Monitoring of atmospheric polycyclic aromatic hydrocarbons through optimization of analytical techniques

by

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Declaration

I, Chiedza Francisca Munyeza declare that the thesis, which I hereby submit for the degree Doctor of Philosophy at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Signature: CF Munyeza

Date: July 2020

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Summary

Atmospheric pollutant monitoring in low to medium-income countries can play a vital role in improving human welfare through reductions in environmental impacts and the global burden of disease. Polycyclic aromatic hydrocarbons (PAHs) have been widely used as markers of environmental pollutants in the context of ambient air, indoors, as well as in working environments. Sampling, extraction, sample clean up and analysis constitute the principal stages required for the determination of airborne PAHs. Most conventional methods utilize high volume samplers and high volume extraction methods for the analysis of atmospheric gaseous and particulate PAHs, which is time consuming and may introduce unreliable data for human exposure estimations. Additionally, large amounts of toxic solvents generate waste and could cause adverse environmental impacts.

In order to counteract these unfavorable environmental effects, recent studies worldwide have been focusing on the miniaturization of sampling and analysis techniques. However, most of these developed portable sampling devices for simple and efficient solvent minimized techniques are not easily available, especially in developing countries which have limited laboratory budgets. This research focused on multi-channel polydimethylsiloxane (PDMS) traps as portable denuder devices for the monitoring of semi-volatile organic compounds (SVOCs), with most attention being given to the United States Environmental Protection Agency (US EPA) priority PAHs. These portable PDMS samplers are currently being analyzed by direct thermal desorption using a commercial desorber, which is quite expensive to obtain, maintain and operate.

In response to challenges faced by laboratories in developing countries, a plunger assisted solvent extraction (PASE) method for multi-channel PDMS rubber trap samplers was developed as an alternative to direct thermal desorption for the monitoring of PAHs. Extraction parameters which are capable of influencing extraction efficiency of target analytes such as choice of extraction solvent, number of sequential extractions and PDMS trap orientation were investigated and optimized. The proposed method used minimum solvent (total 2 mL hexane) and was quicker (approximately 4 min needed for PASE extraction including weighing, compared to the 11.5 min desorption time). Additionally, the PASE technique was

advantageous over thermal desorption (TDS) in that samples could be re-analyzed, as only 1 μL of the final extract was injected. However, limits of detection (LODs) for thermal desorption remained superior, ranging from 0.14 ng m^{-3} for acenaphthylene to 0.9 ng m^{-3} for benzo[g,h,i]perylene, as it analysed the whole sample. In comparison, PASE method LODs ranged from 13.6 ng m^{-3} for naphthalene to 227.1 ng m^{-3} for indeno[1,2,3-cd]pyrene in sampled air.

Two sequential extractions resulted in optimum overall extraction efficiencies of the target PAHs, and ranged from 76% for naphthalene to 99% for phenanthrene, with relative standard deviations (RSDs) below 6%. Although sequential extractions did not result in much improvement in extraction efficiencies of lighter PAHs (2-3 rings), it improved efficiencies for the heavier target analytes (4-6 rings). Notable quality control merits (mean for 15 PAHs) of the proposed PASE method included good repeatability based on intra-day variations, (n=5), which ranged from 0.5% for pyrene to 4.9% for naphthalene and acceptable recoveries (n=3) ranging from 76% for naphthalene to 99% for phenanthrene. Linearity of the calibration curves ranged from 0.983 for naphthalene to 0.999 for acenaphthene and acenaphthylene, which demonstrated the suitability of the method for routine monitoring of PAHs. The PASE procedure was firstly applied to the analysis of domestic outdoor fire (charcoal) air emission samples and naphthalene was the most dominant analyte with maximum concentrations of 9.5 μg m^{-3}. Fluorene, anthracene, phenanthrene, fluoranthene and pyrene were also identified and quantified.

In the next phase of the study, the applicability of the PASE method was evaluated for the analysis of indoor and outdoor air samples from residential homes in rural and urban coastal Kenya (Taita Taveta and Mombasa counties). A concentration step was added to the PASE method, whereby extracts were blown down to 100 μL. Calibrations and quantification were based on 100 μL final extracts and LODs (based on 100 μL final extract, 1 μL injection and an air sampling volume of 5 L) ranged from 1.9 ng m^{-3} for 2-methylnaphthalene to 34.9 ng m^{-3} for indeno[1,2,3-cd]pyrene. A PDMS trap coupled to a portable sampling pump was used to sample combustion emissions (within the breathing zone) using a flow-rate of 500 mL min^{-1} for 10 min. Typical combustion devices in rural and urban residential areas of Kenya included gas, kerosene, charcoal (jiko), 3-stone and improved 3-stone stoves. In addition to the combustion device, other possible influencing factors for PAHs levels in indoor environments such as the type of dwelling, ventilation, geographical location and fuel used were also explored. Indoor area measurements during operation of cooking devices in rural areas resulted in higher total gaseous PAH concentrations per household (ranging from 11.37 to 85.20 µg m^{-3}) compared to urban homes (ranging from <LOQ to 36.40 µg m^{-3}). However, ambient PAH concentrations were higher in urban environments, likely due to traffic contributions. As evidenced by principal component analysis (PCA), the most pronounced variations were observed from wood burning emissions during use of traditional 3-stone stoves in rural households, with total PAH concentrations averaging 46.23 ±3.24 µg m^{-3} (n=6).

In order to evaluate the relative carcinogenic contribution of each individual PAH based on benzo[a]pyrene (BaP), BaP equivalent (BaPeq) values were calculated using selected Toxic Equivalence Factors (TEFs). From an overall analysis of household cooking fuel use in coastal Kenya, gas stoves were found to account for the least (0%) PAH emissions (no detected carcinogenic contribution) in indoor setups. Average BaPeq total concentrations for kerosene, jiko, 3-stone and improved 3-stone stoves were 43.31, 88.38, 309.61 and 453.88 ng m^{-3} respectively. These high variations in PAH concentrations and carcinogenic potencies indicate the importance of good combustion devices and well ventilated conditions to reduce possible health impacts in urban and rural communities.

Further laboratory controlled experiments were performed to shed more light on the principal operating mechanisms of the PDMS traps and quartz fiber filters in a denuder assembly. Efficient transmission of sample particles through the PDMS trap is of paramount importance otherwise gas phase SVOC concentrations would be over-estimated and particle phase SVOC concentrations would be underestimated if SVOCs were associated with these particles. In this light, experiments mainly addressed particle collection and transmission efficiencies for a wider size range of particles than had been previously studied, including more realistic ambient particulate matter for ambient measurements. Ambient aerosol and aqueous suspensions of monodisperse polystyrene latex (PSL) as test particles (0.3, 0.5 and 0.8 µm), were evaluated. A temperature controlled chamber consisting of an aerosol generator, dilution and mixing unit, a flow tube and the sampling apparatus was used to evaluate particle transmission and collection efficiencies. With regards to quartz fiber filters, collection efficiency for the tested

PSL particles was high (>98%) with acceptable variation coefficients all less than 16%. However, the tested ambient particles were collected with lower efficiencies, ranging between 88-95%, most likely due to the higher diffusion coefficients of the smaller ambient particles and electrostatic effects. This data allowed for a better understanding of the denuder operating mechanisms and can provide useful guidelines as well as potential limitations which should be considered in future sampling applications and data interpretation.

In conclusion, the optimized multi-channel PDMS denuder device, extraction and analysis methods investigated in this study could find application in environmental laboratories, especially where cost considerations are important (such as Sub-Saharan Africa). Additionally, the application of these methods would facilitate the widespread monitoring of atmospheric PAHs in a cost effective manner and identify potential hotspots of regional pollution.

Publications and Manuscripts

This thesis is based on the following journal papers:

1. Chiedza F. Munyeza, Egmont R. Rohwer, Patricia B.C. Forbes, (2019). A review of monitoring of airborne polycyclic aromatic hydrocarbons: An African perspective. *Trends in Environmental Analytical Chemistry*, 24. https://doi.org/10.1016/j.teac.2019.e00070.

2. Chiedza F. Munyeza, Onkarabile Dikale, Egmont R. Rohwer, Patricia B.C. Forbes, (2018). Development and optimization of a plunger assisted solvent extraction method for polycyclic aromatic hydrocarbons sampled onto multi-channel silicone rubber traps, *Journal of Chromatography A*, 1555, 20-29. https://doi.org/10.1016/j.chroma.2018.04.053.

3. Chiedza F. Munyeza, Aloys M. Osano, Justin K. Maghanga, Patricia B.C. Forbes, (2019). Polycyclic aromatic hydrocarbon emissions from household cooking devices: A Kenyan case study. *Environmental Toxicology and Chemistry*. https://doi.org/10.1002/etc.4648.

4. Chiedza F. Munyeza, Vesta Kohlmeier, George C. Dragan, Erwin W. Karg, Egmont R. Rohwer, Ralf Zimmermann, Patricia B.C. Forbes (2019). Characterization of particle collection and transmission in a polydimethylsiloxane based denuder sampler, *Journal of Aerosol Science*, 130, 22-31. https://doi.org/10.1016/j.jaerosci.2019.01.001.

An additional paper was produced as a co-author contributing to the literature review and analysis of data.

Osano, A.; Maghanga, J.; Munyeza, C.F.; Chaka, B.; Olal, W. and Forbes, P.B.C. (2019). Insights into household energy use in Kenyan communities. *Sustainable Cities and Society*, 55, 102039. https://doi.org/10.1016/j.scs.2020.102039.

Conference Presentations

Additional outputs based on this work are summarized below:

Oral Presentations

1. Chiedza F. Munyeza, Onkarabile Dikale, Egmont R. Rohwer, Patricia B.C. Forbes, Development and optimization of a plunger assisted solvent extraction method for polycyclic aromatic hydrocarbons sampled onto multi-channel silicone rubber traps, ChromSAAMS **2016**, New Limits - New Applications, 11-14 September 2016, Vanderbijlpark, South Africa.

2. Chiedza F. Munyeza, Onkarabile Dikale, Egmont R. Rohwer, Patricia B.C. Forbes, Development and optimization of a plunger assisted solvent extraction method for polycyclic aromatic hydrocarbons sampled onto multi-channel silicone rubber traps, 9th International Symposium on Modern Principles of Air Monitoring and Biomonitoring (AIRMON **2017**), 11-15 June 2017, Dresden, Germany.

3. Chiedza F. Munyeza, Onkarabile Dikale, Egmont R. Rohwer, Patricia B.C. Forbes, Development and optimization of a plunger assisted solvent extraction method for polycyclic aromatic hydrocarbons sampled onto multi-channel silicone rubber traps, ChromSA Student Symposium **2017**, 8 September 2017, University of Pretoria, South Africa.

Poster Presentation

1. Chiedza F. Munyeza, Vesta Kohlmeier, George C. Dragan, Erwin W. Karg, Egmont R. Rohwer, Ralf Zimmermann, Patricia B.C. Forbes, Characterization of particle collection and transmission in a polydimethylsiloxane based denuder sampler, Analitika **2018**, 22-25, Legend Gold and Safari Resort, Mookgophong, Limpopo, South Africa.

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Abbreviations

Abbreviations from all chapters have been listed below. Abbreviations in the Appendix are not listed here, unless used elsewhere in the thesis, as they are fully defined in the respective paper.

ASE	Accelerated Solvent Extraction
ATSDR	Agency of Toxic Substances and Disease Register
BaPeq	Benzo[a]pyrene Equivalent
CF-SPME	Cold-Fiber Solid-Phase Micro-Extraction
CIS	Cooled Injection System
DCM	Dichloromethane
DSWE	Dynamic Subcritical Water Extraction
ECD	Electron-Capture Detection
GC-MS	Gas Chromatography-Mass Spectrometry
GFF	Glass Fiber Filter
GPC	Gel Permeation Chromatography
HS-SPME	Headspace Solid-Phase Micro-Extraction
IARC	International Agency for Research on Cancer
IS	Internal Standard
LC	Liquid Chromatography
LDI-TOF-MS	Laser Desorption Ionization - Time of Fight-Mass Spectrometry
LIF	Laser Induced Fluorescence
LOD	Limit of Detection
LOQ	Limit of Quantification

LPG	Liquefied Petroleum Gas
MAD	Microwave-Assisted Desorption
PAHs	Polycyclic Aromatic Hydrocarbons
PASE	Plunger Assisted Solvent Extraction
PCA	Principal Component Analysis
PDMS	Polydimethylsiloxane
PUF	Polyurethane Foam
QFF	Quartz Fiber Filter
QuEChERS	Quick, easy, cheap, effective, rugged, and safe
RSDs	Relative Standard Deviations
SDGs	Sustainable Development Goals
SFE	Supercritical Fluid Extraction
SIM	Selected Ion Monitoring
S/N	Signal to Noise
SVOCs	Semi-Volatile Organic Compounds
TEFs	Toxic Equivalence Factors
TEQs	Toxic Equivalence Quotients
US EPA	United States Environmental Protection Agency
WHO	World Health Organisation

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Introduction

1.1 Research Background

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants comprising carbon and hydrogen atoms fused into two or more aromatic ring structures. They are formed and released into the environment through natural and anthropogenic activities due to the incomplete combustion of fossil fuels (coal, natural gas, oil). Sources of emissions include natural fires, volcanic eruptions, household fuel burning, waste incineration and coke production [1]. PAHs have caused major health and environmental concerns due to their carcinogenic, toxic and mutagenic properties [2]. For this reason, the global monitoring of PAHs in different environmental matrices such as water, soil and air have been on the rise. Additionally, several international organisations, including the United States Environmental Protection Agency (US EPA), World Health Organisation (WHO), International Agency for Research on Cancer (IARC) and the Agency of Toxic Substances and Disease Register (ATSDR) have classified some PAHs among the most hazardous and persistent organic pollutants, and have listed them as priority pollutants. The World Health Organisation has raised serious concerns about atmospheric emissions and have reflected these issues in their recent Sustainable Development Goals (SDGs) [3]. Over the past decades, PAHs have been portrayed as an attractive marker for evaluating complex mixtures from atmospheric pollution [4-6].

In South Africa, notable technological improvements in sampling methods and extraction techniques have positively impacted the extent of monitoring of PAHs but further work is still needed to improve the understanding of the status of PAHs in environmental compartments [7]. Our research group has been focusing on the monitoring and risk assessment of PAHs in air samples and has reported several trends and applications. The development of a novel denuder device for the monitoring of gaseous and particulate PAHs in air has been documented in previous work by Forbes *et al.* [8-10] The denuder set-up entails the use of two multi-channel polydimethylsiloxane (PDMS) traps in series joined by a Teflon connector which houses a quartz fiber filter, whereby the PDMS acts as an absorbent for gaseous semi-volatile organic compounds (SVOCs) and the filter collects particulate analytes [11]. A sorbent is often employed behind the filter (secondary trap), to trap analytes desorbed from the filter, and any gaseous analytes not effectively removed by the primary trap (under break-through conditions) [10].

1.2 Problem Statement and Motivation

The efficiency of the multi-channel PDMS denuder device has been investigated from both theoretical and experimental perspectives and it has been utilized in a number of applications including household fire emissions, sugar cane burning emissions, tunnel air pollution studies and in underground mining environments in South Africa [11-13]. However, more research is still needed in this area as there is still an increasing demand to develop methods for the measurement and analysis of PAHs in indoor or outdoor environments, ambient air and in the working environment. The need for this research is not only in South Africa but in most developing countries in Sub-Saharan Africa. Additionally, research on PAHs is still being extensively conducted all over the world since PAHs are a global environmental issue. Currently, the PDMS samplers are being analyzed by direct thermal desorption using a commercial desorber. Many modern laboratories have GC-MS instruments but only a few have commercial thermal desorbers since they are very expensive to obtain, maintain and operate. To date there is no reported literature on a validated liquid extraction procedure for extracting PAHs from multi-channel silicone rubber trap samplers.

1.3 Aims and Objectives

In view of the above mentioned challenges faced by laboratories in developing countries, the main goal and strategy of this work is to develop an alternative extraction technique in an effort to reduce cost and at the same time allow for the widespread use of the multi-channel silicone rubber traps. The main objectives of this work are:

- To develop and validate a new plunger assisted solvent extraction (PASE) technique for extracting PAHs from multi-channel silicone rubber trap samplers, as an alternative to the conventional thermal desorption of samples directly from the traps, in order to enhance accessibility of this sampling technique and reduce analytical costs. (This work only focused on the solvent extraction of the PDMS denuder traps. Filters were not solvent extracted in this study).

- To quantify the PAHs in each extract using an optimized chromatographic technique coupled to mass spectrometry.

- To apply the optimized extraction technique to real field samples, for example samples obtained from Kenyan household fuel emissions, where exposure to PAH emissions are of concern, in order to investigate and justify the suitability of the analytical method.

- To conduct controlled laboratory experiments based on particle transmission efficiencies of PDMS traps and particle collection efficiencies of filters, in order to further elucidate the fundamental operating mechanisms of the denuders.

1.4 Structure of Thesis

This study involved collaborations with a few institutions and academic disciplines encompassing chemists, environmental and occupational health practitioners. In light of this, research chapters are based on published manuscripts.

Chapter 2 (**Paper 1**) is a literature review which gives an overview of the current status of the monitoring of PAHs in living and working conditions as well as in ambient air. Sampling, extraction and analysis methods for atmospheric PAHs employed in several African countries over the period 2000 to 2018 are reviewed. Basic quality assurance data and concentrations measured are also presented.

Chapter 3 (**Paper 2**) summarizes the main methods, results and discussion of this work. A plunger assisted solvent extraction (PASE) method for multi-channel silicone rubber trap samplers was developed and evaluated as an alternative to direct thermal desorption for the monitoring of PAHs. Although preliminary application of the method to real domestic fires was described in Chapter 3, Chapter 4 (**Paper 3**) reports the sampling of gas phase PAHs onto PDMS traps and their extraction using the low cost PASE method, based on a domestic combustion case study in rural and urban coastal Kenya.

In order to shed more light on the fundamental operating mechanisms of the PDMS traps used in this research and the quartz fibre filter employed in associated denuder samplers, Chapter 5

(**Paper 4**) describes additional controlled laboratory experiments regarding particle transmission and collection efficiencies for a wider size range of particles. Lastly, overall conclusions and future recommendations are summarised in Chapter 6.

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Chapter 2: Literature Review (Paper 1)

This chapter presents a general overview of sampling, extraction and analytical methods for atmospheric PAHs employed in several African countries over the period 2000 to 2018.

This chapter was published in Trends in Environmental Analytical Chemistry (TrEAC).

Chiedza F. Munyeza, Egmont R. Rohwer, Patricia B.C. Forbes, (2019). A review of monitoring of airborne polycyclic aromatic hydrocarbons: An African perspective. *Trends in Environmental Analytical Chemistry*, 24. https://doi.org/10.1016/j.teac.2019.e00070.

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A review of monitoring of airborne polycyclic aromatic hydrocarbons: An African perspective

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ABSTRACT

In this review, we focus on the status of the monitoring of polycyclic aromatic hydrocarbons (PAHs) in ambient air as well as in living (indoor) and working environments in Africa from 2000 to 2018. This is important as PAHs are ubiquitous in the environment and are known to be potentially carcinogenic. Aspects of sampling such as collection media for particle bound and gaseous PAHs are discussed. The efficiency and basic quality assurance data of commonly employed extraction techniques for separating target PAHs from sampling media using conventional solvent-based and emerging solvent-free approaches were also evaluated. Polyurethane foam and quartz fiber filters are generally the most commonly used collection media for gaseous and particle bound PAHs, respectively. A wide range of total PAH concentrations in ambient air has been reported across the continent of Africa, with the highest levels found at sampling sites close to high density traffic and industrial areas. A rapidly increasing population, commercial and industrial development, poor urban transportation infrastructure and the use of low quality oil products were the main causes of high total gas and particulate PAH concentrations (1.6–103 $\mu g/m^3$) in West African port cities such as Cotonou, Benin. With regards to indoor environments, gas phase PAHs were detected at the highest total concentrations in rural areas ranging from 1 to 43 $\mu g/m^3$ in Burundi with naphthalene being the most prevalent. Firewood burning was the major emission source in most developing countries and resulted in benzo[a]pyrene concentrations above the European permissible risk level of 1 ng/m^3.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic compounds containing at least two fused benzene rings arranged in various configurations. They are released into the environment from both natural and anthropogenic sources. Domestic heating emissions, vehicle exhausts, waste incineration and industrial processes are some of the major anthropogenic sources releasing PAHs into the atmosphere [1]. Significant natural sources of PAHs include volcanic eruptions and natural fires in forests and grasslands. Globally, PAHs have remained in the environmental spotlight due their adverse effects on humans. The toxicity of PAHs is well known: based on laboratory tests on animals as well as human epidemiologic studies, it has been suggested that most of these compounds are potentially carcinogenic and/ or mutagenic [2–4]. Additional health effects resulting from acute and chronic human exposure to PAHs include pulmonary and respiratory problems, localized skin effects, genetic reproductive and developmental complications, behavioral, neurotoxic, and other organ system effects [5].

In this review we mainly restrict our discussion to unsubstituted PAHs, although the compounds may exist in various substituted forms such as nitro-, amino-, alkyl-, or halogen substituted PAHs. The US Environmental Protection Agency (EPA) includes sixteen PAHs in its priority pollutants list and the names and abbreviations of these are given in Table 1. Although the health effects of individual PAHs differ, certain PAHs have been identified to be of greatest concern due to their highly negative impacts on human health. Ambient air legislation in Europe targets benzo[a]pyrene (with an annual target value of 1 ng/m^3) as this compound is known to carry the highest toxic load (calculated by multiplying toxicity and concentration) of any airborne PAH [6,7].

The physicochemical properties of PAHs (Table 1) determine their high mobility in the environment, allowing them to be widely distributed across water bodies, soil and air [6]. PAHs in the ambient air can be distributed between gas and particle-bound phases. Their phase distribution depends on the nature (origin and properties) of the aerosol, the atmospheric conditions (relative humidity, ambient temperature, *etc*) and the properties of the individual PAH [8–10]. Consequently, lighter PAHs (with 2–4 rings)

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Table 1
Structure and properties of the 16 EPA priority PAHs.

PAH	Abbreviation	Formula	Molar mass (g/mol)	[a]Vapor pressure (Pa 25 °C)	[b]TEF
Naphthalene	Nap	$C_{10}H_8$	128	11.14	0.001
Acenaphthylene	Acy	$C_{12}H_8$	152	3.87	0.001
Acenaphthene	Ace	$C_{12}H_{10}$	154	3.07	0.001
Fluorene	Flu	$C_{13}H_{10}$	166	1.66	0.001
Anthracene	Ant	$C_{14}H_{10}$	178	1.06×10^{-1}	0.01
Phenanthrene	Phen	$C_{14}H_{10}$	178	8.6×10^{-4}	0.001
Fluoranthene	FluAn	$C_{16}H_{10}$	202	8.61×10^{-4}	0.001
Pyrene	Pyr	$C_{16}H_{10}$	202	5.0×10^{-5}	0.001
Benzo [a]anthracene	BaA	$C_{18}H_{12}$	228	5.43×10^{-4}	0.1
Chrysene	Chry	$C_{18}H_{12}$	228	4.0×10^{-6}	0.01
Benzo[b]fluoranthene	BbF	$C_{20}H_{12}$	252	5.0×10^{-7}	0.1
Benzo[a]pyrene	BaP	$C_{20}H_{12}$	252	6.0×10^{-8}	1
Benzo[k]fluoranthene	BkF	$C_{20}H_{12}$	252	5.2×10^{-8}	0.1
Indeno[1,2,3-cd]pyrene	IcdP	$C_{22}H_{12}$	276	1.27×10^{-7}	0.01
Benzo[g,h,i]perylene	BghiP	$C_{22}H_{12}$	276	1.38×10^{-8}	0.1
Dibenz[a,h]anthracene	DahA	$C_{22}H_{14}$	278	1.33×10^{-8}	1

[a] Vapor pressure [19,29].
[b] Toxic equivalence factor [30].

are more volatile and tend to be enriched in the gas phase while the heavier PAHs with low vapor pressure show almost complete association with particles [11]. In light of these phase partitioning processes, it remains a challenge –from sampling to analysis- to acquire an accurate profile of these harmful substances in various environmental matrices, especially in the atmosphere.

Sampling, extraction, sample clean-up, and analysis constitute the principle stages in the measurement of atmospheric PAHs. To date, gas chromatography (GC) in combination with a number of sampling approaches and sample-preparation steps, has been the most common technique for the analysis of PAHs in air. This is because for stable organic compounds, GC has advantages over other systems such as liquid chromatography (LC) and is proven to have greater selectivity, resolution, and sensitivity [1]. Ideally GC is combined with mass spectrometry (MS) to improve selectivity and to ensure the robustness of sample identification and quantification. This has produced powerful GC–MS strategies, which are able to yield lower limits of detection (LODs) compared to other GC methods.

1.1. Background

Globally, there have been a number of reviews concerning the sampling and quantitation of PAHs in gaseous or particulate phases in ambient air. Leinster and Evans [12] summarized the difficulties that can arise in the sampling of airborne PAHs and discussed possible factors which should be considered when devising a sampling plan in order to avoid analyte losses. A similar study was reported by Davis et al. [5] who reviewed the effects of choice of filters and sorbents such as polyurethane foam (PUF), XAD-2 and Tenax on the overall air sampling efficiency. The authors discussed active *versus* passive sampling covering the period 1977-83 and they also described experimental artifacts, especially losses due to blow-off of the more volatile PAHs from particulate matter (PM).

The 21st century saw the introduction of many ground breaking technologies which encouraged numerous studies focusing on the analysis of PAHs. Liu et al. [13] reviewed the improvements and developments of sampling and pretreatment techniques used to determine airborne PM PAHs during 2000–05. With the introduction of spectroscopic approaches for detection and quantitation of PAHs as an important area for future research, Cullum et al. [14] provided an overview of high temperature (150–600 °C) fluorescence and other *in situ* spectroscopic measurements of PAHs in ambient air and in flames. Cecinato et al. [15] briefly reviewed the sampling and analytical methods for assessing semi-volatile organic compounds (SVOCs) such as PAHs, phthalates, and psychotropic substances in the atmosphere. The authors summarized sample collection techniques, extraction, recovery, clean-up, separation and analytical instrumentation. Pandey et al. [1] extensively reviewed the common methodologies employed in the analysis of airborne PAHs, with particular attention to sampling techniques, solvent extraction efficiencies, LODs, and analytical reproducibility of the methods. Similarly, Szulejko et al. [16] presented the next major review in 2014, with the main emphasis being given to all aspects of solvent extraction prior to GC-based analysis of airborne PAHs. More recently, a number of reviews from all over the globe have addressed concentration, distribution, emission factors, human exposure assessment and available control technologies regarding atmospheric PAHs [17–20]. However, not much information has been made available on the current sampling and extraction methodologies for the analysis of airborne PAHs which are employed in African countries, where resource limitations and different sources of PAHs are expected to lead to different approaches to those employed in developing countries.

Air pollution is used as a marker of sustainable development, as sources of air pollution also produce climate-modifying pollutants such as black carbon. Consequently, concerns about air pollution have been reflected in the Sustainable Development Goals (SDGs) by the World Health Organization (WHO) [21]. The WHO report concluded that citizens in Africa, Asia and the Middle East breathe much higher levels of air pollutants than those in other parts of the world. This could be attributed to the fact that Africa (77%) and South-East Asia (61%) have the highest proportion of households using solid fuels [22]. In addition to the prevalence of household biomass burning to provide household energy, low-income countries, especially in sub-Saharan Africa, bear a high burden of PAH air pollution from other sources such as traffic and veld fires, yet they are nearly unrepresented when it comes to researching the health impacts thereof on their citizens. A possible explanation is that the health risk of air pollution is perceived to be overshadowed by risks like tuberculosis, HIV, malnutrition and malaria. A lack of air monitoring resources and infrastructure could also contribute to the limited data available from Africa [23].

Levels, trends and health concerns of atmospheric PAHs have been reviewed for Europe [24] and Asia [25]. Since Africa and these regions have different air quality problems, a comparative analysis of the concentrations of PAHs in air is essential. In cities such as London, air pollution is mainly due to the burning of hydrocarbons for transport, yet African pollution is more complex in nature [24]. In most African urban areas, burning of garbage, cooking indoors using inefficient fuel stoves, large numbers of diesel electricity generators, cars without catalytic converters and petrochemical plants, may all emit air pollutants. In light of the above, a detailed regional overview on the analysis of PAHs in air is required with the ultimate aim of improved air quality and human health.

With regards to reviews of PAH pollution in Africa, Kalisa et al. [26] recently examined epidemiological and toxicological studies conducted in African cities. The authors summarized the association between biological and chemical components of PM and their associated health outcomes, with an emphasis on the 16 EPA PAHs and their nitrated derivatives. Country based reviews have also been documented, whereby Chimuka et al. [27] assessed the status of PAH concentrations in a range of environmental media including surface water, air, sediment, and soil samples in South Africa and Assmaa et al. [28] presented the concentrations of PAHs in suspended particulate matter in Egypt. However, no detailed regional overview which focuses on the sampling, extraction and analysis techniques used for the monitoring of gaseous and particulate PAHs in ambient air, indoor and workplace environments has been published to date.

This review evaluates trends in existing analytical methods and recent developments in sampling, extraction and analysis of airborne PAHs in Africa from 2000 to 2018 as compared to global trends and analytical practices. In order to review concentrations of airborne PAHs found in Africa, we discuss the procedures involved - from sampling, sample preparation or pre-concentration to final detection of PAHs from different sampling sites. The focus is on sampling of both vapor and particulate phases and how conventional solvent-based extraction techniques have been applied and improved over time. Moreover, we also evaluate simplified solvent-free methods as alternatives to solvent-based methods, and present their advantages and disadvantages in each application area.

2. Monitoring of airborne PAHs with a focus on Africa

From Table 2, it is clear that the number of African studies which monitored PAHs in air grew over the period from 2000 to 2018 (Fig.1), which may be attributed to increasing awareness and concerns related to the adverse effects of airborne PAHs on human health as mentioned in Section 1. However, despite this progress in research output, only 30% of the African countries have reported detailed analytical procedures for the monitoring and risk assessment of PAHs in air samples. This is most likely due to hindrances such as socio-political priorities and lack of resources which results in unavailability of funding, suitable equipment and skilled human capital [23]. In an effort to overcome some of these problems, most African studies reviewed involved collaboration with Europe or Asia whereby sampling was performed in Africa with analysis done overseas [31–35]. Egypt and Algeria had the highest number of publications on the monitoring of airborne PAHs, closely followed by South Africa. Table 2 summarizes the methods used to monitor airborne PAHs in studies which have been done across the African region. Table 2 is discussed to determine the distribution of PAHs and their concentrations, as well as sampling, extraction and analysis methods for each exposure type.

2.1. Airborne PAH sampling methods

Sampling is a critical step that can define the success or failure of any measurement campaign for PAHs in ambient air. The main sampling modes for atmospheric PAHs are active (where a known volume of air is drawn through the sorbent) and passive sampling (where vapor is allowed to diffuse into the sorbent). This can be performed with a variety of samplers, including high or low-volume samplers and passive samplers. There are numerous standard reference procedures which have been developed for the determination of PAHs in ambient air such as the EPA compendium method TO-13A [74] and the California Environmental Protection Agency method [75]. These methodologies are typically based on high volume sampling, which makes them not directly applicable to low volume samples. Collection of PAHs usually relies on active sampling rather than passive sampling because of the relatively low concentrations of PAHs present in air. This pattern is clearly shown in Table 2 in which only three African studies employed passive sampling with sampling periods ranging from 7 to 28 days [42,43,49]. Different sampling media have been reported in African literature with most of them being modified and improved over the past few years. Since the distribution of airborne PAHs occurs in both gas and particle-bound phases, sample-collection methods should be designed in such a way that they cover each of the two fractions individually or that they measure the sum fractions at the same time. As indicated in Table 2, a significant number of studies across the African continent aimed to quantify both particle and gas-phase PAHs simultaneously [10,35,50,72,76]. Quantification of the relative contributions of each of the PAH phases is very important as they may have different impacts on human health. In light of this, the collection methods for each of the PAH phases have been summarized in the following sections.

2.1.1. Collection of gas-phase PAHs

Typical sampling media for gas-phase PAHs include polydimethylsiloxane (PDMS), PUF, XAD and mixed sorbents. As detailed by Pandey et al. [1], PUF is the most common sampling medium employed for gas-phase collection since it is applicable for a wide range of PAHs. This is also evident in Table 2, whereby most studies in Africa utilised PUF as sorbent material for different applications. The use of PUF is popular on a global scale and has been recently evaluated for the first time as a tool for occupational PAH measurements [77]. The authors indicated that PUF can reliably and precisely accumulate PAHs after short exposure times (<1 h) and that this sampling medium works for semi-quantitative detection in high-exposure regions in workplaces. Additionally, PUF is considerably cheaper compared to PDMS and other mixed sorbents, which could have influenced sorbent choice in developing countries where funding is scarce. The applicability of PUF samplers has been demonstrated through the use of high sampling volumes ranging from approximately 300–900 m^3 [40,42,49]. As an alternative to PUF, collection of gaseous PAHs on XAD-2 resin cartridges has also been done occasionally across the continent [50,76,78]. Mahgoub and Salih [64] used Teflon membrane filters for the sampling of gaseous PAHs from Dokhan incense in Sudan. Teflon membrane filters are naturally hydrophobic with excellent chemical resistance, making them the ideal choice for gas-phase sample collection. Semi permeable membrane devices were also employed for the evaluation of air contamination in both urban and industrial areas in Morocco [43]. Although not commonly reported, a styrene-divinylbenzene adsorption tube was used to trap volatile PAHs in a study which assessed indoor exposure to PAHs in traditional houses in Burundi [35]. Interestingly, the use of PDMS samplers for airborne PAHs appeared to be common only in South African laboratories [10,70]. This could be attributed to the fact that PDMS is more expensive compared to other sampling media. However, it is advantageous due to its inertness and re-usability. Although other sorbent materials such as Tenax, XAD-4, Carbopack C and mixed sorbent combinations have been reported for the sampling of gaseous PAHs worldwide, their application is limited in Africa.

Table 2
Sampling, extraction and analysis methods for PAHs employed in several African countries over the period 2000–2018. Basic quality assurance data and concentrations measured are also given.

Year of study	Country	Exposure type	Gas/ particle phase	Sampling method/ media	Extraction method & solvent	Analytical method	LODs and Recovery [%]	Concentration	Reference
2000	Burundi	Indoor	Gas and particle	Gilair pump (styrene-divinylbenzene adsorption tube, GFF)	Reflux (acetonitrile)	HPLC-FL	–	1–43 µg/m^3	[35]
2001	Egypt	Ambient	Particle	High volume active sampler (GFF)	Ultrasonic extraction (hexane)	HPLC-DAD/FL	–	7.53–14.79 ng/m^3	[36]
2002	Egypt	Ambient	Particle	High volume air sampler (GFF)	Ultrasonic extraction (hexane)	GC–MS	Recovery:40–120%	14 ng/m^3	[37]
2006	Benin	Indoor and ambient	Particle	Battery operated pumps (GFF)	Soxhlet extraction (DCM)	HPLC-FL	–	76.2–103.2 ng/m^3	[38]
2006	Kenya	Ambient	Particle	Mini-pump (QFF)	Soxhlet extraction (acetone-hexane)	GC–MS	LODs: 0.04–0.1 ng/m^3	0.1–35.8 ng/m^3	[31]
2007	Algeria	Ambient	Particle	Medium volume air sampler (QFF)	Soxhlet extraction (DCM-acetone)	GC–MS	LODs: 0.01–0.025 ng/m^3	13–212 ng/m^3	[39]
2008	Atlantic ocean	Ambient	Gas and particle	High volume active sampler (PUF, GFF)	Soxhlet extraction (*n*-hexane)	HPLC- FL	LODs: 1–9 pg/m^3	23–2560 pg/m^3	[40]
2009	Algeria	Ambient	Particle	High volume active sampler (QFF)	Soxhlet extraction (DCM-acetone)	GC–MS	LOQs: 0.2–2 pg/m^3	0.37–5.14 ng/m^3	[41]
2009	Whole Africa	Ambient	Gas	Passive samplers (PUF disks)	Reflux in DCM	GC–MS	Recovery: 72–102%	80–150 ng/m^3	[42]
2009	Morocco	Ambient	Gas	Semipermeable membrane devices	Microwave extraction, GPC, (DCM)	GC–MS	LOD: 0.4–1.2 ng/m^3	0.4–40 ng/m^3	[43]
2010	Algeria	Ambient	Particle	Medium volume sampler (QFF)	Soxhlet extraction (DCM-acetone)	GC–MS	LODs: 0.01–0.025 ng/m^3	12–24 ng/m^3	[44]
2011	Benin	Ambient, workplace	Gas and particle	GFF	–	HPLC-FL	–	1.6–103 µg/m^3	[45]
2011	Tanzania	Indoor and personal	Gas and particle	Personal aerosol sampler (GFF)	Ultrasonic extraction (DCM)	GC–MS	LOD: 2 ng/m^3	1–5040 ng/m^3	[46]
2011	Egypt	Ambient	Gas phase	High volume air sampler (GFF)	Ultrasonic extraction (benzene-ethanol)	HPLC-FL	Recovery: 87–104%	17.7–65.8 pmol/m^3	[32]
2011	Kenya	Indoor	Particle (soot)	Weighed on filter papers	Soxhlet extraction (DCM)	GC–MS	–	0.2–109.5 µg/g	[47]
2012	Uganda	Ambient	Gas and particle	High volume sampler (PUF, GFF)	ASE (hexane-acetone)	GC–MS	LODs 0.005–0.009 ng/m^3	0.01–160 ng/m^3	[48]
2012	Egypt	Ambient	Gas	Polyethylene passive sampler and high volume sampler (PUF)	Reflux, (DCM), ASE for PUF	GC–MS	–	240–1100 ng/m^3	[49]
2012	Egypt	Ambient (urban traffic area)	Gas and particle	Vacuum pump (GFF, PUF and XAD-2 resin)	Soxhlet extraction (DCM-*n*-hexane)	GC-FID	LOD: 0.029–0.064 ng/m^3 [59.3–107.2%]	Gas: 1.6–1355 ng/m^3 Particle: 2.2–423.1 ng/m^3	[50]
2012	Sierra Leone	Ambient	Particle	Dual impactor (Teflon coated GFF)	Ultrasonic extraction (benzene-ethanol)	HPLC-FL	Recovery: 85–96%	1.38–81.42 ng/m^3	[33]
2012	South Africa	Diesel emissions	Gas and particle	Portable Gilair Plus pump (PDMS traps and QFF)	Solvent free	TD-GC-MS	LOD 1ng	1.8–4.3 µg/m^3	[51]
2012	Nigeria	Ambient	Particle	High volume air sampler (GFF)	Reflux	HPLC-FL	–	0.17 ng/m^3–9.2 µg/m^3	[52]
2012	Sierra Leone	Indoor	Particle	Dual impactor (Teflon coated GFF)	Ultrasonic extraction (benzene-ethanol)	HPLC-FL	–	38–4282 ng/m^3	[34]
2013	Algeria	Indoor	Particle	Low volume sampler (QFF)	Soxhlet extraction (DCM-acetone)	GC–MS	LOQ: 0.2–2 pg/m^3	8–87 ng/m^3	[53]
2013	Algeria	Ambient	Particle	Medium volume sampler (QFF)	Soxhlet extraction (DCM-acetone)	GC–MS	LODs: 0.01–0.025 ng/m^3	1.9–3.5 ng/m^3	[54]
2013	Egypt	Ambient	Gas and particle	High volume air sampler (PUF and QFF)	ASE	GC–MS	–	Gas: 155–1400 ng/m^3 Particle: 14–420 ng/m^3	[55]
2014	Egypt	Ambient	Gas and particle	Low volume air sampler (PUF and QFF)	Soxhlet extraction (DCM-hexane)	HPLC-FL	Recovery: 79–112%	Gas: 0.9–377 ng/m^3 Particle: 0.5–76 ng/m^3	[56]
2014	Ghana	Ambient	Particle	IVL sampler (Teflon filter)	Soxhlet extraction (DCM-hexane)	GC-FID	–	0.2–253 ng/m^3	[57]
2014	Tunisia	Ambient	Particle	Low volume air sampler (GFF)	Ultrasonic extraction (DCM-acetone)	HPLC-FL	LOD: 0.03–1.06 ng/m^3 [31.5–100%]	9.4–44.8 ng/m^3	[58]
2014	Algeria	Ambient	Particle	High volume air sampler (QFF)	Soxhlet extraction (DCM-acetone)	GC–MS	LOQ: 0.2–2 pg/m^3	0.4–11.2 ng/m^3	[59]
2014	Mali	Ambient	Gas and particle	High volume air sampler (PUF, QFF)	ASE	GC–MS	–	0.1–13 ng/m^3	[60]
2014	South Africa	Ambient	Particle	Dual E-sampler (QFF)	Soxhlet extraction (DCM-*n*-hexane)	HPLC-UV	LODs: 0.001–0.03 mg/L [98–101%]	6.7–14.76 ng/L	[61]
2014	South Africa	Ambient	Particle	High volume air sampler (QFF)	Soxhlet extraction (DCM)	GC–MS	LOD: 0.4–38 pg/m^3	0.10–1870 pg/m^3	[62]
2015	Sudan	Ambient	Gas and particle	High volume air sampler (PUF, QFF)	Soxhlet extraction (hexane)	GC–MS	–	0.3–14.3 ng/m^3	[63]

Table 2 (*Continued*)

Year of study	Country	Exposure type	Gas/ particle phase	Sampling method/ media	Extraction method & solvent	Analytical method	LODs and Recovery [%]	Concentration	Reference
2015	Sudan	Indoor	Gas	Sampling chamber (Teflon membrane filter)	Ultrasonic extraction (DCM)	GC–MS	–	–	[64]
2015	Ghana	Ambient	Particle	Low volume air sampler (QFF)	Soxhlet extraction (acetone-hexane)	GC–MS	LOD: 0.02–0.7 ng/ m^3 [81-93%]	0.51–38 ng/m^3	[65]
2015	Sierra Leone	Indoor and outdoor	Particle	Dual impactor (Teflon coated GFF)	Ultrasonic extraction (benzene-ethanol)	HPLC-FL	LOD: 0.001–0.04 ng/ml; [83–97%]	Indoor: 96.5–1279.7 ng/m^3 Outdoor: 13.1–41.2 ng/ m^3	[66]
2015	South Africa	Workplace (underground)	Gas and particle	Portable Gilair Plus pump (PDMS traps and QFF)	Solvent free	TD–GC x GC–TOFMS	LODs 1–68 pg	Gas: 0.01–18 μg/m^3 Particle: 0.47–260 ng/ m^3	[10]
2016	Algeria	Indoor	Gas and particle	Passive sampler (PUF)	Ultrasonic extraction (DCM-acetone)	GC–MS	LODs: 0.04–0.08 ng/m^3	17–182 ng/m^3	[67]
2017	Algeria	Indoor and ambient	Particle	Low volume air sampler (QFF)	ASE	GC–MS	Recovery: 80–110%	0.84–10.8 ng/m^3	[68]
2017	Nigeria	Ambient	Particle	Low volume air sampler (QFF)	Ultrasonic extraction (DCM)	GC–MS	Recovery: 68–112%	72.5–142.9 ng/m^3	[69]
2018	South Africa	Outdoor (domestic fire)	Gas	Portable Gilair Plus pump (PDMS traps)	Plunger assisted solvent extraction (*n*-hexane) & TDS	TD-GC-MS and GC–MS	LODs: 14–227 ng/ m^3 [76–99%]	0.1–9.7 μg/m^3	[70]
2018	Tunisia	Ambient	Particle	High volume air sampler (QFF)	ASE	GC–MS	LOD: 0.2–8 pg/m^3	0.5–17.8 ng/m^3	[71]
2018	Egypt	Ambient	Gas and particle	Low volume air sampler (PUF, QFF)	Ultrasonic extraction (DCM)	GC–MS	Recovery: 54.6–94.4%	Gas: 7.6–267.8 ng/m^3 Particle:1.6–199 ng/m^3	[72]
2018	Rwanda	Ambient	Particle	High volume sampler (GFF)	Ultrasonic extraction (benzene-ethanol)	HPLC-FL	–	19.3–54.9 ng/m^3	[73]

HPLC-FL/UV High Performance Liquid Chromatography with fluorescence or ultraviolet absorption detector; GC–MS/FID: Gas chromatography–mass spectrometry/flame ionization detection; TD–GC x GC–TOFMS: Thermal desorption comprehensive two-dimensional gas chromatography coupled to a time of flight mass spectrometry; PUF: polyurethane foam; QFF: quartz fiber filter; GFF: glass fiber filter; DCM: dichloromethane; LOD: limit of detection; LOQ: limit of quantification; PDMS: polydimethylsiloxane; GPC: gel permeation chromatography; ASE: accelerated solvent extraction.

