Vol. 13(1), pp. 36-51, January 2019
DOI: 10.5897/AJEST2018.2582
Article Number: E438A7659488
ISSN: 1996-0786

http://www.academicjournals.org/AJEST

African Journal of Environmental Science and Technology

Full Length Research Paper

Exploratory study of Polycyclic Aromatic Hydrocarbon (PAH) contributions to household air pollution arising from improved cookstove use in rural Malawi

Kondwani R. Chidziwisano[1,2], Michael O. Rivett[1*], Amornphat Tadsanaprasittipol[1,3], Laura A. McGregor[1,4] and Robert M. Kalin[1]

[1]Department of Civil and Environmental Engineering, University of Strathclyde, Glasgow G1 1XJ, UK.
[2]Department of Environmental Health and WASHTED, Polytechnic, University of Malawi, Blantyre, Malawi.
[3]Pollution Control Department, 92 Soi Phahon Yothin 7, Phahon Yothin Road, Phayathai District, Bangkok 10400, Thailand.
[4]SepSolve Analytical Ltd, 22 Commerce Road, Lynchwood, Peterborough, Cambridgeshire, PE2 6LR, UK.

Received 17 September 2018, Accepted 6 November 2018

Around three million premature deaths annually are ascribed to household air pollution (HAP) arising from inefficient burning of biomass and emissions of products of incomplete combustion. The developing-world response has been widespread adoption of improved cookstove (ICS) technologies. This exploratory study evaluates variation in polycyclic aromatic hydrocarbon (PAH) attached to inhalable particulate matter (PM) in rural Malawi households adopting ICS use. PM literature supports HAP exposure to inhalable PM is lowered, albeit variably, compared to traditional fires, but remains significant. Similar is expected for PAH; however, datasets lack discerning PAH chemical-specific contributions to risks. The study introduces the Malawian context, invokes a PAH reconnaissance approach sampling kitchen soot 'spots' and residential dusts, and relates PAH occurrence to the two sample types collected and ICS types surveyed. The total PAH for dusts was low (*c.* 2 µg/g mean), with volatile 2-ring naphthalene dominant. Soot total PAH was much higher (c. 200 µg/g mean to a maximum of 815 µg/g). Soot from PM emissions poses a major primary health concern. Despite PAH trends not being obvious with ICS type (limited sample size) and the wide range in soot total PAH, soot PAH-fingerprints were well constrained with low variation of diagnostic PAH ratios, exhibiting n-ring fingerprints close to the soot median (0.1% 2-ring, 20% 3-ring, 61% 4-ring, 14% 5-ring, 5% 6-ring PAH). These corroborate the expected wood-related combustions sources, but also point to the needs to understand factors that control wide variations in PM and (total) PAH emitted as these control variations in HAP and differing risks posed to individual households. Further household-based research is thus recommended discerning relationships between PM emissions and PAH contents, driving the chemical-composition health risks. These should establish influences on PAH exposure arising from ICS type/model selected, operational modes, building/ventilation conditions, variable fuel sources and non-optimal ICS use.

Key words: Improved cookstoves (ICS), polycyclic aromatic hydrocarbon (PAH), household air pollution (HAP), particulate matter (PM), Malawi, indoor air pollution (IAP).

INTRODUCTION

Nearly three billion people rely on the burning of biomass for their everyday cooking and heating (IEA, 2017). In the rural developing world, especially Sub-Saharan Africa, 80% use wood, charcoal, animal dung and crop residue biomass fuels within simple 'three stone fires' (TSF) or traditional stoves (Foell et al., 2011). Although biomass use is not unsound as such, unsustainable harvesting and deforestation, alongside inefficient dirty energy-conversion practices has caused unprecedented health impacts (Foell et al., 2011; Wathore et al., 2017). A staggering 2.8 million premature deaths each year, mostly women and children, is ascribed to household air pollution (HAP) (indoor air pollution (IAP)) due to inefficient burning of biomass and emission products of incomplete combustion (PIC) (IEA, 2017). The World Health Organization (WHO) estimate even higher, attributing nearly 4 million premature deaths to illness associated with HAP due to poor cooking practices (WHO, 2018).

Documented health effects include acute respiratory infections, chronic obstructive pulmonary disease, pulmonary tuberculosis, perinatal and infant mortality and various cancers (Gall et al., 2011; WHO, 2018). PIC include CO, CH_4, polycyclic aromatic hydrocarbons (PAHs) and particulate matter (PM) that includes black carbon, 'soot', aerosols (Wathore et al., 2017). Our research concerns risks posed by particle-bound PAH transported on inhalable PM, a long recognised exposure pathway to biomass stove users (Gachanja and Worsfold, 1993; Lawal, 2017; Ramdahl, 1985; Saksena et al., 1992). PM-bound PAH poses significant health concern as 50-75% of emitted particulates are of inhalable size, with greater PAH mass adsorbed to fine soots (Gachanja and Worsfold, 1993; IARC, 2013). Despite its low per capita energy consumption, Africa's per capita PAH emissions are amongst the highest globally due to the high proportion of residential/commercial biomass burning (Shen et al., 2013a). Some 63% of total PAH emissions globally occur within the residential/commercial sector, reaching 67-80% in Africa (Shen et al., 2013b).

Growing use of improved cookstoves (ICS) forms the cornerstone response globally (Grieshop et al., 2011; Thomas et al., 2015; Wathore et al., 2017). ICS sophistication ranges from rudimentary stoves using local materials, up to state-of-the-art forced-draft cookstoves (FDCS) with electric fans (Grieshop et al., 2011; Jetter et al., 2012; Thomas et al., 2015; Wathore et al., 2017). ICS uptake is rapidly growing due to Sustainable Development Goal agenda to reduce air pollution-related disease burden under SDG 3, and to ensure access to clean fuel energy technology under SDG 7. Concerns remain however. Thomas et al. (2015) conclude from their review of 36 studies globally, that despite ICS interventions reducing exposure to HAP, pollutant levels are unlikely to meet WHO recommendations. Laboratory bench-testing indicates ICS performance in reducing HAP varies over two orders of magnitude (Grieshop et al., 2011) and often over-estimates household performance, by 2-5 times for PM emissions (Roden et al., 2009; Shen et al., 2013b) where non-ideal user operation may prove a significant issue (as confirmed in Malawi by Wathore et al. (2017)). Even best performing ICS (FDCS) under controlled Malawian field-test kitchens still resulted in $PM_{2.5}$ (< 2.5 µm 'fine particle') emissions 22% of TSF levels, with others much worse (Jagger et al., 2017). Continuing, variable emissions, alongside less-than-expected health benefits, endorse the need for studies that examine underlying chemical-composition influence (Mortimer et al., 2017; Romieu et al., 2009).

Significant rationale exist to evaluate PAH exposure risks associated with ICS use and chemical toxicity of the complex PAH fingerprint transported on PM (Brook et al., 2010; Keshtkar and Ashbaugh, 2007; Lawal, 2017; Taylor and Nakai, 2012). Fingerprint characterisation is important due to varying individual PAH toxicity and resultant variable chronic exposure risks arising from the carcinogenicity and mutagenicity, especially of higher ring PAH (IARC, 2013). As more volatile 2- to 3-ring PAH are released into the gas phase (Vineis et al., 2004; Brook et al., 2010), attention is more towards very low volatility 5- and 6-ring PAH preferentially associated with ultrafine PM (< 0.1 µm), and moderate volatility 3- and 4-ring PAH predominant in larger particles (Keshtkar and Ashbaugh, 2007). It should be further recognised that the burden of illness due to PAH exposure may be greater than currently estimated from carcinogenicity and cardiovascular morbidity, as respiratory conditions may be significant (Cakmak et al., 2017). Furthermore, PAH are immunosuppressive (White Jr., 2008) with various disease outcomes linked to acute exposure including inflammation of the eye, skin, and respiratory and prenatal exposure associated with, for instance, fetal growth restriction and childhood asthma (Ferguson et al., 2017) and heightened health risks to communities with increased rates of AIDS (acquired immunodeficiency syndrome). Understanding PAH emission sensitivity to ICS design and user operation requires in-household PAH datasets covering a range of ICS design type and use conditions. Lack of data is ascribed to the demands of implementing PAH analysis in developing countries, and primary use of PM and CO to regulate HAP human exposure with PAH risks then being inferred. Of the intervention studies reviewed by Thomas et al. (2015),

*Corresponding author. E-mail: michael.rivett@strath.ac.uk.

Figure 1. Map of Malawi showing study districts sampled.

only the Mexican study of Riojas-Rodriguez et al. (2011) had pollutant outcomes relating to PAH.

Our aim is to undertake an exploratory study of the variation in PAH emissions associated with ICS use within rural Malawian households thereby permitting preliminary evaluation of potential residential occupant exposure to PAH risks via inhalable PM. Objectives were to: review the context of ICS use in Malawi; adopt a simple sampling approach that allowed convenient reconnaissance of PAH occurrence in ICS user households; to measure total and individual PAH to establish PAH fingerprint characteristics and any relationships to the various ICS or sample types evaluated; and, provide forward recommendations on household study research.

MATERIALS AND METHODS

Study setting and review

Rural Malawians are among the poorest of the global poor. Malawi is a low-income country, ranking 170 out of 188 in the 2015 Human Development Index (World Food Program, 2018). It continues to receive significant international aid facilitating its quest to meet a host of SDGs. Current population is 18 million, growing by 2.9% per annum (World Bank, 2018), with the majority rural (*c.* 85%). Most rural inhabitants of the Chikwawa District studied in semi-arid Southern Malawi are subsistence farmers. They live on less than $0.50 (USD) a day with a mean, but increasing, life expectancy of just 45 years (Water for People, 2017). Water, food and energy security is low. Just 2% of Malawian households are estimated to cook with electricity and many are daily exposed to HAP from open fires. In 2010, 99.5% of the rural Malawians and 85% of the urban population were using solid fuels, mostly within TSF for cooking (Malawi-Government, 2010). Biomass fuel will likely remain the most reliable household source of cooking energy in semi urban and rural Malawi due to its accessibility.

