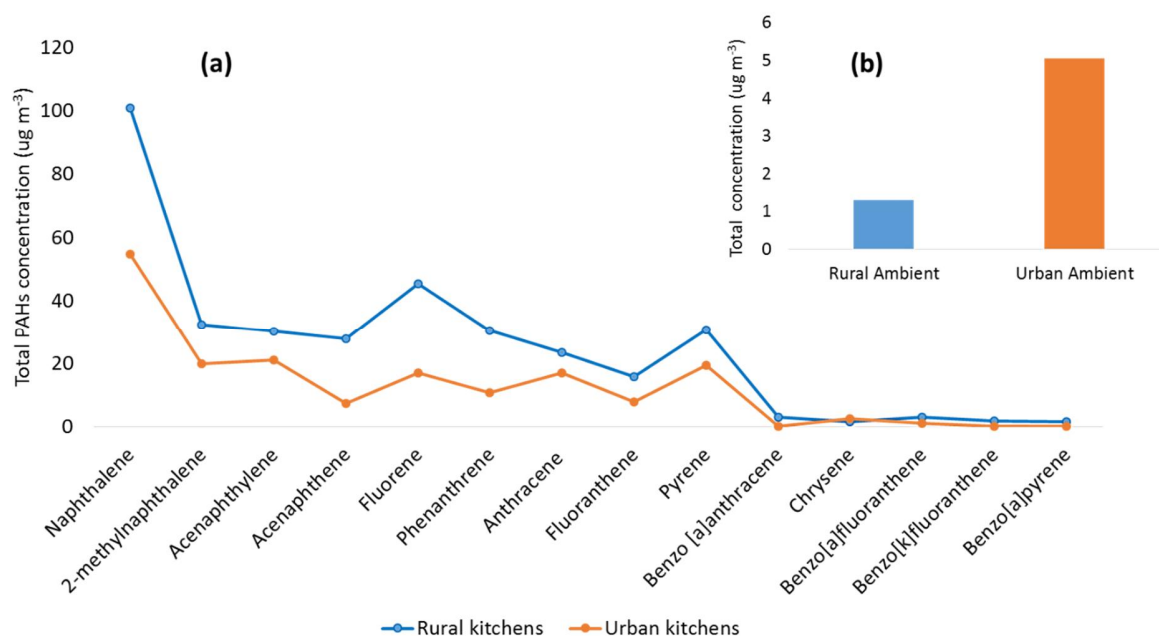


Fig 4 Comparison of total PAH concentrations in (a) rural and urban kitchens (n=12) and (b) in rural and urban ambient environments.

Efforts to characterize differences between urban and rural atmospheric PAHs pollution in Africa have largely been hindered by a paucity sampling data. As illustrated in **Fig 4a**, PAHs showed a strong rural-urban gradient with maximum concentration in rural homes. Although Kilifi rural homes were more ventilated, with some households cooking outdoors in 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. Additionally, they had openings in the walls which served as windows (see **Fig 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 **Fig 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. Additionally, the detection of Nap, Flu, Phen and Ace as main PAHs from wood combustion are 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 ng m^{-3} range have been reported in other African indoor environments for instance in Sierra Leone where total concentrations ranged from 1.38-4282 ng m^{-3} (Munyeza et al., 2019), which could have been a result of only the particle phase being measured.

With regards to ambient variations, the pattern illustrated in **Fig 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 since Mombasa is known as a busy port city. Additionally, there is higher population density in urban areas compared to rural areas where homes are more widely spread out, therefore resulting in greater dilution of pollutants from household activities. The choice of combustion device used in urban and rural areas was based on whether the cost of the device, its availability, energy requirements and fuel consumption rates, as well as cultural issues. 3-stone and improved 3-stone devices were only used in rural areas, and based on the questionnaire results these were preferred since they are cheap and easily available. Subjects in rural areas also gave cultural reasons for using the 3-stone devices, mentioning they were inherited from their parents and that it makes local foods such as ‘ugali’ taste better. LPG, kerosene and charcoal stoves were mainly distributed in urban areas since they are easily available, easier to use and more affordable for urban residents compared to those in rural areas.

3.4 Toxicity assessment of gaseous PAHs

Investigation of PAH concentrations indoors can be considered incomplete if individual PAHs carcinogenic potency is not assessed. In order 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) was calculated for the indoor PAH concentrations using Toxic Equivalence Factors (TEFs) proposed by Nisbet and LaGoy (1992) (Nisbet and Lagoy, 1992). Based on the proposed TEF values, BaP equivalent (BaPeq) or Toxic equivalence quotient (TEQs) values for each household are shown in **Fig S9**. TEF values were applied to the different combustion devices used in this study and the relative toxicity

contribution of each individual PAH in the PAH profile is given in **Fig 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 LPG, 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 light molecular weight PAHs like Nap, 2-mNap, Acy and Ace mostly contributed to total indoor PAH concentrations, total BaPeq values were mainly influenced by the heavier BaA, BaF, BkF and BaP (**Fig 5b**), due to their higher TEFs.