2.1.2. Collection of particle-phase PAHs

Although a number of studies have focused on both phases of PAHs, African research has mainly focused on the particulate phase. Similarly, particulate-bound PAHs are the most studied components of PAHs globally as they have been found to be carcinogenic and have enhanced mutagenic properties [26]. Typical sampling media for particulate phase PAHs include quartz-fiber filters (QFFs), glass fiber filters (GFFs), Teflon coated glass fiber and Teflon membrane filters. From Table 2, it is clear that QFFs and GFFs were the most frequently employed collection devices for particulate phase PAHs in the region. Sampling flow rates and total sample volume for particulate phase collection varied between studies, but most researchers passed large volumes (600–1500 m^3) of air through the filters to ensure enrichment of trace PAH analytes. High volume samplers may introduce analytical artifacts and under- or over-estimation of human exposure to PAHs may result from blow-off and adsorptive effects occurring on the filter. In light of this, relatively low sampling volumes (<5 m^3) have been passed through QFFs to collect particle-phase PAHs in more recent studies [10,65,69,72]. In a South African study, the authors employed a back-up sorbent behind the filter, to trap analytes desorbed from the QFF, and any gaseous analytes not effectively removed by the denuder which sampled gas phase PAHs (i.e. under break-through conditions) [10].

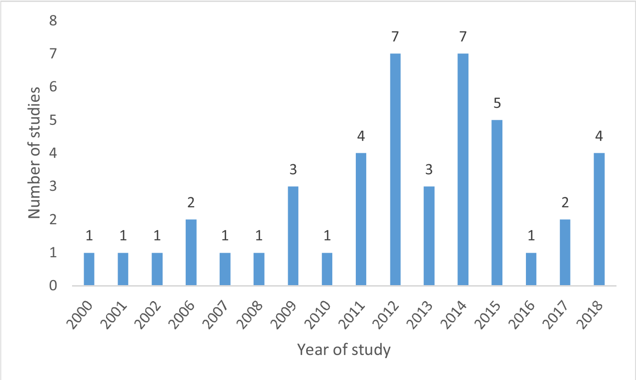

Fig. 1. Trends in research studies based on sampling and quantification of airborne PAHs in Africa from 2000 to 2018.

Advantages of QFFs and GFFs include their low blank levels which are usually below LODs and their resistance to degradation during extraction. Preference is also shown for these sampling materials since their performance and collection efficiencies for SVOCs have been evaluated in previous studies [79–81]. Although not as common as other collection media, Teflon-coated GFFs have also been used for the collection of particle-bound PAHs. The use of these modified GFFs was only reported in three studies done by a group of researchers in Sierra Leone [33,34,66]. The total volume of air passed through these collection devices was very low (approximately 3 m^3) and lower flow rates (1.5 L/min) were used compared to those for unmodified GFFs. Safo-Adu et al. [57] used unmodified Teflon filters for the health risk assessment of exposure to particulate PAHs at a tollbooth on a Ghana highway. The authors preferred Teflon filters because of their low chemical background, low affinity for water vapor and the fact that Teflon filters are not affected by most acids or bases.

2.2. Sample preparation and analysis techniques for airborne PAHs

Pretreatment of airborne samples is a very crucial step for the determination of PAHs since the air matrix is complicated and the concentration of PAHs in air is typically very low. Globally, most studies aiming to investigate the distribution of airborne PAHs (gas or particle phase) have relied on solvent-based extraction. As illustrated in Fig. 2, these conventional solvent-based techniques

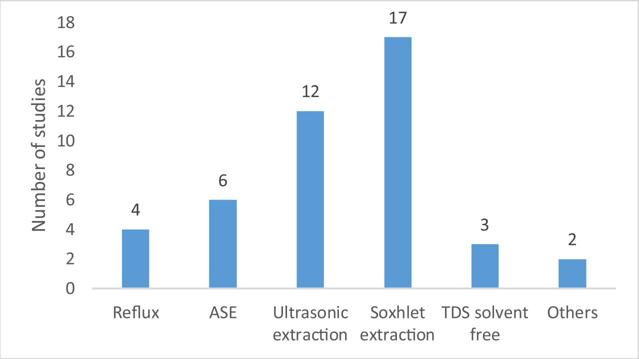

Fig. 2. Commonly employed extraction methods employed in Africa over the period 2000–2018.

have also been successfully employed on a larger scale in African studies. In this section, we discuss the common approaches adopted in the extraction and analysis of airborne PAHs, and note those which have been employed in Africa. The worldwide development of modern extraction methods based on green analytical chemistry principles through miniaturization and use of more environmentally friendly materials and sorbents is briefly discussed. Figures of merit such as LODs and extraction efficiencies are also reviewed.

The most common instruments used for the analysis of PAHs are High Performance Liquid Chromatography (HPLC) with fluorescence or ultraviolet (UV) detection and GC with different detectors such as MS and flame ionization detection (FID). GC coupled with electron-capture detection (ECD) has also been reported particularly for the analysis of oxy- or nitro-PAHs [20].

As stated in Section 1, with regards to PAH analysis, GC has advantages over other systems such as LC since it is proven to have greater selectivity, sensitivity and separation of complex non-polar analytes [1], although fluorescence detection of PAHs with HPLC analysis also provides selectivity (refer to Table 2). GC has relatively low operating costs considering that a tank of gas is generally cheaper than HPLC grade solvents. HPLC requires a complex pressurized system, which adds to the instrument maintenance costs.

2.2.1. Solvent based methods

Solvent extraction of PAHs from samplers typically involves techniques such as ultrasonic, Soxhlet, and accelerated solvent extraction. As shown in Table 2, the most common solvent based methods employed in Africa have been ultrasonic and Soxhlet extraction. A similar global trend was observed in a recent review analytical methods for atmospheric PAHs and their derivatives [20]. Ultrasonication treatment has been tested and validated to retrieve the 16 priority PAHs and gives higher efficiencies compared to other conventional solvent based methods [13]. In most studies, ultrasonic extraction was reported in combination with high performance liquid chromatography using fluorescence detection (HPLC-FL) for analysis as compared to GC–MS due to cost of instrumentation. The performance of this extraction method was highly variable as evidenced by the incomparable analytical figures of merit in Table 2. Although numerous studies showed average recoveries above 70% for most analytes, ultrasonication resulted in very low recoveries (31–40%) for lighter PAHs particularly Nap [37,58]. Ultrasonic extraction is faster than Soxhlet extraction and allows extraction of larger amounts of sample with a relatively low cost. However, it is labor intensive, and filtration is often required after extraction.

Soxhlet extraction is the most popular method that has been employed in the African region for the analysis of airborne PAHs. Similarly this classical method has been utilized extensively worldwide, due to its high extraction efficiency, availability and lower cost [13]. Soxhlet allows use of larger amounts of sample, no filtration is required after the extraction, the technique is not matrix dependent, and many Soxhlet extractors can be set up to operate unattended. However, this technique is known to be time consuming (8–48 h), uses large amount of solvent (300–500 mL) and requires further concentration prior to analysis due to the large amounts of solvent used.

Solvent reflux was also used to retrieve the 16 priority PAHs from gas and particle phases in a few studies [35,42,49,52]. The newer extraction techniques such as accelerated solvent extraction (ASE) and microwave-assisted extraction are very attractive globally because they are a lot faster, use much smaller amounts of solvents, and are environmentally friendly. The application of microwave-assisted extraction for airborne PAHs has not been commonly reported in Africa, most likely due to lack of resources and expertise. Only one study [43] in Morocco reported the use of a Teflon reactor (microwave) for the extraction of gaseous PAHs from semi-permeable membrane devices. Shaking methods use relatively large volumes of organic solvents, which is unfavorable from an environmental and cost perspective. In an effort to reduce extraction solvent use, a low volume PASE method was recently used in the monitoring of domestic fire emissions in South Africa [70].

Although most of the high volume solvent-based techniques have been successfully applied in African studies, their extraction efficiencies are often highly uncertain, and concentrations presented are rarely comparable across different studies using different methods. Due to the negative impact of the use of toxic organic solvents, complexities involved in post extraction clean-up steps, sample concentration and eventually the possible loss of analytes (particularly lighter PAHs), there have been growing efforts to develop solvent-free analytical approaches to PAH analysis.

To date several developments in the solvent-based extraction of airborne PAHs have been reported in literature, yet their application in Africa has not been reported. Cold-fiber solid-phase micro-extraction (CF-SPME), supercritical-CO_2, drop micro-extraction, and dynamic sub-critical water solvent extraction are some of the low-volume pre-treatment techniques for airborne PAHs that have emerged. Supercritical fluid extraction (SFE) has been shown to be suitable for the analysis of relatively non-polar compounds such as aliphatic hydrocarbons and PAHs, using pure CO_2 as extraction fluid [82]. In addition, SFE reduces the extraction time and solvent consumption compared with Soxhlet extraction. However, the recoveries obtained are typically lower for the more polar compounds present in atmospheric aerosols, such as oxy- and nitro-PAHs [82]. SFE has nevertheless been applied for the analysis of oxy- and nitro-PAHs in urban aerosol samples in Barcelona where concentrations were in the range 15–364 pg/m^3 [82]. Lower detection limits in the pg/m^3 range were obtained when a dynamic subcritical water extraction (DSWE) method was developed for the analysis of PAHs from airborne PM [83]. This procedure was environmentally friendly since water is considered a green solvent.

The Quick, easy, cheap, effective, rugged, and safe (QuEChERS) procedure has been developed for organic compounds with the objective to simplify and shorten the extraction step. Albinet et al. [84] were the first to test QuEChERS in the extraction of PAHs from ambient and emission (wood combustion) air samples. The QuEChERS technique has been recently reviewed and is favorable as the total extraction and clean up time ranges from 1 to 5 min and recoveries are high and comparable to ASE [85].

2.2.2. Solvent-free methods

Solvent-free methods rely on the collection of the airborne PAHs on sorbent or filter materials for subsequent direct release by the thermal desorption (TD) into the analytical instrument. Although numerous research based on TD has been performed worldwide, studies involving solvent-free extraction methods for airborne PAHs have generally been scarce in Africa owing to the lack of specialized desorption equipment. The few reported cases in which TD was employed have all been documented and applied in South Africa [10,51,70]. In a typical solvent-free method, multichannel silicone rubber traps, which consist of 22 parallel PDMS tubes of 0.3 mm i.d. housed in a 178 mm long glass tube and their respective quartz fiber filters were thermally desorbed with a Gerstel 3 TD system. This solvent-free method is beneficial in that detection limits are improved as the entire sample (analytes) can be transferred to the GC–MS for analysis. Incomplete desorption of heavier analytes may, however, be a limitation of this technique. Moreover, as portrayed in Table 2, many African laboratories have GC–MS instruments but only a few have commercial thermal desorbers, which are expensive to obtain, maintain and operate.

In addition to TD studies, laser-induced fluorescence (LIF) of atmospheric PAH samples on quartz multi-channel PDMS traps was developed in Africa [86]. The application of laser-desorption ionization time-of-flight MS (LDI-TOF-MS) techniques for particulate matter has also been reported [87,88]. The laser-induced methods are rapid, non-destructive and provide selectivity without the need for sample clean-up and separation processes.

A microwave-assisted desorption (MAD) coupled to headspace solid-phase micro-extraction (HS-SPME) was studied as an *in-situ*, one-step sample preparation method for airborne PAHs collected on XAD-2 adsorbent [89]. This proposed technique was simple, rapid, sensitive, solvent-free and achieved a recovery rate of >80% under optimized extraction conditions [89]. These current leading international trends may become used in Africa due to the growing global effort to reduce solvent use.

3. Concentrations of airborne PAHs found in Africa

3.1. Ambient air

Outdoor air pollution continues to be one of the many environmental problems that need attention in many African countries. It can be seen in Table 2 that most PAH exposure assessments were done in ambient environments compared to indoor and direct occupational exposure sites. Total PAH concentrations varied largely across the reported studies and were heavily influenced by contributing pollution sources close to the sampling sites such as industrial, residential and high density traffic areas. Additionally, environmental factors such as the altitude at which the sample was taken, season in which sampling was undertaken and extraction techniques used for sample analysis would have also contributed to the wide variations.

The atmosphere over the open oceans can serve as the global atmospheric background level of PAHs. Baseline atmospheric levels of PAHs have been established in air over the open Atlantic Ocean [40]. Ten PAHs were measured and concentrations were low and varied from 23 to 2560 pg/m^3. With regards to the African coast, unexpectedly high concentrations were measured in proximity to Mauritania, Senegal, Cape Verde, Guinea Bissau and Guinea. The elevated concentration of PAHs off the northwest coast of Africa could possibly be attributed to the contribution of the emerging oil industry along the African shore, the role of biomass burning and natural sources of PAHs [40]. In a similar study, aerosol samples were collected aboard a cruise ship to investigate the geographical distribution of PAHs over oceans and to assess their continental origin [62]. PAH concentrations over the South Indian ocean were noticeably higher than over other areas of the Indian ocean and this was attributed to air masses from wildfire emissions in Africa. Concentrations of total PAHs ranged from 66 to 1870 pg/m^3 with a geometric mean of 341 pg/m^3 [62].

Klánová et al. conducted the first comprehensive study reporting levels of PAHs and persistent organic pollutants (POPs) in the atmosphere over the African continent [42]. The air samples from 26 sampling sites in 15 African countries were collected during the 6 months of the MONET-AFRICA survey. The sites ranged from continental, rural and urban backgrounds to contaminated sites heavily affected by industrial activities. The highest levels of PAHs were measured at the urban background in Ethiopia (15.5 µg/sample which corresponds to 80–150 ng/m^3 for the sum of 16 EPA PAHs), and at the industrial sites in Egypt (11 µg/sample) and Senegal (9 µg/sample). Significantly higher concentrations were observed at municipal dumpsites in Kenya and a cotton growing region in Mali. The lowest concentrations of PAHs (<0.73 ng/m^3) were found at Mountain Kenya (3600 m above sea level), Tombouctou in Mali (suburb away from industries and traffic), and South Africa (Molopo Nature Reserve) and these represented the background sites for eastern, western, and southern Africa respectively.

Overall, the two major emission sources of PAHs in African ambient air were automobile and industrial activities. As presented in Table 2, Egypt and Algeria had the highest number of reported studies which monitored gaseous and particulate PAHs in ambient air. Benin reported the highest total gas and particulate concentrations ranging from 1.6 to 103 µg/m^3 in its largest and busiest port city of Cotonou [45]. The relatively high PAH levels were attributed to the rapidly increasing population, commercial and industrial development, poor urban transportation infrastructure, an unchecked increase in motorbikes and the use of low-quality oil products in this West-African port city.

With regards to gaseous atmospheric PAHs, the highest concentrations were reported in Alexandria, Egypt [55] and ranged from 300 to 1400 ng/m^3 and 155 to 870 ng/m^3 in the summer and winter seasons respectively. These levels of gaseous PAHs were much higher compared to those reported in other more populated urban cities worldwide such as Guangzhou (China) and Inchon (Korea) [25,90]. Additionally, the higher concentrations of the gas phase PAHs in summer is significantly different from the northern Chinese cities that experience higher PAH concentrations during the heating season (winter) as a result of increased combustion of fossil fuels [91]. In Egypt, centralized heating systems are not common and heating of indoor places depends mainly on electric heaters [55]. In another field study in Alexandria, the higher PAH concentrations observed during the summer season were attributed to the marked increase in the traffic density (mainly with gasoline powered vehicles) as a result of the increased number of visitors for recreational purposes [49]. Khairy and Lohmann applied receptor models seasonally to investigate the source apportionment of PAHs in the city's atmospheric environment at industrial, residential and traffic sites [55]. The results indicated that diesel and gasoline emissions were the major sources of PAHs in Alexandria, Egypt. The PAH traffic contribution to ambient air quality was also assessed by a number of studies in high traffic sites of Egypt [32,37,50,56]. In most studies done in both summer and winter, all the gas phase samples were dominated by 2–3 ring PAHs with the predominant analytes being Nap, Phen, FluAn and Ant. Morocco and Sudan reported lower levels of gaseous PAHs in ambient air of their urban cities [43,63]. In Uganda, air samples collected from sites within the Lake Victoria watershed ranged from 0.01 to 160 ng/m^3 and were used to generate a baseline reference data set for future studies in the East African region [48].

Exposure to airborne particulates is estimated as the largest cause of premature human mortality worldwide and is of particular concern in sub-Saharan Africa where emissions are high and data is lacking. The highest concentration (9.2 μg/m^3) of total particulate PAHs in the air was recorded in Niger Delta communities [52]. This is because the Niger Delta area is characterized by heavy industrial activities such as oil production and refining. The total particulate PAH concentration mostly consisted of BkF, a marker of the petrochemical complex located in this area [92]. BaP and IcdP, which are known to be carcinogenic were also predominant in the samples. The total particulate PAH concentrations found at the Niger Delta sampling stations were among the highest in the world and exceeded the Chinese national ambient air quality standard for total PAHs of 10 ng/m^3 [13].

Egypt had the second highest particulate associated PAHs in ambient air ranging from 2.2 to 423.1 ng/m^3 [50,55,72]. Approximately 40–50% of the total airborne atmospheric particulates were emitted from diesel engine powered vehicles. In light of this, lifetime lung cancer risk from particulate PAHs exposure by inhalation was estimated for tollbooth attendants on a major highway with heavy traffic flow in Ghana and particulate PAHs peaked at 253 ng/m^3 [57]. Toxic equivalence factors were used to calculate BaP equivalents for individual PAHs and BaA, BaP, BkF, BbF, BahA, BghiP and Chry were the most predominant genotoxic PAHs. Lower concentrations were reported in urban cities of other developing countries and levels were generally below 50 ng/m^3 [58,59,71,73]. Overall, higher molecular weight PAHs such as BbF, BaP, IcdP and BghiP and alkylated phenanthrenes predominated in the particle phase. In contrast to the gas phase PAHs, particulate PAHs concentrations showed significantly higher values in winter compared to summer and the trend was observed globally. Based on seasonal trends and spatial variations of particulate PAHs in Italy, Masiol et al. [93] indicated that the lower concentrations in summer may be due to higher temperatures and solar radiation, which favor evaporation and photodegradation of PAHs. During winter seasons, an increase in domestic and vehicular emissions along with lower dispersion conditions and a decrease in photochemical reactions may promote the accumulation of PAHs in the lower atmosphere [94].

3.2. Indoor exposure

Research on the health effects of indoor air pollution in less-developed countries has been hindered by lack of detailed data about exposure and illness outcomes. Inhalation of indoor air is one of the major routes of exposure of the general public to airborne PAHs. Most people in rural communities of developing countries are prone to be exposed to large doses of PAHs since firewood and other organic fuels are used indoors for cooking, lighting and heating purposes. As illustrated in Table 2 and Fig. 3, indoor exposure studies showed the highest PAH concentrations for both phases compared to workplace and ambient exposure studies, most likely due to the burning of biomass fuels in a confined (kitchen) environment. Poor ventilation conditions in rural homes strongly influenced the indoor PAH concentrations. When indoor exposure to PAHs in Burundi's traditional houses was investigated, relatively high total concentrations ranging from 1 to 43 μg/m^3 were reported [35]. Although total PAH concentrations in Burundi were higher than those reported in other developing countries and Chinese households, the predominance of Nap (representing 60–70% of the total PAH concentration), was consistent across most studies. Concentrations of BaP ranged from 0.01 to 0.27 μg/m^3, which largely exceeded the maximum permissible risk level of 0.001 μg/m^3 BaP in ambient air as proposed by the European ambient air legislation [1]. Similarly, high particulate concentrations in soot (109.5 μg/g) were reported in Kenya when PAHs were characterized and quantified from burning various biomass types in the traditional grass-roofed households [47].

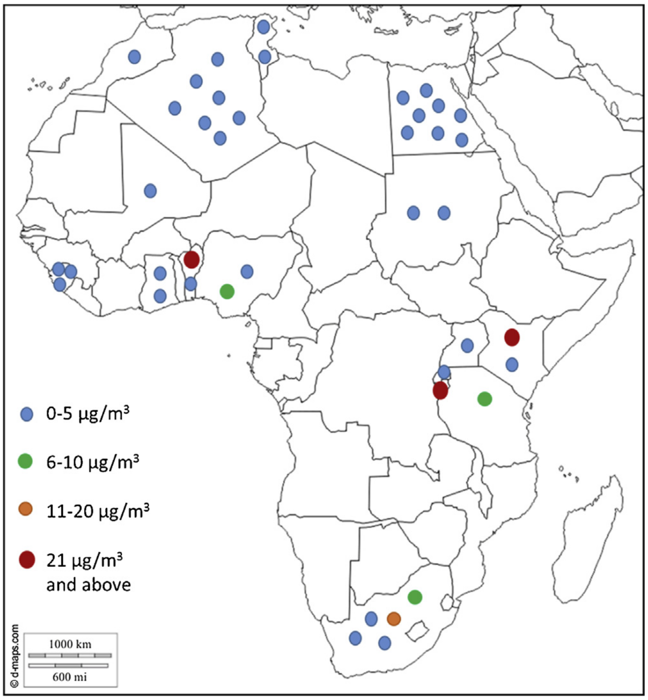

Fig. 3. Geographical distribution of reported PAH studies in air across African countries and the total PAH concentrations. (Source: a blank map was downloaded online (https://d-maps.com/) and modified by the authors).

Overall, the unventilated burning of firewood in Sierra Leone, Tanzania, Burundi and Kenya exposed people living in traditional homes to high doses of PAHs from indoor air pollution. BaP concentrations in soot samples were generally high, which is consistent with other global studies that reported BaP as a major component of wood smoke [95–97]. The authors concluded that when wood is combusted, BaP predominates the particle phase PAHs, regardless of the combustion appliance design, fuel class or combustion environment. The same trend was reported in a household fuel use pilot study in the highlands of Tanzania where BaP equivalent exposures for US EPA priority PAH pollutants were highest for open wood fire (767 ng/m^3), 44 ng/m^3 for charcoal, 8 ng/m^3 for kerosene-charcoal mix and 0 for LPG [46]. However, despite different biomass fuels being used for cooking and heating purposes, it has to be noted that the vast geographic variations in domestic emissions of PAHs could be due to climatic differences.

Although smoking and cooking are the major sources of PAHs indoors, traditional incense burning can also be a significant contributor of indoor particle concentrations although only one study from Africa has been published in this regard [64], likely indicating that it is not a very common practice in Africa. Dokhan incense burning, which is a traditional practice of women in all areas of Sudan, was found to release six PAHs among the 16 PAHs listed by the US EPA as priority pollutants [64]. Unfortunately no quantification data was reported, although the authors concluded that the six identified PAHs may be the cause of different health problems present in the area, including cancer.

3.3. Workplace environments

Occupational exposure to PAHs is largely through the inhalation and skin absorption of these compounds. Workers employed in occupations such as road paving, underground mining, aluminum plants, iron/steel foundries, as well as street vendors, firemen, mechanics, and chimney sweeps are occupationally exposed to carcinogenic PAHs. Considering the studies which have been reviewed in Table 2, monitoring of PAHs in workplace environments has not been given much priority probably due to a lack of portable, rugged instruments for challenging environments often with heavy machinery. Although most African countries do not have occupational exposure limits for airborne PAHs, Benin and South Africa have assessed the levels of PAHs in workplace environments [10,45,51].

South Africa has taken steps towards establishing occupational guidelines by simultaneously characterizing gaseous and particulate PAHs in South African underground platinum mines and at agricultural sugarcane burning sites [10,51]. In underground mines, the most predominant PAHs were found in the gas phase with Nap and mono-methylated Nap derivatives having the highest concentrations ranging from 0.01–18 $\mu g/m^3$. Particle associated PAHs were highest at vehicle exhausts and concentrations ranged from 0.47 to 260 ng/m^3 with a dominance of Pyr, FluAn, BbF, BaP, IcdP and BghiP. Although not much data has been reported globally on airborne PAH levels in underground mines, a similar study in a black coal mine in the Czech Republic and an oil shale mine in Estonia also reported pyrene as a biomarker for PAH occupational diesel exhaust exposure [98].

Ayi-Fanou et al. [45] investigated the formation of bulky DNA-adducts as biomarkers of biologically effective dose of PAHs in people living and working in the city of Cotonou (Benin) in which exposure to PAHs, mainly BaP, has been found. Taxi-motorbike drivers, roadside residents, street vendors and gasoline sellers had significantly higher levels of DNA-adducts than village inhabitants. This was one of the first studies of this kind in an African exposed population. Validation of the urinary excretion of 1-hydroxypyrene as a biological marker of exposure to PAH was also performed. Since DNA-adduct levels correlated with the levels of environmental carcinogenic compounds found in these workplace environments, more studies need to be done for people working close to PAH emission sources.

4. Conclusions and future perspectives

The growing number of reported studies regarding PAH monitoring confirms that clean air is recognized as a key component of a sustainable urban environment both in Africa and globally. Although numerous sampling, extraction and analysis techniques have been utilized in PAH monitoring studies across the continent, further optimization and new technology application is needed in order to address the key environmental problem of elevated levels of airborne PAHs in developing countries, where the air quality problems are pervasive.

Biomonitoring, as a cheap and convenient alternative to traditional sample collection, is becoming more popular, although its main drawback is the lack of standard procedures. Lichens have been characterized as useful biomonitors for airborne PAHs due to their ability to respond to SVOC air pollutants at different levels and their ability to indicate the presence and concentrations of these pollutants [99].

An area that requires further research regarding the monitoring of airborne PAHs in Africa is sample extraction. It is clear from this review that most of the PAH-extraction techniques which have been utilized require large volumes of solvents and there is scope for application of the miniaturized methods and cheaper, greener techniques which are quicker and have high recoveries.

Current state-of-art techniques such as SFE, drop micro-extraction, CF-SPME, supercritical–CO_2 and dynamic sub-critical water solvent extraction have been reported in literature but have not yet been applied in Africa for airborne PAH monitoring. Resource constraints may limit uptake of emerging technologies by the developing world. In terms of analysis of sample extracts, GC–MS was used in most studies. In recent years, there has been a global increase in development of several new products designed specifically for PAH analysis in this regard, such as PAH specific GC columns and SPE cartridges which have assisted in improving selectivity and sensitivity for these target analytes.

Although more studies are still needed in most parts of the continent, especially in central and sub-Saharan Africa, the discussion of spatial and seasonal variations of airborne PAHs in this review has identified potential hotspots of regional pollution. This will provide a useful basis for decision making towards developing environmental management and protection policies. It may also assist in motivating for the filling in of the African gap in terms of understanding the global distribution of atmospheric PAHs.

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Chapter 3: Methods, Results and Discussion (Paper 2)

The development and optimization of a plunger assisted solvent extraction method for polycyclic aromatic hydrocarbons sampled onto multi-channel silicone rubber traps is presented in this chapter. Materials, experimental methods, results and discussion are described.

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Development and optimization of a plunger assisted solvent extraction method for polycyclic aromatic hydrocarbons sampled onto multi-channel silicone rubber traps

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ABSTRACT

A plunger assisted solvent extraction (PASE) method for multi-channel silicone rubber trap samplers was developed and evaluated as an alternative to direct thermal desorption for the monitoring of polycyclic aromatic hydrocarbons (PAHs). The proposed extraction method was simple, fast (a total of 2 min for extraction), and used a small volume of solvent (a total of 2 mL from two sequential 1 mL extractions). The PASE method presented an advantage over thermal desorption in that samples could be re-analyzed, as only a portion of the extract was injected. Additionally, this approach is cost effective and can be applied in laboratories which do not have thermal desorption systems, hence allowing for the more widespread use of the polydimethylsiloxane samplers which can be employed as denuders in the monitoring of gas and particle partitioning of air pollutants. The method was validated over a wide concentration range (0.005–10 ng μL^{-1}) and the limits of detection ranged from 13.6 ng m^{-3} for naphthalene to 227.1 ng m^{-3} for indeno[1,2,3-cd]pyrene. Overall extraction efficiencies of the target PAHs were good (from 76% for naphthalene to 99% for phenanthrene) with relative standard deviations below 6%. The PASE method was successfully applied to the analysis of domestic fire air emission samples taken at 10 and 20 min after ignition, using a sampling flow rate of 500 mL min^{-1} for 10 min in each case. The samples were found to contain primarily naphthalene (maximum concentration of 9.5 $\mu g\, m^{-3}$, 10 min after ignition), as well as fluorene, anthracene, phenanthrene, fluoranthene and pyrene.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are abundant environmental pollutants, which are released in gaseous and particulate-associated phases from the incomplete combustion or pyrolysis of organic materials [1]. PAHs may persist in the environment and are well known for their potential carcinogenic and mutagenic properties. They are mostly released as a result of human activities, especially in urban and industrial areas. Sources of PAHs include vehicular emissions, coal-powered plants, petroleum refineries, domestic fires and burning of biomass [2]. Principal stages in the measurement of PAHs in ambient air generally consist of sampling, extraction, sample clean-up and analysis. Most conventional atmospheric analyte sampling methods for gas and particulate phases are based on high volume samplers which may introduce analytical artefacts and unreliable estimations of human exposure to PAHs [3,4]. Typical sampling media for particulate phase PAHs include quartz-fibre, glass fibre, Teflon coated glass fibre and Teflon membrane filters, whilst sampling media for gas-phase PAHs include polydimethylsiloxane (PDMS), polyurethane foam (PUF), XAD and mixed sorbents [5–7]. Over the past years, PAHs have been monitored globally in different environmental matrices such as water, air, soil, food and beverages [8–11]. Significant technological improvements in sampling methods and extraction techniques have had an impact on the extent of environmental monitoring of PAHs but further monitoring is still needed to improve the understanding of the status of PAH concentrations in developing countries [12].

Recent research activities in sample collection and preparation are mainly focused on the development of miniaturized, simple, efficient and solvent minimized techniques. The sampling of gaseous semi-volatile organic compounds (SVOCs) has developed very rapidly in terms of the technology employed and the applications thereof [13–15]. Our research group has been focusing on the monitoring and risk assessment of PAHs in air and water samples and has reported several trends and applications for portable sampling devices [16,17]. Multi-channel silicone rubber traps, which consist of 22 parallel PDMS tubes of 0.3 mm i.d. housed in a 178 mm

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long glass tube, have been prepared in our laboratory for gaseous semi-volatile organic analyte sampling [18]. The efficiency of these multi-channel silicone rubber traps as novel denuder devices has also been investigated from both theoretical and experimental perspectives and they have been utilized in a number of applications including household fire emissions, sugar cane burning emissions, tunnel air pollution studies and in underground mining environments in South Africa [16,19,20]. However, more research is still needed in this area, as there is an increasing demand to develop guidelines for the measurement and analysis of PAHs in both ambient air and working environments in developing countries, as well as globally.

Extraction methods for PAHs from PDMS-based air samplers typically involve techniques such as shaking silicone rubber samplers in about 360–500 mL of organic solvent for 48 h [21] or Soxhlet extraction using approximately 60 mL of organic solvents for 8 h [22]. In addition, post extraction clean-up steps such as solid phase extraction or gel permeation chromatography are also performed in these protocols which are time-consuming. In addition, the shaking methods, in particular, use relatively large volumes of organic solvents, which is unfavorable from cost and environmental perspectives. However, in some cases where resin cartridges are used for sample collection, only certain extraction methods, such as microwave or accelerated solvent extraction, are effective [5,23]. In recent years, there has been a growing effort to reduce solvent use when extracting analytes of interest from various matrices and hence limit the impact of solvent waste on the environment. Solvent-less or low-volume solvent-extraction pretreatment for environmental analysis has emerged, for example thermal desorption and single-drop microextraction. Thermal desorption has the advantages of being time efficient and solvent free, therefore the silicone rubber traps were designed to be thermally desorbed for analysis [16,17,19]. In addition, detection limits are improved with some TD systems as the entire sample (analytes) can be transferred to the gas chromatograph-mass spectrometer (GC–MS) for analysis. Incomplete desorption of heavier analytes may, however, be a limitation of this technique.

Despite the introduction of many solvent-free procedures over the past decades, solvent extraction techniques remain the most common option for PAHs in gas or particle phases. In light of this, our aim was to develop and optimize a new method in which a plunger system is used to extract PAHs from silicone rubber traps. Our method uses a plunger made of steel wire and a carefully sized Teflon tip which is inexpensive and easy to assemble. This proposed novel and miniaturized plunger assisted solvent extraction (PASE) setup provides an alternative procedure to thermal desorption that is time-efficient and uses low volumes of organic solvents, in addition to not requiring specialized desorption equipment and associated liquid nitrogen. PASE reduces costs and at the same time allows for the widespread use of the silicone rubber traps. The PASE method was applied to the monitoring of domestic fire emission samples from a traditional *imbawula* stove. Furthermore, the liquid splitless injection method was compared to direct thermal desorption in terms of extraction versus desorption efficiencies. General parameters of the methods such as analysis time, equipment requirements and cost, limits of detection (LODs) and limits of quantitation (LOQs) are also compared.

2. Materials and methods

2.1. Chemicals and reagents

The overall analytical procedure, including calibration, was performed using a certified standard PAH mix solution obtained from Supelco (St Louis, MO), containing 15 priority PAHs. The nominal concentration of each compound in the mixture dissolved in methylene chloride was 2000 ng μL^{-1} and the names and abbreviations of the PAHs included are given in Table 1. Stock solutions at a concentration of 100 ng μL^{-1} were prepared in toluene and working solutions were prepared by appropriate dilutions of the stock solutions before use. Pure individual PAH standards were obtained from Sigma Aldrich. All solvents were of analytical grade (99% purity) including toluene, dichloromethane (DCM) and n-hexane which were purchased from Sigma Aldrich. Acetone was obtained from Associated Chemical Enterprises (ACE, South Africa). Deuterated internal standards (IS), d8-naphthalene, d10-phenathrene, d10-pyrene and d12-chrysene were obtained from Isotec Inc (Sigma Aldrich, Bellefonte, USA).

Table 1
List of PAHs included in the study in order of elution and increasing molar mass. Internal standards (IS) used for each group of PAHs are shown. Linear regression analysis results of both liquid splitless injection (PASE) and TDS experiments are included (n = 3).