Malawi targets adoption of ICS in two million homes, some 65% of its households, by 2020 (Jagger and Jumbe, 2016). The programme is inextricably linked with the plight of Malawi's forests, depleting at 2.8% per annum due to illegal logging by communities (Gercama and Bertrams, 2017). Gercama and Bertrams (2017) report on the progress indicated by the National Cook Stove Steering Committee (a coordinating body of officials, NGOs, etc.), that half-a-million 'clean and efficient' cookstoves are now in use. Illegal logging is attributed to surging charcoal demand in Malawi's cities. According to the government, 54% of urban women now use the 'black gold' for cooking, recognising it cleaner and quicker burn than firewood with use considered a status symbol (Gercama and Bertrams, 2017). Unless sustainably sourced, charcoal production and sale is banned; however, only one commercial licence for production has been issued. Quoting Gercama and Bertrams (2017), "the illegal trade is booming, serviced by rural residents who scrape a living turning timber into charcoal in a highly inefficient process which wastes enormous amounts of wood".

The above is indicative of the Malawian climate in which ICS research and development finds itself. Cookstoves are foremost in Malawian policy agenda, cutting across energy, environment, health, and gender sectors (Jagger et al., 2017). ICS implementaion is supported by a growing diversity of cookstove research in Malawi, including: Wathore et al. (2017) evaluating the impacts of traditional, natural- and forced-draft cookstoves, and Piddock et al. (2014) on periurban domestic biomass use; Fullerton *et al.* (2011) on wood smoke impaired lung function, Fullerton et al. (2009) on biomass fuel emissions and respirable dust, and Mortimer et al. (2017) confirming interventions failed to prevent pneumonia; Timko et al. (2016) on tree species preference and Fisher and Shively (2005) on forest use; O'Shaughnessy et al. (2014) on an electricity-producing portable ICS, Orr et al. (2015) on integrated food-energy systems; Jagger and Jumbe (2016) on household willingness to adopt ICS and Cundale et al. (2017) on household costs and benefits; Das et al. (2017) on health outcomes for women; and Jagger et al. (2017) on controlled field testing of TSF and ICS and up-scaling ICS programmes. None of these studies directly focuses upon PAH and hence our research is viewed complimentary.

Field survey of households: dust and soot sampling

Our exploratory study on PAH emissions from ICS use was afforded as an opportunity implemented alongside other (unrelated) health-based research in Malawi that facilitated field survey household access. Field collection of household kitchen soot and residential dust samples for PAH analysis was undertaken from randomly selected traditional households equipped with ICS located in Balaka District and Chikwawa District of rural semi-arid Southern Malawi (Figure 1). Households typically comprised mud walls, dirt floors, small wooden windows and doors with grass-thatched roofs. Structural conditions are characterised by poor ventilation, including smoke generated from cooking. Although these areas support both indigenous and exotic trees, including bush species that are used for fuel, scarcity of fuel wood has led to some community members using any combustible material such as animal dung, crop residues and even plastic materials. Subsistence agriculture provides the predominant source of income with open burning of crop residues common practice posing greater PAH risks to the male population

(Gonçalves et al., 2011). Automobile use is limited and exposure to related-PAH emissions not common.

Residential dust samples were obtained via careful collection of indoor sweepings from 38 households in Chikwawa District (Chidziwisano, 2012). Samples are expected to include coarse particle sizes generated during combustion that are rapidly deposited due to their relatively high mass. They provide a readily collected (for an exploratory study) aggregate sample of deposited PM of varying size fraction associated with the ambient air and may contain PAH originating from a variety of sources – not only from fire or cooking stove origins, but, say, environmental tobacco smoke, or PM entry to households from field burning, vehicle or machinery emissions. Recent quantification of 24 h average elevated total inhalable dust concentrations of 268 µg m^{-3} and 185 µg m^{-3} in rural Chikwawa and urban Blantyre (Fullerton et al., 2009) underscore requirements to evaluate PAH exposure associated with dust inhalation.

Soot samples, again a readily available sample type, were collected from the inside walls of domestic kitchens where soot 'spots' had accumulated. Samples were obtained by scrubbing with a clean brush and anticipated to contain fine-particle size ranges from combustion particulate matter that becomes dispersed and suspended in the household to eventually deposit on inside walls. Fifteen households in Balaka were randomly selected where ICS were in daily use (Chidziwisano, 2012). Five ICS brands (types) of differing designs were investigated including the PCI mud stove (at 5 household sites), Chitetezo Mbaula (7 sites), Briquette (1 site), Aleva (1 site) and Esperanza stove (1 site) (Chidziwisano, 2012). Achieving similar coverage of each ICS type was not possible at the time of this exploratory study due to the uptake of ICS being emergent and quite limited. Most ICS in use were generally simple to construct with NGOs providing training. The Chitetzo Mbaula stove is the only portable design; this could ideally be used outside, or the most ventilated area of a residence, to minimise indoor smoke. The Aleva and PCI mud stoves are built using compacted soil and mud respectively; they hence circumvent problems in locally sourcing clay required for some ICS. The Esperanza stove is a larger and more expensive ICS with ceramic-lined air and combustion chambers; it is perceived, due to its expense, less popular. The exploratory study nature did not allow opportunity to evaluate factors such as type (and seasonality) of fuel burnt, nor influential design features of the residence (kitchen size, ventilation, etc.).

Dust and soot samples were kept in tightly capped glass vials then transferred to the University of Strathclyde laboratory in Scotland where they were stored at -80°C until extraction and analysis. PAH analysis facilities were not available in Malawi.

Laboratory extraction of PAH

A growing wealth of methods exists for environmental sample PAH analysis (Lawal, 2017). Samples were analysed within our programme of wider research developing analytical methods for the analysis of PM-bound PAHs (Tadsanaprasittipol, 2016), developing rapid extraction and analysis of the 16 US EPA priority PAHs (Ong et al., 2003; US EPA, 1999). The detail of Tadsanaprasittipol's (2016) method development (mostly completed in urban Thailand with supporting work in rural Malawi) was not provided, but a key outcome was the accelerated solvent extraction (ASE) method developed and used herein. It is a highly efficient extraction technique for particulate-bound PAH with a sample extraction time of 30 min, significantly less than conventional Soxhlet extraction.

Solvents used (n-hexane, dichloromethane, toluene) were of analytical grade (Fisher Scientific, Loughborough, UK). All PAHs and deuterated PAHs were purchased from Sigma–Aldrich (Gillingham, UK). Anhydrous sodium sulphate, silica gel 60 and diatomaceous earth were activated for 8 h at 450°C prior to use. Silica gel 60 was then deactivated by 10% water (w/w). Extraction of target analytes was performed using an accelerated solvent extraction system (ASE 350, Dionex, Camberley, UK) equipped with 34 ml extraction cells. Soot sample extractions were performed at 150°C with a heating time of 7 min and using 3 cycles with a static time of 6 min. The solvent used for all extractions was a mixture of hexane and toluene (4:1 v/v). A flush-volume of 60% cell volume and purge time of 60 s was used. Dust sample were extracted at 110°C, otherwise conditions were similar to soot sample extraction.

Deuterated surrogates (D8-naphthalene, D10-fluorene, D10-fluoranthene and D12-chrysene prepared as a 500 µg/ml stock solution in dichloromethane) were added to each sample to monitor extraction efficiency. ASE extraction cells were prepared by lining the lower lid with two filter papers to collect unwanted particulates, then filling the cell with 3 g of silica gel/sodium sulphate (4:1 ratio w/w). A portion of soot sample (approximately 5 g) was then added and the remaining cell volume was packed with diatomaceous earth (inert filtration agent). A Büchi Syncore Analyst (Oldham, UK) was used to concentrate the sample extracts to approximately 1 ml. The final sample volume was adjusted to 1.5 ml and spiked with internal standards for subsequent analysis. All extracts were spiked with 60 µl of internal standard (550 µg/ml stock solution of D10-phenanthrene in dichloromethane) prior to analysis and stored at -80°C between analyses.

GC-MS analysis of PAH

A Thermo Scientific (Hertfordshire, UK) Trace Ultra GC equipped with a DSQII quadrupole mass spectrometer and Triplus autosampler was used for all GC-MS analyses. Helium (BOC Ltd., 99.999% purity) was used as the carrier gas at a flow rate of 1 ml min^{-1}. A J&W Scientific DB-5MS column with dimensions 30 m × 0.25 mm i.d. × 0.25 µm film thickness was used for all GC-MS analyses. The injector temperature was set at 230°C, with 1 µl of each soot sample extract was injected at a split ratio of 1:10. All standards and extracts were analysed with the oven temperature programmed at 55°C with 2 min isothermal, then increased at 10°C min^{-1} to 110°C, increased at 3°C min^{-1} to 210°C, then at 8°C min^{-1} to 320°C (maintained for 15 min), with a transfer line temperature of 330°C. The MS was operated in full scan mode using an ion source temperature of 200°C. Dust sample extracts were analysed using splitless mode at the inlet temperature of 230°C. Helium carrier gas was set at 1 ml min^{-1}. All standards and extracts were analysed with the oven temperature programme at 60°C with 3 min isothermal then increased at the rate of 5°C min^{-1} to 310°C (maintained for 1.5 min). The MS was operated in full scan mode with the mass range of 50-650 µ at the scan rate of 500 µ s^{-1}. The ion source temperature was 220°C.

Target PAHs in the soot and dust extracts were quantified by GC-MS using a calibration series containing 16 of the US EPA priority pollutant PAHs. The following PAHs were quantified: naphthalene (N), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHR), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenz[a,h]anthracene (DBA), indeno[l,2,3-cd]pyrene (IP), and benzo[g,h,i]perylene (BP). All samples and standards were analysed in triplicate.