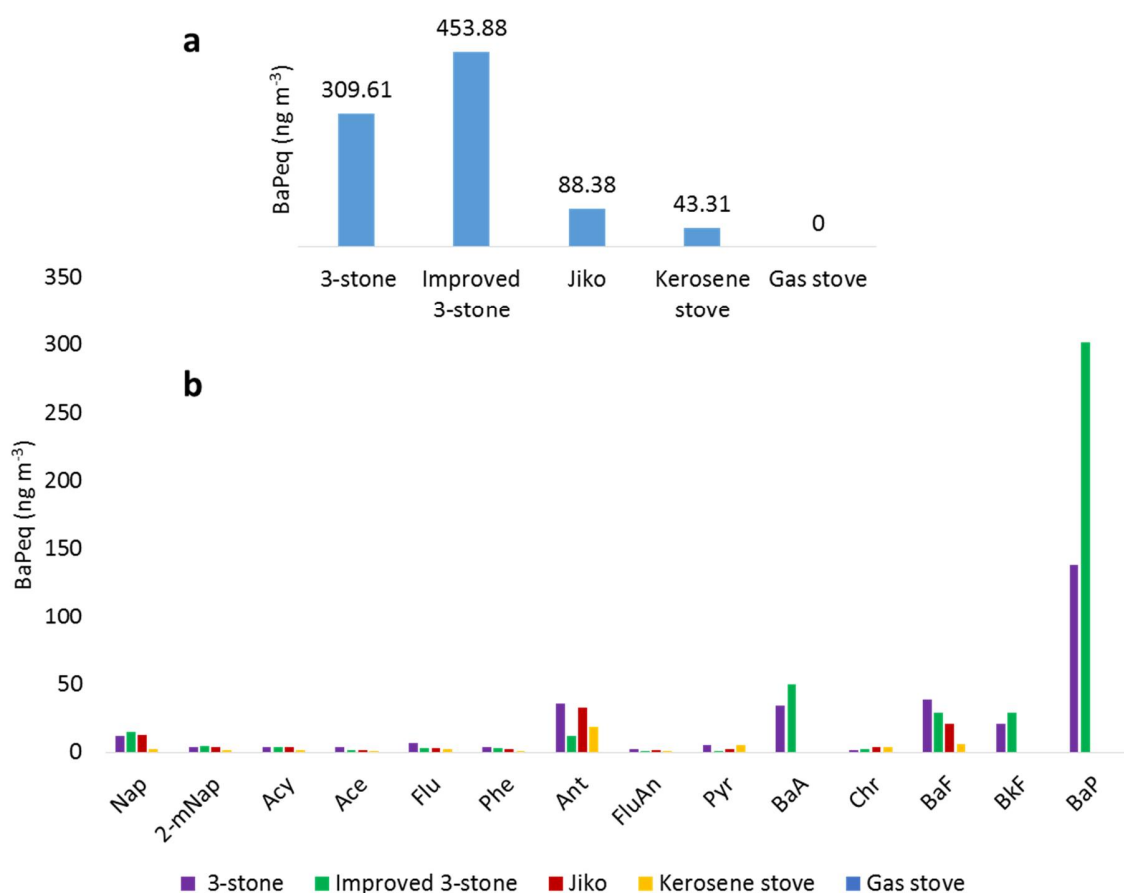


Fig 5 Comparison of benzo[a]pyrene equivalent (BaPeq) total concentrations. **(A)** Total average BaPeq concentrations from different combustion devices, and **(B)** the relative toxicity contribution of each individual polycyclic aromatic hydrocarbon. Ace = acenaphthene; Acy = acenaphthylene; Ant = 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

3.5 Principal component analysis

PCA was done on the results given in **Table S3** using mean centered data and correlation based variance. Although PCA is often used for modelling purposes, in this study it was strictly used to identify potential differences between our samples. PCA plots were used to visualize the interdependence between datasets and two different plots were employed, namely score plots (**Fig S10a**) and loadings plots (**Fig S10b**). It was observed that the 1st principal component accounted for 61.1% of the explained variance between samples whilst the 2nd principle 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 LPG (green ellipsoid, samples 12 and 17) combustion samples. A biplot (**Fig 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 in section 3.1, it was also observed that the samples from the first two houses in Taita Taveta rural area (TTR-H1, TTR-H2A and TTR-H2B) were very different from all the other samples. The rest of the combustion devices and sampling sites did not show any substantial grouping patterns as they were irregularly distributed on the plot. The loadings plot clearly illustrated the PAHs which were responsible for the inter-sample variations. The loadings plot illustrated that the increased concentrations of Nap, 2m-Nap, Phen, Ace, Ant, FluAn and BaF accounted for the variation of the TTR-H1, TTR-H2A and TTR-H2B.

4. Conclusions and recommendations

For rural communities, this 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 averages of $46.23 \mu\text{g m}^{-3}$). Exposure to PAHs could cause great health risks especially for the poorly ventilated households. Charcoal combustion using jiko stoves contributed to the highest PAH emissions in urban areas, although less 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 LPG combustion for cooking purposes is a step in the right direction toward use of clean fuel for near elimination of household PAHs pollution. Our 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 Nap. However, the contribution of Nap to BaPeq concentrations was insignificant and only heavier analytes such as Ant, BaA, BaF, BkF and BaP displayed high concentrations that are equivalent to toxic levels. The estimated BaPeq 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 LPG and electric stoves are 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 PAH indoors. These kitchen ventilation improvements together with household energy transitions can play a significant role towards improved 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 towards clean cooking.

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