Analyte	Abbreviation	Quantification ion *m/z*	R^2	
			PASE	TDS
Naphthalene d_8	**IS**	**136**		
Naphthalene	Nap	128	0.983	0.988
Acenaphthylene	Acy	152	0.999	0.995
Acenaphthene	Ace	154	0.999	0.999
Phenanthrene d_{10}	**IS**	**188**		
Fluorene	Flu	166	0.998	0.995
Phenanthrene	Phe	178	0.998	0.994
Anthracene	Ant	178	0.994	0.996
Pyrene d_{10}	**IS**	**212**		
Fluoranthene	FluAn	202	0.997	0.995
Pyrene	Pyr	202	0.996	0.993
Benz[a]anthracene	BaA	228	0.997	0.995
Chrysene d_8	**IS**	**240**		
Chrysene	Chr	228	0.998	0.998
Benzo[b]fluoranthene	BbF	252	0.994	0.996
Benzo[a]pyrene	BaP	252	0.991	0.996
Indeno[1,2,3-cd]pyrene	IcdP	276	0.994	0.990
Benzo[g,h,i]perylene	BghiP	276	0.993	0.994
Dibenz[a,h]anthracene	DahA	278	0.992	0.993

2.2. Multi-channel silicone rubber traps

The PDMS traps were prepared according to the method described by Ortner and Rohwer [18]. Each trap consisted of 22 parallel PDMS tubes (55 mm long, 0.3 i.d., 0.6 mm o.d. Sil-Tec, Technical Products, Georgia, USA) in a 178 mm long glass tube (6 mm o.d., 4 mm i.d.). The plungers consisted of carefully sized Teflon tips which were designed and machined in- house. 10 μL Hamilton syringes (Supelco, Nevada, USA) were used to spike standards onto traps and the traps were then end-capped with Teflon sleeved glass stoppers to prevent analyte loss. In order to avoid unnecessary sample dilution and extraction solvent use, the open volume in the traps was calculated as illustrated in Fig. 1a, where V_A represents the volume of the empty tube portion and V_B the open volume in the silicone portion of the trap, respectively.

The total volume (V_{total}) of the multi-channel silicone rubber trap that the extraction volume would occupy was *ca.* 0.7 mL, therefore 1 mL of organic solvent was used for extractions (full calculation is given in Equation S1). All the multi-channel silicone rubber traps used in this study were pre-conditioned before use at 280 °C for approximately 24 h with a hydrogen gas flow of *ca.* 10 cm^3 min^{-1}.

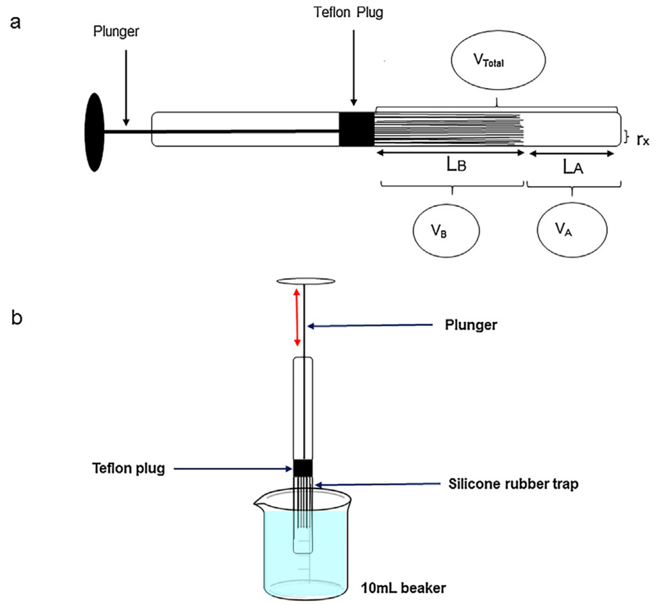

Fig. 1. Schematic diagram of (a) a multi-channel silicone rubber trap illustrating how the maximum open volume in the trap was calculated. V_A represents the volume of the empty tube portion, V_B the open volume in the portion of the trap containing PDMS tubes, and (V_{total}) the total volume of the multi-channel silicone rubber trap that the extraction solvent would occupy and (**b**) the plunger assisted solvent extraction (PASE) setup.

2.3. *Sample extraction procedures*

2.3.1. *Selection of extraction solvent*

The experimental setup for PASE is shown in Fig. 1b which illustrates how the plunger is used to draw solvent through the silicone trap. In experiments to determine the optimal solvent for use in PASE of PAHs from multichannel silicone rubber traps, four solvents were tested: toluene, n-hexane, DCM and acetone: hexane (1:1). In order to evaluate possible co-extraction of siloxane compounds, preliminary experiments were carried out by carefully drawing up each of the four pure solvents from a beaker, making sure all the silicone tubes were immersed and then releasing the solvent back into the beaker (plunging).

A 5 μL volume of a 100 ng μL^{-1} mixed PAH standard (giving a total mass of 500 ng on the trap) was injected onto a multi-channel silicone rubber trap and the trap was then capped and left to dry for 10 mins before sequentially plunging 10 times with 1 mL of solvent in a 10 mL beaker. The beaker containing solvent was pre-weighed on a Sartorius analytical balance (Sarto Mass Services CC) and then weighed again after plunging to account for any solvent loss. Parafilm was used to seal the beaker during the weighing steps to minimise solvent evaporation. The final optimized extraction procedure required a total solvent volume of 2 mL (resulting from two sequential extractions of 1 mL each). Extracts were pipetted into sealed 2 mL amber vials and refrigerated (−18 °C) until further analysis by GC–MS. Each PASE experiment was conducted in triplicate and each of the PASE extracts thus obtained was analysed in triplicate to determine an average concentration and to discard outliers. Standard deviations were based on uncertainties between the average triplicate extract analyses (ie n = 3).

2.3.2. *Air flow through the multi-channel silicone rubber trap*

5 μL of the 100 ng μL^{-1} PAH standard was injected onto a multi-channel silicone rubber trap. The trap was then connected to a battery operated air sampling pump (Sensidyne Gilair 3, Envirocon, South Africa), and air was allowed to flow through the trap at 500 mL min^{-1} for 8 min, which is below the PAH breakthrough volume of 5 L (specifically that of the most volatile PAH, namely naphthalene) for these PDMS traps as determined in previous studies [24]. The trap was then plunged with the optimum solvent and all extracts were placed in sealed 2 mL amber vials and refrigerated until further analysis by GC–MS. These laboratory controlled experimental trials were done to better mimic the actual sampling and use of our extraction method in air monitoring applications.

2.3.3. *Adsorption of PAHs onto Teflon*

In order to avoid biased extraction results and to evaluate adsorption losses, the effect of contact with Teflon on PAH peak areas was tested and observed over time. A piece of Teflon with the same dimensions as that of the Teflon tip on the wire plunger was placed into a 4 mL amber vial containing 2 mL of 0.5 ng μL^{-1} PAH mix standard in toluene. The vial was kept refrigerated away from light, and a 200 μL aliquot was removed into a labelled vial after 0, 5, 15, 30, 60 min and 24 h. These were refrigerated until further analysis by GC–MS.

2.4. *GC–MS analysis*

PAH analysis was performed using a gas chromatograph (GC, Agilent 6890) connected to a mass spectrometer (MSD, Agilent 5975C) in electron impact ionisation mode. The analytes (1 μL splitless injection) were separated on a Restek Rxi®-PAH column with the following column dimensions: 60 m long, 0.25 mm internal diameter and 0.10 μm film thickness. Helium gas of high purity (Afrox, Gauteng) was used as the carrier gas in a constant flow mode of 1 mL min^{-1}. The inlet temperature was at 275 °C and the GC oven temperature was held at 80 °C for 1 min, then ramped at 30 °C min^{-1} to 180 °C, then subsequently to 320 °C at 2 °C min^{-1}. The ionization potential was 70 eV, the source temperature was 230 °C and the quadrupole temperature was 150 °C. A mass range of m/z 40–350 was recorded in full scan mode. Compounds were identified based on comparison of retention times and mass spectra to those of pure individual standards which had been dissolved in toluene. For better sensitivity, the SIM mode was also employed to detect compounds and quantify the analytes.

2.5. *Quality control*

PAHs were quantified using seven-point calibration curves with concentrations ranging from 0.005 to 10 ng μL^{-1}. Calibration curves were derived from the ratio of the target analyte peak area to that of the internal standard (IS) versus the amount of analyte in pg. The IS mixture, containing d8-naphthalene, d10-phenathrene, d10-pyrene and d12-chrysene (0.5 ng μL^{-1}) was spiked into all samples prior to GC–MS analysis. A quality control standard mixture (0.5 ng μL^{-1}) containing all the analytes was analysed before and after each sample batch in order to check the validity of the calibration curves. Other quality assurance measures included monitoring the performance of the GC–MS and the mass selective detector daily by tuning the mass detector and monitoring the sensitivity and linearity of the calibration curve. Procedure and reagent blanks were run between each analysis to ensure that there was no carry over and to confirm that there was no contamination of the samples. The LOD of each target compound was calculated as three times the signal to noise (S/N) ratio and the LOQ as ten times the S/N ratio. For each PAH at each concentration, intra-day (VC_{intra}) and inter-day variations (VC_{inter}) were expressed using variation coefficients.

2.6. *Comparative thermal desorption experiments*

Thermal desorption experiments were conducted for comparison, whereby the PDMS traps were thermally desorbed directly

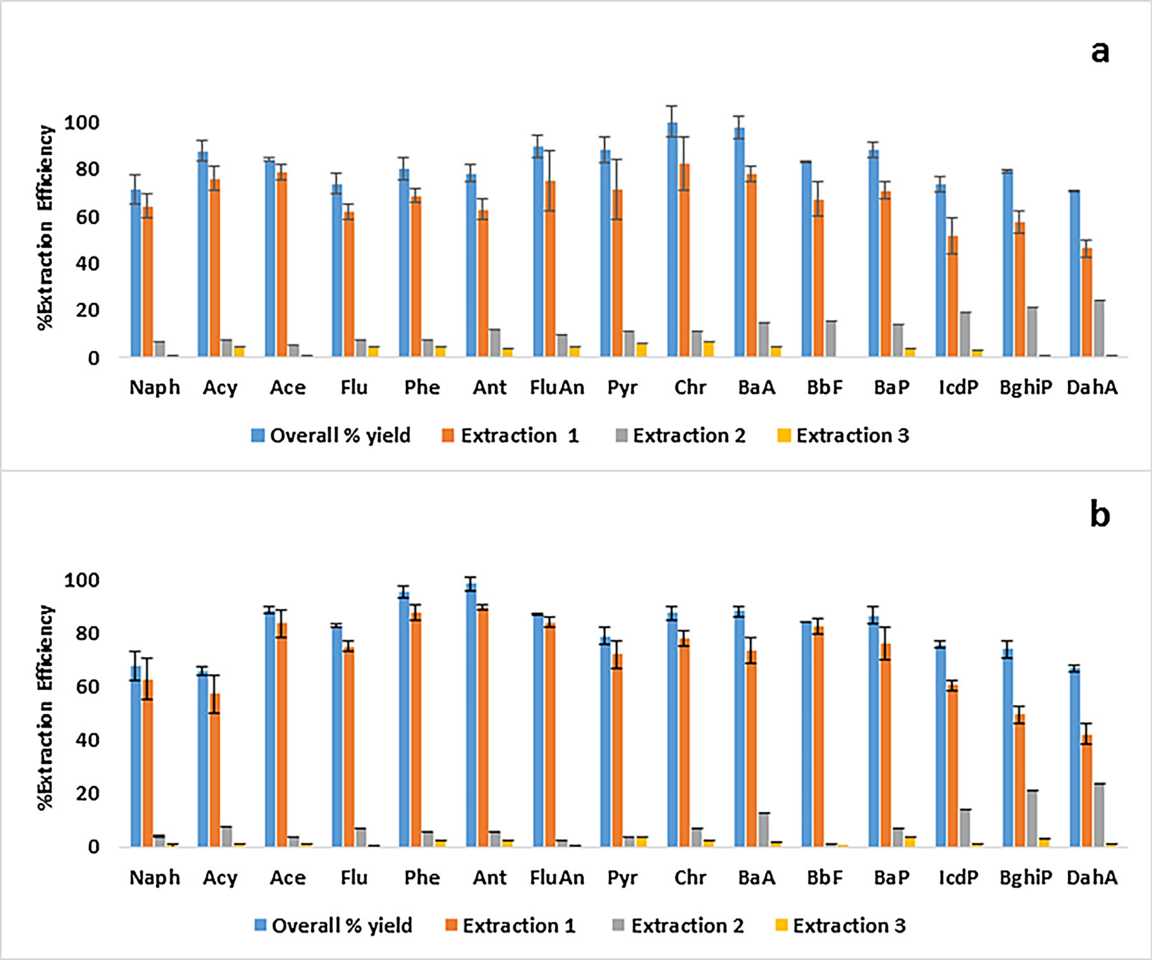

Fig. 2. Sequential PASE extraction efficiencies of PAHs using toluene (**a**) and n-hexane (**b**). The overall extraction yield is also given and error bars show ± standard deviation, n = 3.

in order to compare the desorption efficiency to the extraction efficiency of the PASE experiments. For this purpose, a PDMS trap was spiked with 1 μL of a 1 ng μL^{-1} PAH standard mix. The same instrument as described in Section 2.4 was used in this experiment with a Gerstel 3 thermal desorber system (TDS) operating in splitless mode for sample introduction. The GC inlet was in the solvent vent mode with helium (Ultra High Purity, Afrox) as the inlet gas. Thermal desorption was carried out from 30 °C to 280 °C (5 min hold time) at 60 °C min^{-1}. The desorbed PAHs were cryogenically focused via a cooled injection system (CIS) at −50 °C using liquid nitrogen. A Gerstel baffled liner was employed. The CIS temperature was rapidly ramped at 10 °C s^{-1} to 280 °C in order to introduce the analytes onto the GC column and the inlet purge time was 3 min. The desorption flow rate was 100 mL min^{-1} and the TDS transfer line was set at 280 °C. The remaining GC–MS conditions mentioned in Section 2.4 were maintained.

2.7. *Field application*

A domestic fire was lit in a traditional brazier or *imbawula* stove (Fig. S1) using the traditional method of lighting a fire with a pine wood and charcoal fuel mix. The fire ignition method and experimental set-up for sampling gaseous PAHs were adapted from Makonese et al. [25]. In this experiment, approximately 1 000 g of commercial charcoal was placed onto a grate at the bottom of the brazier followed by about 40 g of rolled paper and 500 g of pine wood chips. After ignition, approximately 2 000 g of charcoal was added on top of the already burning kindling. Air samples were taken at the fire using a PDMS trap coupled to a portable Gilair 3 sampling pump operated at 500 mL min^{-1} for 10 min. The traditional fire was sampled at 10 and 20 min after ignition and at 1 and 1.5 m above the brazier. In all cases the sampler location was 1 m from the combustion device, in the stream of effluent gases. The burn was conducted in the morning of the 1st of December 2016 at the LC de Villiers recreational site on a very sunny day with a temperature of approximately 29 °C. After sampling, the traps were end-capped and wrapped in aluminium foil. Samples and field blanks were then refrigerated prior to analysis.

3. Results and discussion

3.1. *Chromatographic results*

After suitable optimization of the chromatographic parameters, a reproducible and complete separation of individual compounds in the 15 priority PAH mix was achieved. A representative GC–MS-SIM chromatogram of PAHs in a PASE extract obtained from a spiked (1 ng μL^{-1}) PDMS trap is provided in the Supplementary Data (Fig. S2). Priority compounds such as phenanthrene and anthracene, which are normally difficult to separate, were well resolved using this PAH specific column, which also provides for the separation of the numerous analytes usually present in complex environmental samples. A mixture of internal standards was used instead of just one IS to better represent the varying volatilities and extraction efficiencies of the different PAHs (Table 1).

3.2. Evaluation of siloxane background

Plunging of pure solvents showed only minor, reproducible silicone degradation peaks which were easily identified as electron impact (EI) mass spectral fragments of *m*/*z* 73 (Fig. S3). The mass spectral library search identified the degradation products as cyclosiloxanes, which correlated with those found in the literature [18]. The siloxane peaks were found at repeatable retention times and hence did not interfere with the analysis of extracted PAHs in samples. Furthermore, these degradation peaks were not found when analysing solvent blanks indicating that there was no carry-over of the siloxane compounds. In contrast, TDS experiments showed major reproducible silicone degradation peaks when a blank trap was analysed.

3.3. Effects of different solvents

The volume and type of extraction solvent employed are crucial to enhance extraction efficiencies. In addition to effectively dissolving the analytes, it is also important that the solvent should have a sufficiently low vapour pressure to prevent potential loss during the extraction procedure [26]. Furthermore, the extraction solvent should not cause undue swelling of the polymer which would increase fragility and potentially reduce the flow of solvent during extraction [27]. Based on these considerations and on available literature, toluene, n-hexane, DCM and acetone-hexane (1:1) were chosen as extraction solvents for evaluation.

Fig. S4 shows the mean recoveries obtained after a single extraction using the four different solvents whilst all other extraction conditions were kept the same. The recoveries of individual PAHs extracted using n-hexane ranged from 42% (DahA) to 90% (Ant) with relative standard deviations (%RSDs) ($n = 3$) of 0.8-9.5%, respectively. Similar recoveries were found for toluene, which ranged from 46% (DahA) to 82% (Chr) with%RSDs ($n = 3$) of 0.2-9.6%, respectively. For acetone-hexane (1:1), the recoveries obtained were from 56% (Nap) to 101% (Ant) with%RSDs ($n = 3$) of 0.3-14.7%, respectively. For DCM as an elution solvent, the recoveries were considerably lower, ranging from 46% (Nap) to 73% (Chr) with%RSDs ($n = 3$) of 0.3-13.4%, respectively. In most cases, lower recoveries were obtained for both the lighter and heaviest PAHs. This is likely due to the fact that the lighter PAHs are more volatile and thus may have been lost during the extraction procedure. An increase in PAH ring numbers results in an increased interaction between the PAHs and the PDMS therefore heavier PAHs sorbed into the PDMS would be more difficult to extract, leading to slightly lower recoveries. In addition, adsorption losses of heavier PAHs to glass would be expected to be higher [28], however the internal standard correction employed in this study would have corrected for this.

Among the four solvents tested, n-hexane and toluene provided the most favourable results for PAH extractions, which were about 20–30% higher than those obtained using DCM. The results also indicated that acetone:hexane gave higher extraction efficiencies compared to the other solvents but this could be attributed to evaporation effects since acetone is very volatile. This hypothesis can also be confirmed by the higher%RSD values which were obtained with this extraction solvent, indicating that the extraction was less reproducible.

In order to extract PAHs that might have remained on the PDMS after the first extraction, a sequential extraction experiment was performed employing the two most promising solvents (toluene and *n*-hexane). The extract yields obtained in each extraction step are illustrated in Fig. 2. In the first step of extraction, both toluene and n-hexane showed similar recoveries as those obtained in the previous single extraction step, as expected. In the second extraction step, a significant amount of PAHs were still recovered, with the additional amounts extracted ranging from 3 to 23% and 5–24% of the total spiked amount for n-hexane and toluene extractions, respectively. The third extraction step recovered negligible amounts of PAHs (all additional amounts were less than 5% of the spiked amount) and this step was therefore omitted in further experiments. The results showed that a sequential extraction step is necessary for heavier PAHs (four or more benzene rings) to be efficiently extracted. Furthermore, as shown in Fig. 2, the overall extraction yield of the sequential extraction was superior to the single extraction yield of individual PAHs. Toluene and n-hexane provided comparable results for all extraction steps but considering the general toxicity of toluene and its higher%RSD values, n-hexane was chosen as the most suitable extraction solvent for further applications and analyses. The optimized method thus uses a total of 2 mL of n-hexane and requires 2 min for the extraction (1 mL and 1 min for each step in the sequential extraction), hence making it a ‘greener’ and faster solvent extraction method compared to traditional shaking extractions. Air flow experiments were done primarily to better reflect the actual sampling procedure used in PDMS air sampling applications and satisfactory results were obtained (Fig. S5). This demonstrated that our PASE method could yield promising results when applied to real atmospheric samples.

According to Kremser et.al, PAHs may readily adsorb onto almost any available surface, therefore it is always best to check this in order to avoid biased results [8]. In this study, adsorption of PAHs onto Teflon was investigated. The results presented in Fig. 3 show that there was no analyte loss due to sorption to the Teflon plunger since the PAH peak areas were not reduced over time and had minimal variation (%RSD of less than 10.5%, n = 3), with Nap values being slightly higher than other PAHs due to evaporative losses. As illustrated in recent literature, PAH loss due to sorption onto glassware and the Teflon septa of sample vial caps are typically below 5% [8], hence loss of analytes onto these additional surfaces could be neglected.

3.4. Method evaluation

3.4.1. Comparison of methods

Resolution, peak shape, retention times and peak heights for both the PASE and TDS methods were comparable (Fig. S3). However, chromatograms from the TDS experiments showed more noise and interferences from 0 to 15 min which was attributed to additional siloxane peaks.

A series of experiments were performed as explained in the methods section, to indirectly determine the method linearity, repeatability, reproducibility, LODs and LOQs, in order to compare the methods. The internal standard method of quantification was employed in both methods and optimized PASE conditions were used. The results are summarized in Tables 1 and 2. The linear concentration range of the liquid splitless injection and TDS methods was 0.005–10 ng μL^{-1}, depending on the analytes, with coefficients of determination (R^2) all greater than 0.98. Calculated LODs and LOQs corresponding to airborne concentrations with a sampling volume of 5 L were also calculated and are reported in Table 2. The LODs for PAHs in air ranged from 13.6 to 227.1 ng m^{-3} and from 0.13 to 0.9 ng m^{-3} for PASE and TDS experiments, respectively. The TDS method utilized the whole sample whilst only a small fraction (0.15%) of the final solvent extract was utilized in the liquid splitless injection. LODs for TDS were therefore on average 100–500 times better than in the solvent extraction method, which is in agreement with literature [29]. From the data in Table 2, it is evident that the difference in LODs between the two methods is less than 300 times in most cases. This may be due to incomplete desorption of some analytes by TDS or incomplete trapping of analytes by the CIS during

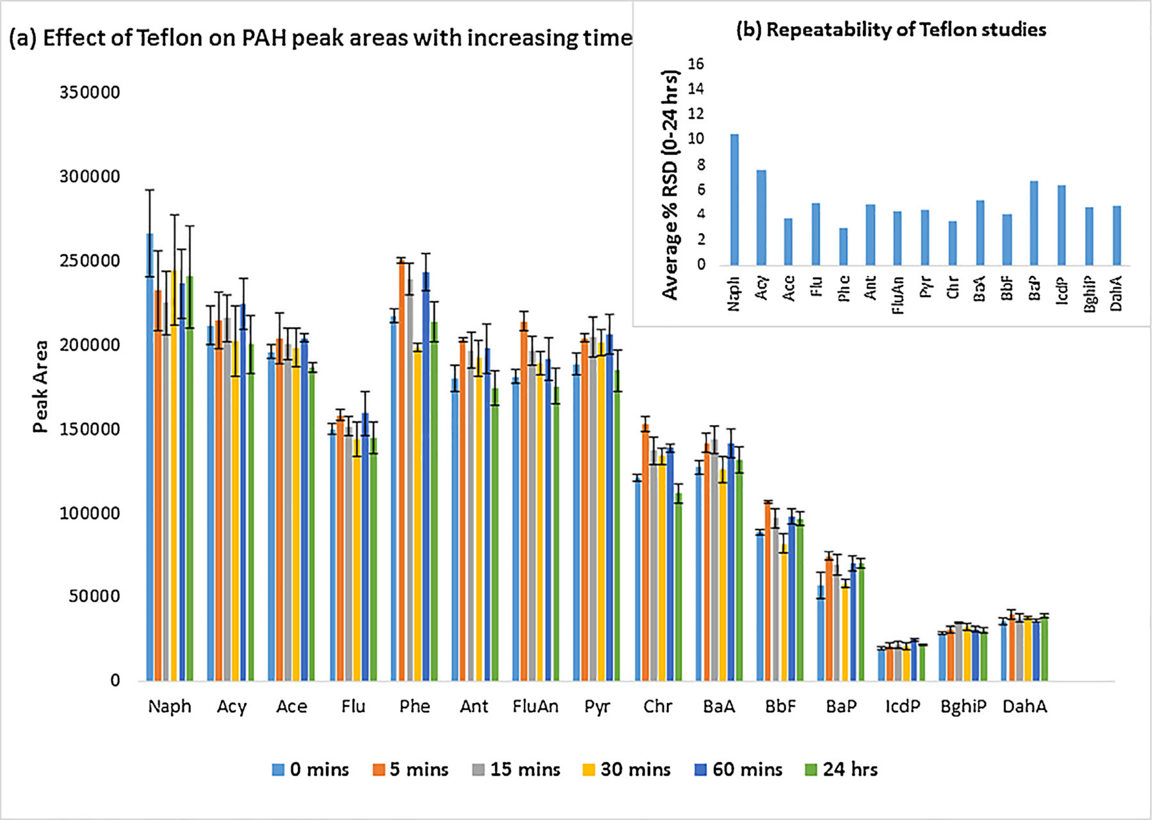

Fig. 3. Effect of the Teflon plunger on peak areas of PAHs with increasing exposure time from 0 to 24 h (a), error bars show ± standard deviation, n = 6; the top right figure (b) illustrates the average error (%RSD) over the different time intervals.

Table 2
Limits of detection (LODs) and limits of quantitation (LOQs) of PAHs based on SIM ions for both PASE and TDS methods. The LOD was calculated based on a signal to noise (S/N) ratio of 3 and the LOQ on a S/N ratio of 10.

Analyte	LOD pg		Calculated air sample LOD[a] (ng m^{-3})		LOQ pg		Calculated air sample LOQ[a] (ng m^{-3})	
	PASE	TDS	PASE	TDS	PASE	TDS	PASE	TDS
Nap	68.0	0.9	13.6	0.18	204.0	2.9	40.8	0.58
Acy	74.8	0.7	14.9	0.14	258.4	3.1	51.7	0.62
Ace	136	0.8	27.2	0.17	544.0	3.5	108.8	0.70
Flu	115.6	0.9	23.1	0.19	408.0	3.0	81.6	0.60
Phe	129.2	0.8	25.8	0.17	646.0	3.3	129.2	0.66
Ant	170.0	1.0	34.0	0.20	360.4	3.3	72.1	0.66
FluAn	122.4	0.9	24.5	0.17	421.6	3.3	84.3	0.66
Pyr	156.4	1.1	31.3	0.21	618.8	3.3	123.8	0.66
BaA	414.8	1.5	82.9	0.30	850.0	4.9	170.0	0.98
Chr	639.2	2.3	127.8	0.46	1366.8	7.1	273.4	1.42
BbF	714.0	1.8	142.8	0.36	2652.0	5.5	530.4	1.10
BaP	884.0	2.1	176.8	0.42	2808.4	6.2	561.7	1.24
IcdP	1135.6	1.9	227.1	0.38	3162.0	5.9	632.4	1.18
BghiP	1020.0	4.5	204.0	0.90	3638.0	13.8	727.6	2.76
DahA	986.0	3.8	197.2	0.76	3264.0	12.1	652.8	2.42

[a] LOD and LOQ for PASE considering the airborne concentration obtained by sampling a volume of 5 L (0.005 m^3) and based on a pre-analysis sample extract volume of 680 μL.

transfer from the TDS. In our work, the final volume of the extract was on average 680 μL and the liquid splitless LODs reported were based on this volume. In cases where sensitivity could be a problem, the final pre-analysis volume of the extract could be reduced to 100 μL, which would result in a 7-fold improvement in LODs.

In the liquid splitless injection studies, VC_{inter} for an injected concentration of 1 ng μL^{-1}, ranged from 1.2% for Pyr to 7.7% for Nap. Intra-day variations were lower ranging from 0.5% for Pyr to 4.9% for Nap (Table 3). VC_{intra} for TDS experiments was evaluated as the trap desorption repeatability which was performed within one day by spiking a conditioned PDMS trap with 1 ng of a PAH mix standard. In the TDS experiments, VC_{intra} varied from 2.2% for Pyr, to 7.1% for Nap and 11% for BaP. A similar trend was observed for inter day variations whereby the%RSD values were all below 12.4%, which shows that the reproducibility of all analyses was acceptable. To better assess the performance of the proposed PASE method, the precision and LODs of the PASE method were compared with values in literature and the results are summarized in Table 4. The

Table 3
Intra and inter day variations for PASE and TDS methods, with recovery data from PASE liquid samples and desorption efficiency values.

PAHs	VC_{intra} (%), $n = 5$		VC_{inter} (%), $n = 3$		(%)Recovery/Desorption 1 ng, $n = 3$			
	PASE	TDS	PASE	TDS	PASE	%RSD	TDS	%RSD
Nap	4.9	7.1	7.7	7.6	76	5.2	89	5.3
Acy	3.4	7.8	5.4	5.4	89	3.2	73	1.4
Ace	2.7	9.2	4.5	9.8	86	3.2	83	1.2
Flu	0.7	6.6	1.4	4.7	95	3.0	84	2.6
Phe	1.3	5.8	3.2	6.7	99	2.9	85	2.4
Ant	0.9	3.4	1.3	3.4	98	4.7	83	2.7
FluAn	1.3	3.4	3.0	4.2	96	2.9	86	3.2
Pyr	0.5	2.2	1.2	2.7	88	2.7	75	3.4
BaA	2.3	5.4	3.1	2.9	90	1.4	93	2.5
Chr	2.0	3.8	2.2	3.1	88	3.3	78	2.0
BbF	2.5	5.8	3.9	6.0	86	5.4	68	4.0
BaP	1.1	11	2.2	9.8	93	3.6	78	3.4
IcdP	1.4	10	2.1	12	81	5.7	79	1.4
BghiP	1.9	8.8	3.1	11	83	4.9	66	3.3
DahA	1.2	8.7	3.7	6.4	85	3.6	71	1.2

Table 4
Comparative data of PASE-GC–MS and other solvent extraction and TD-GC–MS approaches described in literature for the determination of airborne PAHs in the vapour phase. All analyses were done by GC–MS.

Extraction	Sample loading	Sampling volume (L)	LOD (ng m^{-3})	Precision (%RSD)	Reference
PDMS traps	TD	–	0.1	–	[24]
Sorption tubes (PDMS + foam)	TD	144	0.007 (Ant) to 0.026 (Nap)	3.7 (Pyr) to 12.9 (Nap)	[31]
Toluene	DI	–	1	–	[32]
Hexane	DI	60	$1–10 \times 10^{-6}$	below 5	[30]
No solvent	TD		0.3		[33]
PASE (hexane)	DI	5	13.6–227.1	1.4 (BaA) to 5.7 (IcdP)	This study
PDMS traps	TD	5	0.18 to 0.9	1.2 (Ace, DahA) to 5.3 (Nap)	This study

DI = direct injection.

extraction method developed in this study had a similar precision (%RSDs below 6%) to that of other reported direct injection methods for the target PAHs (for example, %RSDs below 5% [30]).

3.4.2. *Comparison of recoveries and desorption efficiencies*

The PASE extraction recoveries and thermal desorption efficiencies were assessed. Recovery experiments were done by spiking the PDMS traps with the PAH standard mix solution at low (0.3 ng) and high (1 ng) quality control levels to better represent both trace analysis of environmental samples and those at higher concentrations closer to sources. PASE studies and TDS experiments were each done in triplicate and recoveries were calculated with repeatability expressed as%RSD. As can be seen from Table 3, individual recoveries ranged from 76% to 99% for PASE and from 66% to 93% for thermal desorption. The recovery and repeatability results showed that PASE extraction was superior to the TDS method in this regard. Although there were more losses of Nap with PASE, the remainder of the PASE PAH recoveries were better (Fig. S6) especially for the heavier analytes which were not desorbed as efficiently using the TDS method.

3.5. *Application to real domestic fires*

The applicability of the PASE method was investigated by determining the concentration of PAHs in real domestic fire air emission samples under the established optimum analytical and extraction conditions for both PASE and TD of samples. The proposed method was applied to the analysis of four different sets of samples acquired during an outdoor fuel burning experiment. Sample set A represents duplicate samples collected 10 min after ignition at 1 m above the brazier, sample set B was similarly collected 10 min after ignition but at 1.5 m above the brazier, sample set C related to 20 min after ignition at 1 m above the brazier and sample set D to 20 min after ignition at 1.5 m above the brazier. As Table 5 shows, some of the compounds included in this study could be found at very low levels in the fire emission samples despite the short sampling time (10 min) and small air sample volume (5 L).

As illustrated in the PAH composition profiles (Fig. 4), total PAH fractions for the whole burning cycle showed that the 2–3 ring PAHs (from Nap to Ant) accounted for about 72% of total emissions. In general, the profile of the eight quantified gaseous PAHs was similar to emissions from wood, crop residues and other combustion sources reported in literature [34,35]. Hellen et al. recently noted that emission rates of PAHs heavily depend on many different factors, such as the type and construction of the fireplace, operating procedures, quality of the wood used and meteorological conditions, hence making it difficult for direct comparison of PAH concentration levels [36]. In addition, sampling parameters such as flow rate employed may influence the variations in reported concentrations of PAHs. Emissions are expected to be higher in a traditional wood stove (such as an *imbawula*) due to under-ventilated conditions. The overall PAH profiles for the trap samples are presented as bubble plots in Fig. 4, which give an indication of which PAHs were predominantly detected using the PASE and TDS methods. The high concentrations of Nap (9.58 $\mu g\, m^{-3}$) are in agreement with residential wood combustion PAH profiles previously reported [34,37,38]. Although higher Nap concentrations (28.7 and 29.0 $\mu g\, m^{-3}$ in Burundi and Japan respectively) have been reported for indoor air environments [39,40], other studies have reported lower concentrations in the ng m^{-3} range, especially outdoors where dilution occurs [41,42].

Both methods in this study detected Nap, Acy and Phen as the most abundant PAH contaminants in the fire emissions. Samples A and D were taken concurrently adjacent to each other, and the results of the two methods indicated a similar order of magnitude in PAH concentrations. Variations in concentrations observed

Table 5
Analytical results of PAHs ($\mu g\,m^{-3}$) in real domestic fire air emission samples by PASE-GC–MS and direct TD-GC–MS.%RSDs for PASE results were based on three repeat injections of each sample extract (n = 3).

Compound	Sample A			Sample B*		Sample C*		Sample D		
	PASE	%RSD	TDS	PASE	%RSD	PASE	%RSD	PASE	%RSD	TDS
Nap	9.6	9.7	8.4	9.0	8.5	3.8	9.1	3.2	7.2	3.9
Acy	1.6	3.5	1.7	1.1	4.3	0.6	3.8	0.4	5.1	1.2
Ace	0.3	4.7	0.4	0.2	3.2	0.2	4.4	0.1	3.7	0.1
Flu	1.5	6.8	0.1	1.3	4.7	0.5	3.9	0.4	5.7	0.1
Phe	1.9	5.2	0.7	1.9	5.6	0.6	2.7	0.4	2.6	0.4
Ant	0.7	2.9	0.1	0.7	3.1	0.3	3.3	0.2	4.0	0.1
FluAn	0.7	4.4	0.1	0.6	2.5	0.3	2.9	0.1	3.5	0.1
Pyr	0.3	3.3	0.1	0.1	3.8	<LOQ	<LOQ	<LOQ	<LOQ	0.1

A = samples collected 10 min after ignition at 1 m above brazier.
B* = samples collected 10 min after ignition at 1.5 m above brazier.
C* = samples collected 20 min after ignition at 1 m above brazier and.
D = samples collected 20 min after ignition at 1.5 m above brazier.
< LOQ = analytes were detected but were below the limit of quantification.
* Sample sets B and C were not available for analysis by TDS due to a pump malfunction.

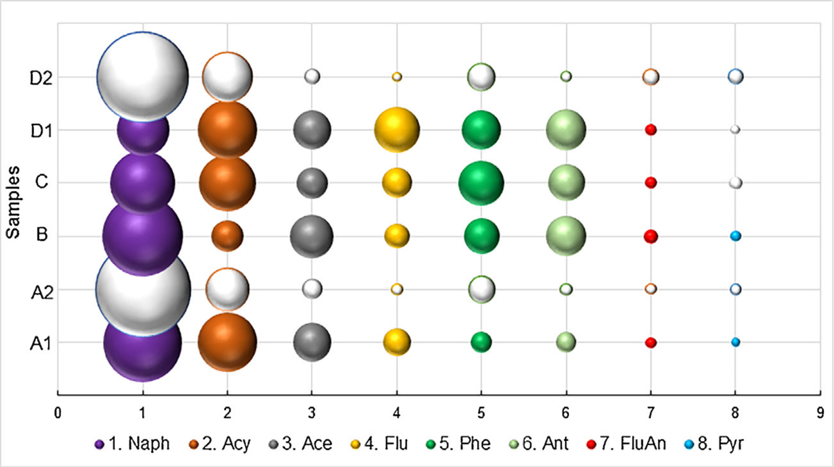

Fig. 4. Bubble plots to show the relative% peak areas per cubic meter of air sampled of gas phase PAHs found in the PDMS trap. Samples A1, B, C and D1 were analysed by the PASE method, illustrated as shaded bubbles and samples A2 and D2 were analysed by direct thermal desorption and are illustrated as open bubbles.

between the methods may have been due to slight variations in the concentrations of analytes in the air sample at each trap location, due to air dispersion effects. In addition, different multi-silicone rubber traps were used for each sample, which may have introduced sampling variations.

Although direct comparison is fairly rare, a few studies have compared the relative performance of thermal desorption-based methods and conventional solvent-based methods for PAH determinations. Wauters et al. compared their TD-GC–MS method to a classical liquid extraction method for the quantitative analysis of 16 PAHs and found that concentrations for higher molecular weight PAHs were significantly higher than the classical method [31]. This was catered for in our present study through sequential plunging and superior extraction efficiencies were therefore achieved for heavier analytes. In another study, conventional liquid extraction and TD-GC–MS were assessed and the authors reported that the methods had equivalent results although TD-GC–MS gave lower uncertainties [43]. In an extensive review of the analysis of airborne PAHs, Pandey et al. reported that although TD appears to be a superior choice for certain PAHs, acquiring good recovery of all PAHs is still a challenge since TD is sensitive to the physicochemical properties of individual PAHs [7]. Hence the use of PASE surpasses most limitations of TD without compromising original sampling methods and the use of multi-channel silicone rubber traps.

4. Conclusions

The PASE method allowed for both the more volatile PAHs (such as naphthalene), as well as the higher molecular weight PAHs to be efficiently extracted and quantified without excessive use of organic solvents. PASE is an environmentally friendly approach since small volumes of organic solvent were consumed (a total of 2 mL per extraction), whilst extraction efficiencies were good (from 76% for Nap to 99% for Phen). Some figures of merit (mean for 15 PAHs) of the proposed PASE method include excellent repeatability (0.5%), accuracy (98%) and linearity (0.999) and this demonstrated the suitability of the method for routine monitoring of PAHs. Low intra-day variations were observed for PASE and ranged from 0.5% for Pyr to 4.9% for Nap. Although all extraction efficiencies were generally good, the PASE method showed enhanced results compared to the TDS method for most of the PAHs under consideration, especially the heavier analytes. Therefore PASE can be used as a reliable and cheaper alternative to TDS for the analysis of PAHs from PDMS traps in applications where concentrations are above the LODs for this method. The proposed PASE technique required less total analysis time compared to TDS, since TDS required an extra 11.5 min for cryofocusing of analytes, whilst the PASE extraction was completed in 2 min. Losses were minimized with the PASE method since only Teflon was in contact with the sample and solvent. The application of the PASE method has been illustrated for the analysis of PAHs from domestic fuel burning, whilst it opens interesting perspectives for the similar determination of other semi-volatile organic pollutants which are also effectively sampled onto the PDMS traps. In addition to being a cheaper alternative, PASE allows for the re-analysis of samples and does not require any modification of existing samplers or low volume sampling methods. Although the entire sample is not analysed, as in the case of TD, this is not a problem in many applications due to the sensitivity of the analytical method. Large volume injections or pre-concentration of PASE extracts are possible means to further enhance detection limits. Application is possible in laboratories which do not have thermal desorption systems, hence facilitating the widespread use of PDMS traps for airborne PAH monitoring, as well as in denuder applications for the simultaneous monitoring of gas and particle associated PAHs.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.chroma.2018.04.053.