Figure 2 shows a box plot of recovery percentages of surrogate deuterated PAH (d-PAH) spiked onto dust samples collected from the 38 households. The surrogate D-PAHs adsorbed by dust particles were demonstrated to be extracted at high recoveries, for both the 2-ring and 4-ring PAH shown. The mean recovery of naphthalene-d8 was 85% ± 18% and that of chrysene-d12 higher at 89 ± 16%. The ASE extraction method hence gave very satisfactory results for dust samples. The shown efficient extraction of deuterated surrogate concentrations is within the US EPA

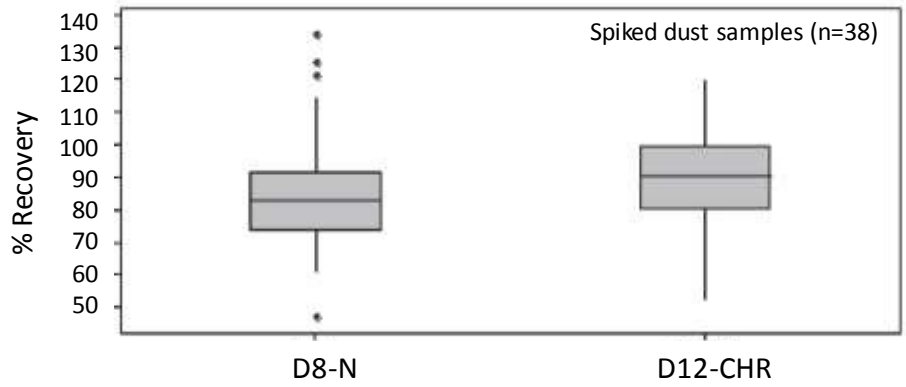

Figure 2. Box (25th and 75th percentile) and whisker (5th and 95th percentile) plots of recovery percentages of naphthalene-d_8 and chrysene-d_{12} PAH spiked in survey dust samples (Tadsanaprasittipol, 2016).

approved range of 70-120%.

Data processing and chemometrics

As the samples contained a range of compounds outside of the 16 quantified PAHs, the peak areas of a variety of compounds were also compiled for each sample (normalised to the peak area of internal standard) and compared statistically. These include methoxyphenol and sulphur-containing compounds.

Matlab statistical software (version R2011a, Mathworks Inc.) was used for principal component analysis (PCA) of the two datasets. Principal component analysis is a multivariate statistical technique that allows the simplification of complex datasets into principal components (PCs) which account for the majority of the total variance (Meglen, 1992). The sample score determine the position of each sample in the two-dimensional plot. Samples that are more similar show alike scores on each PC. The loadings can also be examined to show the contribution of each variable (PAH in this case) towards the formation of each principal component.

RESULTS

PAH in dust samples

PAH in dust samples from 38 households, shown in order of increasing total PAH concentration (Figure 3a), ranged from 0.37-7.07 µg/g total PAH (16 US EPA priority). Individual PAH concentrations ranged from below detection limits (0.002 to 0.005 µg/g across the various PAH) up to 6.52 µg/g. Naphthalene (N), the lowest molecular weight and most volatile PAH, accounted for this dataset maximum concentration and the maximum individual PAH concentration within all dust samples. N dominance is evident in the PAH fingerprint composition resolved within the individual sample plotted bars (Figure 3a).

Dominance of 2-ring PAH arising from N presence is obvious in Figure 3b. Whilst some 3-ring PAH, and to a lesser extent 4-ring PAH, are present in the dust samples; their concentrations remain low. Concentrations of 5-ring and 6-ring PAH were below, or barely exceeded, detection limits. Examination of the relative proportion of the various ring PAH (Figure 3c) reveals that greater mass proportions of the higher ring categories are found in some, but not all, samples with lower total PAH concentrations around 1 µg/g where 2-ring mass proportions decline to around 35-55%. Otherwise, 2-ring proportions typically account for around 65-90% of the dust PAH mass. Dust sample PAH associated with this coarse particle size range is hence dominated by the low molecular weight, most volatile PAH fraction. With one marginal exception, total PAH of dusts samples were below 5 µg/g.

PAH in soot samples

Soot samples from 15 households are shown in Figure 4a ordered in cookstove type, and then with each type, by increasing total PAH. Concentrations spanned two orders of magnitude from 13.7 to 815 µg/g total PAH. Marked variation of total PAH within individual cookstove types is apparent where multiple samples were available for comparison. For example, the total PAH for PCI cookstoves (n = 5) varies from 52-226 µg/g, with no samples exhibiting similar values. For Chitetezo cookstoves (n = 7), total PAH is also quite dissimilar across samples that range from the soot minimum of 13.7 up to 678 µg/g. Individual PAH concentrations were mostly above detection limits leading to a complex and varied PAH fingerprint composition being apparent across the dataset shown by the sample fingerprint detail (Figure 4a). Highest individual PAH concentrations detected were in the *c.* 100-250 µg/g range; these occurred for 3-ring phenanthrene (PHE) up to a maximum of 117 µg/g, for 4-ring fluoranthene (FLT) up to 217 µg/g, and 4-ring pyrene (PYR) up to 217 µg/g.

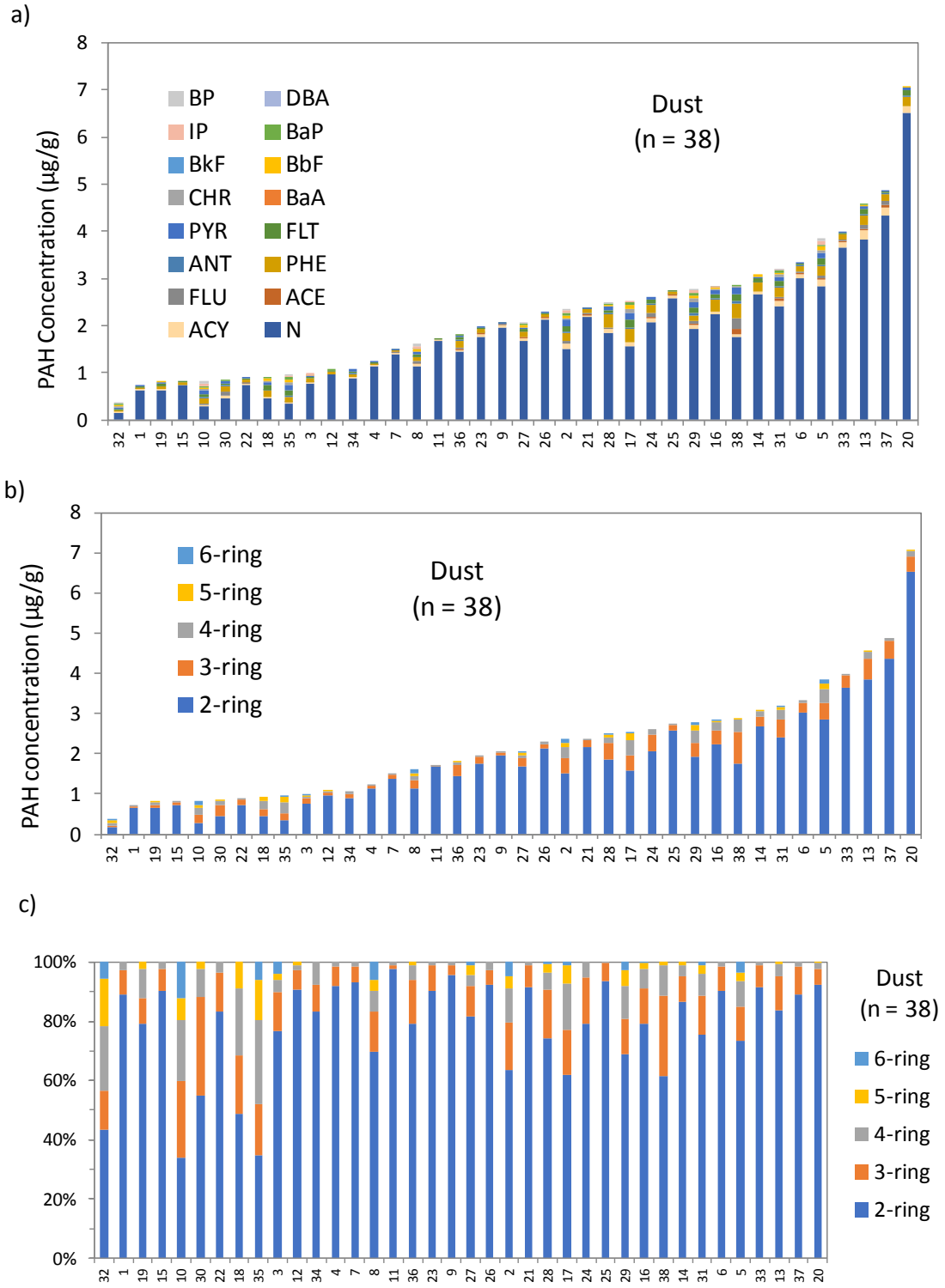

Figure 3. Dust samples (n=38) ordered with increasing total PAH concentration: (a) individual PAH composition; (b) concentration composition classified by number of rings in molecule; (c) mass proportion of total PAH mass classified by number of rings.