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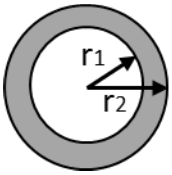
Paper 2 Supplementary Information

Equation S1. illustrates how the maximum volume in the trap was calculated. V_A represents the empty space in the empty tube portion, V_B the open volume in the trap portion and (V_{total}) the total volume of the multi-channel silicone rubber trap that the extraction solvent would occupy.



Silicone rubber tube dimensions

$V_A = \pi r_x^2 L_A$ (where r_x and L_A are internal radius of the glass tube and length L_A, respectively). Total volume (V_T) occupied by 1 silicone rubber tube of length $L_B = \pi r_2^2 L_B - \pi r1^2 L_B$ (Where r_2 and r_1 are external and internal radius of each silicone rubber tube respectively and L_B is length B). Therefore $V_B = \pi rx^2 L_B - 22V_T$; (where 22 is the number of silicone rubber tubes). Hence the total open volume was obtained by using the equation $V_{total} = V_A + V_B$.

Figure S1: Illustration of an imbawula stove used in this study, showing a medium ventilation case

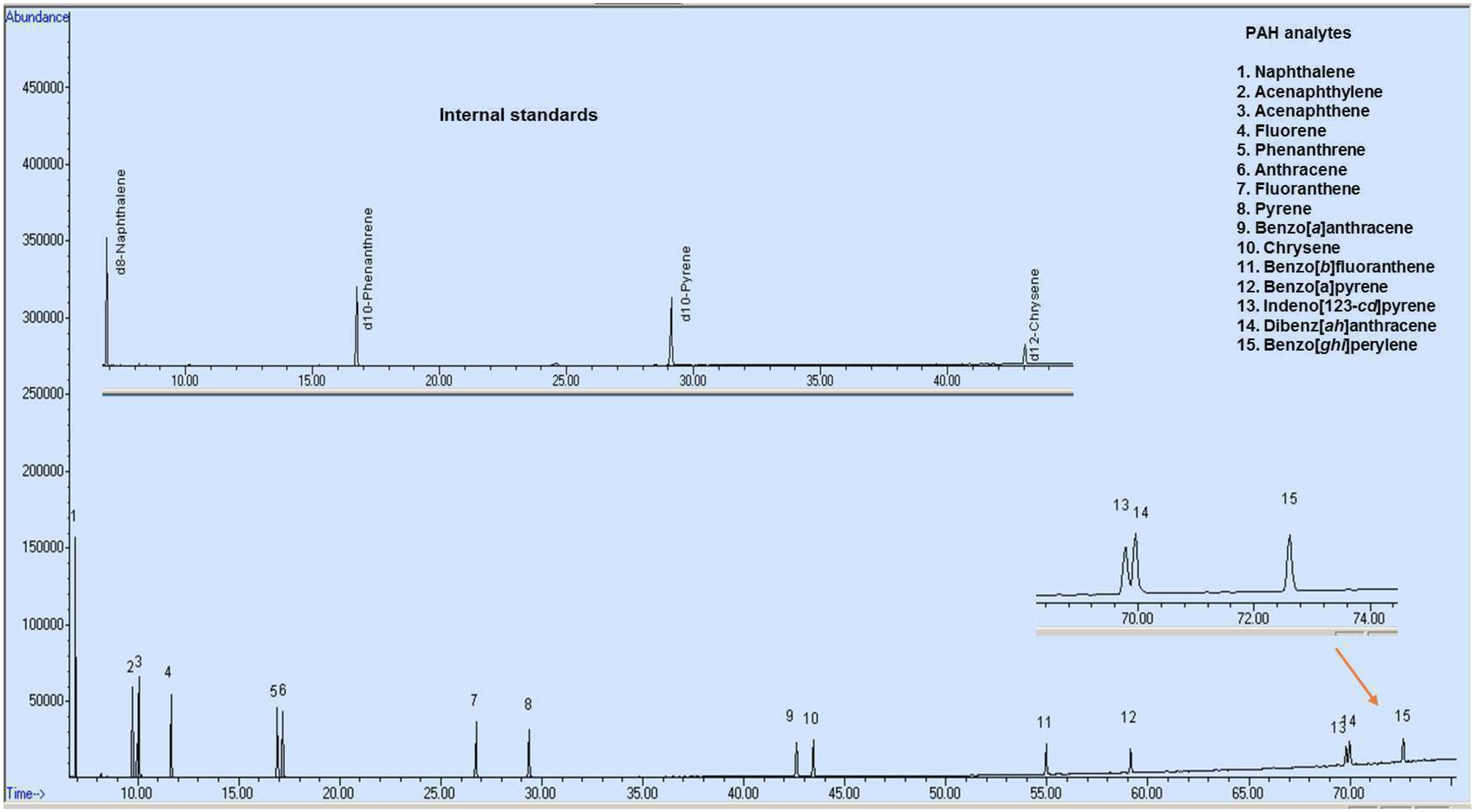


Figure S2: Representative GC-MS-SIM chromatograms of PAHs in a PASE extract from a spiked (1000 ng µL $^{-1}$) PDMS trap. The IS mixture contained d8-naphthalene, d10-phenathrene, d10-pyrene and d12-chrysene in toluene.

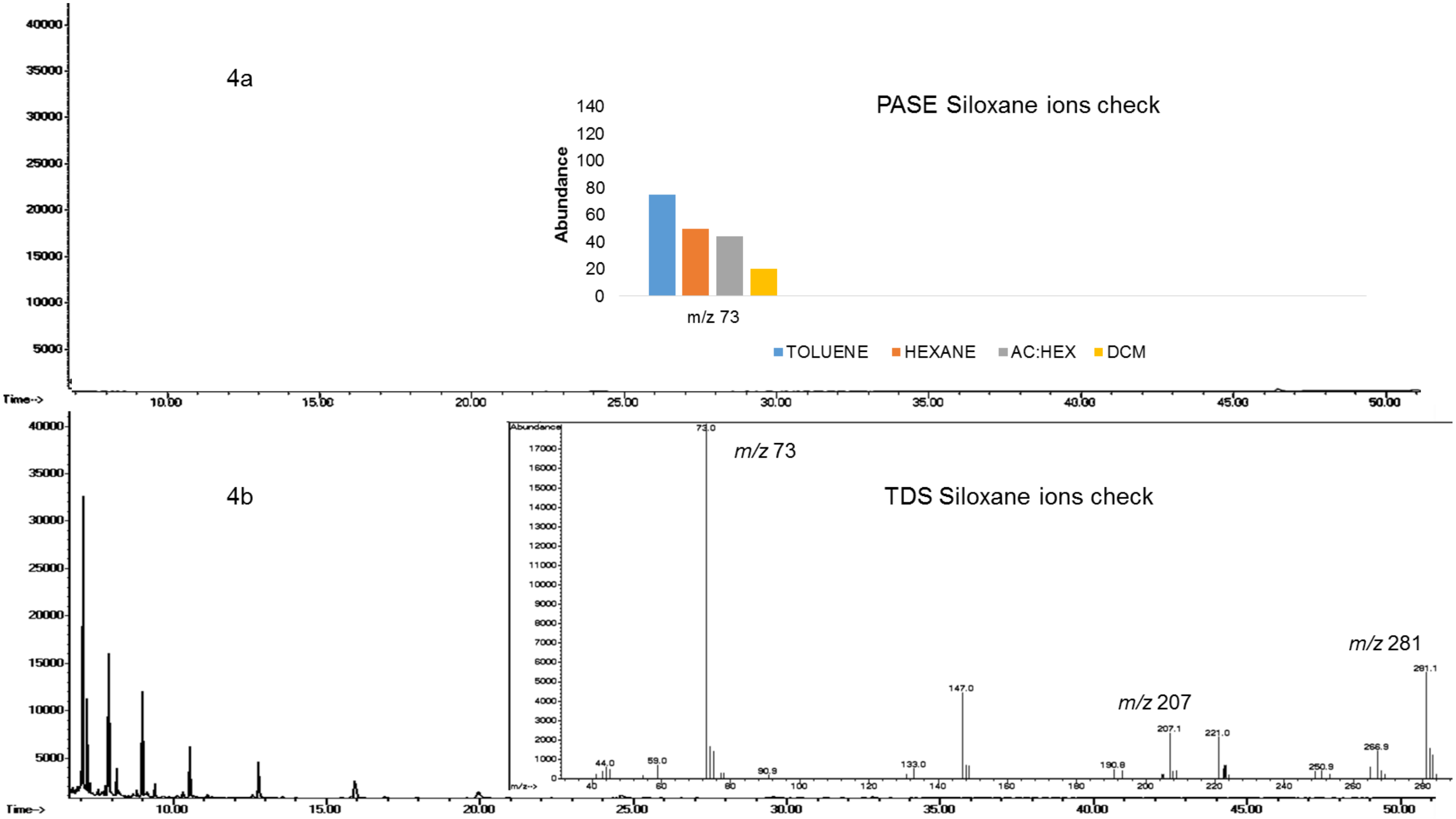
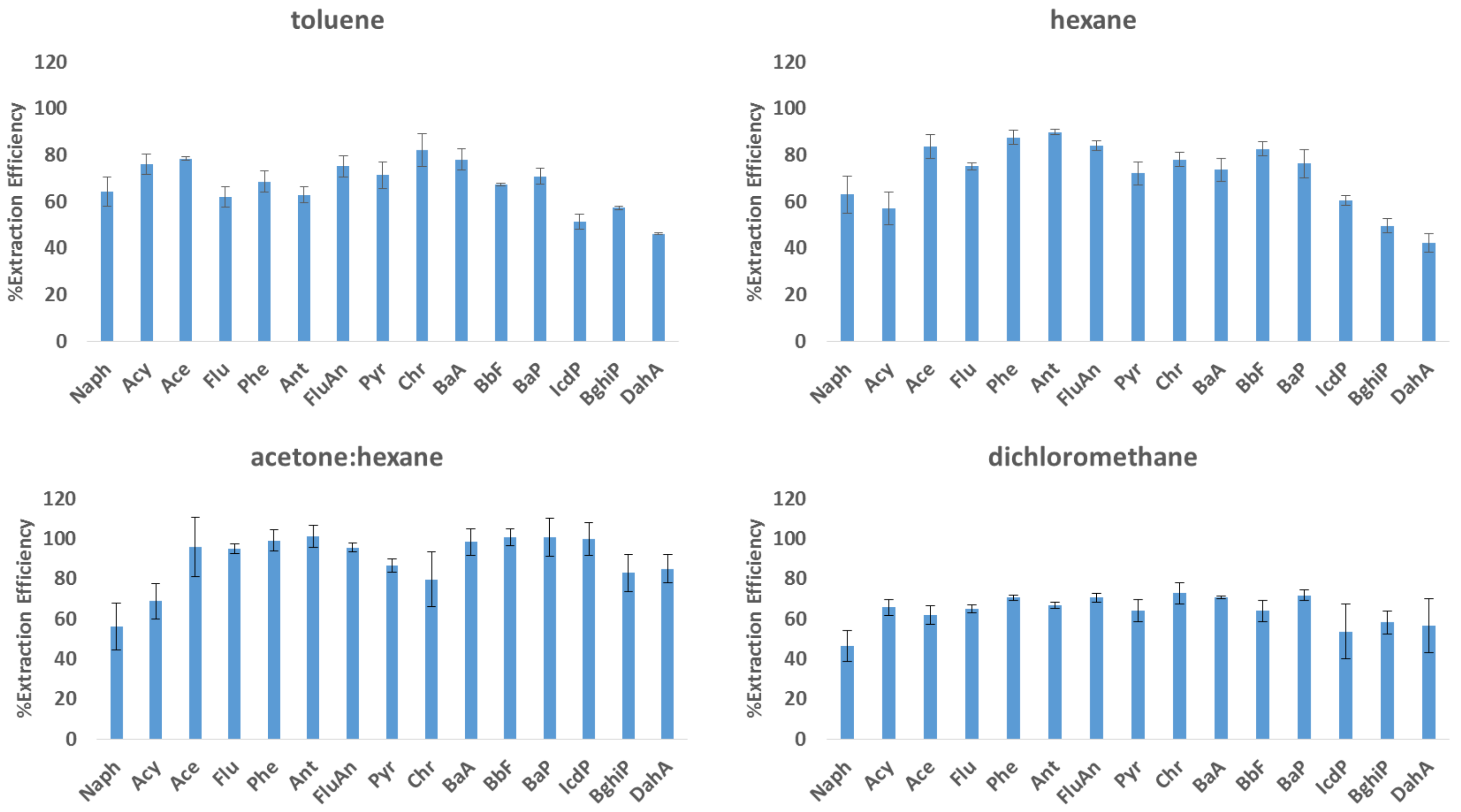


Figure S3: A representative total ion chromatogram (TIC) showing no interfering peaks when the silicone rubber trap was plunged in pure toluene solvent, where the siloxane peak abundance was taken from the highest peak in a given TIC for each solvent. Fig. 4b displays a representative TIC at the same scale and mass spectrum (peak at 12.2 min) obtained from the direct thermal desorption of a blank silicone rubber trap. Silicone degradation peaks are illustrated which were easily identified as cyclosiloxanes with mass spectral fragments of m/z 73, 207, 211 and 281.


toluene

hexane

acetone:hexane

dichloromethane

Figure S4: Average extraction efficiencies for individual PAHs obtained by PASE with different extraction solvents. Error bars show ± standard deviation, n=3.

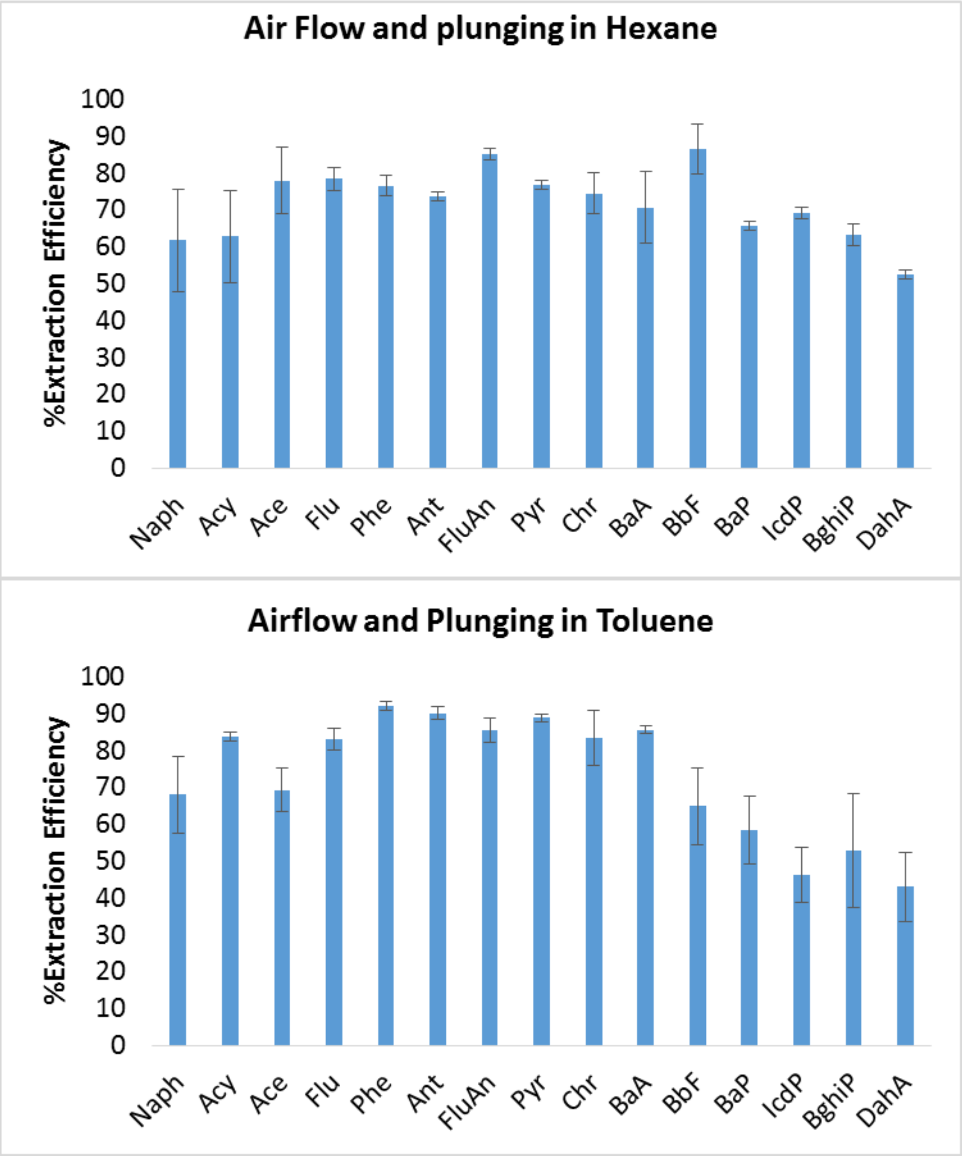


Figure S5: Single extraction efficiencies of individual PAHs using n-hexane and toluene as extraction solvents. Air was pumped through a trap spiked with PAHs (1ng.µL^{-1}) at 500 mL.min^{-1} for 8 min and this was then followed by PASE. Error bars show ± standard deviation, n=3.

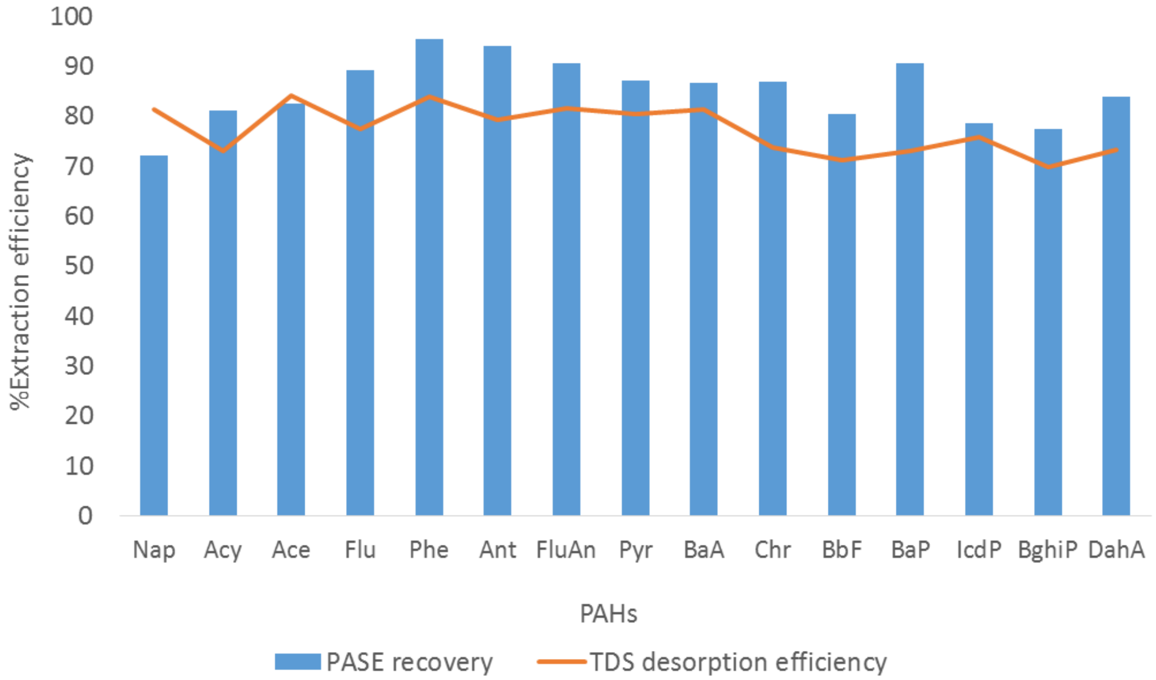


Figure S6: Comparison of individual PAH recoveries obtained for PASE (hexane extraction solvent, 680 µL) and TDS thermal desorption efficiencies, (n=3).

Chapter 4: PASE Application: A Kenyan Case Study (Paper 3)

The monitoring of gas-phase PAH emissions from household cooking devices in Kenya utilizing the developed PASE method as a solvent extraction technique is reported in this chapter.

This chapter was published in Environmental Toxicology and Chemistry. Additional information is provided in the Addendum.

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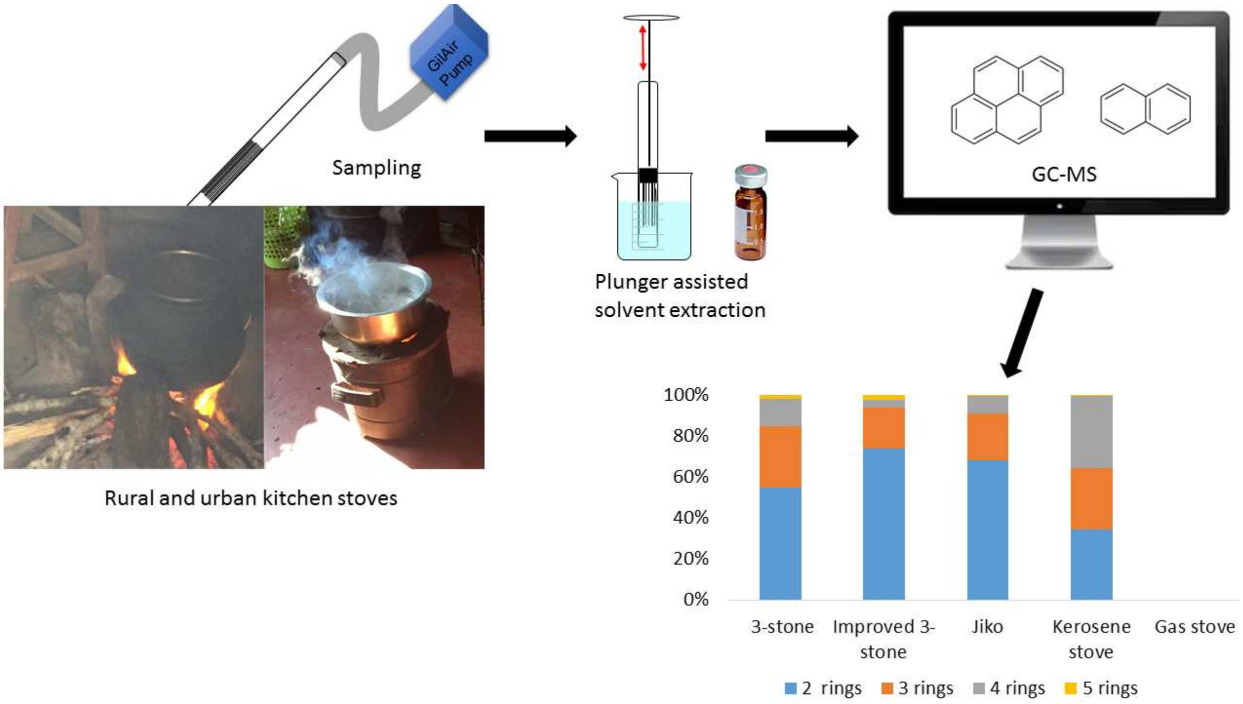
Chiedza F. Munyeza contributed to the design of the paper, performed sampling, sample preparation and quantification experiments, data analysis and wrote the paper. Aloys M. Osano and Justin K. Maghanga contributed to the design of the paper, participated in the sampling campaign and edited the paper. Patricia B.C. Forbes conceptualized the study, contributed to the design of the paper and data interpretation, participated in the sampling campaign, edited and submitted the paper.

Graphical Abstract



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

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Abstract: In developing countries, household energy use is highly variable and complex, yet emissions arising from fuel combustion indoors are typically poorly quantified. Polycyclic aromatic hydrocarbons (PAHs) are emitted during the combustion of organic fuels such as charcoal and biomass. In the present study, multichannel polydimethylsiloxane rubber traps were used for gas-phase PAH sampling and extracted using a low–solvent volume plunger-assisted solvent extraction method. Sixteen US Environmental Protection Agency priority PAHs, primarily in the gas phase, were investigated in indoor air of rural and urban residential homes in coastal Kenya (Mombasa and Taita Taveta Counties) using typical combustion devices of each area. Average gaseous PAH concentrations per household were higher in rural (ranging 0.81–6.09 $\mu g\ m^{-3}$) compared to urban (ranging 0–2.59 $\mu g\ m^{-3}$) homes, although ambient PAH concentrations were higher in urban environments, likely attributable to traffic contributions. The impact of fuel choice and thereby combustion device on PAH emissions was very clear, with the highest concentrations of PAHs quantified from wood-burning emissions from 3-stone stoves (total PAH averages $46.23 \pm 3.24\ \mu g\ m^{-3}$ [$n = 6$]). Average benzo[*a*]pyrene equivalent total concentrations were evaluated for the priority PAHs and ranged from not detected to 43.31, 88.38, 309.61, and 453.88 $ng\ m^{-3}$ for gas, kerosene, jiko, 3-stone, and improved 3-stone stoves, respectively. *Environ Toxicol Chem* 2020;00:1–10. © 2019 SETAC

Keywords: Polycyclic aromatic hydrocarbon; Household air pollution; Combustion device; Clean energy; Plunger-assisted solvent extraction; Gas chromatography-mass spectrometry

INTRODUCTION

It is well into the twenty-first century, yet an estimated 2.8 billion people in countries with developing economies still rely on solid fuels (dung, coal, crop wastes, wood, charcoal, etc.) and traditional stoves for heating and cooking (International Institute for Applied Systems Analysis 2012; Bonjour et al. 2013). According to recent data, 600 million Africans have limited access to electricity or clean cooking energy and still rely on traditional sources of energy to meet their basic energy needs (World Health Organization 2016; Makonese et al. 2018). As a result, most households in developing countries without access to clean energy provisions use inefficient combustion devices and fuels that have high pollutant emissions, hence significantly increasing the disease burden in these communities. According to the national human activity pattern survey sponsored by the US Environmental Protection Agency (Klepeis et al. 2001), indoor air quality is an important determinant of health globally because humans spend up to 90% of their time indoors. The recent Global Burden of Disease studies have also estimated that exposure to smoke from household air pollution is responsible for approximately 3.5 million premature deaths worldwide and various health issues such as cancer and cardiovascular diseases (Patelarou and Kelly 2014; Health Effects Institute 2018; Suter et al. 2018).

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

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This article includes online-only Supplemental Data.

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potential mutagenicity and carcinogenicity (Boström et al. 2002; Umbuzeiro et al. 2008). Combustion of fuels of all types, including wood, charcoal, coke, gas, and diesel, is the major anthropogenic activity that produces PAHs, whereas volcanic eruptions and forest fires are the primary natural sources. Total global emissions of the 16 US Environmental Protection Agency priority PAHs (ΣPAH16) were estimated at 504 Gg in 2007, of which more than half (~60%) was ascribed to residential solid fuel combustion (Shen H et al. 2013). Thus, PAHs have remained among the toxic organic pollutants of most concern; and in certain industrialized countries, residential wood combustion is still a major source of PAH emissions. For example, in Finland, Chile, and the United States, ΣPAH16 values from residential wood combustion are 78, 72, and 46% of the national PAH emission totals, respectively (Shen H et al. 2013; Shen et al. 2017). However, recent reviews on the current status of atmospheric PAHs in Africa have indicated that there are few data on the measurement of these organic compounds and their associated health outcomes (Kalisa et al. 2019; Munyeza et al. 2019).

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

The characteristics of indoor PAH pollution in African developing countries such as Kenya are significantly different from those in developed countries because of the traditional cooking methods employed. In addition, Kenya Vision 2030 has identified fuel as one of the infrastructural enablers of its social economic pillar, stating that the availability of sustainable, affordable, and reliable fuels for all citizens is a key factor in the realization of the national development blueprint (Rambo 2013). In this light, more baseline studies on levels of PAHs in both rural and urban Kenya households using different fuel types and cook stoves are needed to better understand exposure levels and to quantify future improvements. Gachanja and Worsfold (1993) analyzed particulate-bound and gaseous PAHs from 2 charcoal stoves generally used in the Kenyan highlands (ceramic-lined and traditional metal) and concluded that the ceramic stove produced notably lower PAH emissions than the traditional stove. In a related study, Lisouza et al. (2011) characterized and quantified PAH emissions in soot samples collected from traditional thatched rural households of the Western Province of Kenya. Although variance in PAH levels among houses using different biomass fuels such as cow dung, crop residues, or firewood was reported by the authors, there was no comparison of gas-phase PAH concentrations in the breathing zone of urban and rural kitchens based on combustion devices. In addition, levels in ambient air surrounding rural and urban households were not reported in these 2 previous Kenyan studies.

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

MATERIALS AND METHODS

Area of study

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

Sampling

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

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

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

[a] Mud houses had grass or leaf roofs, whereas brick houses had tiled roofs.
LPG = liquefied petroleum gas.

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

Extraction of PAHs

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

Characterization and quantification of PAHs

The analysis of gas-phase samples was based on the method previously developed (Munyeza et al. 2018) as described in the Supplemental Data. The PAHs were identified using retention times, verified by GC (Agilent 6890) connected to an MS (Agilent 5975C) and quantified from peak area responses using the internal standard method. Seven-point matrix-matched analytical curves (concentrations 0.05–1.5 ng μL^{-1}) were used for the quantification of PAHs, where the target PAH analyte peak area ratio to that of the internal standard versus the amount of analyte in nanograms was employed. The internal standard mixture was spiked onto all traps prior to extraction. Losses of PAHs during sample concentration were investigated by analyzing 1 ng μL^{-1} pure PAH mix standards before and after nitrogen blowdown and reconstitution in n-hexane. Analyte to internal standard ratios between pure standards injected before and after concentration were compared. A 2-tailed *t* test was used to determine the significance of PAH losses in the evaporated samples based on these ratios, and it was concluded that losses were not significant at the 95% confidence interval ($p > 0.05$). Although the relative standard deviations (RSDs) were highest for 2- and 3-ringed PAHs (ranging from 0.2% for acenaphthylene to 19.4% for acenaphthene), no significant losses of PAHs, regardless of their boiling points, were found. This was consistent with a previous study which investigated PAH losses when using nitrogen for sample blowdown (Chang et al. 2001). In addition, vaporization of lighter PAHs was not problematic because an internal standard mixture was added before extraction and concentration, therefore compensating for any losses. Matrix-matched calibration point samples were also blown down to near dryness using pure nitrogen and reconstituted in 100 μL hexane. This step was performed to match the field sample extraction and to correct for the optimized and acceptable recoveries (ranging 76–99%). The limit of detection (LOD) and limit of quantification (LOQ) for each target compound was calculated as 3 times and 10 times the S/N ratio, respectively.

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

Statistical analysis

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

RESULTS AND DISCUSSION

PAH quantitation

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

Fourteen PAHs out of the initial target 17 PAHs were identified in field samples. The concentrations of gas-phase PAHs found in the traps are presented in Supplemental Data, Table S3. Gas-phase indoor concentrations were high and varied widely, ranging from 0.12 to 25.92 $\mu g\,m^{-3}$. Similar elevated gas-phase concentration ranges, with naphthalene being the most abundant analyte, have been reported in Burundi (Viau et al. 2000) and Japanese kitchens (Ohura et al. 2004). Low–molecular weight PAHs are predominant in the gaseous phase and are known to be less toxic to humans, whereas high–molecular weight PAHs tend to be found in the particulate phase because of their low vapor pressures and are more carcinogenic and/or mutagenic (Dat and Chang 2017). Although considered less toxic, low–molecular weight PAHs exist in higher concentrations and can react with other pollutants such as O_3 and NO_x to form highly toxic nitrated and oxy-PAH compounds and are therefore of importance in risk assessments.

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

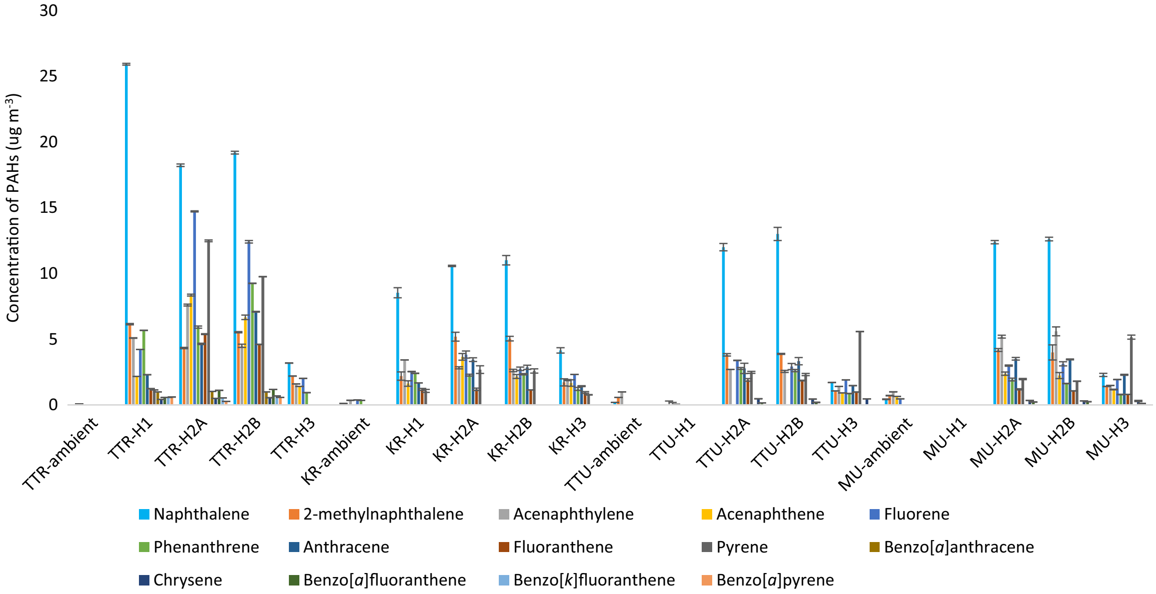

FIGURE 2: Gas-phase polycyclic aromatic hydrocarbon (PAH) concentrations in 12 selected households and ambient backgrounds in urban and rural areas. Error bars show ± standard deviation, $n = 2$. KR = Kilifi rural; MU = Mombasa urban; TTR = Taita Taveta rural; TTU = Taita Taveta urban.

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

Variation in levels of PAHs with combustion device employed

Because emission performance often varies dramatically with fuel type and stove design, previous studies have recommended evaluation of various PAH concentrations based on the fuel–stove combination (Shen G et al. 2013). This is because dirty fuels may burn relatively clean in improved-efficiency stoves and, conversely, clean fuels may also produce more pollutants under substandard combustion conditions. A number of studies have investigated and compared emissions from wood combustion based on different stoves or heating appliances in laboratory-controlled conditions (Orasche et al. 2012, 2013). A variety of fuel and cook stove combinations which were investigated in the present study are summarized in Table 1. Cook stoves are commonly called "improved" if they are more efficient, visually emit less emissions, or are safer than the traditional cook stoves or 3-stone fires. In the present study, an improved 3-stone cook stove refers to a built-in or constructed structure in which firewood is placed (see Supplemental Data, Figure S4). Generally, traditional wood stoves are expected to produce higher emissions because of their underventilated conditions.

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

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

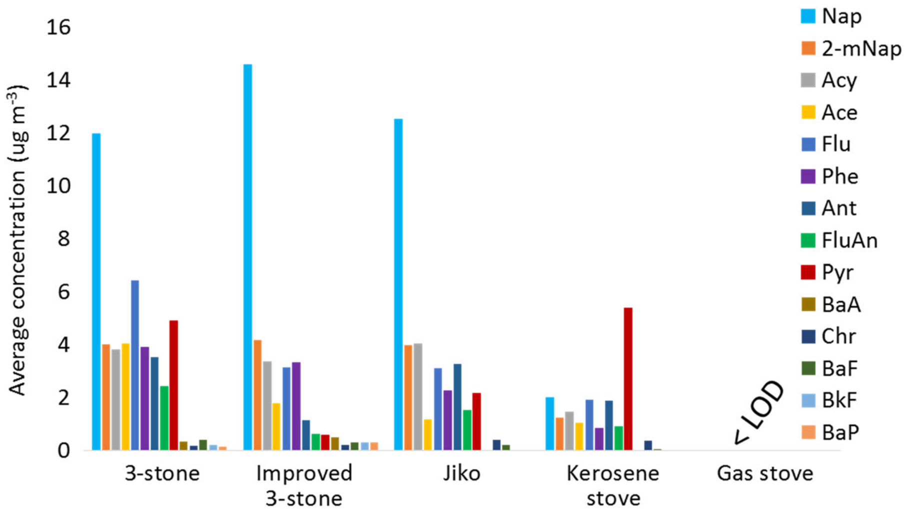

FIGURE 3: Average polycyclic aromatic hydrocarbon concentrations for various combustion devices. Ace = acenaphthene; Acy = acenaphthylene; Ant = anthracene; BaA = benzo[*a*]anthracene; BaF = benzo[*a*]fluoranthene; BaP = benzo[*a*]pyrene; BkF = benzo[*k*]fluoranthene; Chr = chrysene; Flu = fluorene;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

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

The improved 3-stone cook stove did not demonstrate a significant advantage over the traditional 3-stone because gas-phase analytes were still present at high concentrations, which was likely attributable to the types and quality of fuels which were used. A 2-tailed *t* test confirmed that levels of PAHs from these 2 combustion devices were not significantly different at the 95% confidence interval ($p > 0.05$). Although high concentrations were quantified from improved 3-stone cook stoves, a marked decrease in the emission of the heavier 4- to 5-ring PAHs was observed with these devices, which is promising because heavier PAHs are known to be more toxic (see Supplemental Data, Figure S6). For example, when the woman tending the fire was interviewed, it was reported that the cyprus firewood which was used in household TTR-H1 (for improved 3-stone) was not dry, resulting in poor combustion and leading to high PAH concentrations and choking smoke in the kitchen. However, when dry sawdust was used with another improved 3-stone stove in TTR-H3, lower PAH emissions were found compared to those in TTR-H1. These findings are consistent with those of a previous study, which showed that, apart from type of combustion device, particle concentration of smoke and associated PAH concentration also depend on the wood moisture content and burning period involved (Chomanee et al. 2009). In addition to the type of fuel influencing the evaluation of cook stoves, differences in ventilation sources could have contributed to PAH variation because most rural households had no chimneys but a small door and a window (see pictures in Supplemental Data, Figure S7).

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

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

Distribution of PAHs in rural and urban households

Efforts to characterize differences between urban and rural atmospheric PAH pollution in Africa have largely been hindered by a paucity of sampling data. As illustrated in Figure 4A, PAHs showed a strong rural to urban gradient, with maximum concentration in rural homes. Although Kilifi rural homes were more ventilated, with some households cooking outdoors on open fires, most rural kitchens had poor ventilation in general. Rural Kilifi kitchens had poorly structured roofing made from coconut palm fronds, and thus the roofs had many holes and were well ventilated. In addition, they had openings in the walls which served as windows (see Supplemental Data, Figure S8). Lack of properly designed and installed chimneys or exhaust was evident in Taita Taveta rural households, yet urban kitchens were typically more ventilated (see Supplemental Data, Figures S7 and S8). This coupled with the low-efficiency cook stoves and a large amount of firewood used could have attributed to the higher concentrations in rural compared to urban homes. In addition, the detection of naphthalene, fluorene, phenanthrene, and acenaphthene as main PAHs from wood combustion is clearly seen as values doubled from urban to rural households. Elevated PAH levels were also found in rural homes of Burundi (average of 43 $\mu g\,m^{-3}$ for 12 PAHs; Viau et al. 2000), Vietnam (total of 957 $\mu g\,m^{-3}$ for 18 ΣPAHs; Kim Oanh et al. 1999), and Thailand (total of 366 $\mu g\,m^{-3}$ for 17 ΣPAHs) when firewood, sawdust briquettes, or kerosene were used in domestic cook stoves. However, lower total concentrations, in the nanograms per cubic meter range, have been reported in other African indoor environments (Munyeza et al. 2019), for instance, in Sierra Leone, where total concentrations ranged from 1.38 to 4282 $ng\,m^{-3}$, which could have been a result of only the particle phase being measured.

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

Toxicity assessment of gaseous PAHs

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

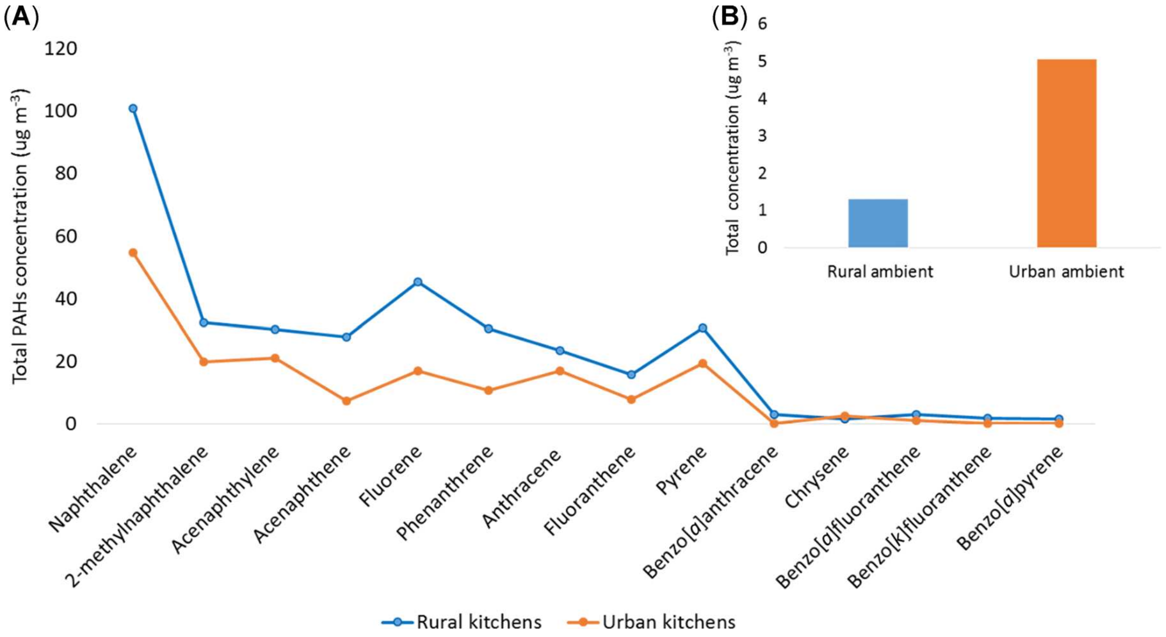

FIGURE 4: Comparison of total polycyclic aromatic hydrocarbon (PAH) concentrations in (**A**) rural and urban kitchens ($n = 12$), and (**B**) rural and urban ambient environments.

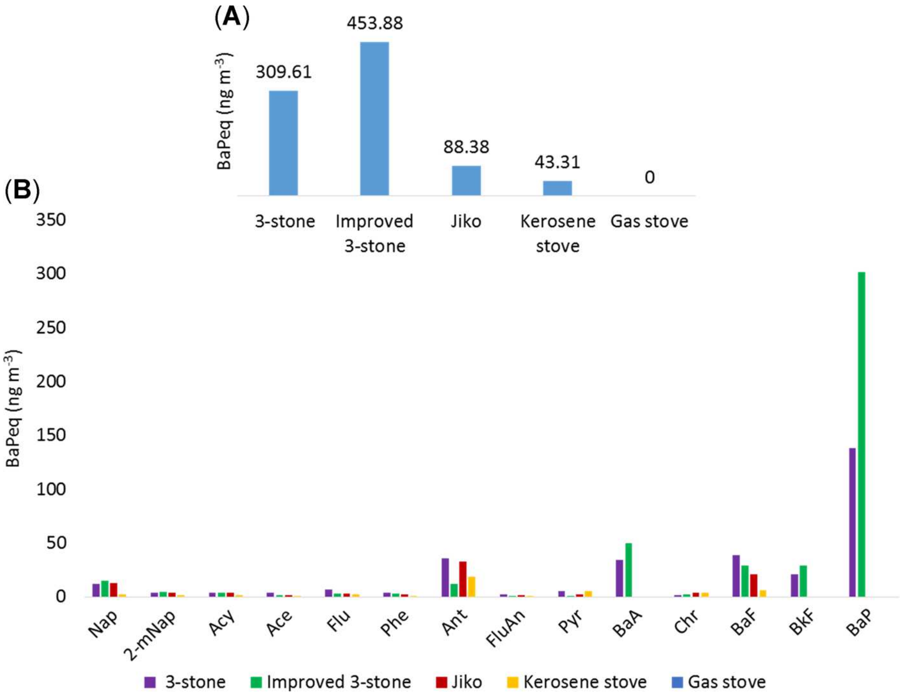

FIGURE 5: Comparison of benzo[*a*]pyrene equivalent (BaPeq) total concentrations. (**A**) Total average BaPeq concentrations from different combustion devices, and (**B**) the relative toxicity contribution of each individual polycyclic aromatic hydrocarbon. Ace = acenaphthene; Acy = acenaphthylene;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

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

PCA

We performed PCA on the results given in Supplemental Data, Table S3, using mean centered data and correlation-based variance. Although PCA is often used for modeling purposes, in the present study it was strictly used to identify potential differences between our samples; PCA plots were used to visualize the interdependence between data sets, and 2 different plots were employed, namely score plots (Supplemental Data, Figure S10a) and loading plots (Supplemental Data, Figure S10b). It was observed that the first principal component accounted for 61.1% of the explained variance between samples, whereas the second principle component accounted for 30.1%. The scores plot illustrated that good grouping of samples was only observed with respect to ambient (orange ellipsoid, samples 1, 6, 11, and 16) and liquefied petroleum gas (green ellipsoid, samples 12 and 17) combustion samples. A biplot (Supplemental Data, Figure S11) was used to further illustrate that the increased concentrations of BaA accounted for the variation of samples MU-H2A (18) and MU-H2B (19). As mentioned previously (*PAH quantitation*), it was also observed that the samples from the first 2 houses in Taita Taveta rural area (TTR-H1 and TTR-H2A + TTR-H2B) were very different from all of the other samples. The rest of the combustion devices and sampling sites did not show any substantial grouping patterns because they were irregularly distributed on the plot. The loading plot clearly illustrated the PAHs which were responsible for the intersample variations. The loading plot illustrated that the increased concentrations of naphthalene, 2m-Nap, phenanthrene, acenaphthene, anthracene, fluoranthene, and BaF accounted for the variation of TTR-H1 and TTR-H2A + TTR-H2B.

CONCLUSIONS AND RECOMMENDATIONS

For rural communities, the present study has shown that the use of wood-burning 3-stone combustion devices exposes people indoors to the highest number of carcinogenic gaseous PAHs (total average of 46.23 μg m^{-3}). Exposure to PAHs could cause great health risks, especially for poorly ventilated households. Charcoal combustion using jiko stoves contributed to the highest PAH emissions in urban areas, although lower amounts of high–molecular weight compounds were quantified. Kerosene stoves showed an approximately 50% reduction in PAH emissions compared to jiko, 3-stone, and improved 3-stone stoves. No PAHs were detected from the gas stoves, which shows that liquefied petroleum gas combustion for cooking purposes is a step in the right direction toward use of clean fuel for the near elimination of household PAH pollution. The present results suggest that the use of clean energy sources in combination with more efficient combustion devices could reduce global PAH emissions from the residential sector.

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

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

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

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Paper 3 Supplementary Information

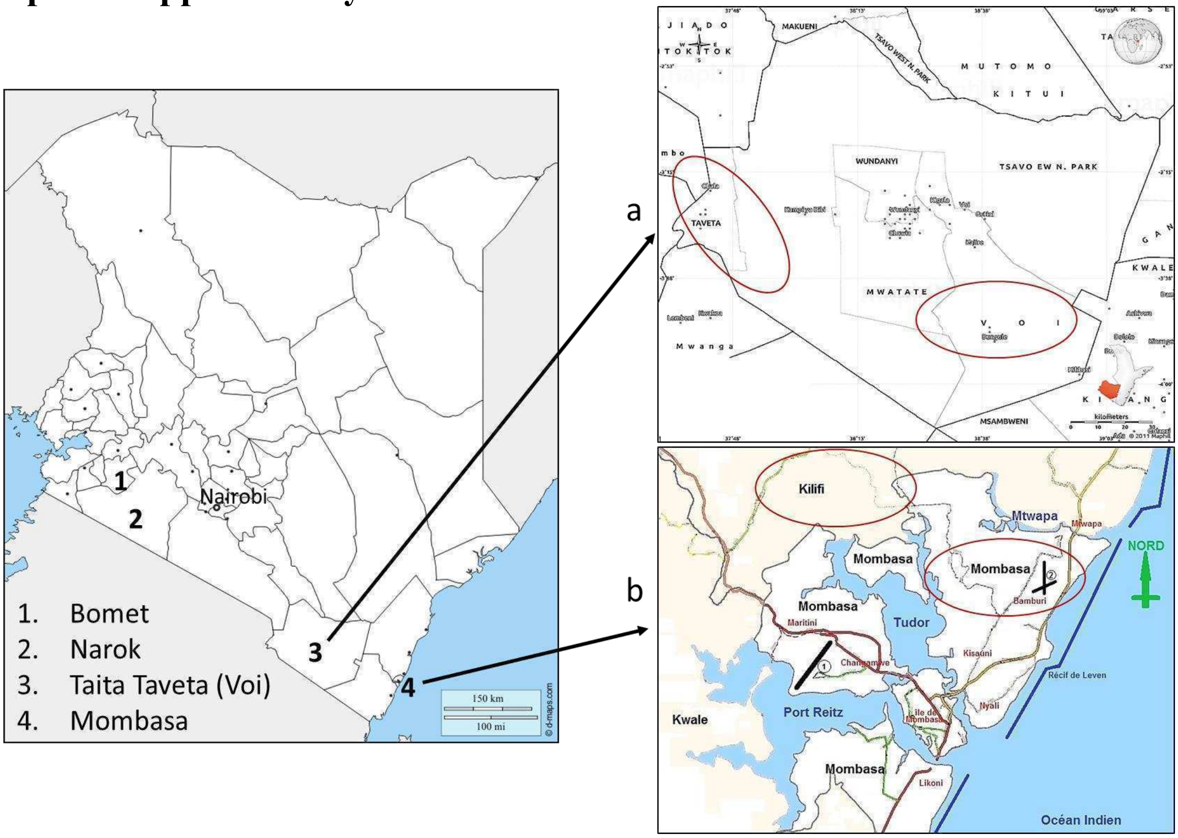

Figure S1: Maps of Kenya and the coastal counties, showing the sampling areas. (a) Map of Taita Taveta county showing the sampling locations (Taveta rural and Voi urban) and (b) map of Mombasa sampling locations (Mombasa urban and Kilifi rural). (Source: maps were downloaded online (https://d-maps.com/) and were modified by the authors).

Chemicals and reagents

The overall analytical procedure, including calibration, was performed using a certified standard PAH mix solution obtained from LGC Standards (Manchester, USA) containing 16 priority PAHs plus 2-methylnaphthalene. The nominal concentration of each compound in the mixture dissolved in methylene chloride was 2000 ng µL^{-1} and the names and abbreviations of the PAHs included are given in Table S1. Stock solutions were prepared in n-hexane and working solutions were prepared by appropriate dilutions of the stock solutions before use. Pure individual PAH standards were obtained from Sigma Aldrich (Bellefonte, USA). All solvents were of analytical grade (99% purity) including toluene and n-hexane and were purchased from Sigma Aldrich (Bellefonte, USA). Deuterated internal standards (IS), namely d8-naphthalene, d10-acenapthene, d10-phenanthrene, d12-chrysene and d12-perylene were obtained from LGC Standards (Labor GmbH, Augsburg, Germany). The IS standards used for respective PAH groups are given in Table S1.

GC-MS Procedure

Briefly, sample analysis was performed using a gas chromatograph (GC, Agilent 6890) connected to a mass spectrometer (MSD, Agilent 5975C) in electron impact ionisation mode. The analytes (1 µL splitless injection) were separated on a Restek Rxi®-PAH column (60 m long, 0.25 mm internal diameter and 0.10 µm film thickness). Helium gas of high purity (Afrox, Gauteng) was used as the carrier gas in a constant flow mode of 1 mL min^{-1}. The inlet temperature was at 275 ^{o}C and the GC oven temperature was held at 80 ^{o}C for 1 min, then ramped at 30 ^{o}C min^{-1} to 180 ^{o}C, then subsequently to 320 ^{o}C at 2 ^{o}C min^{-1}. The ionization potential was 70 eV, the source temperature was 230 ^{o}C and the quadrupole temperature was 150 ^{o}C. A mass range of m/z 40-350 was recorded in full scan mode. Compounds were identified based on comparison of retention times and mass spectra to those of pure individual standards. For better sensitivity, the selected ion monitoring (SIM) mode was also employed to detect compounds and quantify the analytes. In order to confirm the validity of the calibration curves, a quality control standard mixture (1 ng µL^{-1} of all PAH analytes and IS mixture) was analyzed before and after each sample batch.

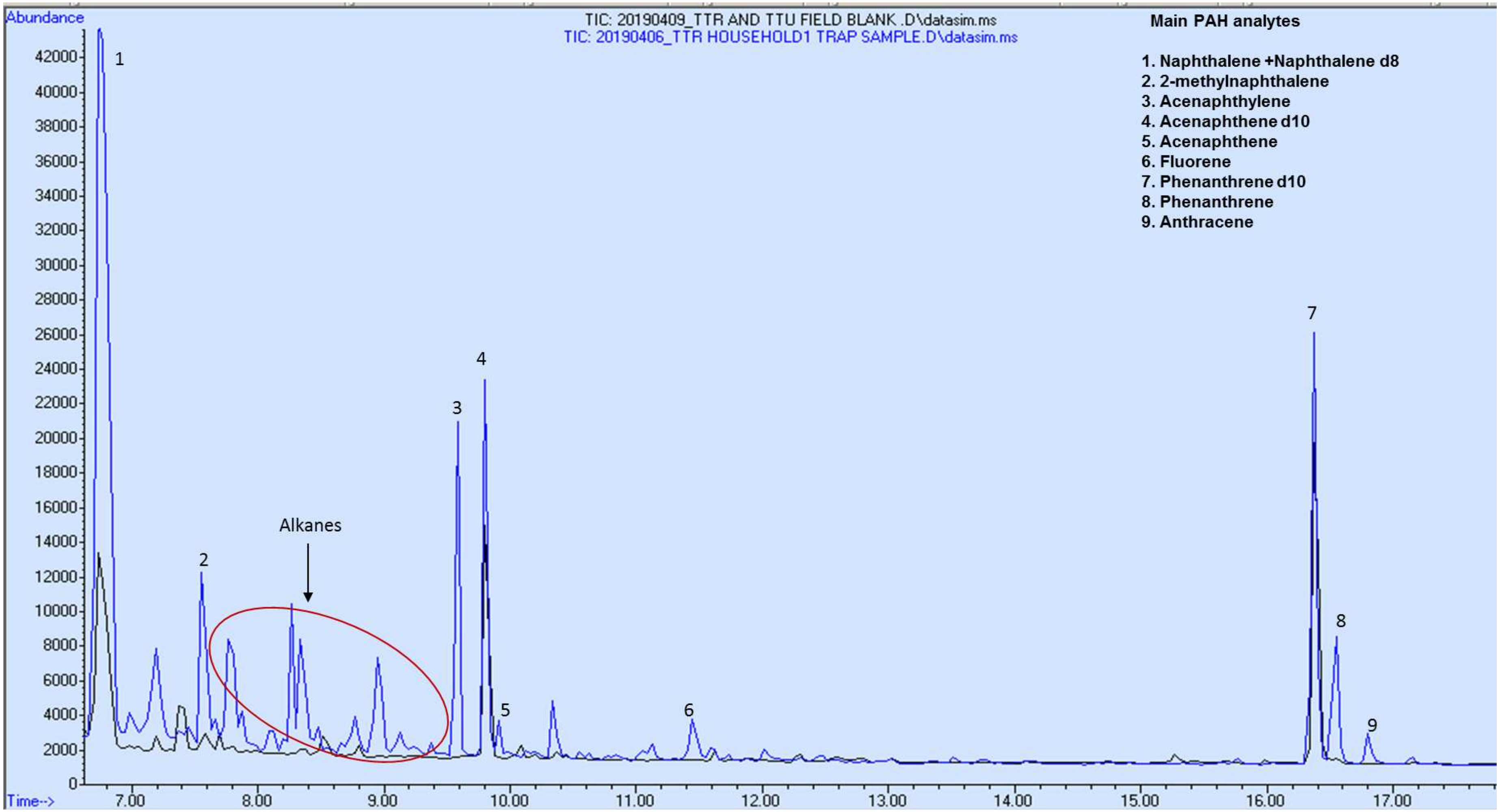

Figure S2: Representative GC-MS-SIM chromatograms of a PASE field blank sample spiked with IS mix (black) and PAHs in sample PASE extracts (blue). Alkanes tentatively identified were docosane, octadecane, tricosane and eicosane.

Table S1: List of PAHs included in the study in order of elution and increasing molar mass. Chemical formulas, number of fused benzene rings and internal standards (IS) used for each group of PAHs are shown. Linear regression (R^2) analysis results are included (n=3).

Analyte	**Abbreviation**	**Quantification ion m/z**	**Formula**	**Number of rings**	**R^2**
Naphthalene d8	**IS**	**136**			
Naphthalene	Nap	128	$C_{10}H_8$	2	0.996
2-methylnaphthalene	2-mNap	142	$C_{11}H_{10}$	2	0.975
Acenaphthylene	Acy	152	$C_{12}H_8$	3	0.954
Acenaphthene d10	**IS**	**164**			
Acenaphthene	Ace	154	$C_{12}H_{10}$	3	0.989
Fluorene	Flu	166	$C_{13}H_{10}$	3	0.983
Phenanthrene d10	**IS**	**188**			
Phenanthrene	Phen	178	$C_{14}H_{10}$	3	0.984
Anthracene	Ant	178	$C_{14}H_{10}$	3	0.992
Fluoranthene	FluAn	202	$C_{16}H_{10}$	4	0.989
Pyrene	Pyr	202	$C_{16}H_{10}$	4	0.988
Benzo[a]anthracene	BaA	228	$C_{18}H_{12}$	4	0.999
Chrysene d12	**IS**	**240**			
Chrysene	Chry	228	$C_{18}H_{12}$	4	0.975
Benzo[a]fluoranthene	BaF	252	$C_{20}H_{12}$	5	0.978
Benzo[k]fluoranthene	BkF	252	$C_{20}H_{12}$	5	0.970
Benzo[a]pyrene	BaP	252	$C_{20}H_{12}$	5	0.985
Perylene d12	**IS**	**264**			
Indeno[1,2,3-cd]pyrene	IcdP	276	$C_{22}H_{12}$	6	0.938
Dibenz[a,h]anthracene	DahA	278	$C_{22}H_{14}$	6	0.928
Benzo[g,h,i]perylene	BghiP	276	$C_{22}H_{12}$	6	0.912

Table S2: Limits of detection (LODs) and limits of quantitation (LOQs) of PAHs based on SIM ions for the PASE method. The LOD was calculated based on a signal to noise (S/N) ratio of 3 and the LOQ on a S/N ratio of 10.

Analyte	LOD (ng)	Calculated air sample [a]LOD (ng m^{-3})	LOQ (ng)	Calculated air sample [a]LOQ (ng m^{-3})
Nap	0.01	2.09	0.03	6.07
2-mNap	0.01	1.93	0.03	5.60
Acy	0.01	2.30	0.03	6.67
Ace	0.02	4.18	0.06	12.14
Flu	0.02	3.55	0.05	10.32
Phe	0.02	3.98	0.05	11.53
Ant	0.03	5.23	0.08	15.17
FluAn	0.02	3.77	0.05	10.92
Pyr	0.02	4.81	0.07	13.96
BaA	0.06	12.76	0.19	37.01
Chr	0.10	19.67	0.29	57.04
BaF	0.11	21.97	0.32	63.71
BkF	0.13	25.05	0.36	72.64
BaP	0.14	27.20	0.39	78.88
IcdP	0.18	34.94	0.51	101.33
BghiP	0.16	31.38	0.46	91.02
DahA	0.15	30.34	0.44	87.98

[a]LOD and [a]LOQ considering the airborne concentration obtained by sampling a volume of 5 L (0.005 m^{3}) and based on column concentrations from 1 µL of injected final extract.

Table S3: PAH concentrations in µg m^{-3} in in indoor and ambient air from rural and urban areas in coastal Kenya (average of duplicate injections).

RURAL SAMPLES										
	TTR-Ambient	TTR-H1	TTR-H2A	TTR-H2B	TTR-H3	KR-Ambient	KR-H1	KR-H2A	KR-H2B	KR-H3
Nap	*	25.92	18.24	19.19	3.19	0.12	8.54	10.58	11.01	4.16
2-mNap	-	6.15	4.33	5.54	2.20	*	2.21	5.20	5.05	1.73
Acy	0.09	5.10	7.60	4.50	1.61	0.36	3.43	2.83	2.62	1.89
Ace	*	2.18	8.36	6.67	1.40	*	1.64	3.66	2.17	1.67
Flu	*	4.24	14.73	12.42	2.03	0.39	2.54	3.84	2.75	2.31
Phe	-	5.68	5.93	9.26	0.94	0.35	2.41	2.27	2.34	1.22
Ant	-	2.31	4.65	7.09	*	*	1.68	3.45	2.87	1.44
FluAn	-	1.25	5.39	4.61	*	-	1.18	1.20	1.14	0.96
Pyr	-	1.15	12.49	9.76	*	-	1.08	2.69	2.59	0.78
BaA	-	0.99	1.04	1.00	-	-	*	-	-	-
Chr	-	0.41	0.51	0.56	-	-	*	*	*	*
BaF	-	0.57	1.12	1.20	-	-	-	*	*	*
BkF	-	0.58	0.54	0.69	-	-	-	*	*	*
BaP	-	0.60	0.27	0.56	-	-	-	*	*	*
URBAN SAMPLES										
	TTU-Ambient	TTU-H1	TTU-H2A	TTU-H2B	TTU-H3	MU-Ambient	MU-H1	MU-H2A	MU-T2B	MU-T3
Nap	0.21	*	12.01	13.01	1.71	0.44	*	12.15	12.62	2.29
2-mNap	0.59	*	3.82	3.89	1.08	0.71	-	4.38	3.99	1.41
Acy	0.99	*	2.71	2.56	1.42	1.01	-	4.79	5.60	1.49
Ace	*	-	*	*	0.90	0.64	-	2.54	2.24	1.18
Flu	-	-	3.39	2.93	1.91	0.47	-	2.86	3.14	1.94
Phe	*	-	2.78	2.62	0.87	*	-	2.25	1.63	0.80
Ant	*	-	2.79	3.34	1.48	*	-	3.57	3.47	2.30
FluAn	*	-	1.91	1.86	0.98	*	-	1.32	1.07	0.79
Pyr	*	-	2.49	2.32	5.59	*	-	2.14	1.81	5.16
Chr	-	-	0.48	0.45	0.46	-	-	0.38	0.31	0.31
BaF	-	-	0.16	0.20	-	-	-	0.19	0.25	0.12

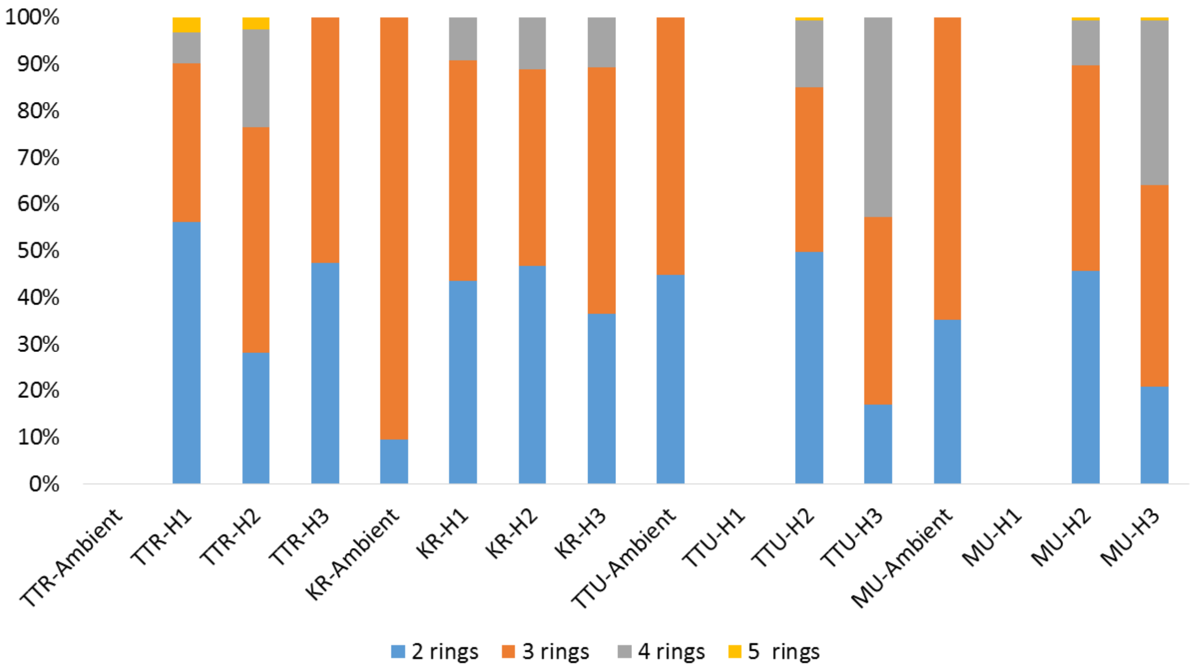

Figure S3: Relative percentage of 2-, 3-, 4- and 5- ring PAHs from each individual household sample.

Table S4: Variation (%RSD) between duplicate trap samples which were taken from each second household.

	%RSD, n=2			
	Taita Taveta Rural	Taita Taveta Urban	Kilifi Rural	Mombasa Urban
Nap	2.5	4.0	1.9	0.9
2-mNap	12.2	0.9	1.4	2.3
Acy	25.6	2.9	3.7	3.7
Ace	11.2	0	25.6	3.2
Flu	8.5	7.4	16.4	2.3
Phe	21.9	2.9	1.5	8.6
Ant	20.8	8.9	9.1	0.7
FluAn	7.8	1.3	2.5	5.3
Pyr	12.3	3.4	1.9	4.3
BaA	1.7	0	0	0
Chr	4.3	2.9	0	5.1
BaF	3.4	11.7	0	5.9
BkF	12.1	0	0	0
BaP	35.1	0	0	0

Improved
3-stone stove

Figure S4: Typical improved stove in rural Taita Taveta

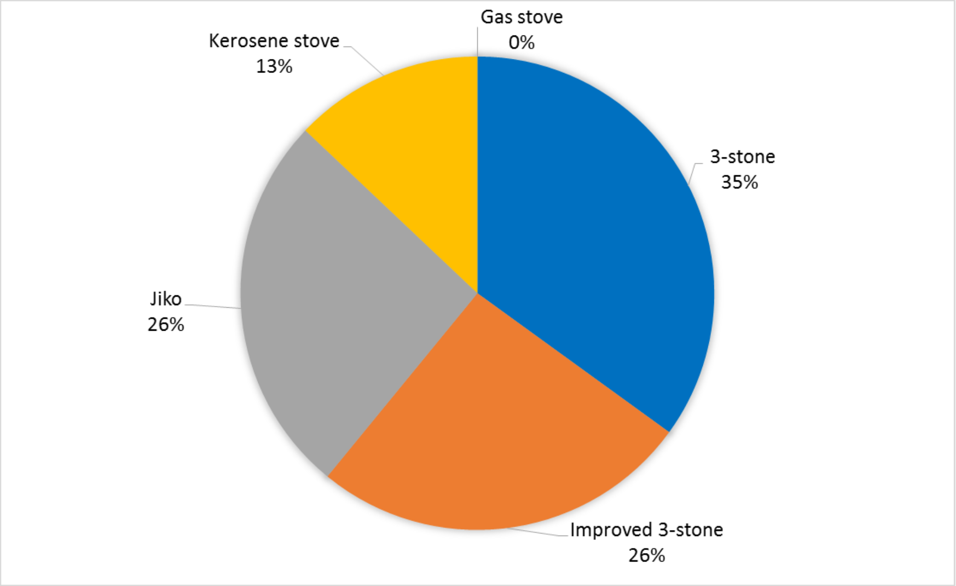

Figure S5: Average total gas phase PAHs from different combustion devices

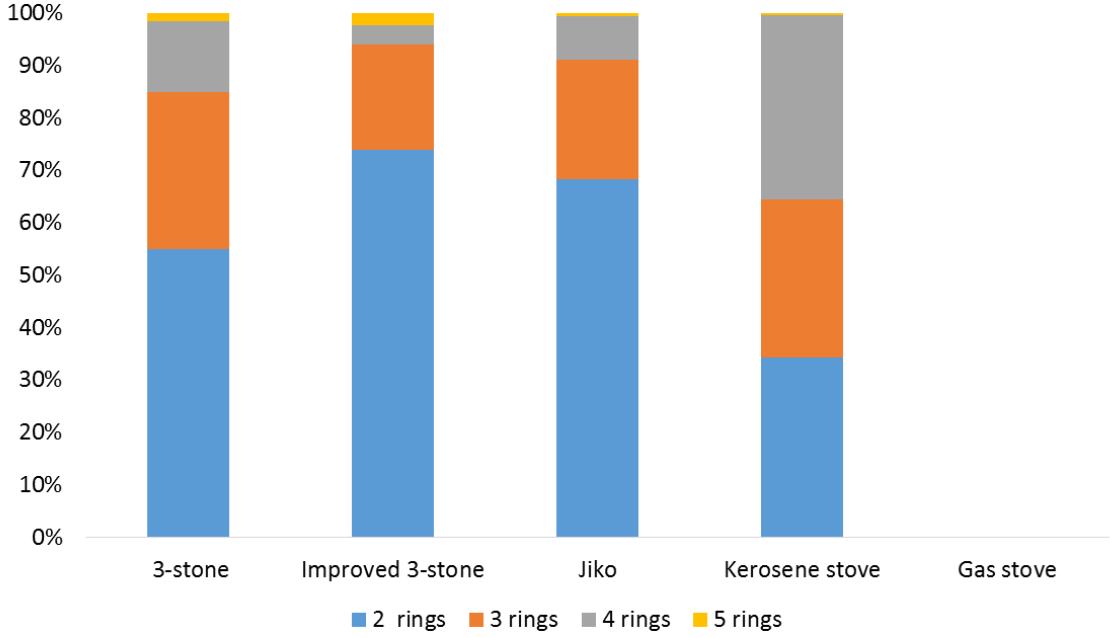

Figure S6: Relative percentage of 2-, 3-, 4- and 5- ring PAHs from each combustion device

Figure S7: Typical houses where samples were collected in rural Taita Taveta county showing poor ventilation

Figure S8: Typical houses where samples were collected in more ventilated conditions in (a) Mombasa urban and (b) rural Kilifi.

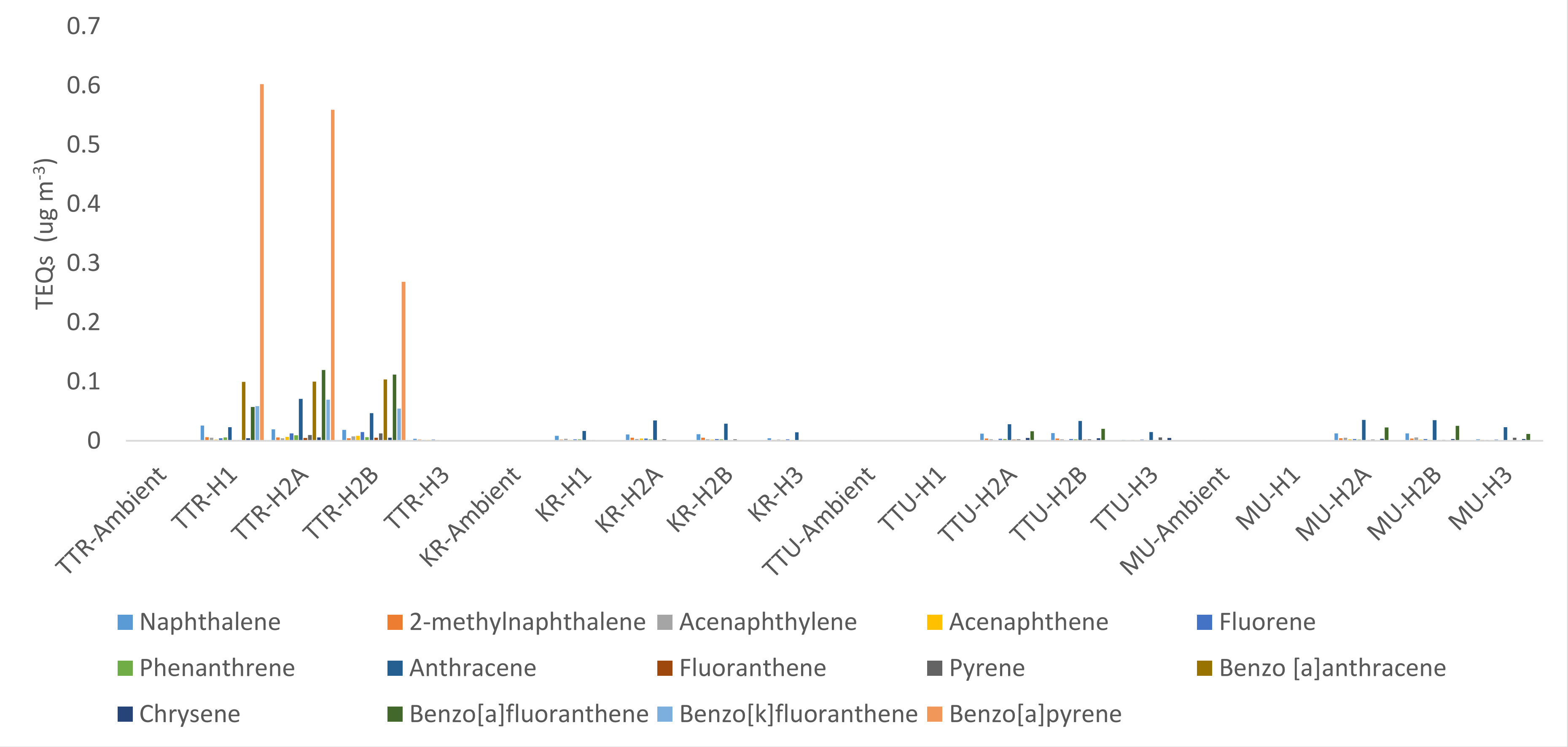

Figure S9: Toxic equivalence quotient (TEQs) values for individual PAHs in each household

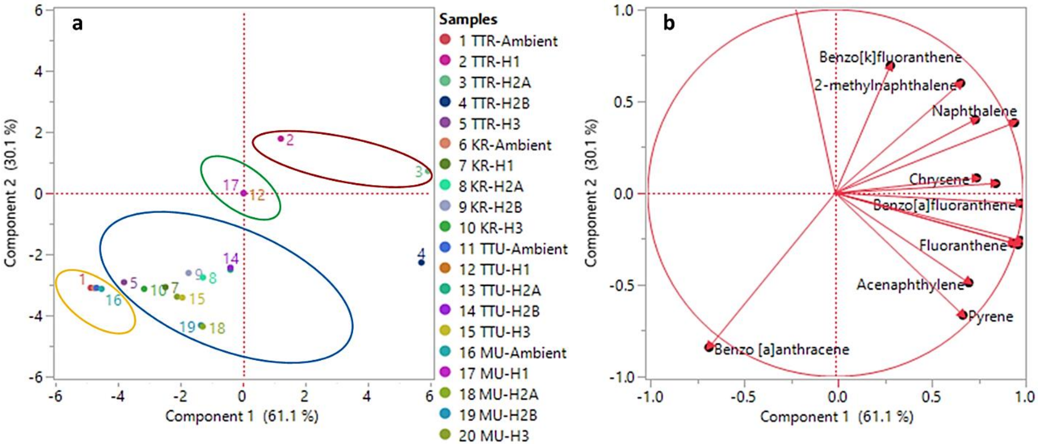

Figure S10 Principal component analysis scores plot (a) and loadings plot (b) for the ambient and indoor samples from 12 selected households. TTR-Taita Taveta Rural, MU-Mombasa Urban, TTU-Taita Taveta Urban, KR-Kilifi Rural, H-Household. The legend shows the sample and household numbers, red ellipsoid shows TTR samples, green ellipsoid shows LPG samples, orange ellipsoid shows ambient samples and blue ellipsoid represents all the other samples.

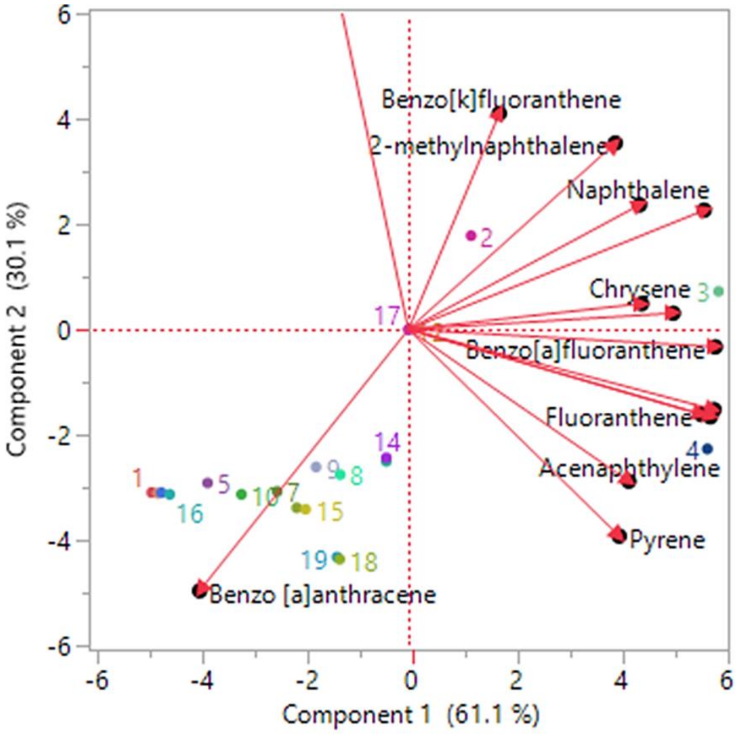

Figure S11: Principal component analysis biplot for ambient and indoor samples from 12 selected households.

Chapter 5: Denuder Sampler Characterization (Paper 4)

In this chapter, controlled laboratory experiments were performed to shed more light on the fundamental operating mechanisms of the PDMS traps and quartz fiber filters, specifically with respect to particle sampling. Particle collection and transmission efficiencies for a wider size range of particles than had previously been studied, including more realistic ambient particulate matter for ambient measurements, were addressed in this chapter.

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Chiedza F. Munyeza contributed to the design of the paper, performed experiments, data analysis and wrote the paper. Vesta Kohlmeier and George C. Dragan contributed to the design of the paper, assisted with experimental setup and data interpretation and edited the paper. Erwin W. Karg, Egmont R. Rohwer and Ralf Zimmermann contributed to the editing of the paper. Patricia B.C. Forbes conceptualised the idea, contributed to the experimental methods, data interpretation and the design of the paper, edited and submitted the paper.