Dominance of the 4-ring PAH composition within the soot PAH mass is clearly shown in Figure 4b. Lesser contributions from 3-ring, with more minor contribution of 5-ring PAH, and trace contributions from 6-ring PAH are

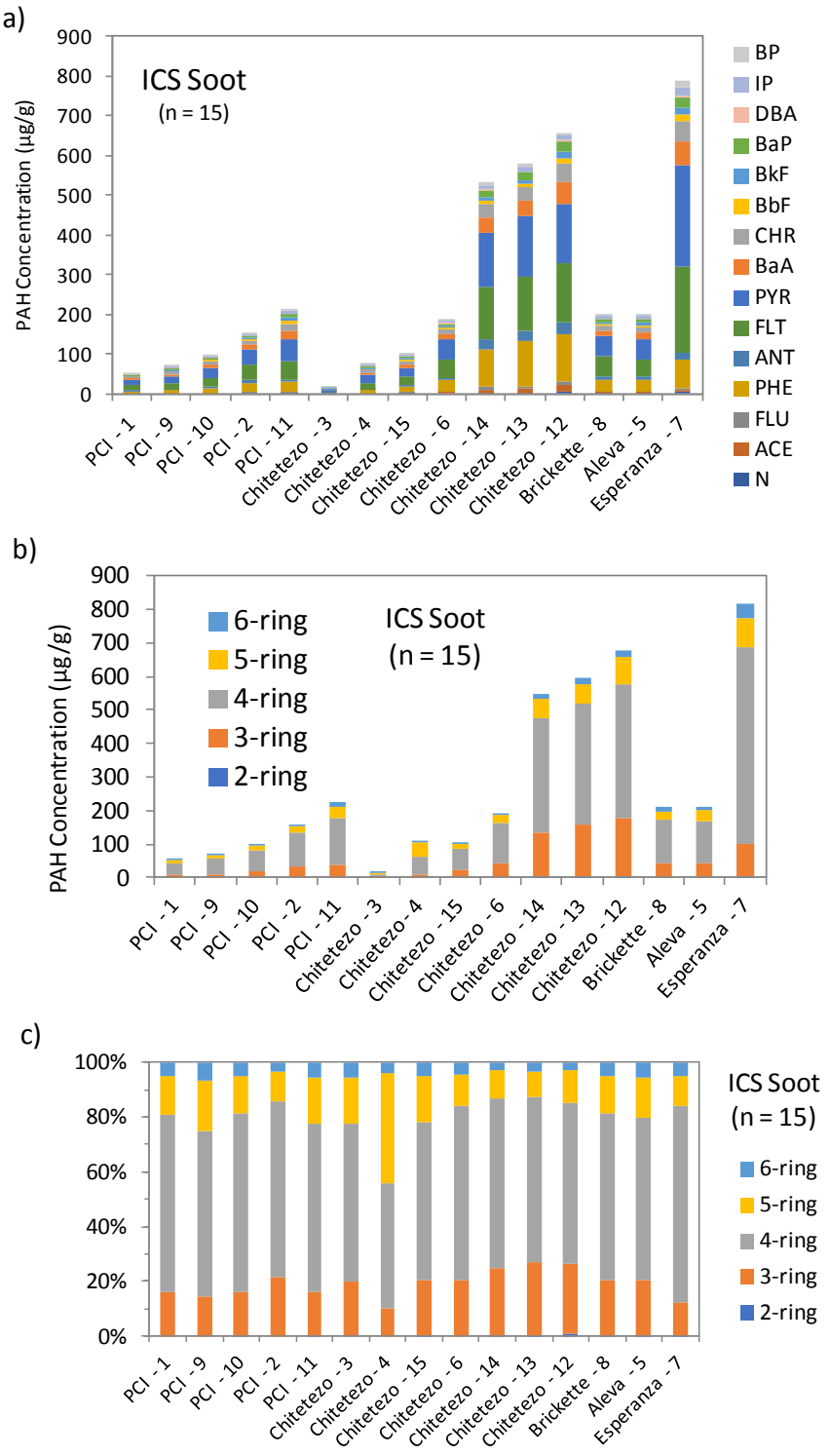

Figure 4. ICS soot samples (n=15) grouped by ICS type and increasing total PAH within that group: (a) individual PAH composition; (b) concentration composition classified by number of rings in molecule; (c) mass proportion of total PAH mass classified by number of rings.

discernible across the soot dataset. Examination of the relative proportion of the various ring PAH within the soot (Figure 4c) indicates the relative proportion of the various ring PAHs remains quite similar across the soot dataset,

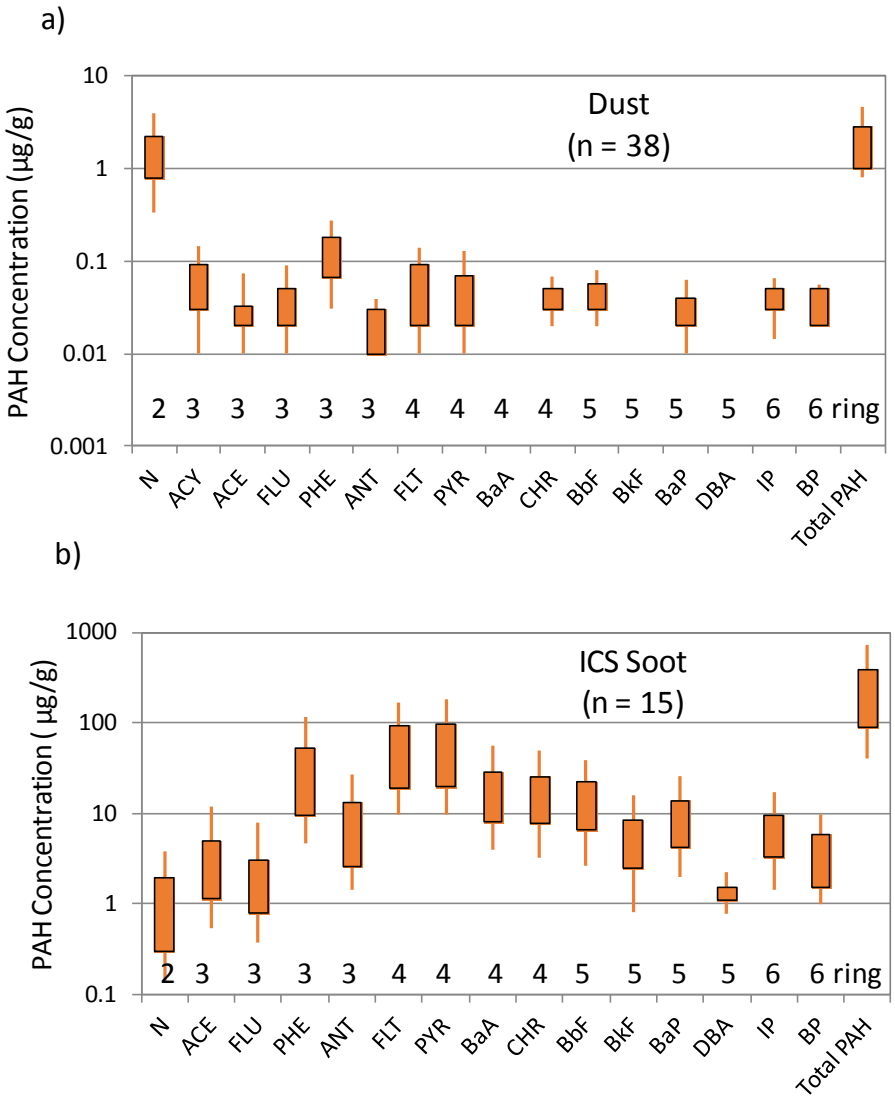

Figure 5. Box (25th and 75th percentile) and whisker (5th and 95th percentile) plots of individual and total PAH concentrations in: (a) dust samples; (b) ICS samples.

and the range of ICS sampled. The arithmetic averages and standard deviations for the soot dataset relative mass proportions displayed in Figure 4c is: 3-ring PAH at 19.1 ± 4.4%, 4-ring PAH at 62.4 ± 3.7%, 5-ring PAH at 13.6 ± 2.9%, and 6-ring PAH at 4.7 ± 1.1%. The presence of 2-ring PAH is barely discernible in the soot samples.

In summary, whilst total PAH concentration within the fine particle size range soots varies significantly across the dataset, and within cookstove types, the proportional ring-based PAH composition appears similar across the various soots. This composition is dominated by 4-ring PAH, but with contributions from 3-ring and 5-ring PAH and a minor 6-ring presence. Although variable, typically total PAH, exceeded 100 µg/g with mean and median soot values respectively approaching and exceeding 200 µg/g.

Comparison of dust and soot PAH

PAH concentrations associated with kitchen soot are consistently much higher than the household dust as illustrated in Figure 5 comparative box plots (note the differing (log) concentration scales). Total PAH for the dust exhibit an average and median of 2.22 and 2.06 µg/g respectively. These compare to soot values of 270 and 193 µg/g, around two orders of magnitude higher. 2-Ring naphthalene (N) of average and median concentration in the dust of respectively 1.80 µg/g and 1.68 µg/g and range 0.16-6.52 µg/g dominates the dust PAH content. N concentrations are similar across the soots sampled, but lower, at average and median concentrations of 1.4 µg/g and 0.5 µg/g respectively, with a range of < 0.1- 4.4 µg/g. Contrasting with the dusts, the

median contribution of 2-ring N to the total PAH soot mass is negligible at 0.1%.

Excluding N, all other individual PAH with detectable concentrations in the dust occur almost exclusively in the range 0.01- 0.1 µg/g (Figure 5a). Exceptions to this are for 3-ring PHE with a median of 0.11 µg/g and maximum of 0.32 µg/g and a few concentrations of 3-ring ACY and 4-ring FLT and PYR that just exceed 0.1 µg/g. Interestingly, three of these PAH (PHE, FLT and PYR) are the aforementioned individual PAH maxima encountered in the soot samples. Their more elevated occurrence within the soot compared to other PAH is illustrated in Fig. 5b; median concentrations at 26.8 µg/g PHE, 43.4 µg/g FLT and 49.5 µg/g PYR compared to soot medians for all other PAH spanning 0.5- 13.3 µg/g with an overall median of those PAH around an order of magnitude lower at 4.5 µg/g. It is surmised from the similarity of the 3-ring and 4-ring PAH higher concentration fingerprint between the dust and soot, that some soot particles are quite likely deposited and incorporated within the household dust sampled and may account for this similarity.