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Characterisation of particle collection and transmission in a polydimethylsiloxane based denuder sampler

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ABSTRACT

Denuder sampling devices consisting of two multi-channel silicone rubber traps separated by a quartz fibre filter, have been effectively employed for the simultaneous sampling of gas and particle associated semi-volatile organic compounds. Here controlled laboratory experiments were conducted to further elucidate the fundamental operating mechanisms of this portable denuder with respect to particle transmissions. Particle collection efficiency of the quartz fibre filters as well as particle transmission efficiency through the silicone rubber traps using ambient aerosol and aqueous suspensions of monodisperse polystyrene latex (PSL) as test particles (0.3, 0.5 and 0.8 µm), were evaluated for various scenarios. Particle size and number concentration were measured with a scanning mobility particle sizer. Transmission efficiency of the denuder was determined from the ratio of particle concentration transmitted by the denuder to that of a bypass line. All sizes of PSL particles were collected with high efficiency and reproducibility by the quartz fibre filter (> 98% with variation coefficients < 16%). Overall transmission efficiencies for all particles > 100 nm ranged from 91% to 100% (variation coefficients of 2–14%). Transmission efficiencies decreased when PDMS tubes were twisted but were not significantly different for traps made by different individuals. Ambient particles, which were studied for the first time, were collected with 88–95% collection efficiency. Losses of smaller particle size fractions in the trap portion of the denuder were likely due to diffusion and electrostatic effects. The high particle collection and transmission efficiencies of all tested particle sizes indicated that these denuders are very effective tools for aerosol measurements.

1. Introduction

Aerosols can be defined as disperse systems of liquid and/or solid particles suspended in air, with particle sizes ranging from about 0.002 µm to more than 200 µm (Hinds, 2012). Particulate and gaseous phases of aerosols remain unchanged at thermodynamic equilibrium, however this is rarely the case in real workplace atmospheres (Breuer, 1999; Dragan et al., 2014). Gas–particle distribution is known to be constantly changing. Therefore sampling of hazardous aerosols containing semi-volatile organic compounds

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(SVOCs) by occupational hygienists still remains a challenge. It is very important for proposed measurement systems and instrumentation to quantify the relative contributions of each of the aerosol phases, as they may have different impacts on human health. This is of particular relevance with respect to toxicity studies impacting human health, since deposition and uptake of inhaled toxic species depends on phase distribution (Forbes, Karg, Zimmermann, & Rohwer, 2012; Temime-Roussel, Monod, Massiani, & Wortham, 2004).

Over the past years, most research on indoor and workplace air quality has been focused on developing and improving aerosol measurement instrumentation to enable quantification of a variety of aerosol properties with high temporal resolution and accuracy (Breuer, Dragan, Friedrich, Möhlmann, & Zimmermann, 2015; Dragan et al., 2014, 2015; Grimm & Eatough, 2009; Howe et al., 2011; Makonese, Forbes, Mudau, & Annegarn, 2014; Ogura et al., 2014; Zhang, Williams, Goldstein, Docherty, & Jimenez, 2016; Zimmerman et al., 2015). Despite the challenges, sampling and measurement of SVOC aerosols still remains a priority due to their abundance in the indoor environment and their potential negative health effects on humans. Aerosols of SVOCs can be released as a result of mechanical and thermal processes (evaporation and condensation) (Breuer et al., 2015). Polycyclic aromatic hydrocarbons (PAHs), alkanolamines, inorganic acids, bitumen fumes and metalworking fluids used as lubricants and coolants are a few common examples of SVOCs generated or utilized in workplaces (Breuer et al., 2015; Breuer, 1999; Howe et al., 2011). In order to avoid significant bias in measurement results and for effective sampling of the two phases of SVOCs, it must be ensured that analytes are not lost from the sampling process. In terms of particles, mechanisms leading to losses during sampling should be accounted for in order to avoid erroneous measurement results (McMurry, 2000; Von der Weiden, Drewnick, & Borrmann, 2009). These include sedimentation, diffusion, turbulent inertial deposition, inertial deposition in a bend, electrostatic deposition and interception (Hinds, 2012; Kulkarni, Baron, & Willeke, 2011; Von der Weiden et al., 2009).

Denuders are sampling devices which have been effectively employed in various atmospheric partitioning applications. Several denuder geometries have been developed, with annular and cylindrical denuders being reported the most in literature (Forbes & Rohwer, 2015). Separation in denuders is achieved as a result of gas phase analytes having high diffusion coefficients, thus they are retained by a sorptive surface perpendicular to the gas flow (typically on the walls of the denuder) (Forbes et al., 2012; Geldenhuys, Rohwer, Naudé, & Forbes, 2015). Particles, on the other hand, will flow through the denuder channels, and can be collected on a downstream filter. In a fibrous filter, the pressure drop across the filter is caused by the combined effects of the resistance of each fibre to the flow of air past it (Hinds, 2012). The pressure drop represents the total drag force on all the fibres. Therefore, the lower the pressure drop, the better the performance of the filter. For a filter with a unimodal fibre diameter, the pressure drop is a function of its thickness, solid volume fraction (SVF), air viscosity and face velocity (Li, Wang, Zhang, & Wei, 2014). A sorbent is normally employed behind the filter, to trap analytes desorbed from the filter, and any gaseous analytes not effectively removed by the denuder (under break-through conditions) (Forbes et al., 2012). The denuder device evaluated in this study consisted 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 SVOCs and the filter collects particle phase analytes. The efficiency of these portable denuders has been investigated from both theoretical and experimental perspectives by Forbes et al. (2012) and recently by Kohlmeier et al. (2017). One limitation of the former study is the fact that the particles used were not monodisperse, as a broad range of diameters of ammonium sulfate particles was investigated. Although Kohlmeier et al. did further studies using PSL particles with unimodal diameters of 0.30, 0.51, 0.75, 0.99, 1.54 and 2.00 μm, ambient particles were not tested in both studies.

Additional experiments to further elucidate performance parameters regarding particle collection and transmission efficiencies for a wider size range of particles, including more realistic ambient particulate matter for ambient measurements, are addressed in this work. Controlled laboratory experiments were performed to shed more light on the fundamental operating mechanisms of the PDMS traps and quartz fibre filters, specifically with respect to particle sampling. The suitability of collection of a range of particle sizes by the quartz fibre filter paper in the assembly used for denuder applications (in terms of filter paper diameter and housing) was thus investigated. It is also vital that particles are efficiently transmitted through the denuder (PDMS trap), otherwise gas phase SVOC concentrations would be over-estimated and particle phase SVOC concentrations would be underestimated if SVOCs were associated with these particles. Furthermore, PDMS trap-to-trap variations can bias the indoor or workplace particle measurements. The variation was investigated including multi-channel silicone rubber traps manufactured by different individuals and twisted traps with an intentionally introduced kink were used to investigate worst case conditions where additional particle losses occur via inertial deposition in the bends. The results provide a better understanding of the fundamental operating principles of these denuder devices as well as potential limitations which should be considered when interpreting results.

2. Materials and methods

2.1. Chemicals and reagents

Aqueous suspensions of National Institute of Standards and Technology (NIST) certified monodisperse polystyrene latex (PSL) particles, (Polysciences Inc., Warrington, USA) with diameters of 0.3, 0.5 and 0.8 μm were used in all the laboratory particle transmission tests in this work. The PSL particles were prepared in water (HPLC-MS grade, Merck KGaA Germany), stored in the refrigerator and sonicated for 15 min before use. All other solvents were of analytical grade (99% purity) including methanol, dichloromethane (DCM) and *n*-hexane which were purchased from Sigma Aldrich.

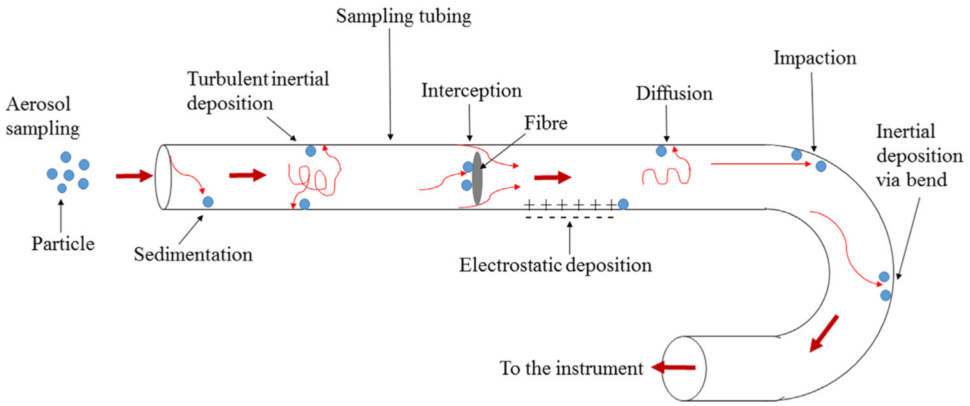

Fig. 1. Possible particle loss and collection mechanisms during transport through a sampling tube.

2.2. *Multi-channel silicone rubber traps*

The PDMS traps were prepared according to the method previously described (Ortner & Rohwer, 1996). Each trap consisted of 22 parallel PDMS tubes (55 mm long, 0.3 mm i.d., 0.6 mm o.d. Sil-Tec, Technical Products, Georgia, USA) in a 178 mm long glass tube (6 mm o.d., 4 mm i.d.). The traps used in this study were prepared by two individuals hence they were classified into two batches A and B for further evaluation. Twisted multi-channel silicone rubber traps were prepared by deliberately introducing a single kink in the parallel PDMS tubes, in order to test a worst case scenario in terms of particle losses. Pressure drop across the twisted traps and straight traps used in this study was measured in triplicate using the GilAir Plus sampling pump and the mean values were reported in inH$_2$O (Supplementary information). All the multi-channel silicone rubber traps used in this study were pre-conditioned before use at 280 °C for approximately 24 h with a hydrogen gas flow of ca. 10 cm^3 min^{-1}. An empty trap was used as a bypass in the experimental setup illustrated in Fig. 2. The glass tubes were cleaned by sonication in pure *n*-hexane and dichloromethane and then baked overnight in an oven at 250 °C before use.

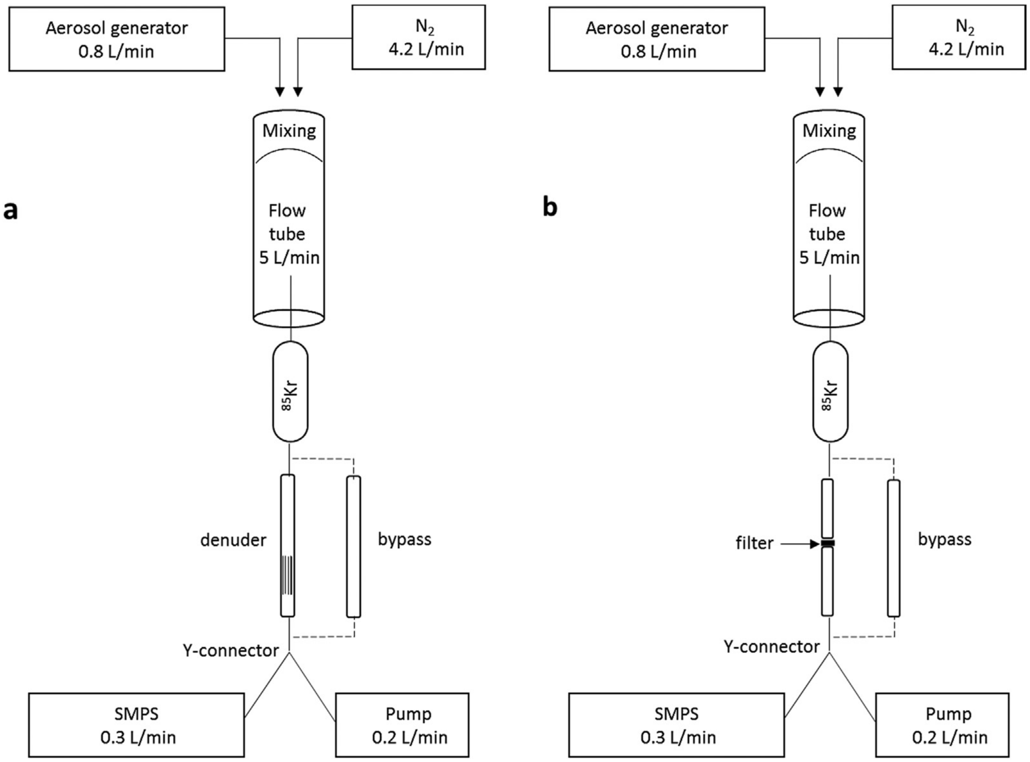

Fig. 2. Experimental setup for **(a)** particle transmission studies through silicone rubber traps and **(b)** particle collection efficiency studies on filters.

2.3. Filters

Quartz fibre filter punches (6 mm diameter punched from QMA 20.3 × 25.4 cm, Whatman, GE Healthcare, UK) were placed in a 100 mL beaker. Methanol was added to the beaker and swirled for approximately 1 min and decanted off. This procedure was repeated with DCM, taking extra care not to break the now fragile punches. The clean filter punches were then placed in an oven at 200 °C for 30 min to dry before storage in an amber vial in a dessicator.

2.4. Experimental setup

Experiments were conducted in a temperature controlled chamber (with a preset temperature of 25 °C) as shown in Fig. 2. It consisted of four main components: an aerosol generator, dilution and mixing unit, a flow tube and the sampling apparatus. An ATM 220 type aerosol generator (Topas, Dresden, Germany), was used to nebulize the PSL particles at a flow rate of 0.5 L min^{-1}. A poly (methyl methacrylate) (PMMA) flow tube preceded by a dilution and mixing unit was employed to allow the aerosol to mix with the particle- and humidity free dilution gas, nitrogen.

A Krypton-85 (^{85}Kr) neutralizer was used prior to the denuder to prevent electrostatic interferences in measurements due to charge distribution on the particles. All tubing connecting the denuder or the bypass line in the experimental setup were of identical length and diameter. An initial zero particle measurement using N_2 gas was done on a daily basis to ensure that a stable experimental setup had been established and that there was no carryover of particles from previous experiments.

The particle sizer employed was a scanning mobility particle size spectrometer composed of a differential mobility analyzer (DMA, Model 3080, TSI, USA), and a condensation particle counter (CPC Model 3022, TSI, USA). The DMA separated aerosols based on the mobility of the charged particles in air induced by an electric field (electrical mobility), whilst the CPC was used to measure the particle number concentration for ambient and PSL particle measurements. The sampling pumps used for this study were designed to maintain a constant flow rate up to a certain backpressure. For the investigation of the particle transmission efficiency at a flow rate of 0.5 L min^{-1} per trap, the CPC (sample flow rate of 0.3 L min^{-1}) was connected in parallel to a battery operated GilAir Plus personal sampling pump (Sensidyne Inc., USA). The sampling flow rate was therefore maintained at 0.5 L min^{-1} using the GilAir pump (which was set at a sample flow rate of 0.2 L min^{-1}). All instruments were set to a sampling time of 120 s, which is the scan time of the scanning mobility particle sizer (SMPS) for a single run measuring particle size and number concentration.

2.5. Determination of particle collection efficiency

To evaluate the performance and suitability of the quartz fibre filter with respect to particle collection efficiency in a denuder configuration, two empty glass tubes were connected in series and these were separated by a quartz fibre filter which was held in place by Teflon connectors (Fig. 3). Aerosol particles (0.3, 0.5 and 0.8 µm PSL) were generated and aerosol concentration and size distribution upstream and downstream of the filter were measured by means of an SMPS. Measurements were also done with ambient air particles, whereby laboratory doors were opened to allow free circulation of outside ambient air. The bypass was made up of two empty glass tubes connected by a Teflon connector in series without any filter. For each experiment, particle collection efficiency was determined by switching five times between the denuder and a bypass line and averaging these data sets obtained (giving a total measurement time of 10 min). After bypass/denuder switching the sample flow rate was allowed to stabilize before the next measurement was taken. At least three independent experiments using different filters were performed to ensure reproducibility of the results. All independent measurements for 0.3 and 0.5 µm PSL particles were done for 10 min. Filter clogging was assessed by doing measurements with 0.8 µm PSL aerosol particles (total concentration of approximately 164,000 particles/cm^3) which were generated for 30 min. The pressure drop was measured before and after the 30 min measurement using a portable sampling pump.

2.6. Laboratory particle transmission tests for multi-channel silicone rubber traps

Multi-channel silicone rubber traps made by different individuals were also evaluated as denuders in terms of their particle

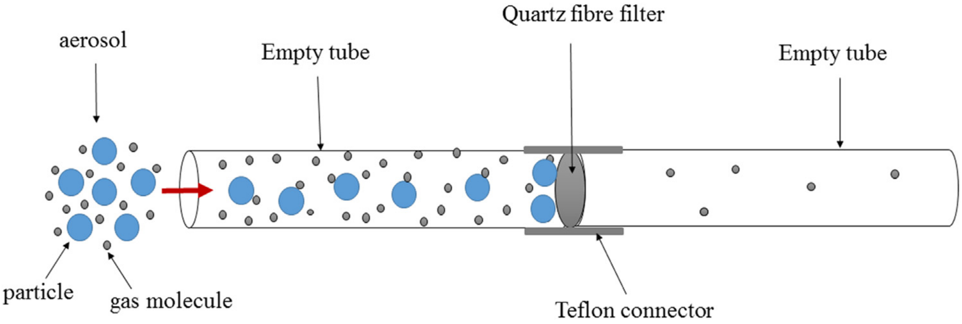

Fig. 3. Collection of PSL particles on the quartz fibre filter.

Table 1
Results of measured average percent particle collection efficiencies for ambient air and PSL particles (0.3, 0.5 and 0.8 μm) for filters. Collection efficiencies were averaged (n = 5) over particle diameters (d_p) in the range 100 – 661 nm for 0.3, 0.5 and 0.8 μm PSL particles.

Particle type	Particle size d_p [μm]	% Average collection efficiency	Variation coefficient [%]
PSL	0.3[a]	98.8	8.2
	0.3[a]	99.8	7.9
	0.5[a]	98.5	2.9
	0.5[a]	98.8	7.7
	0.8[a]	99.2	3.4
	0.8[b]	99.9	15.7
Ambient	–	88.0	1.8
	–	89.5	4.3
	–	94.8	4.7

[a] 10 min independent measurement.
[b] 30 min measurement.

transmission efficiencies. With reference to the setup in this work, each trap was referred to as the denuder. Since each trap was handmade, five different traps were used for each setup to account for inter-denuder variability. The denuders were either operated in the horizontal or vertical position for comparison and determination of the contribution of gravitational settling to transmission losses. The denuders were operated at a flow rate of 0.5 L min^{-1} and the transmission efficiency was investigated for ambient particles and PSL particles with optical diameters of 0.3 and 0.5 μm. All measurements were repeated five times for each denuder.

3. Results and discussion

3.1. Laboratory particle collection efficiency tests on filters

Experimental results for the overall average collection efficiencies of ambient and PSL particles in the horizontal configuration are summarized in Table 1. Penetrations of particle diameters (dp) in the ranges 100 – 661 nm are shown in Fig. 4. Fig. 4a shows an illustrative zero particle measurement from which it is evident that no significant particle numbers were measured when only N_2 was flowing through the system.

The results showed that our punched filters were efficient in collecting aerosol particles in the given denuder configuration. The 10 min independent measurements for 0.3 and 0.5 μm PSL particles ensured reproducibility of the results across different filters. These independent measurements also confirmed that there was no significant variation between two different punched filters when the same sized particles are being collected. The Whatman quartz fibre filters did not become clogged or misaligned as evidenced by

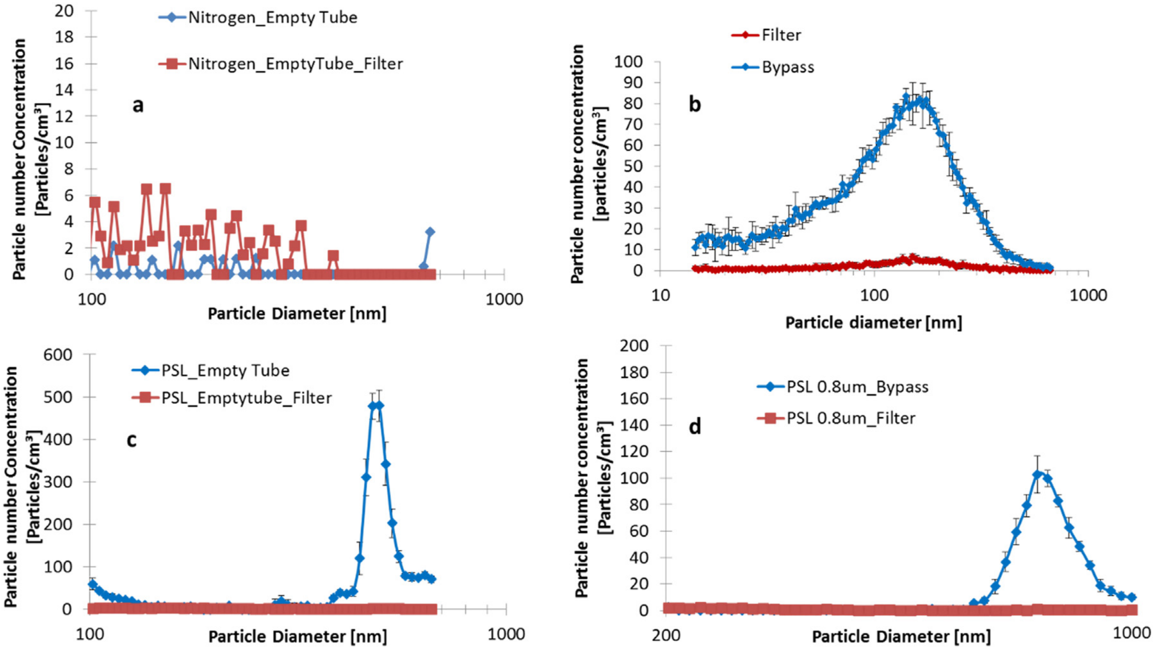

Fig. 4. (a) Averaged size distributions of filter and bypass collection efficiencies of (a) zero particle measurement, (b) ambient particles, (c) 0.5 μm PSL particles and (d) 0.8 μm PSL particles. Error bars show ± standard deviation of the number concentration, n = 5.

Table 2

Structure and performance of some common aerosol-sampling filter materials for $d_p = 0.3\ \mu m$.

Filter type	Material	Thickness (mm)	Test particles	%Efficiency	Reference
Whatman 41 fibre	Cellulose	0.19	PSL	72.0	(Lippmann, 2001)
Nuclepore CPM[a]	Polycarbonate	0.01	PSL	90.0[b]	(Hinds, 2012)
Microsorban fibre	Polystyrene	1.5	PSL	99.5	(Hinds, 2012)
MSA 1106B fibre	Glass	0.23	PSL	99.9	(Lippmann, 2001)
Millipore AA membrane	Cellulose ester	0.15	PSL	99.9	(Lippmann, 2001)
HEPA[c]	CNT[d]/ quartz fibre	–	NaCl	99.9	(Li et al., 2014)
Whatman QMA fibre	Quartz	–	PSL	99.5	This study

PSL = polystyrene latex particles.

[a] CPM = capillary pore membrane.

[b] Estimated.

[c] High-efficiency particulate air filters.

[d] Carbon nanotubes.

the constant pressure drop measured before and after each measurement. However, when mass loading was greater (0.8 µm PSL), it was observed that the pressure drop doubled when it was monitored before and after a 30 min measurement. This could have been caused by a cake of particles forming on the filter, which would conceivably enhance particle collection as indicated by the higher collection efficiency of 99.9%. Ambient particles were collected with significantly lower efficiencies (88.0–94.8%) compared to the PSL particles. This was primarily due to higher particle losses of the smaller (< 0.1 µm) ambient particles with higher diffusion coefficients. Theoretical calculations in literature have confirmed that for particles smaller than 0.1 µm (particularly those < 0.04 µm), the particle trapping (collection) efficiency decreases rapidly with the size of the aerosols because their diffusion coefficient increases (Temime-Roussel et al., 2004). Very small particles behave similarly to gas phase molecules both in terms of sampling as well as in the human respiratory system, therefore analytical results would still be meaningful for guiding risk assessments.

The collection efficiencies were comparable to literature regarding common aerosol-sampling filter materials as summarized in Table 2. Comparisons of filter quality and collection efficiency are normally encouraged for the same test aerosol particle size. Additionally, standard tests for the collection efficiency of filters use 0.3 µm particles, on the assumption that this size is near the minimum efficiency point and efficiency will be greater for all other sizes or size distributions (Hinds, 2012). In Table 2 we mainly report the comparison of filter quality and collection efficiency for the same sized test particles (0.3 µm PSL and NaCl particles). The results of this study give confidence that the filter assembly used in the PDMS denuders efficiently collects particles and is fit for purpose.

3.2. Laboratory particle transmission tests for multi-channel silicone rubber traps

The particle transmission efficiency was determined from the particle concentration ratio between the denuder and bypass. Fig. 5 shows an example of the size distributions plotted for transfer through both the denuder and bypass in the horizontal configuration.

For particle sizes above 100 nm, the bypass and denuder graphs display fairly identical concentrations, which shows a transmission efficiency of nearly 100% through the denuder. The size resolved transmission was found to be close to 100% for particles larger than 200 nm and this was consistent with previous studies (see Fig. S1 for comparison with literature values for ammonium sulfate particles) (Forbes et al., 2012). This was also confirmed by the denuder/bypass ratio lines in Fig. 5b and d which become stable with an approximate value of 1 for particles > 100 nm. With regards to PSL particles, graphs were plotted from a particle size of 200 nm since particles smaller than this were derived from surfactants in the PSL solution and impurities in the water used. In Fig. 5b, the cumulative size distribution curve increased in the smaller particle size range between 10 and 100 nm and leveled off at about 200 nm, which showed that the maximum summed number concentration had been reached as there were very few larger particles present in the ambient air. Loss of small particles (< 20 nm) by diffusion is commonly reported and may be improved by reducing their residence time in the denuder, however, this would negatively impact the collection efficiency of gaseous analytes. Variability in particle transmission efficiency of different denuders (handmade by the same individual or different individuals) is summarized in Table 3, Table S1 and pressure drop information is available in Table S2. Two sided Student's *t*-tests were used as a tool to determine the statistical significance of the measured data, where a Gaussian distribution of data was assumed whenever this test was used. With regard to denuders operated vertically at a flow rate of 0.5 L min^{-1}, our results were also comparable to a previous study in which high transmission efficiencies from 91% to 100% (variation coefficients 3.69–9.65%) were obtained (Kohlmeier et al., 2017).

Variability between measurements performed with traps from the same manufacturer (i.e A1-A5) was insignificant as shown by the low standard deviations which were all below 3%. The denuder/bypass ratios were computed to determine statistical variations and it was found that particle transmission efficiencies for traps manufactured by different individuals were not significantly different at 95% confidence interval. A high level of agreement between the two sets of data is also evident from the A/B ratio given in Table 3, whereby the deviation from the ideal value of 1 did not exceed 7%. However, it is always important to use a minimum of three traps for each measurement since traps are handmade and variations in efficiency are possible. Average %transmission efficiencies for ambient air and PSL particles (0.3 and 0.5 µm) in the vertical configuration are shown in Table S1. Vertical and horizontal setup

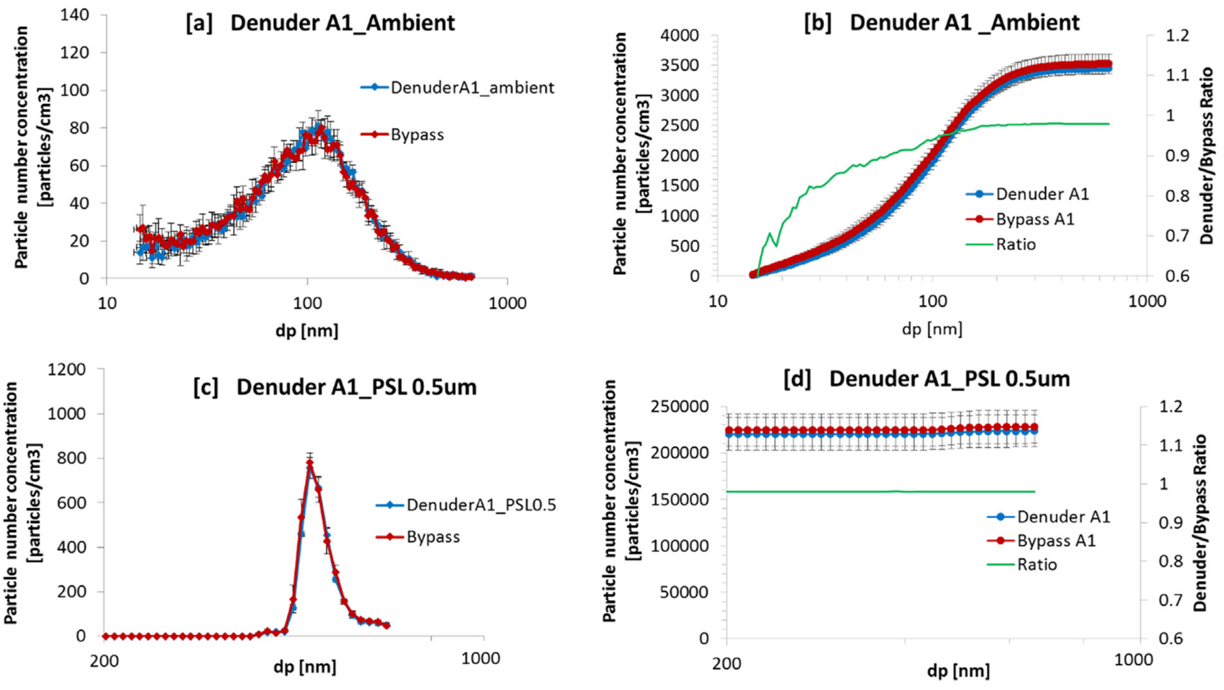

Fig. 5. Average size distributions for transfer through a PDMS denuder in the horizontal configuration and the bypass line of (a) ambient particles and (c) 0.5 µm PSL particles. 5(b) and 5(d) show the integral counts of summed number concentration for ambient and 0.5 µm PSL particles respectively. Error bars show ± standard deviation of the number concentration, n = 5.

Table 3

Comparison between traps made by different individuals. Average %transmission efficiencies for ambient air and PSL particles (0.3 and 0.5 µm) in the horizontal configuration are shown. Transmission efficiencies were averaged over particle diameters (d_p) in the range 10–661 nm for ambient particles and 100–661 nm for 0.3 and 0.5 µm PSL particles.

Particle type	Individual A trap number	%Transmission efficiencies (variation coefficient)	Individual B trap number	%Transmission efficiencies (variation coefficient)	A/B Ratio[a]
Horizontal setup					
Ambient	A1	96 (4.2)	B1	94 (11.4)	1.02
	A2	97 (2.8)	B2	96 (3.0)	1.01
	A3	93 (6.5)	B3	96 (3.0)	0.97
	A4	96 (3.8)	B4	95 (5.8)	1.01
	A5	96 (3.6)	B5	96 (3.9)	1.00
	Average	**96**		**95**	**1.01**
	SD	**1.4**		**0.8**	
PSL, 0.3 µm	A1	100 (2.8)	B1	95 (7.1)	1.05
	A2	95 (5.5)	B2	99 (5.5)	0.96
	A3	93 (7.6)	B3	93 (10.0)	1.00
	A4	100 (7.7)	B4	98 (8.2)	1.02
	A5	94 (9.9)	B5	94 (3.9)	1.00
	Average	**96**		**96**	**1.00**
	SD	**3.0**		**2.3**	
PSL, 0.5 µm	A1	98 (4.0)	B1	96 (4.6)	1.02
	A2	97 (13.9)	B2	97 (8.4)	1.00
	A3	98 (6.5)	B3	98 (7.0)	1.00
	A4	97 (4.5)	B4	97 (4.0)	1.00
	A5	93 (7.7)	B5	100 (3.7)	0.93
	Average	**97**		**98**	**0.99**
	SD	**1.9**		**1.4**	

SD = standard deviation.

[a] The ratio was the transmission efficiency of manufacturer A to that of manufacturer B. A ratio of 1 signifies perfect agreement between the two measurements.

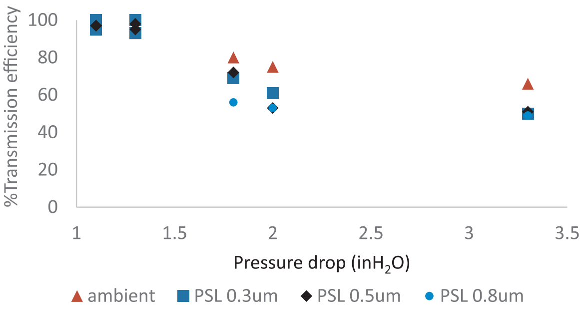

Fig. 6. Effect of pressure drop variability across different straight silicone rubber traps (pressure drops 1.1 and 1.3 inH_2O) and twisted silicone rubber traps (pressure drops 1.8–3.3 inH_2O) on overall transmission efficiency of particles of different sizes.

comparisons revealed minimal losses due to sedimentation. Measurements carried out with vertically operated denuders resulted in average transmission efficiencies in the range of 93–97% with variation coefficients between 2.3% and 13.3%. Measurements with denuders operated horizontally showed only a slight difference in the transmission efficiency, ranging from 95% to 98% with variation coefficients between 2.8% and 13.9%. Minimal differences were observed in this study for vertical and horizontal setups because particles smaller than about 0.5 μm are less likely to be affected by gravitational forces (Von der Weiden et al., 2009). The highest particle losses by sedimentation and impaction are associated with large particles (Kohlmeier et al., 2017).

The trends observed for different particle sizes with regards to twisted traps and effects of pressure drop with respect to transmission efficiencies are illustrated in Fig. 6 (and Fig. S2). These are in agreement with a theory (Von der Weiden et al., 2009) which states that for a bend or twist in tubing, the streamlines of the flow change their direction and large particles cannot follow them perfectly due to their inertia. Measurements with twisted denuders showed that smaller ambient particles were transmitted more efficiently through the twisted PDMS channels due to less impaction losses.

The larger particles could be deposited on the walls of the tubing in the bend as a result of their inability to follow stream lines, however, this depends on particle stopping distance (Von der Weiden et al., 2009). Therefore, PSL particles (particularly 0.8 μm) were transmitted less easily through the twisted PDMS channels compared to the smaller ambient particles. As summarized in the literature section (Fig. 1), the larger particles could have been lost via impaction near the bend in the tubing. The kink in the twisted traps resulted in higher pressure drops compared to traps with straight channels, as determined experimentally. Surprisingly, at higher pressure drops of 2.0 and 3.3 inH_2O, the transmission efficiencies were almost the same for 0.3, 0.5, and 0.8 μm PSL particles. This showed that inertial effects and pressure drop alone could not fully explain the measurement discrepancies displayed. One possible additional explanation could be drawn from the displayed trend, which illustrated that as the pressure drop for traps increased, the standard deviation for the measurements also increased. This higher variation might be the reason why substantial differences were not visible between the different sized PSL particles at a higher pressure drop. Overall, it was shown that the higher the pressure drop, the lower the particle transmission efficiencies.

4. Conclusions

The selected quartz fibre filter and related sampling assembly are suitable for use in the denuder configuration since PSL particles tested were collected with high efficiency ($>$ 98% with variation coefficients $<$ 16%). Overall collection efficiencies for ambient particles were lower, ranging between 88% and 95%, due to the higher diffusion coefficients of the smaller ambient particles, particularly those $<$ 100 nm, which resulted in losses. Particle transmission efficiencies for traps manufactured by different individuals were also compared and were not statistically significantly different at 95% confidence interval. Though trap-to-trap variations were minimal, this study recommends the use of a minimum of three traps per given measurement to ensure unbiased results. Additionally, silicone rubber tubes utilized during sampling campaigns should not be twisted or bent to prevent further particle impaction losses. Visual inspection of traps and the determination of pressure drop across each trap are important quality control checks prior to use.

Acknowledgements

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaerosci.2019.01.001.

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Paper 4 Supplementary Information

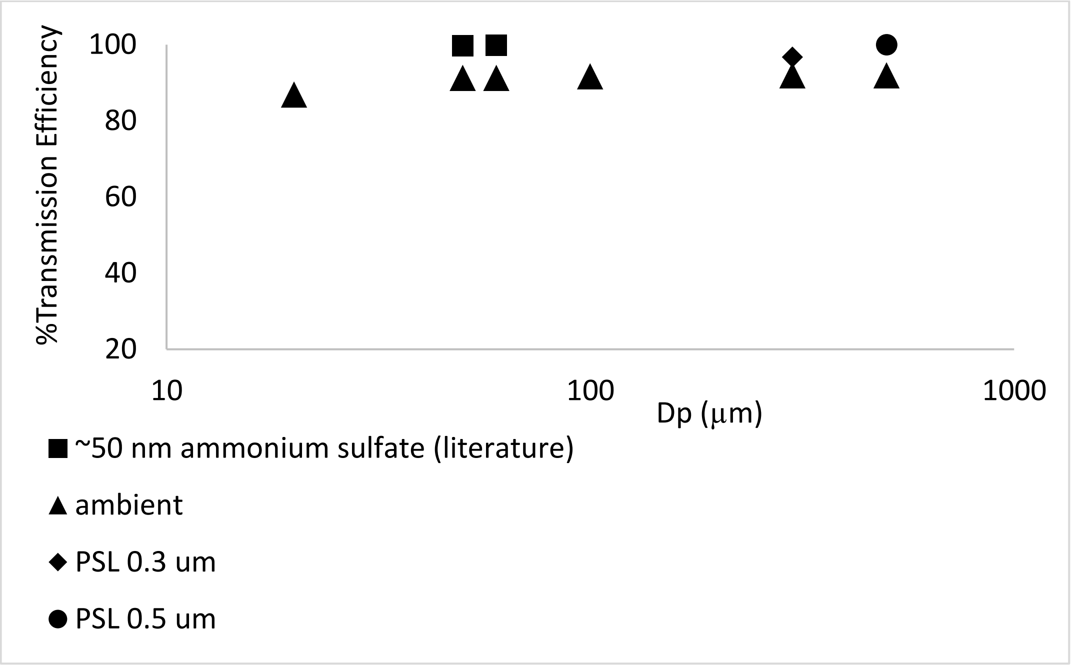

Figure S1: Comparison of transmission efficiencies of test particles in this study (ambient, PSL 0.3 µm and 0.5 µm) and test particles in literature (ammonium sulfate) through a denuder.