Comparison of dust and soot samples by n-ring classification illustrates the dominance of the 2-ring concentration mass in the dust samples compared to the dominance of the 4-ring concentration mass in the soot with contributions to that soot mass from the 3-ring and then 5-ring PAH mass (Figure 6a and b). Expressing the n-ring concentration mass as a relative percentage proportion of the total PAH mass furnishes a more normalised comparison of the n-ring fingerprint composition differences between dust and soot samples (Figure 6c and d). The dust dataset exhibits a marked decline from the dominance of the 2-ring mass to declining contributions from successively higher n-ring mass. Whilst recognising the inter-quartile and overall ranges in the individual n-ring percentages are quite large, especially for the 2-ring, the median dust PAH mass proportional composition calculated is: 84% 2-ring: 11% 3-ring : 4% 4-ring : 1% 5-ring PAH (with 6-ring trace). The soot dataset (Figure 6d) exhibits a clear 4-ring peak proportion and a notably small inter-quartile and overall range in observed individual n-ring percentages (Figure 6d). This low variation endorses the median soot PAH mass composition calculated is reasonably representative of all soots sampled, this being: 0.1% 2-ring, 20% 3-ring, 61% 4-ring, 14% 5-ring, 5% 6-ring PAH. This ratio hence appears to offer a well-constrained proportional PAH mass fingerprint of the sampled Malawian kitchen soot.

PAH diagnostic ratios

PAH diagnostic ratios, commonly used to identify pollution emission sources (Tobiszewski and Namieśnik, 2012; Yunker et al., 2002), are calculated for the soot and dust datasets (Table 1). Ratio comparison with the provided literature diagnostic ranges corroborates, as anticipated, the soots arise from combustion sources. For three of the four ratios, all samples are categorised in the 'Solid/grass/wood/coal' category range. For the other ratio, FLT / FLT+PYR, all samples are indicative of combustion sources, with some ratio just within the above category and the remainder a touch outside (the mean plus standard deviation equates to the lower threshold of that category). Comparison with the example literature combustion ratio given likewise supports wood-related sources (Table 1). Mean ratio for the dust dataset all fall in the combustion 'Solid/grass/wood/coal' category. Individual dust ratios could not be calculated for all samples (where relevant PAH were below detection), nevertheless 80% of those calculated were in the above category (all exceptions were for ANT/178). Use of the PAH diagnostic ratios thus usefully confirms the influence of wood-related combustions source for kitchen soots, as expected, but also the dusts. This is consistent with the rural environment and the low expected, still possibly masked, influence of other PAH sources.

Comparison of the two ICS types where multiple soot samples were taken (PCI and Chitetzo stoves) reveals similar ranges in the various PAH ratios and hence their distinctive influence is not apparent (Table 1). In fact, once the outlier low total PAH sample is removed (that yields anomalous ratio), variation in ratio for the entire soot dataset is small with standard deviations corresponding to just 3–7% of the ratio mean. This again points to a reasonable consistent PAH fingerprint regardless of the ICS sampled, and despite the wide variation in total PAH of the soot sampled.

Improved cookstove type influence on soot PAH

Using Figure 4a to compare variation inherent to a specific ICS type, there appears considerable variation in kitchen soot total PAH concentrations, especially for the Chitetezo (by a factor of 50 (or 9 ignoring the anomalous low sample 3 concentration)), but also for the PCI (factor of 4). Hence, there must be other influences to cookstove type. These influences were not assessed, but could include variable modes of user operation of a specific ICS type, varying fuel type, and spatial variation in PAH occurrence within a household soot. Isolated sampling of the other ICS types precludes any definitive statements on these factors. It was noted that the Brickette and Aliva stoves show similar total PAH that compare to the highest concentration observed from the PCI stove dataset (Figure 4a). In addition, the single sample from the Esperanza stove is prominent for it being the highest total PAH surveyed.

In terms of varying PAH composition fingerprints, the absolute individual PAH concentrations vary within and between ICS type in accordance with the overall variation in PAH (Figure 4a). The key finding displayed by Figure

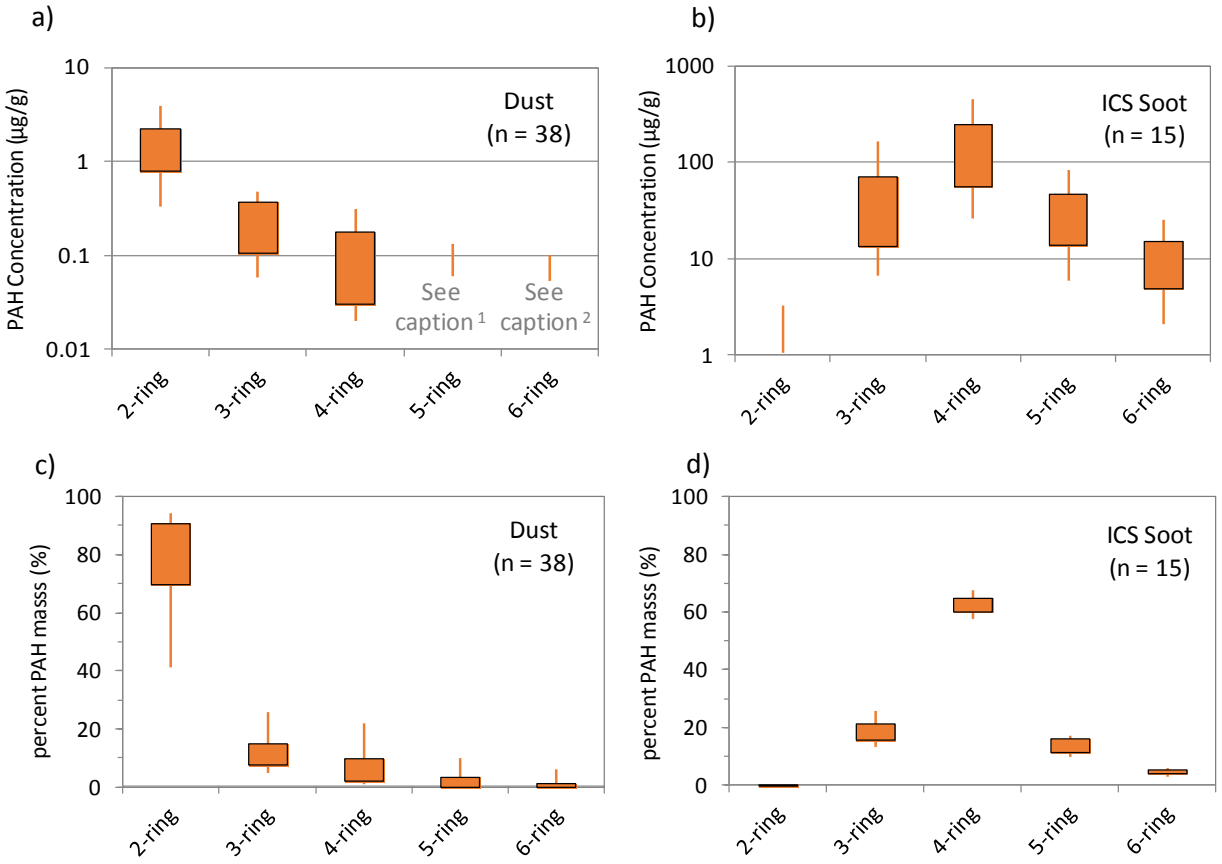

Figure 6. Box (25th and 75th percentile) and whisker (5th and 95th percentile) plot comparison of PAH compositions classified by numbers of rings for: dust sample (a) concentrations and (b) percent mass proportions; and, ICS sample (c) concentrations and (d) percent mass proportions. Footnotes: [1] 76% of n=152 sample 5-ring concentrations < detection limit (0.003-0.004 µg/g) with median of detections 0.03 µg/g; [2] 74% of n=76 sample 6-ring concentrations < detection limit (0.004-0.006 µg/g) with median of detections 0.04 µg/g.

6d of little variation of the entire soot dataset from the median soot PAH mass proportional composition, means that differences in proportional n-ring PAH fingerprints between the various ICS types may potentially be minimal (endorsed by the detail of Figure 4b and n-ring proportions in Figure 4c). Generally, the fingerprints are quite comparable without obvious differences between, or within ICS types. Nevertheless, some further observations can be made. For instance, the three highest total PAH Chitetezo samples (-12, -13 and -14) exhibit the maximum 3-ring proportions (Figure 4c) due to the disproportionately high PHE concentrations compared to other samples (Figure 4a). Whist such observations appear minor, they suggest possible scope for diagnostic insight from more detailed evaluation of the 16-PAH fingerprint.

Principal components analysis (PCA)

Discrimination of individual PAH influence is further examined through PCA. Figure 7 plots PC scores for the soot samples with an inset showing the PC scores for the dust dataset and their local extent within the former (Figure 7a [soot samples are labeled with a 'b' to distinguish from similar numbered dust samples]). Loading plots for the dust (Figure 7b) and soot (Figure 7c) are also shown for the individual PAH. The maximum total PAH concentration Esperanza stove (Sample 7) was an outlier in the PC scores for the soot samples (Figure 7a); its positioning is attributed to the influence of high PYR (Figure 4a and Figure 7c). Otherwise, most soot samples cluster in the area labeled 'A', inferring similar individual PAH concentrations in soot samples within those specified clusters. The remaining soot samples are the aforementioned three highest total PAH Chitetezo samples, 12, 13 and 14 with the former pair at cluster locality 'B' and the latter sample 14, somewhat outlying from there (Figure 7a). Their positioning is consistent with the influence of higher PHE noted above and apparent on the loading plot (Figure 7c).

The N-dominated dust samples (Figure 7b) are shown

Table 1. PAH diagnostic ratios observed for kitchen soot and household dust (mean) samples compared to literature diagnostic ranges for petroleum an combustion sources and example environmental samples.

	'ANT/178' =	**'BaA/228' =**		
	ANT / ANT+PHE	**FLT / FLT+PYR**	**BaA / BaA+CHR**	**IP / IP+BP**
		Literature diagnostic ranges		
Fuels/oil products:				
- petroleum	< 0.1	< 0.4	< 0.2	< 0.2 (< 0.1)
Combustion sources:				
- Liquid/petroleum fossil fuel	> 0.1	0.4-0.5	> 0.35	0.2-0.5 (0.1-0.3)
- Solid/grass/wood/coal	> 0.1	> 0.5	> 0.35	> 0.5 (> 0.3)
ICS sample (Total PAH)		**Kitchen soot samples**		
PCI – 1 (52 µg/g)	0.21	0.50	0.52	0.65
PCI – 9 (73 µg/g)	0.23	0.48	0.55	0.67
PCI – 10 (100 µg/g)	0.21	0.47	0.47	0.69
PCI – 2 (156 µg/g)	0.22	0.49	0.52	0.73
PCI – 11 (226 µg/g)	0.18	0.46	0.51	0.62
Chitetzo – 3 (14 µg/g) [outlier]	0.37	0.54	0.76	
Chitetzo – 4 (76 µg/g)	0.21	0.47	0.54	0.75
Chitetzo – 15 (107 µg/g)	0.19	0.51	0.51	0.68
Chitetzo – 6 (194 µg/g)	0.21	0.47	0.51	0.67
Chitetzo – 14 (549 µg/g)	0.21	0.48	0.53	0.64
Chitetzo – 13 (595 µg/g)	0.18	0.47	0.53	0.69
Chitetzo – 12 (678 µg/g)	0.21	0.50	0.53	0.64
Brickette – 8 (209 µg/g)	0.19	0.49	0.53	0.63
Aleva – 5 (210 µg/g)	0.21	0.47	0.51	0.68
Esperanza – 7 (815 µg/g)	0.20	0.46	0.54	0.62
Kitchen soot mean	0.22 ± 0.045	0.48 ± 0.021	0.54 ± 0.064	0.67 ± 0.039
Kitchen soot mean (less outlier)	0.20 ± 0.015	0.48 ± 0.016	0.52 ± 0.019	0.67 ± 0.039
		Household dust sample set		
Household dust mean	0.13 ± 0.041 (n = 23)	0.55 ± 0.092 (n = 35)	below detection (n = 0)	0.51 ± 0.021 (n = 7)
		Literature combustion data (for comparison)		
Wood soot (n=2)	0.26	0.5	0.46	0.55
Wood (n=19)	0.19	0.51	0.46	0.64
Grasses (n=6)	0.17	0.58	0.46	0.58
Kerosene (n=3)	0.14	0.5	0.37	0.37
Bush fire (n = not indicated)		0.61	0.23	0.7

Literature data sources are: Granberg and Rockne (2015) based on Yunker et al. 2002 modified by Yunker et al. (2012) (tabulated values in parentheses).

by the Figure 7a inset locality to plot as a very tight cluster at locality 'C', close to 'A' within the soot plot. This demonstrates that there is minimal variation in the concentration of PAHs in dust compared to soot samples. The dust samples plot closest to the soot sample 3 Chitetezo stove concentration (plotted 3b on the Figure 7a dust inset for reference); this is the anomalously low minimum total PAH soot sample (Figure 4a). The other soot samples that plot closest to the dust cluster (soot samples 1, 2, 4, 9 and 10) form the lower total PAH samples of the PCI and Chitetezo stove sample sets.

Other compounds present

Whilst not the study focus, methoxyphenols and organo-

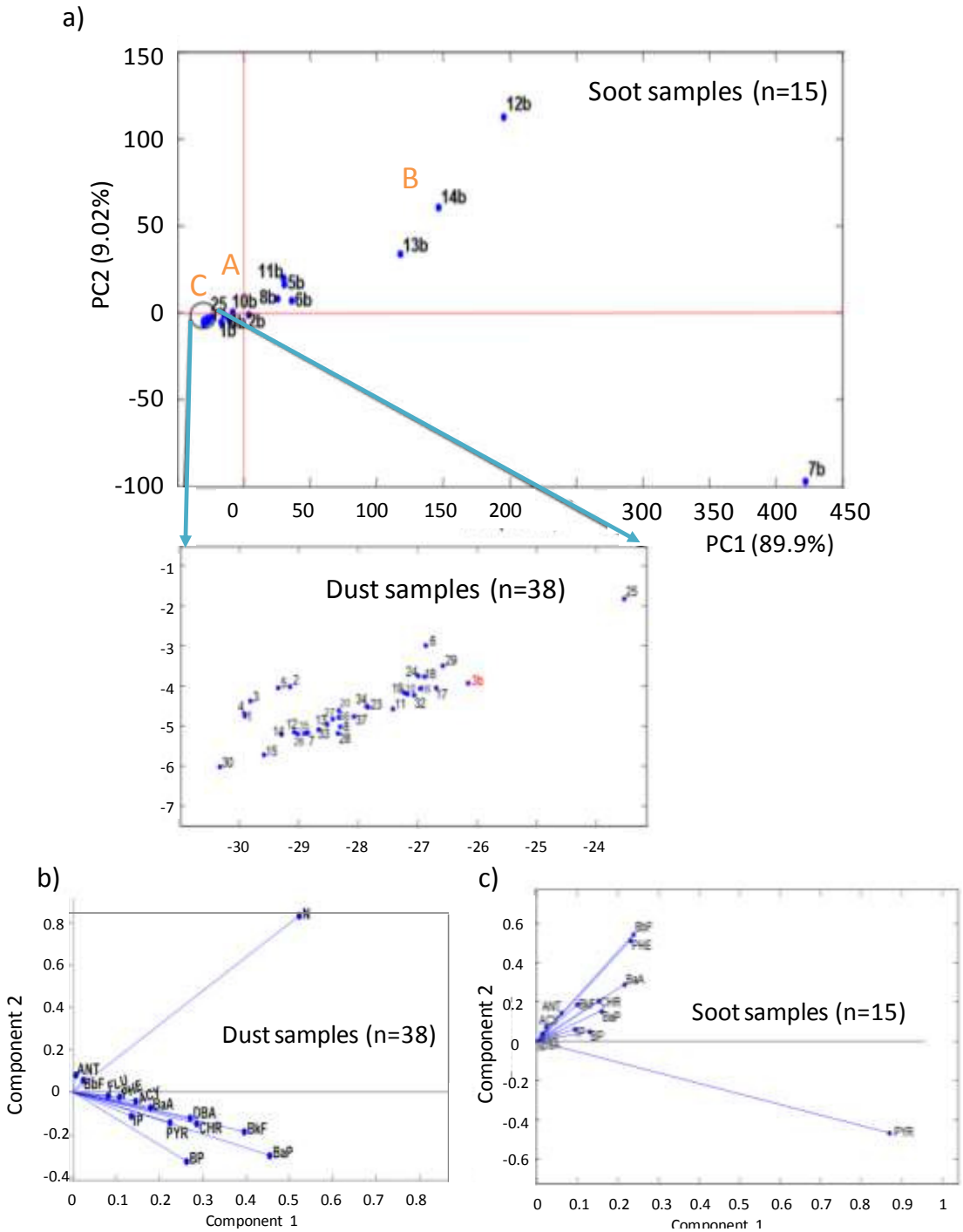

Figure 7. Soot samples principal component analysis (modified from Chidziwisano, 2012.): (a) score plot for soot samples with inset showing dust samples; (b) loading plot for dust samples; (c) loading plot for soot samples.

sulfur compounds were identified in some dust and soot samples in the course of the GC-MS analysis. Each are associated with significant human health effects when present in the ambient air environment. Brief observations follow.

Methoxyphenol compounds are emitted from wood burning (pyrolysis of lignin) and have long been used as biomarkers of smoke exposure from wood burning with human exposure typically via inhalation (Clark et al., 2007). Methoxyphenols were detected in seven soot samples, but no dust samples. Sample peaks areas relative to the internal standard are shown in Figure 8a