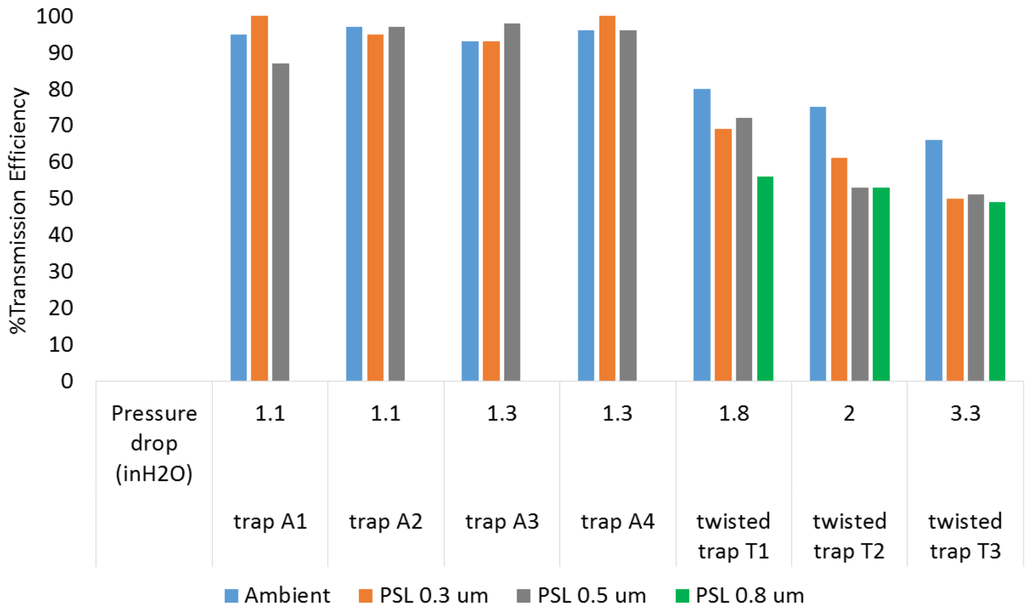

Figure S2: Effect of pressure drop changes in straight PDMS traps (A1-A4) and twisted PDMS traps (T1-T3) on overall particle transmission efficiencies of different particle sizes.

Table S1. Comparison between traps made by different individuals. Average %transmission efficiencies for ambient air and PSL particles (0.3 and 0.5 µm) in the vertical configuration are shown.

Particle type	Individual A trap number	%Transmission efficiencies (variation coefficient)	Individual B trap number	%Transmission efficiencies (variation coefficient)	A/B Ratio[a]
Vertical setup					
Ambient	A1	92 (3.6)	B1	93 (7.5)	0.99
	A2	97 (11.2)	B2	94 (2.3)	1.03
	A3	91 (7.3)	B3	92 (4.3)	0.99
	A4	91 (5.9)	B4	95 (2.8)	0.96
	A5	93 (7.1)	B5	97 (3.8)	0.96
	Average	**93**		**0.94**	**0.99**
	SD	**2.2**		**1.7**	
PSL, 0.3 µm	A1	92 (5.4)	B1	95 (9.7)	0.97
	A2	94 (6.9)	B2	97 (7.6)	0.97
	A3	93 (7.9)	B3	100 (13.3)	0.93
	A4	98 (4.8)	B4	97 (8.0)	1.01
	A5	96 (9.1)	B5	96 (7.0)	1.00
	Average	**95**		**97**	**0.98**
	SD	**2.2**		**1.7**	
PSL, 0.5 µm	A1	92 (3.2)	B1	99 (6.0)	0.93
	A2	97 (7.3)	B2	95 (5.7)	1.02
	A3	100 (8.8)	B3	96 (5.4)	1.04
	A4	98 (5.9)	B4	96 (4.9)	1.02
	A5	97 (11.5)	B5	98 (5.0)	0.99
	Average	**97**		**97**	**1.00**
	SD	**2.6**		**1.5**	

SD=standard deviation

[a] The ratio was the transmission efficiency of manufacturer A to that of manufacturer B. A ratio of 1 signifies perfect agreement between the two measurements.

Table S2: Pressure drop values for different straight PDMS traps (A1-B5) and twisted PDMS traps (T1-T3) used

Trap number	**Pressure drop (inH2O)**
A1	1.1
A2	1.1
A3	1.3
A4	1.3
A5	1.2
B1	1.0
B2	1.1
B3	1.2
B4	1.0
B5	1.2
T1	1.8
T2	2.0
T3	3.3

Chapter 6: Conclusions and Future Work

6.1 Overall Conclusions

The literature review chapter clearly identified scope for application of miniaturized methods and cheaper, greener extraction techniques which are quicker and have high recoveries. A global surge in the development of several advanced products which are designed specifically for atmospheric PAH analysis was also highlighted. However, uptake of emerging technologies by the developing world appears to be very low, which is probably due to resource constraints.

To address key environmental challenges in developing countries (especially in Sub Saharan Africa), and to overcome problems associated with extraction and analysis of atmospheric PAHs, a plunger assisted solvent extraction (PASE) method for multi-channel silicone rubber trap samplers was developed in Chapter 3. Compared to toluene, dichloromethane and acetone: hexane (1:1), hexane resulted in higher extraction recoveries which ranged from 76% for naphthalene to 99% for phenanthrene. Although thermal desorption (TDS) is environmentally friendly in that no toxic solvents are used, the PASE method used small volumes of organic solvent (a total of 2 mL per extraction), hence minimizing solvent use and waste.

PASE can therefore be used as a reliable and cheaper alternative to TDS for the analysis of PAHs from PDMS traps in applications where concentrations are above the LODs for this method. TDS provides higher sensitivity since the whole sample is analyzed, yet only a portion of the extract is injected for PASE. However, this was not problematic in the application performed in this study since elevated concentrations of PAHs were expected as sampling was performed close to the source. A notable drawback for TDS is that it presents a one-time sample analysis, yet possible repeat analyses with the PASE procedure makes it advantageous. The PASE procedure required less total analysis time (approximately 4 min needed for PASE extraction including weighing), compared to TDS which requires 11.5 min for cryofocusing of analytes (desorption time). Additionally, PASE chromatograms showed minimum silicone degradation products yet these were abundant in TDS analyses. Thermal degradation of the PDMS (which occurs during desorption) can cause potential chromatographic peak interferences. Analyses of PDMS traps has become possible in laboratories which do not have thermal desorption systems, hence facilitating their widespread use for airborne PAH monitoring.

Informed by results from Chapter 3, which demonstrated the potential suitability of the PASE method for routine monitoring of PAHs, Chapter 4 successfully identified and quantified PAH emissions from household cooking devices in a Kenyan case study. PAH emissions between selected households were highly variable and showed highest average gaseous PAH concentrations in rural areas (ranging from 0.81 to 6.09 µg m^{-3}) compared to urban homes (ranging from 0 to 2.59 µg m^{-3}). Type of dwelling, ventilation, geographical location, cultural factors, fuel used and type of combustion device used were the factors that chiefly influenced PAHs levels in indoor environments. Barriers to clean household energy in this study were clearly multifaceted, combining social, economic and technological challenges.

Firewood combustion in the traditional and improved 3-stone stoves contributed to the highest (35% and 26%, respectively) PAH concentrations followed by charcoal burning using the jiko stove (26%). Kerosene burning produced relatively lower (13%) PAH emissions compared to the traditional combustion devices and gas stoves produced no quantifiable PAH emissions. Individual PAH carcinogenic potency was successfully assessed and resulted in average BaPeq total concentrations of 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.

In addition to optimization of extraction and analysis procedures, this body of work successfully explored fundamental operating mechanisms of the PDMS traps and quartz fibre filters, specifically with respect to denuder based sampling. High particle collection onto the filters (>98%) and transmission efficiencies through the traps (>91%) of all tested particle sizes indicated that denuders are very effective tools for aerosol measurements. Trap-trap variations and high pressure drops due to kinks in PDMS traps were suggested as potential limitations which should be considered when interpreting results.

Overall, this research could provide a useful basis for decision making towards developing environmental management and protection policies. It may also assist in motivating for the filling in of the African gap in terms of sampling devices, extraction, analysis and understanding the global distribution of atmospheric PAHs.

6.2 Future Outlook

The work presented in this thesis could be improved and expanded further. Future work will focus on the application of PASE to other semi-volatile organic compounds which have similar boiling points to selected PAHs in this study. The occasional slight mismatch between plunger and multichannel silicone rubber trap (due to differences in manufacturing) means one has to carefully handpick traps before the sampling campaign or secure a range of different sized plungers if PASE is to be applied for extraction. This could be overcome by further optimization of the plunging technique. For example, traps could be set up in a customized chamber similar to a SPE manifold using flexible Teflon connectors to allow plunging without the need for the plunger to fit directly into the glass tube itself. This might accommodate the shorter traps (same PDMS tube length but shorter glass tubes) as well, which are currently being used by some research groups for aerosol measurements, and could eventually lead to automation of the extraction procedure. Alternatively, original Gerstel empty tubes could be used to make the traps since they have reproducible inner diameters, unlike the cheaper glass blown tubes employed in this study.

Since this study only focused on domestic fuel burning for cooking purposes, lighting and heating energy could be considered in future. Collection of soot and sampling of particulate PAHs would also be valuable in case studies. Larger sample sets including replicates should be taken in future for statistical purposes and a better understanding of data sets.

Appendix

Appendix

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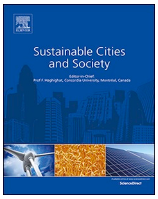

Insights into household fuel use in Kenyan communities

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ABSTRACT

Clean household fuel use is a cornerstone of the development of sustainable cities, in order to minimise household combustion emissions in communities and the negative air quality and human health impacts associated with this. In developing countries, factors determining fuel use are multi-faceted and complex. A survey was thus conducted to better understand the current household fuel usage profile in four regions of Kenya; namely Bomet, Voi, Mombasa and Narok. The fuel use parameters investigated covered bio-data and economic status, dwelling type, fuel choice and usage, combustion devices and ventilation in kitchens. The fuel type usage was distributed between firewood (25 %), charcoal (24 %), kerosene (24 %) and liquefied petroleum gas (LPG) (23 %). Three-stone stoves were still predominant in rural communities, whilst cleaner devices burning kerosene and LPG were used more widely in urban Mombasa. With the exception of Voi, there were more chimneys in urban dwellings than in the rural homes, even though brick houses were the most popular dwelling type overall (52 %). The results of this study will provide a useful basis for decision making regarding potential future clean energy intervention strategies in Kenya in order to promote sustainable development.

1. Introduction

Household air pollution arising from the use of solid fuels for cooking and heating purposes is the eighth leading global risk factor contributing to disease in developing communities (State of Global Air, 2018). 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 (Bonjour et al., 2013; HosgoodIII et al., 2013; State of Global Air, 2018; Suter et al., 2018). Moreover, there is evidence that exposure to air pollution is associated with adverse pregnancy outcomes such as low birth weight, pre-term births and still births (Abusalah et al., 2012; Patelarou & Kelly, 2014; Pope et al., 2010). Firewood, animal dung, crop waste and coal are examples of solid fuels which are dominant in rural communities of developing African countries, where open fires and simple stoves are used for residential activities. Due to the fact that roughly half of the world's population relies on solid fuels (Adkins, Tyler, Wang, Siriri, & Modi, 2010), there is growing public concern over emissions of air pollutants from inefficient combustion thereof, which significantly contributes to both indoor and ambient air quality (Sharma, Ravindra, Kaur, Prinja, & Mor, 2019). An example of these airborne pollutants are polycyclic aromatic hydrocarbons (PAHs), which are ubiquitous by-products of incomplete combustion of carbonaceous and organic matter such as charcoal, wood, gas, tobacco and diesel (Szulejko, Kim, Brown, & Bae, 2014). PAHs usually persist in the environment and have a negative impact on human health due to their well-known potential carcinogenic and mutagenic properties. PAHs contain two or more fused benzene rings and they are produced from domestic, industrial processes and vehicular combustion processes.

Systematic measurements of $PM_{2.5}$ in households using solid fuels around the world are not well documented. Quantitative estimations of the contribution of household fuel burning to atmospheric particulate matter levels are difficult to obtain, because emission factors vary greatly with wood type, combustion equipment and operating conditions (Martins & da Graça, 2018; Munyeza, Rohwer, & Forbes, 2019; Roden et al., 2009; Vicente & Alves, 2018). Bonjour et al (2013) developed a multi-level model to allow for the estimation of household solid fuel use for cooking purposes over the period 1980–2010 (Bonjour et al., 2013). However, statistics on household fuel use require updated field surveys, particularly from poor and vulnerable populations, in order to validate modeled results (Duan et al., 2014). Most previous surveys worldwide have focused on fuel use over short time periods, making it difficult to identify changing temporal trends, such as progress towards the establishment of sustainable cities based on clean fuel usage.

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There is a scarcity of reported information on current household fuel patterns for cooking and space heating purposes across the African continent. A recent study using household fuel data from a Demographic and Health Survey found that 66 % of sampled sub-Saharan households rely on biomass for cooking whilst only 25 % have access to electricity (Makonese, Ifegbesan, & Rampedi, 2018). In Kenya, which is one of the few African countries enjoying high growth rates with a positive impact on the income level of its citizens, an estimated 82 % of households still use traditional cooking fuels every day (Rahnema, Sanchez, & Giordano, 2017).

Several field testing surveys in Kenya have evaluated the general performance and usability of biomass cook stoves (Adkins et al., 2010; Lozier et al., 2016; Muindi, Kimani-Murage, Egondi, Rocklov, & Ng, 2016; Pilishvili et al., 2016; Tigabu, 2017). These studies mainly focused on the effectiveness of new improved combustion cook stoves in reducing household air pollution and their acceptability in some Kenyan societies. However, in practice, not all urban and rural households have access to these improved stoves. The choice of fuel and combustion device is expected to vary between provinces and also between rural and urban communities due to the influence of multiple factors. This study aimed to investigate these current factors and their impact on communities in order to facilitate progress towards increasing clean fuel and sustainable resource use.

In this study, we report on the fuel use patterns among urban and rural communities in four different counties in Kenya, namely Narok, Voi, Mombasa and Bomet. Possible influencing factors were explored such as geographical location, economic level (occupation and monthly income), type of dwelling, and fuel(s) and combustion device(s) used. The resulting data on household fuel use for domestic purposes is useful for comparison to and evaluation of previous estimations, and contributes to meeting the research gap on current solid fuel use in the World Health Organization (WHO) database. Additionally, the results are useful for domestic comprehensive risk analyses and burden of disease studies. Importantly, such information can motivate for further sampling campaigns and development of household air pollution control strategies for clean energy interventions, thereby improving quality of life, reducing human health impacts, and promoting environmentally sustainable development.

2. Research methodology

2.1. Background to the survey

Kenya is composed of 42 communities who live in varied climatic conditions, with different fuel consumption behaviors. In identifying suitable regions for sampling, the factors considered were: climatic conditions, cultural issues, dominant tree species present, economic status, fuel wood consumption patterns, and prevalence of burning of charcoal, respectively. The country was partitioned into two broad regions namely the coastal region of Kenya, a part of the country which is at sea level and mainland Kenya, representing areas which are above sea level and are inland. For each of the two regions, two counties were selected according to similarities and differences based primarily on: altitude, types of fuels used, climatic conditions, cultural practices and beliefs, and combustion devices used.

Urban and rural communities in each county were identified, namely Narok and Bomet counties which are located inland in the Rift Valley area where the climate is warm and temperate, and Mombasa and Voi counties in the coastal area of Kenya which have a tropical climate (Fig. 1).

In determining suitable sampling sites, variability in settlement areas which would lead to different fuel consumption behaviors was considered. In urban areas, the choice of sampling sites was based on level of income in order to cover both middle and low level income earners. A total of 106 questionnaires were administered as detailed in Table 1.

2.2. Survey methodology

Variability of about 10 km^2 between any two respondents was considered to avoid similarities hence sampling was purposive and randomized. Questionnaires were administered during September and October 2017 by means of face to face interviews, which lasted between 10 and 20 min. Respondents were requested to fill in their bio-data; income status; settlement types; fuel wood use; types, volumes, and cost of fuels used; and combustion devices employed, as detailed in the questionnaire (refer to Appendix (in Supplementary material)). In terms of fuel consumption, amounts were estimated by respondents, based on the fact that fuel is purchased on a mass basis. Respondents were also asked to give their perceptions and preferences regarding fuel sources and sustainability thereof. Data analysis and presentation was carried out using descriptive statistics (Microsoft Excel).

3. Results and discussion

3.1. Bio-data and economic status

The use of a particular type of cooking fuel is usually seen as a proxy for socioeconomic status in most African countries. This is also supported by the energy ladder theory which states that as incomes rise, households tend to substitute traditional solid biomass cooking fuels with those that are cleaner, more efficient, and more expensive (Schlag & Zuzarte, 2008). However, in the case of Kenya, a correlation between income and fuel switching is not always observed (refer to Table S1 in the Supplementary material), as it is also driven heavily by fuel availability in each region and other factors.

Out of the total population sampled in this survey, 80 % of the respondents were self- employed. In the urban areas of Kenya, half the population lives below the poverty line while a third of the rural population is generally poor (Kwach, 2018). In terms of earnings, in this study it was found that 53 % of households were earning below Ksh 10,000 (~100 USD) per month. The majority of respondents were female (84 %), which may be attributed to cultural issues especially in the rural areas, where it is a common practice for men not to go into the kitchen. Traditionally, women and children are responsible for the preparation of meals and in some cases the collection of firewood. Consequently, women and children typically suffer the most from indoor air pollution and burns, with young children being particularly susceptible to diseases that result in premature deaths and lung problems (Rahnema, Sanchez, & Giordano, 2017). In terms of age, 69 % of the respondents were between 21–40 yrs, while 20 % were 41–60 yrs, 6 % were below 20 yrs and 6 % were above 61 yrs. Most respondents were married (79 %), whilst the family size ranged widely from less than three (35 %), between 4–6 (38 %), to more than 6 members (27 %).

3.2. Types of dwellings

A total of 106 households were sampled. There were three types of dwellings found in the sampling regions namely; brick houses, informal shelters and traditional houses. Brick houses were the most prevalent dwelling type found in all the regions (67 %) followed by traditional dwellings (21 %) and then informal houses (12 %). Details regarding the presence of a dedicated kitchen in the dwellings as well as ventilation details are described under section 3.5.

3.2.1. Brick houses

In the urban areas, the highest number of brick houses was found in Narok (52 %), whilst the least was found in Voi and Mombasa (45 %) (Fig. 2). Brick houses, for the purposes of this study, comprised of stone, concrete or brick-built structures roofed with brick tiles or corrugated iron sheeting (Fig. 3a). Of the four regions, Narok is a highly agricultural area, where commercial farming like wheat production is

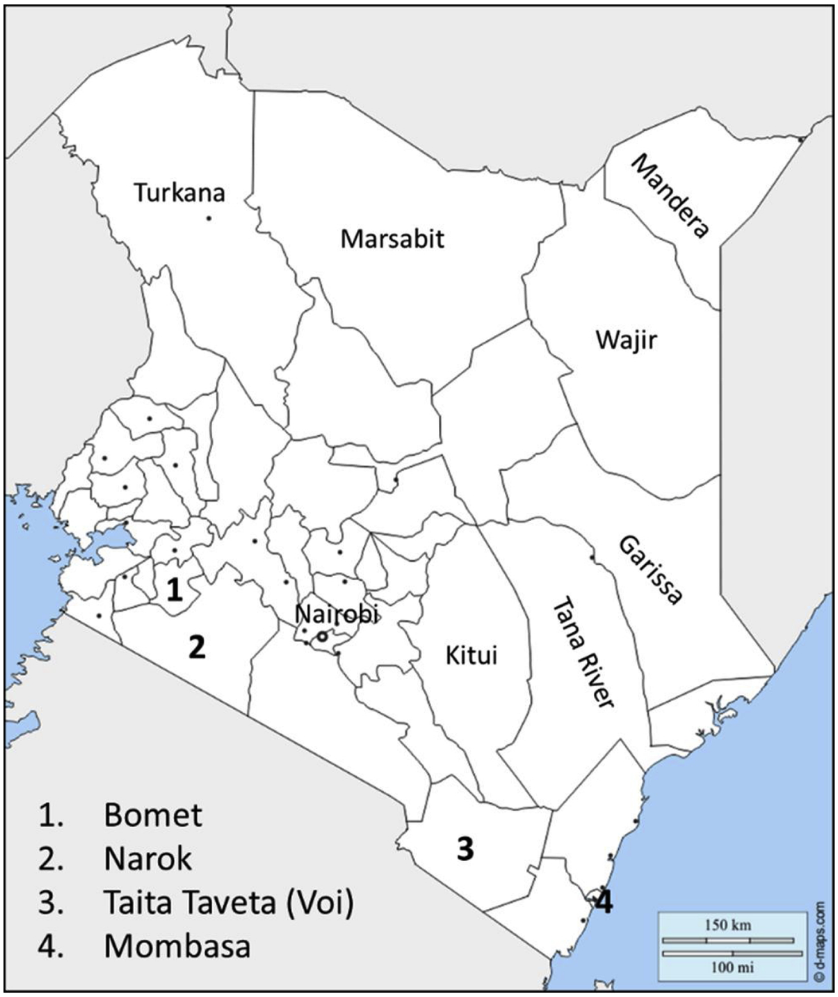

Fig. 1. Map of Kenya showing the four sampling regions (Source: a blank map was downloaded online (https://d-maps.com/) which was modified by the authors).

practiced, as compared to the rest of the study areas. Voi lies on an arid and semi-arid land (ASAL) area with most economic activities being small scale enterprises, hence the income level is low on average compared to the other sampled regions. In the rural areas, Voi had the highest number of brick houses (45 %) while Narok had the least (5 %). Bomet, Mombasa and Narok had more brick houses in the urban than rural areas, whilst Voi had the same number of brick houses in both rural and urban areas.

3.2.2. *Informal shelters*

Informal shelters were classified as those houses with iron sheeted walls and roofs or mud walled structures with iron sheet roofs (Fig. 3b). This kind of informal housing was highest in Narok (52 %) and lowest in Bomet (4 %). The community living in Narok is mainly Maasai who are pastoralists, which could be the reason for the high number of informal dwellings as compared to the other regions. The Maasai people still follow a traditional semi-nomadic lifestyle and observe their age old customs. Interestingly, no informal shelters were found in the urban areas of all the four regions. The displayed pattern could be a result of the urban redevelopment programs such as the Kenya Informal Settlements Improvement Project (KISIP, 2014). This programme was intensified by the Ministry of Lands, Housing and Urban Development, which eventually resulted in forced evictions and demolition of informal settlements in Kenya (Miyandazi, 2015). Voi and Mombasa had the same proportion of informal shelters.

3.2.3. *Traditional houses*

Traditional houses were classified as mud walled structures with thatched roofs or steel roof tops. The Maasai people traditionally rely on local, readily available materials and indigenous technology to construct their own traditional houses known as the Maasai Manyattas. As illustrated in Fig. 4, the structural framework of Manyattas is made

Table 1
Distribution of questionnaires completed in the four sampling regions in both rural and urban households and related climatic information.
Source of climatic data: https://en.climate-data.org/africa/kenya.

Region number	Region name	Total number of households	Number of rural households	Number of urban households	Average annual temperature (°C)	Average annual rainfall (mm)
1	Bomet	24	11	13	17.5	1247
2	Voi (Taita Taveta)	20	10	10	23.3	616
3	Mombasa	20	10	10	26.7	1196
4	Narok	42	20	22	17.1	771

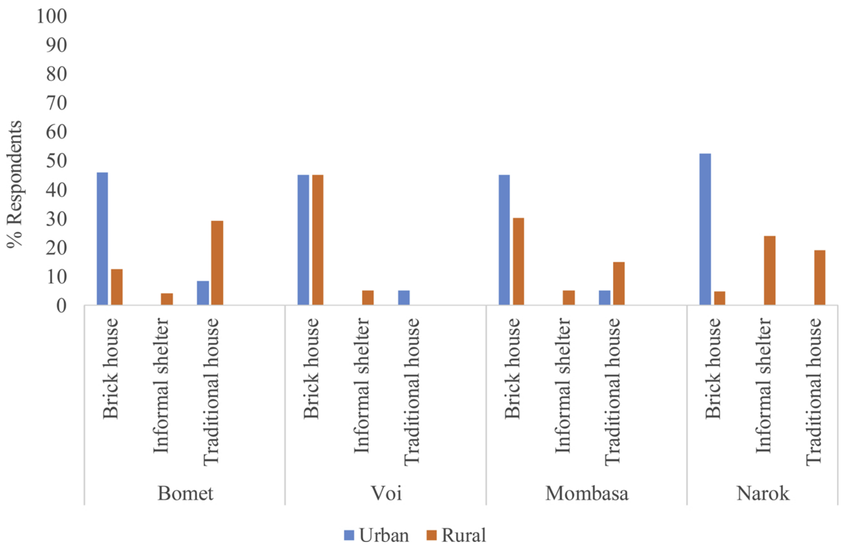

Fig. 2. Types of dwellings in urban and rural areas of the sampling regions.

up of timber poles fixed directly into the ground and interwoven with a lattice of smaller branches of wattle, which is then plastered with a mix of mud, sticks, grass, cow dung, and ash. In Bomet, the highest number of traditional houses (29 %) was recorded, whilst the lowest was found in Voi and Mombasa respectively (5 %). In the rural areas, Bomet had the highest number of traditional houses followed by Narok, Mombasa then Voi. In the urban areas, Bomet had the highest number followed by Mombasa and Voi, whilst they were not found in Narok.

3.3. Fuel use

3.3.1. Types of fuels used

It was found that over the four regions, 25 %, 24 %, 24 % and 23 % of Kenyan households relied on firewood, charcoal, kerosene, and LPG for cooking, respectively (Fig. 5). Only 4 % of the population used other types of fuels such as cow dung, biogas and sawdust. In terms of the urban-rural difference in regional household fuel use patterns, it was observed that urban residents used slightly more clean and non-solid fuels for cooking, such as LPG and kerosene. In rural households, firewood was still the predominant fuel used with only 25 % of the respondents reporting use of LPG.

The fuel use pattern is known to vary dramatically among different regions due to many factors such as household income, fuel accessibility and cost, as well as household cooking habits (Duan et al., 2014; Makonese et al., 2018). Fig. 6 shows how different regions preferred different fuel types. Charcoal appeared to be the most popular fuel in all the four regions, with saw dust being the least preferred fuel. Interestingly, the proportion of households who relied on firewood was lower for the Mombasa and Voi regions compared to Bomet and Narok. This is because these regions lie in the coastal area of Kenya which is mostly humid throughout the year resulting in a lack of dry firewood. For this reason, an increased use of sawdust, charcoal and kerosene was observed in these coastal communities.

3.3.2. Amount of fuel used daily in the studied communities

Most households were found to consume less than 2 kg/day of fuel, with a few exceptions of more than 3 kg/day. This could be attributed to the large number of fuel regimes being used at the same time. Charcoal was found to be consumed more in urban areas (Table 2) with the highest consumption of 3.0 kg/day in Voi and lowest of 0.8 kg/day in Narok compared to rural areas which ranged from 1.3 kg/day in Mombasa to 0.2 kg/day in Voi. No use of biogas was reported by any respondent.

Firewood use was more dominant in rural communities, as previously mentioned, with the highest usage of 6.8 kg/day in rural Bomet and lowest of 2.3 kg/day in rural Voi, compared to 1.5 kg/day in urban Bomet. This could be attributed to the fact that the kitchens in these types of rental dwellings in urban areas are typically not designed for

Fig. 3. A typical brick house (a) and informal shelters (b) in the study areas.

Fig. 4. Typical traditional houses in the study area, **a–b** shows traditional houses with iron sheet roofing, **c–d** shows Maasai Manyattas traditional homes and the ventilation holes in the walls thereof whilst **e** shows a traditional house with thatched roofing.

firewood use. LPG use was overall less than the other fuels, although it was used more in urban areas, with the highest consumption of 0.2 kg/day in urban Mombasa.

3.3.3. Fuel expenditure

Daily expenditure on fuels by communities varied widely (Table 3). Of the four regions, Bomet urban and rural communities had the highest number of respondents who chose their fuel based on its low cost. Such choices are highly related to household income and abundance of the fuel which impacts on its cost, as evidenced by the small amount spent daily on fuel. Bomet was also declared one of the poorest counties in Kenya based on a 2015 GDP per capita of 282 USD (Kwach, 2018).

3.3.4. Sources of fuels

The majority of the respondents in rural areas obtained their fuels

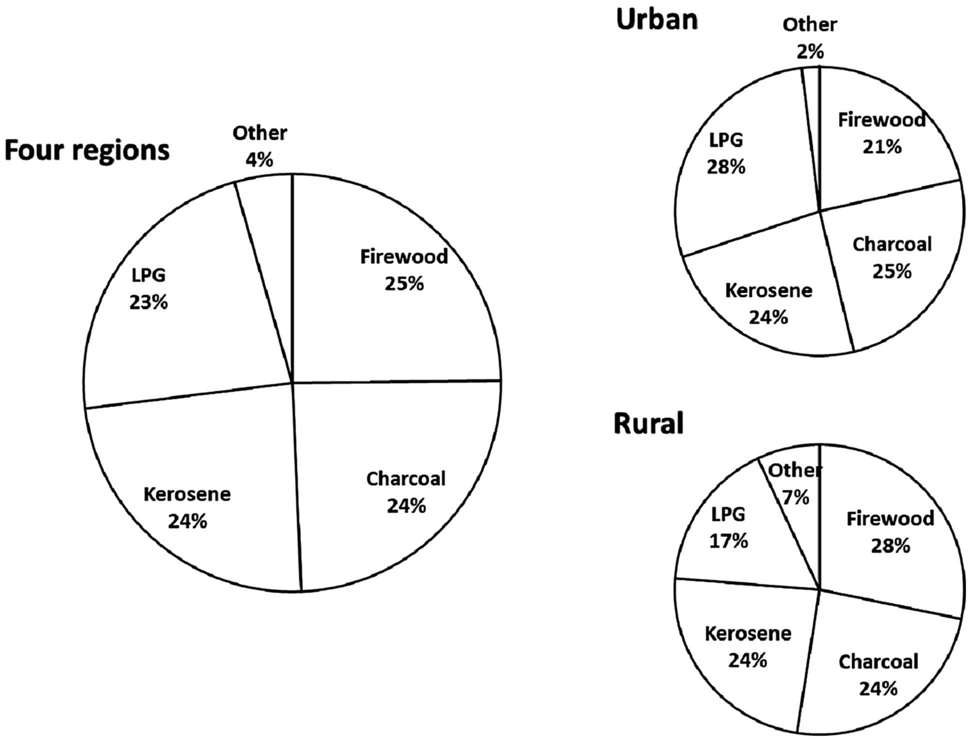

Fig. 5. Average household fuel use patterns over the four selected regions, in rural and urban areas.

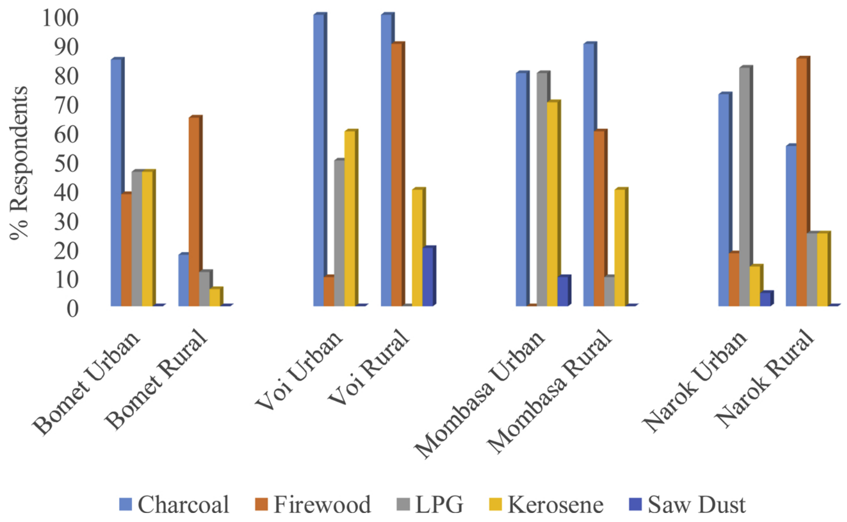

Fig. 6. Types of fuels used per region.

through self-collection (70 % in Mombasa and 60 % in Narok and Voi) (Fig. 7), whilst this was considerably less in urban areas (5–20%). Purchasing from informal vendors was highest in rural Voi (90 %) and lowest in rural Bomet (45 %). Those in urban areas obtained their fuel from shops (100 % of rural Mombasa respondents). Informal vendor supply was the highest at urban Voi (100 %) and lowest in urban Mombasa (30 %). Rural areas recorded correspondingly low responses regarding purchasing of fuel from shops, with the highest of 40 % in rural Mombasa and none in Bomet rural. This could be attributed to their heavy reliance on firewood and charcoal which are obtained locally as well as less dependence on LPG which is obtained from shops.

Table 3
Daily expenditure on fuels in KSh. (KSh. 100 ≈ $1 USD).

	Charcoal	Firewood	LPG	Kerosene	Sawdust
Bomet Urban	27	5	10	8	0
Bomet Rural	12	28	6	5	0
Voi Urban	69	0	27	13	0
Voi Rural	6	8	0	4	2
Mombasa Urban	37	0	29	24	0
Mombasa Rural	23	1	4	11	0
Narok Urban	15	0	23	2	0
Narok Rural	5	2	5	3	0

3.3.5. *Frequency of fuel collection*

Most households collected their fuels on a monthly basis, especially in the urban areas (80 % in urban Mombasa) (Fig. 8). This could be attributed to the availability of income based on monthly earnings. Weekly fuel collections were most common in rural Mombasa (50 % of respondents). Daily fuel collections had the highest response of 54 % in urban Bomet and none in both rural Voi and urban Mombasa. In a few counties, especially Narok and Bomet, some households would collect fuel two to three months in advance.

3.3.6. *Factors influencing the choice of fuel used*

The choice of which kind of fuel households used depended primarily on availability and ease of use factors. The importance of availability varied between 55 and 90 %, while ease of use ranged between 60 and 90 % (Fig. 9). This factor was likely linked to the primary combustion devices which were most accessible to many households; namely a charcoal stove called a Jiko and a three-stone stove. The importance of cost ranged from 10 to 46 %. This could be attributed to the fact that most people access firewood and charcoal for free or very cheaply, as they are near the source or they make it themselves, respectively. The least important factor considered was that of cultural issues, which was 0 % for almost all the regions except in rural Narok and Bomet (20 % and 9 % respectively). This could be attributed to strong cultural beliefs still being practiced by both the Maasai and Kalenjin communities living in each of these regions, respectively. No seasonality in terms of fuel use was noted by respondents, as all but one household used their chosen fuel(s) throughout the year.

3.4. *Combustion devices (cook stoves)*

In order to address health and environmentally related challenges resulting from traditional cooking practices in Kenya, most development efforts have been focusing on improved solid fuel combustion devices. Additionally, a recent survey has reviewed the experience in Kenya regarding the promotion of improved solid fuel cook stoves (Tigabu, 2017). The survey showed that the main focus has been on

Table 2
Estimated quantity of fuel used on a daily basis in each community studied.

		Amount of fuel used per day			
	Charcoal (kg)	Firewood (kg)	LPG (kg)	Kerosene (L)	Sawdust (kg)
Bomet Urban	1.0	1.5	0.1	0.1	0.0
Bomet Rural	0.5	6.8	< 0.1	0.1	0.0
Voi Urban	3.0	1.4	0.2	0.2	0.0
Voi Rural	0.2	2.3	0.0	0.1	0.1
Mombasa Urban	1.4	0.1	0.2	0.4	0.0
Mombasa Rural	1.3	4.6	< 0.1	0.2	0.0
Narok Urban	0.8	0.1	0.2	0.0	0.0
Narok Rural	0.5	2.4	< 0.1	< 0.1	0.0

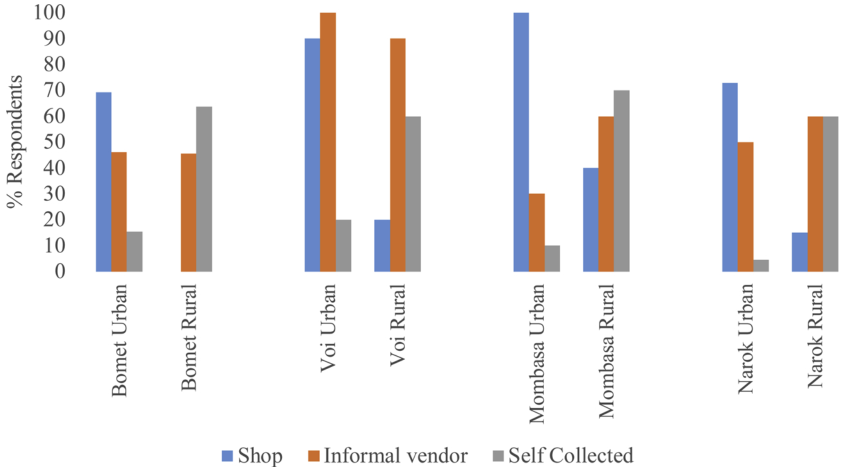

Fig. 7. Sources of fuels used by households in urban and rural communities in the study regions.

increasing production and distribution of improved cook stoves, overlooking the fact that some of the disseminated combustion devices are used less regularly or are even abandoned.

Traditional cook stoves, specifically the Jiko charcoal stove and wood burning three-stone stove, are popular in rural areas (Fig. 10). Personal and kitchen level concentrations of particulate matter < 2.5 μm and carbon monoxide (CO) measured during the use of these traditional and improved cooking devices have been documented in literature (Lozier et al., 2016; Pilishvili et al., 2016; Raiyani et al., 1993). With regards to levels of smoke and toxic emissions (such as PAHs), most findings illustrated that traditional biomass stoves resulted in more household air pollution compared to improved cook stoves (Adkins et al., 2010; Gachanja & Worsfold, 1993). Field measurements and estimations of gaseous and particle pollutant emissions from cooking processes in high population countries such as China and India also reported higher emissions from their traditional biomass stoves which use wood or cattle dung as fuel (Chen et al., 2016; Raiyani et al., 1993). Households using modern LPG or kerosene stoves had the lowest levels of indoor pollution since the stoves have been confirmed to be fuel efficient. Intensified research to design and disseminate clean fuel stoves which are cost-effective is still needed. Therefore, our study examined the current combustion devices being used in the four regions of interest and noted that most households still use traditional combustion devices, which indicates the need for more effective intervention strategies.

The combustion devices used in a particular Kenyan county depended on the type of fuels used. Most of the households in urban areas used a Jiko (charcoal stove) as a combustion device due to the fact that any household using charcoal requires a Jiko (Fig. 11). The highest Jiko use recorded was in urban Voi (100 %), while the least was 62 % in urban Bomet. Rural communities recorded slightly lower rates of Jiko use, with the highest for both rural Voi and Mombasa (90 %) and the lowest in rural Bomet (27 %).

Unsurprisingly, the rural areas dominated in the use of three-stone combustion devices which could be attributed to their high use of firewood. This is because three-stone stoves are cheap and are easy to obtain and assemble compared to other combustion devices. As for rural areas of Narok, the semi-nomadic Maasai rely mostly on the three-stone stove as these are easily discarded when they migrate. However, a few exceptions indicated that other forms of combustion devices, such as improved Jikos which use firewood, are being used by some households. Rural Bomet households recorded the highest use of the three-stone stove (91 %), while only 30 % of rural Voi respondents used it, as they used primarily improved firewood Jikos.

Use of kerosene stoves was higher in urban than rural areas, with the highest use rate of 70 % in urban Mombasa. This could be attributed to the fact that in Mombasa there are fewer choices of fuel while kerosene is cheaper than in other places. In rural areas this kind of combustion device was not widely used (highest in rural Mombasa (50 %) and lowest in rural Narok (0 %)).