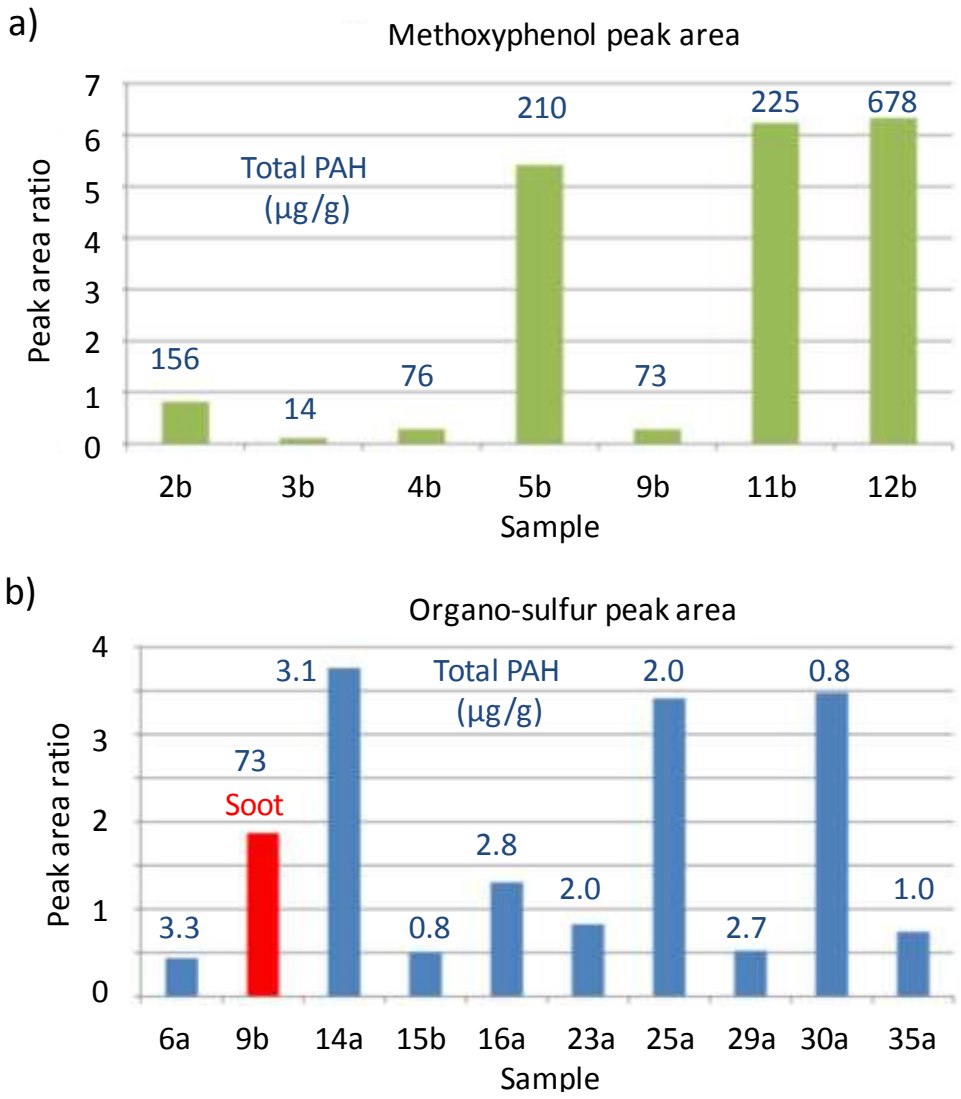

Figure 8. (a) Soot samples with methoxyphenol compounds present – analysed peak area ratio present in sample; (b) sulfur peak area ratio present in certain dust and a single soot sample.

that illustrates increased methoxyphenol concentrations occur with elevated concentrations of total PAH.

Atmospheric emission of sulfur compounds from biomass burning depends on the sulfur content and quantity of volatile sulfur in the biomass with plant type and combustion temperature critically controlling volatile sulfur emitted (Badr and Probert, 1994). Organo-sulfur related compounds were identified in 10 samples, of which 9 were dust samples at generally very minimal (non-quantified) concentrations with low levels of total PAH (Figure 8b). The only soot sample (9 from a PCI stove) that contained organo-sulphur had a low soot (third lowest) total PAH. The general conclusion is that low organo-sulphur concentrations were found in around a quarter of the low PAH dust samples with no evidence of occurrence in moderate to higher PAH concentration kitchen soot.

Conclusions

In line with the Government of Malawi policy and SDG agenda, the present decade is witnessing a marked increase in ICS use across Malawi, supported by a growing body of Malawian research. Similar increase is apparent across the developing world. This exploratory study has novelty within the enabling Malawian research effort, and internationally, examining risks posed by PAHs on inhalable PM posed to households that may remain in spite of ICS adoption. Cooking areas in most

rural Malawian households are usually integral to the main house, often poorly ventilated, and pose greater HAP exposure risks to women and children more commonly present. Although increasing use of ICS facilities over traditional fires is reasonably expected to reduce exposure risks. Recent studies cited increasingly confirm that exposure risks to harmful PM remain significant and variable across ICS type and household-use environments. There is, however, a lack of datasets on PM-bound PAH contents and fingerprint compositions associated with ICS use; these appear increasingly needed given PM emission variability and less-than-expected health benefits of ICS interventions to gain understanding of specific chemical-based risks. This exploratory study through a straightforward approach of reconnaissance sampling of household dusts and kitchen soot has demonstrated that PAH associated with inhalable PM may continue to pose health risks to household occupants, even when ICS use is adopted.

This study confirms that total PAH for household dusts was always low, with means around 2 µg/g and volatile 2-ring naphthalene always dominant. Kitchen soot samples exhibited total PAH means some two orders of magnitude higher, around 200 µg/g to a maximum of 815 µg/g. Total PAH in kitchen soot displayed a wide range, both across the entire soot dataset, and for individual ICS type. Trends were not obvious with ICS type (recognising limited sample size in this exploratory study). Despite the wide range in soot total PAH and various ICS sampled, the soot PAH fingerprint appeared well constrained with most soot having n-ring fingerprints close to the median soot of: 0.1% 2-ring, 20% 3-ring, 61% 4-ring, 14% 5-ring, 5% 6-ring PAH. In addition, commonly used diagnostic PAH ratios were quite similar across the soot dataset. These ratio for soot and dusts, confirmed the expected influence of wood-related combustions sources for the PAH and is consistent with the rural African environment confirming the anticipated current low influence of other PAH sources. Increased total PAH and greater proportions of the higher carcinogenicity, 4- to 6-ring PAH than less toxic 2- to 3-PAH within soot causes their inhalation and ingestion to pose much greater health risks than the coarser, but still inhalable, PM dusts. Exposure risks remain greatest for women and children who spend more time in the indoor environment.

With the very limited developing-world availability of analytical facilities for micro-organic pollutant (incl. PAH) analysis in Malawi (and likely elsewhere) and greater ease of PM measurement, it is expected PM measurements will remain the primary metric for management of PM-associated pollutants such as PAH. This exploratory study, however, endorses the need for household-based research studies that characterise not only factors that control PM emissions, but also within those assessments, characterisation of the total PAH, its fingerprint composition and temporal/spatial PAH variation within PM emissions driving the chemical-based health risks. Whilst the soot PAH fingerprint (n-ring proportions and diagnostic PAH ratios) observed appear quite consistent and may usefully underpin PAH-related health risk assessments, this consistency requires evaluation across larger datasets. Of key importance, is to understand the factors that control total PM emission quantities and associated total PAH that may cause significant variation between, and within, ICS types and modes and conditions of use; and in turn, marked variation in HAP and differing PAH exposure risks to individual households.

Hence relationships between PAH risks and more facile PM measurements need to be investigated within the context of expanding ICS use and possible influence of the plethora of ICS designs, operational modes, building/ventilation design, variable fuel sources and recognised non-optimal use. There is need for household studies to sample the airborne PM and associated PAH concentrations and fluxes. A variety of study types are possible to include before and after ICS installation to households (with controls). Long-term studies to ensure reductions in emissions and health risks are sustained as well as cross-sectional studies where PAH-related aspects of ICS design/efficiency HAP or health outcomes are measured simultaneously in households with traditional stoves and households with ICSs in a similar geographic area (Chaigneau, 2012). It will be important to address here the concern noted by Thomas et al. (2015) that many households continue to use both traditional fires/stoves and ICS, even reverting back to the former. Such studies are vital to the optimisation of ICS designs and household user practice improvements to secure delivery of SDG 3 and SDG 7.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

ACKNOWLEDGEMENTS

The authors appreciates Prof. Anthony Grimason and Vincent Doyle of Concern Universal for arranging the collection and transportation of all soot samples analysed in this study. They also gratefully acknowledge the support in final manuscript preparation provided by the Scottish Government under the Scottish Government Climate Justice Fund Water Futures Programme research grant HN-CJF-03 awarded to the University of Strathclyde (R.M. Kalin).

REFERENCES

Badr O, Probert S (1994). Atmospheric sulphur: Trends, sources, sinks and environmental impacts. Applied Energy 47(1):1-67.
Brook RD, Rajagopalan S, Pope CA, Brook JR, Bhatnagar A, Diez-Roux

AV, Holguin F, Hong YL, Luepker RV, Mittleman MA, Peters A, Siscovick D, Smith SC, Whitsel L, Kaufman JD (2010). Particulate matter air pollution and cardiovascular disease. An update to the Scientific Statement from the American Heart Association Circulation 121:2331-2378.

Cakmak S, Hebbern C, Cakmak JD, Dales RE (2017). The influence of polycyclic aromatic hydrocarbons on lung function in a representative sample of the Canadian population. Environmental Pollution 228:1-7.

Chaigneau L (2012). Evaluation of small scale cookstove programs. Masters thesis in Toxicology and Environmental Health, Institute for Risk Assessment Sciences, Utrecht University.

Chidziwisano KR (2012). Variation of Polycyclic Aromatic Hydrocarbons levels in soot from improved cook stoves and residential dust in rural Malawi. M.Sc. Environmental Health Sciences thesis (unpublished), Department of Civil and Environmental Engineering, University of Strathclyde.

Clark M, Paulsen M, Smith KR, Canuz E, Simpson CD (2007). Urinary methoxyphenol biomarkers and woodsmoke exposure: Comparisons in rural Guatemala with personal CO and kitchen CO, levoglucosan, and PM2.5. Environmental Science & Technology 41(10):3481-3487.

Cundale K, Thomas R, Kenala MJ, Havens D, Mortimer K, Conteh L (2017). A health intervention or a kitchen appliance? Household costs and benefits of a cleaner burning biomass-fuelled cookstove in Malawi. Social Science and Medicine 183:1-10.

Das I, Jagger P, Yeatts K (2017). Biomass cooking fuels and health outcomes for women in Malawi. EcoHealth 14:7.

Ferguson KK, McElrath TF, Pace GG, Weller D, Zeng L, Pennathur S, Cantonwine DE, Meeker JD (2017). Urinary polycyclic aromatic hydrocarbon metabolite associations with biomarkers of inflammation, angiogenesis, and oxidative stress in pregnant women. Environmental Science & Technology 51(8):4652-4660.

Fisher M, Shively G (2005). Can income programs reduce tropical forest pressure? Income shocks and forest use in Malawi. World Development 33(7):1115−1128.

Foell W, Pachauri S, Spreng D, Zerriffi H (2011). Household cooking fuels and technologies in developing economies. Energy Policy 39(12):7487-7496.

Fullerton DG, Suseno A, Semple S, Kalambo F, Malamba R, White S, Jack S, Calverley PM, Gordon SB (2011). Wood smoke exposure, poverty and impaired lung function in Malawian adults. International Journal of Tuberculosis and Lung Disease 15(3):391-398.

Fullerton DG, Semple S, Kalambo F, Suseno A, Malamba R, Henderson G, Ayres JG, Gordon SB (2009). Biomass fuel use and indoor air pollution in homes in Malawi. Occupational and Environmental Medicine 66(11):777-783.

Gonçalves C, Evtyugina M, Alves C, Monteiro C, Pio C, Tomé M (2011). Organic particulate emissions from field burning of garden and agriculture residues. Atmospheric Research 101(3):666-680.

Granberg KJ, Rockne KJ (2015). Source apportionment of polycyclic aromatic hydrocarbons in Illinois river sediment. Illinois Sustainable Technology Center Report TR-058. http://www.istc.illinois.edu/info/library_docs/TR/TR058.

Gachanja A, Worsfold P, (1993). Monitoring of polycyclic aromatic hydrocarbon emissions from biomass combustion in Kenya using liquid chromatography with fluorescence detection. Science of the Total Environment 138(1-3):77-89.

Gall ET, Carter EM, Earnest M, Stephens B (2011). Indoor air pollution in developing countries: Research and implementation needs for improvements in global public health. American Journal of Public Health 103(4):e67-e72.

Gercama I, Bertrams N (2017). Illegal logging in Malawi: can clean cooking stoves save its forests?. The Guardian (Guardian sustainable business), 23 Feb 2017. https://www.theguardian.com/sustainable-business/2017/feb/23/illegal-logging-in-malawi-can-clean-cooking-stoves-save-its-forests (accessed 06-03-2018)

Grieshop AP, Marshall JD, Kandlikar M (2011). Health and climate benefits of cookstove replacement options. Energy Policy 39(12):7530-7542.

International Agency for Research on Cancer (IARC) (2013) IARC Monographs on the evaluation of carcinogenic risks to humans. Volume 109. International Agency for Research on Cancer, Lyon, France. https://monographs.iarc.fr/wp-content/uploads/2018/06/mono109.pdf

International Energy Agency (IEA) (2017). World Energy Outlook 2017, Paris. https://www.iea.org/weo2017/

Jagger P, Pedit J, Bittner A, Hamrick L, Phwandapwhanda T, Jumbe C (2017). Fuel efficiency and air pollutant concentrations of wood-burning improved cookstoves in Malawi: Implications for scaling-up cookstove programs. Energy for Sustainable Development 41:112-120.

Jagger P, Jumbe C (2016). Stoves or sugar? Willingness to adopt improved cookstoves in Malawi. Energy Policy 92:409-419.

Jetter J, Zhao Y, Smith KR, Khan B, Yelverton T, DeCarlo P, et al. (2012). Pollutant emissions and energy efficiency under controlled conditions for household biomass cookstoves and implications for metrics useful in setting international test standards. Environmental Science & Technology 46(19):10827-10834.

Keshtkar H, Ashbaugh LL (2007). Size distribution of polycyclic aromatic hydrocarbon particulate emission factors from agricultural burning. Atmospheric Environment 41:2729-2739.

Lawal AT (2017). Polycyclic aromatic hydrocarbons. A review. Cogent Environmental Science 3:1-86.

Malawi-Government (2010). Malawi Millennium Development Goals Report, Zomba, Malawi: Malawi Government Print.

Meglen RR (1992). Examining large databases: A chemometric approach using principal component analysis. Marine Chemistry 39:217-237.

Mortimer K, Ndamala CB, Naunje AW, Malava J, Katundu C, Weston W, Havens D, Pope D, Bruce NG, Nyirenda M, Wang D, Crampin A, Grigg J, Balmes J, Gordon SB (2017). A cleaner burning biomass-fuelled cookstove intervention to prevent pneumonia in children under 5 Years old in rural Malawi (the Cooking and Pneumonia Study): A cluster randomised controlled trial. Lancet 389(10065):167-175.

Ong R, Lundstedt S, Haglund P, Marriott P (2003). Pressurised liquid extraction–comprehensive two-dimensional gas chromatography for fast screening of polycyclic aromatic hydrocarbons in soil. Journal of Chromatography A 1019(1):221-232.

Orr A, Kambombo B, Roth C, Harris D, Doyle V (2015). Adoption of integrated food-energy systems: Improved cookstoves and pigeonpea in Southern Malawi. Experimental Agriculture 51(2):191-209.

O'Shaughnessy SM, Deasy MJ, Doyle JV, Robinson AJ (2014). Field trial testing of an electricity-producing portable biomass cooking stove in rural Malawi. Energy for Sustainable Development 20:1-10.

Piddock KC, Gordon S B, Ngwira A, Msukwa M, Nadeau G, Davis KJ, Nyirenda MJ, Mortimer K (2014). A cross-sectional study of household biomass fuel use among a periurban population in Malawi. Annals of the American Thoracic Society, 11(6):915-924.

Ramdahl T (1985). PAH emissions from combustion of biomass. In: A. Bjorseth and T. Ramdahl (Eds.), Handbook of Polycyclic Aromatic Hydrocarbons, Vol. 2, Dekker, New York pp. 61-85.

Riojas-Rodriguez H, Schilmann A, Marron-Mares AT, Masera O, Li Z, Romanoff L, et al. (2011). Impact of the improved patsari biomass stove on urinary polycyclic aromatic hydrocarbon biomarkers and carbon monoxide exposures in rural Mexican women. Environ Health Perspectives 119(9):1301-1307.

Roden CA, Bond TC, Conway S, Osorto Pinel AB, MacCarty N, Still D (2009). Laboratory and field investigations of particulate and carbon monoxide emissions from traditional and improved cookstoves. Atmospheric Environment 43(6):1170-1181.

Romieu I, Riojas-Rodríguez H, Marrón-Mares AT, Schilmann A, Perez-Padilla R, Masera O (2009). Improved biomass stove intervention in rural Mexico. American Journal of Respiratory and Critical Care Medicine 180(7):649-656.

Saksena S, Prasad R, Pal RC, Joshi V, 1992. Patterns of daily exposure to TSP and CO in the Garhwal Himalaya. Atmospheric Environment 26(11):2125-2134.

Shen H, Huang Y, Wang R, Zhu D, Li W, Shen G, Wang B, Zhang Y, Chen Y, Lu Y, Chen H, Li T, Sun K, Li B, Liu W, Liu J, Tao S (2013a). Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions. Environmental Science & Technology 47:6415-6424.

Shen G, Tao S, Wei S, Chen Y, Zhang Y, Shen H, Huang Y, Zhu D, Yuan

C, Wang H, Wang Y (2013b). Field measurement of emission factors of PM, EC, OC, parent, nitro-, and oxy- polycyclic aromatic hydrocarbons for residential briquette, coal cake, and wood in rural Shanxi, China. Environmental Science and Technology 47(6):2998-3005.

Tadsanaprasittipol A (2016). Development of analytical methods for particulate-bound polycyclic aromatic hydrocarbons (PAHs) in Thailand. PhD thesis, Department of Civil and Environmental Engineering, University of Strathclyde.

Taylor ET, Nakai S (2012). Monitoring the levels of toxic air pollutants in the ambient air of Freetown, Sierra Leone. African Journal of Environmental and Science Technology 6(7):283-292.

Thomas E, Wickramasinghe K, Mendis S, Roberts N, Foster C (2015) Improved stove interventions to reduce household air pollution in low and middle income countries: a descriptive systematic review. BMC Public Health 15:650.

Timko JA, Kozak RA (2016). The influence of an improved firewood cookstove, Chitetzo Mbaula, on tree species preference in Malawi. Energy Sustainable Development 33:53-60.

Tobiszewski M, Namieśnik J (2012). PAH diagnostic ratios for the identification of pollution emission sources. Environmental Pollution 162:110-119.

US EPA (1999). Compendium Method TO-13A: Determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography/mass spectrometry (GC/MS). EPA/625/R-96/010b, US EPA Office of Research and Development. https://www3.epa.gov/ttnamti1/files/ambient/airtox/tocomp99.pdf

Water for People (2017). Malawi – Statistics, Our work, Chikwawa. https://www.waterforpeople.org/where-we-work/malawi (Accessed 10/02/2017)

Wathore R, Mortimer K, Grieshop AP (2017). In-use emissions and estimated impacts of traditional, natural- and forced-draft cookstoves in rural Malawi. Environmental Science & Technology 51(3):1929-1938.

World Bank (2018). Malawi Data. https://docs.wfp.org/api/documents/WFP-0000073745/download/?_ga=2.159010418.932160188.1536781160-1100854252.1536781160

White Jr KL (2008). An overview of immunotoxicology and carcinogenic polycyclic aromatic hydrocarbons. Environmental Carcinogenesis Reviews 4 (2):163-202.

World Food Program (2018). WFP Malawi country brief. https://docs.wfp.org/api/documents/WFP-0000073745/download/?_ga=2.159010418.932160188.1536781160-1100854252.1536781160

WHO (2018). Household air pollution and health – Key facts. http://www.who.int/news-room/fact-sheets/detail/household-air-pollution-and-health

Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S (2002). PAHs in the Fraser River Basin: A Critical Appraisal of PAH Ratios as Indicators of PAH Source and Composition. Organic Geochemistry 33(4):489-515.

Yunker MB, Perreault A, Lowe CJ (2012). Source apportionment of elevated PAH concentrations in sediments near deep marine outfalls in Esquimalt and Victoria, BC, Canada: Is Coal from an 1891 shipwreck the source? Organic Geochemistry 46:12-37.