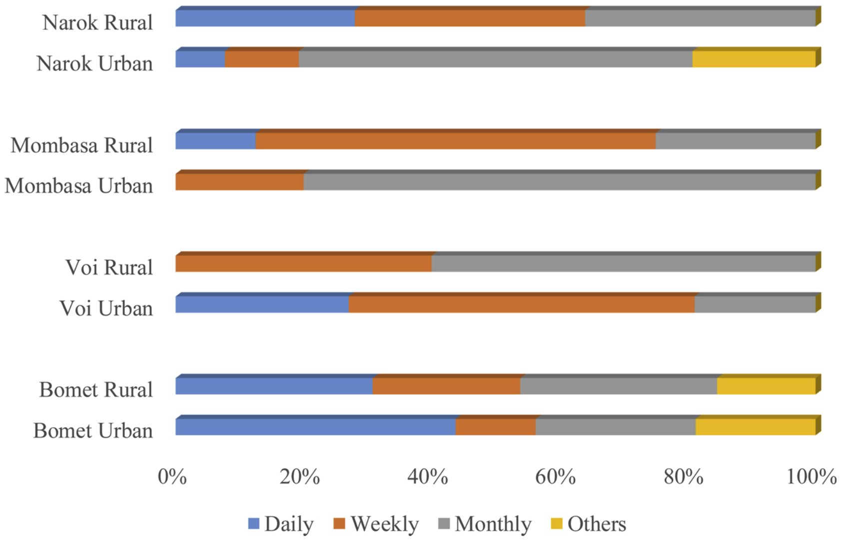

Fig. 8. Frequency of fuel collection by different communities in the study regions.

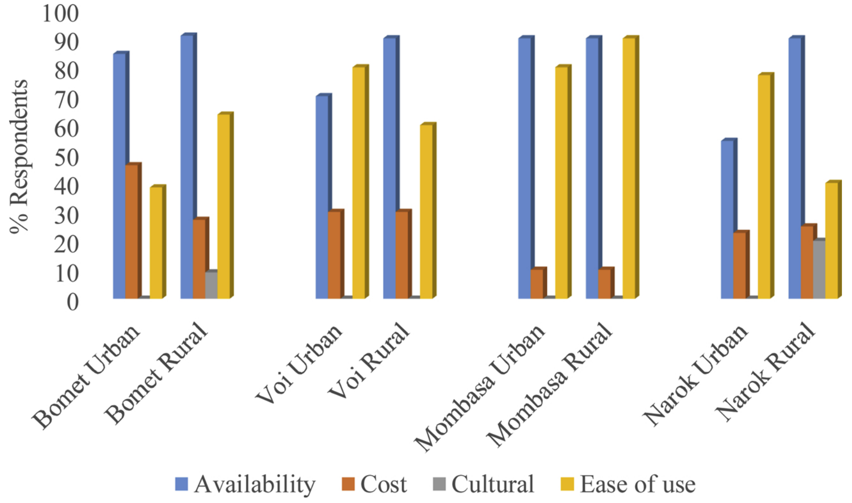

Fig. 9. Reasons given for the choice of fuel used by households in the study regions.

Gas cookers dominated in urban areas with the highest use rate in urban Narok (82 %), which could be attributed to LPG availability, affordability and its convenience in use. Very low or no usage of LPG was found in rural areas with the highest usage in rural Bomet (18 %). This could be a result of low levels of income in these rural communities and inaccessibility of LPG supply.

3.5. Combustion area within dwellings

The nature of the combustion area in the households studied was inspected and analyzed for its potential impact on indoor air quality (and related human health effects) and to some extent the combustion efficiency of various stoves (Fig. 12). A number of parameters were investigated, such as existence or absence of a dedicated kitchen, whether the combustion area was temporary or permanent, the presence or absence of ventilation in the form of windows and chimneys, and the general space available for combustion activities. These parameters provide valuable information when quantitative indoor air pollution studies are performed as the exposure of residents to potentially harmful pollutants such as PAHs and particulate matter generated during combustion is directly influenced by ventilation of homes. Good ventilation allows for dilution of emitted pollutants and efficient removal thereof, and also provides sufficient oxygen for efficient combustion. Poor insulation on the other hand, may increase the need for combustion for space heating purposes during the winter season, particularly in colder regions.

In this study, the number of windows in kitchens was higher in the Narok and Bomet regions which was consistent with the fact that firewood was their main choice of fuel, and would require good ventilation for efficient burning. With the exception of Voi, there were more chimneys in urban dwellings than in the rural homes. The existence of chimneys could be attributed to financial factors with most households in the rural areas not being able to afford a chimney structure.

3.6. Perceived negative aspects of fuel types

The evaluation of the perceived negative aspects of the different fuel types is shown in Fig. 13. The negative effect of the type of fuel used

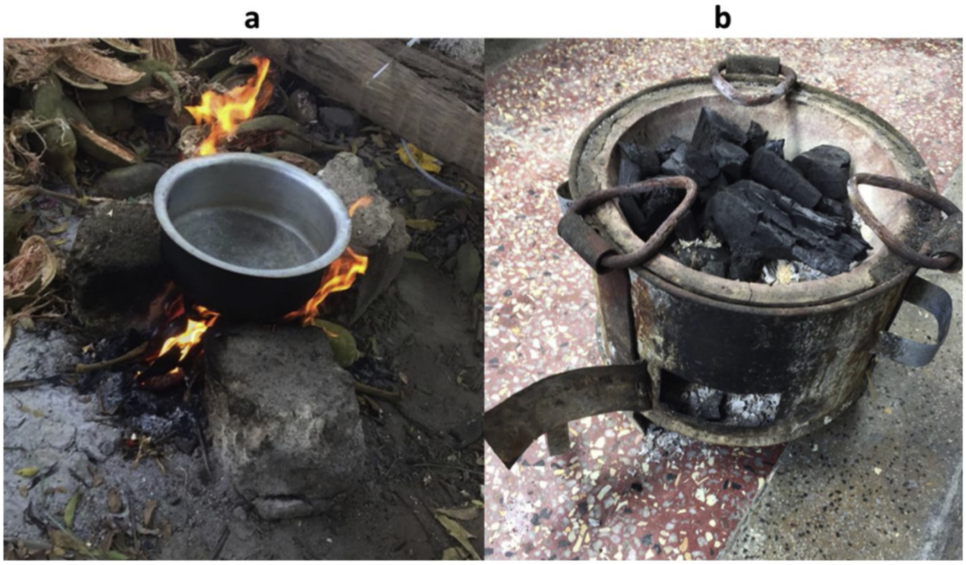

Fig. 10. Typical traditional combustion devices in use in Kenya are the wood burning three-stone stove (a) and a Jiko which uses charcoal fuel (b).

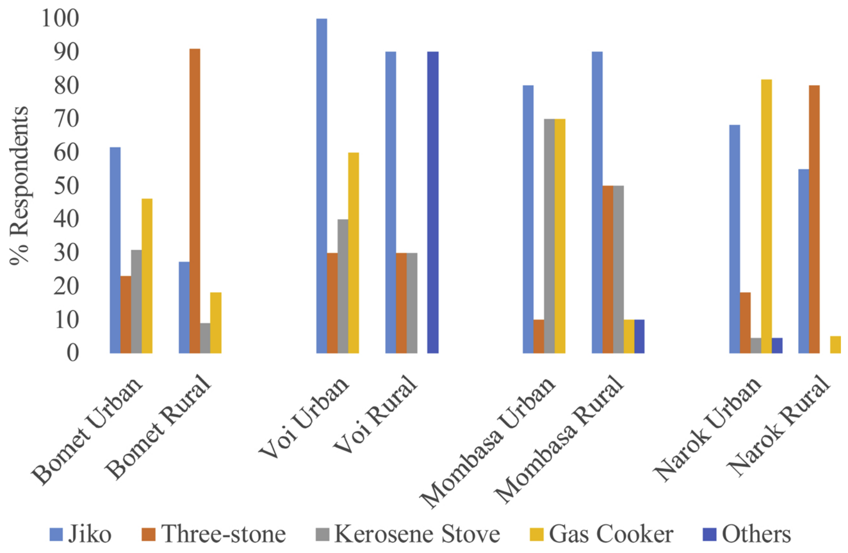

Fig. 11. Types of fuel cook stoves used in urban and rural areas of the four study regions.

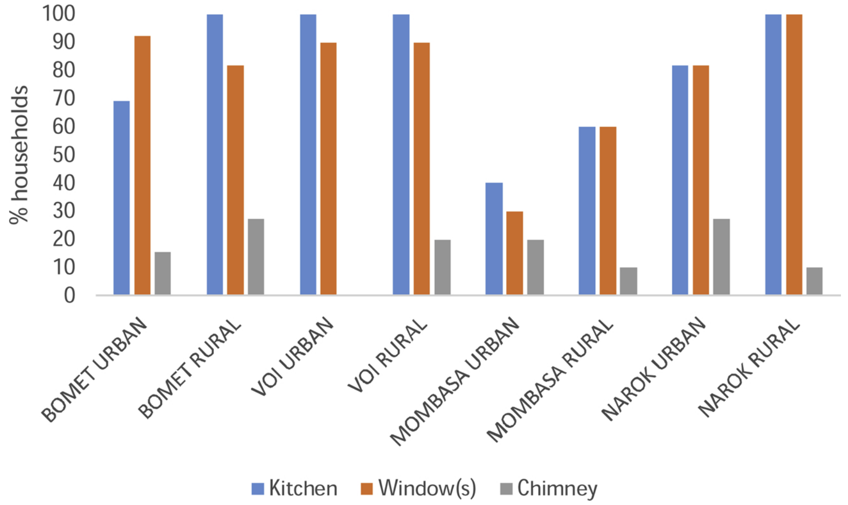

Fig. 12. Percentage of households in each urban and rural area which had kitchens, kitchens with window(s) and kitchens with chimneys respectively.

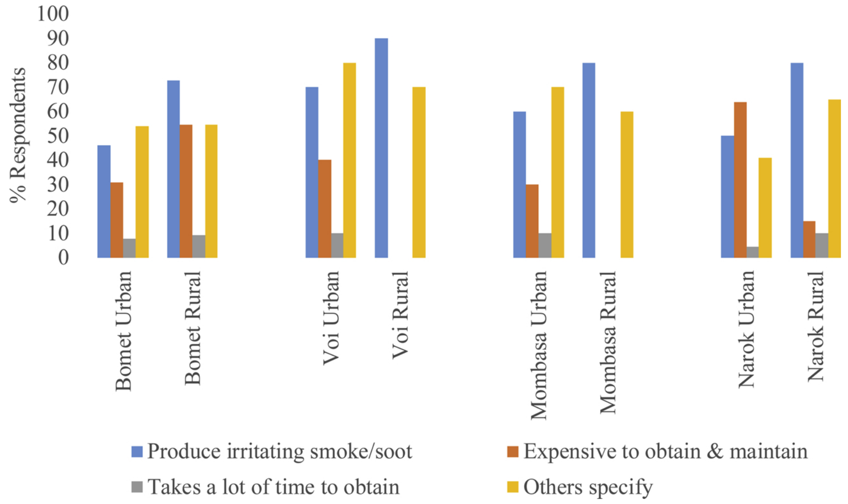

Fig. 13. Perceived negative aspects related to fuel types in the four surveyed regions.

which was evident in almost all households was the production of irritating smoke/soot, particularly in rural communities (90 % of respondents in rural Voi reported this). Urban areas recorded lower negative effects in this regard, where firewood is used less.

The other negative aspects mentioned by respondents were: large amounts of firewood required for complete cooking; causes coughing; risky with children (LPG); and dangerous when used with closed doors (charcoal). Others aspects were deforestation (with respect to firewood and charcoal) and difficulty in lighting when wet (charcoal and firewood). Expense of fuels was more of a problem in urban than rural areas. The time that it takes to obtain the fuel was not found to be a significant negative aspect.

4. Conclusions

The field survey provided firsthand data for household fuel use analysis, including perceptions of respondents in this regard. Household fuel use varied among the four regions, and differed between rural and urban areas. Overall, the most widely used fuel type was firewood (25 %) followed closely by charcoal (24 %), kerosene (24 %) and LPG (23 %). It was found that availability and ease of use of fuel were the key determinants regarding the fuel type utilized, whilst the perceived negative aspects related to fuels were found to be primarily the production of irritating smoke/soot; associated health matters; danger in use; and high costs.

The results of this study provide a useful basis for decision making regarding future intervention strategies in Kenya to reduce household combustion emissions and thereby to enhance air quality and improve human health. Education of communities regarding the benefits of clean fuel use as well as improved indoor air quality will invariably be key factors in achieving environmentally sustainable development.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.scs.2020.102039.

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Appendix: Questionnaire:

NRF KENYA Energy for Domestic Use

NRF National Research Foundation

PAHs Domestic Combustion Emissions Baseline Survey of Ten Selected Regions in Kenya

(A Kenya- South Africa Collaborative Research)

Hello. My name is ______________________. I am working with the Kenya- South Africa Collaborative Research Team. In order to get more information about type of Energy issues and quality of life in Kenya, we are conducting a survey of households Energy usage in the area. Your household has been selected by chance from all households in the area. I would like to ask you some questions related to your household Energy use.

The information you provide will be useful to find out type of energy and the status of quality of life in your community, and will be used to plan future Energy development programs in this area and also in the country. It is part of a survey that Kenya- South Africa Collaborative Research Team are conducting in five other counties in Kenya. Participation in the survey is voluntary, and you can choose not to take part.

All the information you give will be confidential. The information will be used to prepare general reports, but will not include any specific names. There will be no way to identify that you are the one who gave this information.

If you have any questions about the survey, you can ask me, my survey field supervisor who is here with the survey team, or the Principal Investigator Dr. Aloys Osano of Maasai Mara University or Co-Principal Investigator at Dr. Justin Maghanga of Taita Taveta University. At this time do you have any questions about the survey?

(Request for consent from household head to proceed)

Signature of interviewer: ____________________

Date: ____________________

Respondent agreed to be interviewed
☐ 1. Yes
☐ 2. No

Energy for Domestic Use

QUESTIONNAIRE SURVEY ON ENERGY USE IN BOTH KENYA'S URBAN AND RURAL DOMESTIC PLACES

SECTION 1: RESPONDENT PROFILE

Please put a tick (✓)

Gender: Male ( ) Female ( )

Age: Less than 20 years ( ) 21-40 ( ) 41- 60 ( ) 61and above ( )

Marital Status: Married ( ) Single ( )

Family size: Below 3 members ( ) 4-6 members ( ) above 6 members ( )

1. Location: ____
2. Classification: Rural or urban: ________________________________
3. Occupation:____
4. Income of a monthly basis in KSh: Below 10,000 ( ) 10,000- 15,000: ( ) 15,001-20,000: ( ) 20,000 and above ( )

SECTION 2 Dwelling

1. Type of dwelling: i. Stone/brick house ( ), ii. Informal shelter ( ), iii. traditional house ( )
2. Material of construction of the roof: i. Iron Sheets ( ), ii. Grass/Makuti ( ), Others specify, -------------( )
3. Material of construction of the walls: i. Stone/bricks ( ), ii. Earth/clay ( ), iii. Others specify, -------------------( )

SECTION 3 Fuels Used

1 a. What type of fuel do you use for domestic purposes and in what order? Please rank the as 1,2.

Charcoal ------ ( )

Firewood -------- ( )

LPG (gas) ----------- ( )

Kerosene ----------- ( )

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Cow dung ---------- (   )

Biogas --------- (   )

Napier grass rhizomes----------- (   )

b. Why do you use these source of energy?

Availability (   )
Cost (   )
Culture (   )
Ease of use (   )

c. If firewood, which types of trees are used?
Wattle Tree (   )
Blue gum (   )
Acacia (   )
Others (specify) ______________________________ ( )

d. Where do you obtain this fuel from? i. Shop ( ), ii. Informal vendor (   ), iii. Collected themselves ( )

e. How often do you buy or collect fuel? i. Daily ( ), ii. Weekly ( ), iii. Monthly (   ), iv. Other (specify)-- -( )

2. a. Which Combustion devices do you use?
   i. Jiko ( )
   ii. 3-stone ( )
   iii. Kerosene stoves ( )
   iv. Gas cookers (   )
   v. Others (specify) ____________________( )

b. Who uses which kind of combustion device? i. Male ---------- ( ), ii. Female, -------------- ( )

3. Which lighting devices do you use?
   Electricity (   )
   Solar (   )
   Kerosene lamps (   )
   Others (specify)

   ____

____

4. Do you have a kitchen? Yes(   ) No ( )
   If yes, how many windows does it have? 1(   ), 2(   ), 3(   ), None specify..........( )
Is there a chimney in the kitchen? Yes ( ) No ( )

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5. In which of the following seasons do you use your fuel?
   Rainy season (   )
   Dry season (   )
   All (   )
   If not All seasons, then what is the Alternative Fuel? ____________________

6. Rate the availability of the source of energy with reference to the scale below.
   5= Excellent, 4=Very good, 3= Good, 2= Fair, 1= Poor

   i. Firewood ( ); ii. Charcoal ( ); iii. Kerosene ( ); iv. LPG ( ); v. Any other………………… ( )

7. What volume, in litres/mass in Kg of fuel do you use on daily basis?

   Charcoal ____________________

   Firewood ____________________

   LPG (gas) ____________________

   Kerosene ____________________

   Cow dung ____________________

   Biogas ____________________

   Napier grass rhizomes ____________________

8. How much do you spend on fuel on a daily basis?
   Charcoal ____________________

   Firewood ____________________

   LPG (gas) ____________________

   Kerosene ____________________

   Cow dung ____________________
   Biogas ____________________

   Napier grass rhizomes ____________________

9. What are the benefits of the source of energy?

____
____
____

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10. What are the negative aspects of the source of energy?

____

____

____

11. Have you tried to use other sources of energy? Yes(   ) No(   )
    If Yes which ones?

12. Apart from your source of energy for domestic purposes, which other one would you like to use?

    ____

    Give reasons why?

    ____

    ____

    ____

13. Do you think the source of energy can be improved? Yes (   ) No (   )

If yes, how?____

14. Are you happy (satisfied) with the combustion device you currently use? Yes ( ) No ( )
    Give reasons why…………………………………………………………………………………

15. Why do you use this combustion device?
    i. It is cheap ( ),
    ii. Cultural issues ( ),
    iii. Easy to use ( ),
    iv. Conserves energy ( ),
    v. others specify-- ( )

16. Have you always used the same fuel source? Yes ( ) No ( ).
    If not what did you previously use?

    ____

17. Have you always used the same combustion device? Yes ( ) No ( ).
    If not what did you previously use? --

Addendum

This section provides additional information to the published manuscripts in Chapters 3 and 4.

Addendum to Chapter 3 (Paper 2)

1.) Optimization of chromatographic techniques

During method development, different options such as: type of sample solvent, GC column length, polarity of GC stationary phase with respect to target PAHs, vapour pressure (boiling points) of target compounds to be included in the study, carrier gas flow rate, solvent delay and amount of material injected onto the column were evaluated to optimize chromatography and mass spectrometry parameters, which are provided in Table A1.

Table A1: Optimized GC-MSD conditions for the analysis of PAHs in PASE extracted samples

Parameter	**Optimal conditions**
Column	Restek Rxi®-PAH
Column dimensions	60 m, 0.25 mm ID, 0.10 µm d_f
Oven program	80 °C (1 min), 30 °C/min to 180 °C, 2 °C/min to 320 °C
Injection	1 µL
Inlet mode	Splitless, purge flow 30 mL/min (1 min)
Inlet liner	Restek SKY™ Precision splitless liner without wool
Solvent delay	6.5 min
Inlet temperature	275 °C
Carrier gas	Helium, constant flow mode, 1 mL/min
Transfer line temperature	300 °C
Detector settings	-70 eV, electron impact mode
Mode of detection	Selected ion monitoring mode (SIM)
MS ion source temperature	230 °C (ion source), 150 °C (quad temperature)
Total run time	75.33 min

2.) Sampler cost analysis

Each PDMS trap (glass tube, PDMS tubing and glass caps) cost approximately R 120 excluding labour costs (ZAR 1 ~ USD 0.060). In addition to this, active sampling pumps required by PDMS trap samplers makes them generally more expensive than PUF disk passive samplers [3]. With regards to the overall PDMS sampler, the trap and conditioning costs were the same for both TDS and PASE. Although PASE required plungers, they are reusable and they cost approximately R150 each including material and labour costs. GC-MS grade pure solvents introduced extra costs for the PASE method but these were minimal since only 2 mL was utilized per extraction. TDS, on the other hand, had significant additional costs primarily due to the cost of the TD itself, as well as liquid nitrogen.

3.) Spiked PASE concentrations and expected concentrations

Table A2: PASE spiking details

Amount spiked	*Amount expected in 1 mL of first extract	*Amount expected on GC column from 1 μL injection
300 ng	300 ng	0.3 ng
500 ng	500 ng	0.5 ng
1000 ng	1000 ng	1.0 ng

*These amounts were reported as true values in the absence of solvent or other losses.

It should be noted that spike amounts were chosen to provide a final theoretical (expected) concentration in 1 uL injected based on 1 mL total extract volume. Since some solvent was lost through evaporation or through wetting the dry PDMS tubes, volume differences had to be considered for PASE LODs and extraction efficiencies in the preliminary studies:

Extraction efficiency was calculated based on mass balance and gravimetric methods as per the following example:

m1: mass of beaker with toluene (before plunging) = 11.23 g

m2: mass of beaker with toluene (after plunging) = 10.95 g

m1 – m2: mass of toluene lost during plunging = 0.28 g

Density of toluene: 0.865 g/mL

Volume lost during plunging: (0.28 g) / (0.865 g/mL) = 0.32 mL

Volume remaining in the beaker after plunging: 1 mL (initial volume of solvent) – 0.32 mL = 0.68 mL = 680 μL (A).

Using calibration curve of naphthalene (Nap) (from neat standards), we obtain a concentration of 0.6788 μg/mL after injection of 1 μL of (A).

Thus the mass of Nap in an extracted sample was (0.6788 μg/mL) (0.68 mL) = 0.46 μg

Loaded amount of the analytes before extraction was 0.50 μg (i.e. 500 ng)

Therefore extraction efficiency = 0.46 µg/ 0.50 µg x 100 = **92%**

Extraction volume was also included in LOD calculations. An example of a PASE LOD calculation for benzopyrene (BaP) reported in Table 2 is shown below:

100 ng spiked onto trap and extracted in 1 mL hexane, 1 µL (100 pg on column) from the extract gave a calculated S/N ratio of 230.8 (using instrument software), therefore 1.3 pg on column (i.e. in 1 µL) would give a S/N ratio of 3.

Considering a pre-analysis sample volume of 680 µL, 1.3 pg x 680 µL, LOD = 884 pg.

Considering a sample volume of 5 L (0.005 m^3) = 884 pg/5 L, LOD = 176 ng m^{-3}.

LOD and LOQs reported in Paper 2 were based on concentrations which would theoretically give a S/N of 3 and 10 respectively. A more cautious approach would be to set the lower limit of detection of the instrument to 1 pg. Taking Nap as an example, this would relate to 680 pg Nap in the total extract volume of 680 µL (for a 1 µL injection) and a Nap LOD of 136 ng m^{-3} based on 5 L sample volume, and a LOQ of 453 ng m^{-3}. However, as reported in Table 5, Nap was in the µg m^{-3} range in the real samples and the higher (more conservative) LODs would not have had an impact on the reported results.

LOD for TDS in text (Section 3.4.1, Comparison of methods): 0.13 ng m^{-3} should be reported as 0.14 ng m^{-3} since it was rounded off as shown in Table 2.

4.) Use of pure PAH standards

Pure (or neat) PAH standards (for all 15 target analytes) were used in initial method development to confirm the identity of PAHs in the samples. In addition to comparison with library mass spectra, the retention times of the pure standards were used to confirm the presence of analytes in the samples.

5.) PASE vs TDS comparison

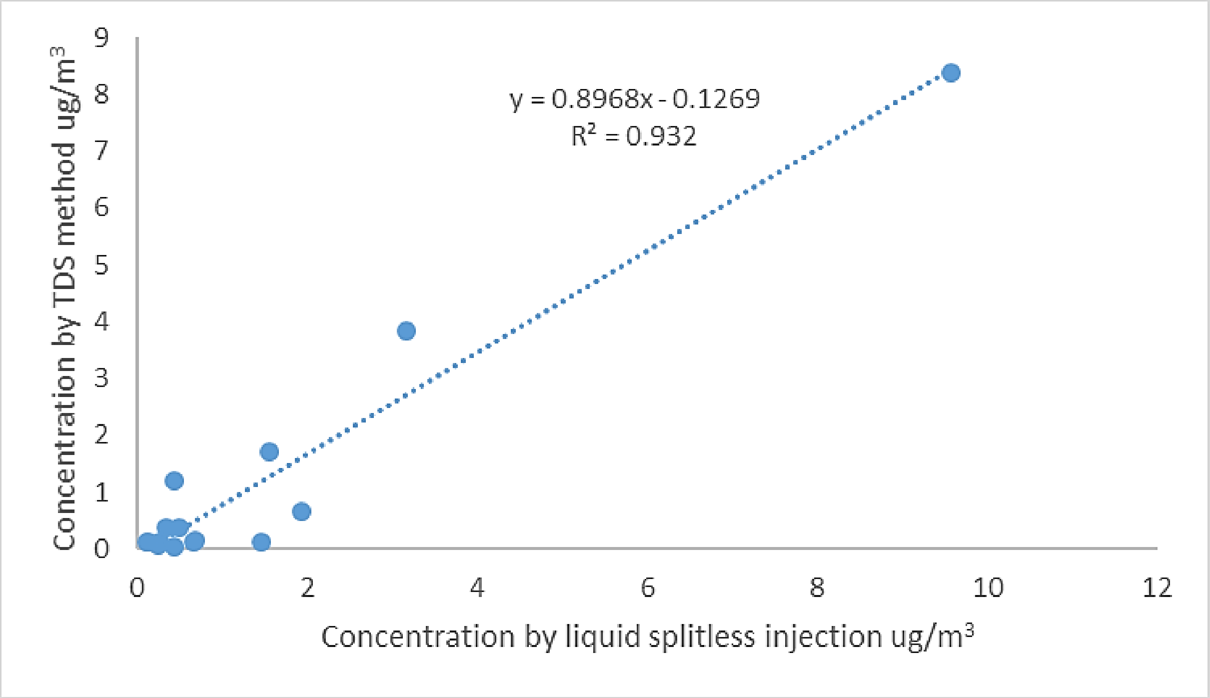


Fig.A1 Comparison of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene concentrations (in µg m^{-3}) obtained using TD vs those obtained using the PASE method from combustion emission samples A and D respectively.

A good correlation between the two methods can only be possible if the two real samples used are the same. In this work, sample A and sample D referred to samples taken at same location but using different multi-silicone rubber traps, which could introduce variations. In addition, the number of samples taken in this study could not statistically validate the extent of agreement of the PAH concentrations in the air therefore for future studies more samples need to be collected. However, as discussed in the cited literature in the paper, direct comparison of the exact concentrations quantified is fairly rare for thermal desorption and liquid extraction. The main aim which was achieved for this work was to alternatively and selectively extract, detect and quantify the analytes of interest.

Therefore in this context a fair comparison was only given in terms of which contaminants were predominantly quantified by the two methods and the trends displayed by the two methods. The PASE method for sample A reported higher concentrations from Nap up to pyrene compared to the TDS concentrations. As shown in Fig. S6, PASE recoveries for most of these analytes (particularly fluorene to pyrene) were superior to those for TDS. Although inefficient desorption could have been the cause of the variations, variations in concentrations of analytes on the respective traps could have been a possible additional cause.

6.) Stock solutions and working solutions

As stated under the sample extraction procedure, four solvents (toluene, n-hexane, DCM and acetone: hexane (1:1)) were tested in order to evaluate the optimal solvent for use in PASE of PAHs from multichannel silicone rubber traps. Solvents for extraction and calibration were matched in all cases (i.e if working standards were prepared in hexane, extraction and calibration was also done using hexane).

7.) Internal standards

In **Paper 2**, deuterated internal standards (IS), d8-naphthalene, d10- phenathrene, d10-pyrene and d12-chrysene were purchased in their crystalline form from Isotec Inc (Sigma Aldrich, Bellefonte, USA). 1 mg of each deuterated standard was separately weighed out and made up in 1 mL of toluene to give stock solutions (1 mg mL^{-1}). These were used to prepare a 500 ng µL^{-1} stock solution in toluene, consisting of mixed IS standards (i.e giving a nominal concentration of each compound as 500 ng µL^{-1}). Working solutions were prepared in respective solvents (hexane or toluene) and PASE samples were spiked before GC-MS analysis (final concentrations of 0.5 ng µL^{-1} on column). For example, 1 µL of 340 ng µL^{-1} added to the 680 uL extract = 0.5 ng µL^{-1} injected.

It should be noted that after reviewers' comments from **Paper 2** and a few analytical considerations, the method for **Paper 3** was subsequently modified to spiking IS standards onto sample traps directly before extraction (see section '*Extraction of PAHs'* in Paper 3). Additionally, the deuterated standards used in **Paper 3** came as a ready-made mixture which was obtained from LGC Standards (Labor GmbH, Augsburg, Germany). IS in **Paper 3** were namely d8-naphthalene, d10-acenapthene, d10-phenanthrene, d12-chrysene and d12-perylene.

8.) Denuders

As stated in the Introduction (Chapter 1), the denuder set-up entails the use of two multi-channel polydimethylsiloxane (PDMS) traps in series joined by a Teflon connector which houses a quartz fiber filter, whereby the PDMS acts as an absorbent for gaseous semi-volatile organic compounds (SVOCs) and the filter collects particulate analytes.

It should be noted that the PDMS trap alone functions as a denuder: it strips gas phase from particle phase analytes in air samples. This holds regardless of whether the particle phase is collected or analysed. This is stated in a number of literature studies [1, 2]. For example, "Small and portable denuders like multi-channel silicone rubber traps are very suitable for both the vapour collection of non-polar SVOCs and the transmission of particles in the 0.3 – 2 µm size range" [1].

9.) Plungers

Fig.A2 Typical plungers used in PASE experiments. Specifications for these are provided in Table A3.

Table A3 Typical specifications for plungers used in this study (slight variations were needed in some cases to provide a snug fit inside the glass tubes).

Outer diameter of Teflon tip	3.9 mm
Length of Teflon tip	5.0 mm
Supplier of Teflon	Maizey Plastics
Length of steel wire	316 mm
Outer diameter of steel wire	2.1 mm
Supplier of steel wire	Gem Tool Co (Pty) Ltd

10.) Trap conditioning

The traps were pre-conditioned in an off-line Gerstel^{TM} TC 2 Tube conditioner (Chemetrix, Midrand, South Africa) using a hydrogen gas flow of 100 mL.min^{-1}.

11.) Outliers

An outlier was defined as an extreme value that was much higher or much lower than the other obtained values. The graphing calculator method was used to determine whether a value was an outlier. The criterion used was that a value that was more than 3 standard deviations from the calculated mean value was discarded as an outlier.

Note that in this work the term ‘outlier’ was not used as a full statistical tool. If an outlier was observed as a result of suspected measurement error, that specific experiment or injection would be repeated (i.e. for n=3 if one value was a suspected outlier, this was not reported as n=2, but an additional injection was performed to give n=3).

12.) Parafilm®M use

Parafilm®M was only used for a short time period during weighing to reduce evaporation losses.

13.) TDS calibration

TDS calibration was performed via injection of liquid standards onto PDMS traps. For example at 1 ng µL^{-1} calibration level, 1 µL was drawn from a 1 ng µL^{-1} PAH mix and spiked onto a PDMS trap. Similarly, 1 µL was drawn from a 0.5 ng µL^{-1} internal standard mix and spiked onto a PDMS trap. This was followed by PDMS traps being thermally desorbed directly. Note that LODs for some PAHs are identical as they were rounded off.

14.) Typical TDS chromatogram (with IS)

In addition to the PASE chromatogram given in Supplementary information, a typical TDS chromatogram is given in Fig. A3.

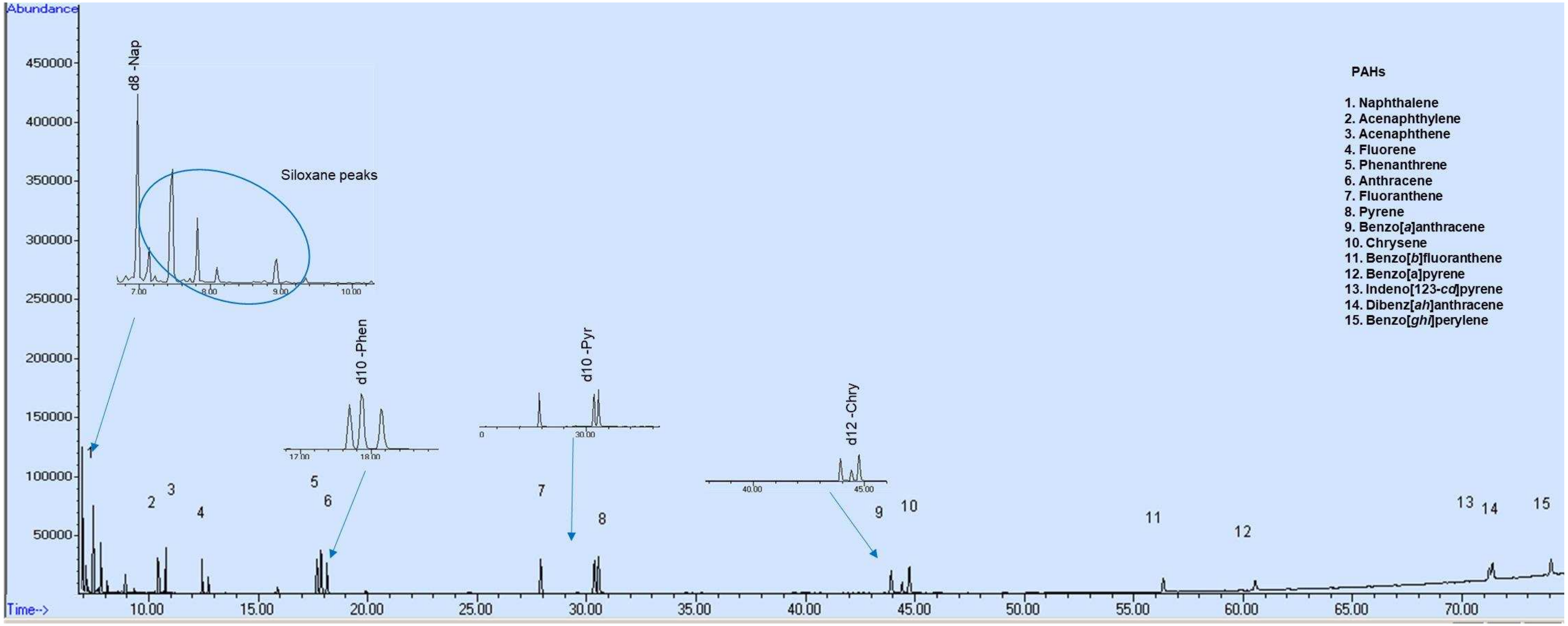


Fig. A3 TDS chromatogram showing siloxane peaks which are absent from the PASE chromatogram. The trap was spiked with 1 µL of 1 ng µL^{-1} PAH mixed standard and 1 µL of 0.5 ng µL^{-1} IS mixture containing d8-naphthalene, d10-phenathrene, d10-pyrene and d12-chrysene in toluene.

15.) Field blanks

Field blanks were taken to the sampling site but were not used for sampling (i.e. end-caps were not removed). They were similarly wrapped in aluminium foil and refrigerated before analysis as were the samples. Field blank samples were spiked with internal standard mix, extracted and analysed in the same manner as field samples. There were no target analytes detected in the field blank extracts therefore concentrations were reported as <LOD. Consequently, no blank subtraction was performed on the processed field samples.

16.) Average extract volumes for different solvents

Table A4 Averages, standard deviations (SD) and relative standard deviations (%RSD) of final extract volumes recovered from each 1 mL of plunging solvent.

Solvent	Average extract volume (µL)	SD	%RSD
Toluene	690	0.01	1.9
Hexane	672	0.05	6.9
Acetone:Hexane (1:1)	562	0.11	19.7
DCM	632	0.02	3.6

17.) Loss of solvent when using PASE

680 µL is mean extract volume for a 1 mL solvent extraction and not 2 mL since sequential extracts were treated separately in preliminary studies (see Fig. 2 in Paper 2 and section 3 under extraction efficiency in this Addendum). Invariably, some solvent will remain in the PDMS tubes and it will contain traces of analyte as solvent extraction is an equilibrium process. That is why sequential extractions were performed with fresh solvent to reduce these losses. From the results presented (Fig. 2), it can be seen that the concentration of analyte in any solvent remaining in the tubes would have been low after two sequential extractions. Regardless of where (how) the solvent was lost, a correction was made for this.

18.) Adsorption losses of analytes to glass

Adsorption losses of heavier PAHs to glass refers to adsorption losses onto the glass vials. Due to the sequential extraction of the trap with fresh solvent in a dynamic (flowing) manner over a short time period, it is unlikely that adsorption losses in the trap itself would be significant as compared to that in the sample vials.

19.) Fig.3 Standard deviation here refers to standard error of the mean based on repeat injections.

20.) Incomplete desorption by TDS

The detector response is not the same if the same amount of a compound is injected into the GC as a liquid standard and if it is spiked onto a trap and is thermally desorbed. This is due to incomplete desorption of some analytes by TDS or incomplete trapping of these by the CIS during transfer from the TDS. The exact origin of the discrepancies would require further studies (and could be optimized further, but this was outside the scope of this thesis).

21.) **Table 3** now clarified as **Table A5** to correct typesetting error in column header.

Table A5: Intra and inter day variations (VC_{intra} and VC_{inter}) for PASE and TDS methods. Recovery data from PASE liquid samples (1000 ng spiked onto trap to give 1 ng on column) and desorption efficiency values (1 ng spiked onto trap). SD = Standard deviation of mean from repeated experiments (n=3) and %RSD = Relative Standard Deviation.

PAHs	VC_{intra} (%), *n=5*		VC_{inter} (%), *n=3*		(%)Recovery/Desorption 1 ng, *n=3*			
	PASE	TDS	PASE	TDS	PASE	%RSD	TDS	%RSD
Nap	4.9	7.1	7.7	7.6	76	5.2	89	5.3
Acy	3.4	7.8	5.4	5.4	89	3.2	73	1.4
Ace	2.7	9.2	4.5	9.8	86	3.2	83	1.2
Flu	0.7	6.6	1.4	4.7	95	3.0	84	2.6
Phe	1.3	5.8	3.2	6.7	99	2.9	85	2.4
Ant	0.9	3.4	1.3	3.4	98	4.7	83	2.7
FluAn	1.3	3.4	3.0	4.2	96	2.9	86	3.2
Pyr	0.5	2.2	1.2	2.7	88	2.7	75	3.4
BaA	2.3	5.4	3.1	2.9	90	1.4	93	2.5
Chr	2.0	3.8	2.2	3.1	88	3.3	78	2.0
BbF	2.5	5.8	3.9	6.0	86	5.4	68	4.0
BaP	1.1	11	2.2	9.8	93	3.6	78	3.4
IcdP	1.4	10	2.1	12	81	5.7	79	1.4
BghiP	1.9	8.8	3.1	11	83	4.9	66	3.3
DahA	1.2	8.7	3.7	6.4	85	3.6	71	1.2

22.) PASE and TDS low spike recovery results

Table A6: Recovery data from PASE liquid samples (300 ng spiked onto trap to give 0.3 ng on column after 1 µL injection) and thermal desorption efficiency values (0.3 ng spiked onto trap). SD = Standard deviation of mean from repeated experiments (n=3) and %RSD = % Relative standard deviation.

PAH	**%PASE Recovery Average**	**SD**	**%RSD**	**%TDS Recovery Average**	**SD**	**%RSD**
Nap	73.0	4.0	5.5	81.7	3.5	4.3
Acy	81.3	1.5	1.9	78.0	3.0	3.8
Ace	82.0	4.0	4.9	82.3	3.2	3.9
Flu	88.7	3.5	4.0	78.0	2.0	2.6
Phe	91.0	2.6	2.9	87.7	2.5	2.9
Ant	92.0	3.0	3.3	89.0	4.6	5.1
FluAn	89.7	1.5	1.7	83.3	4.7	5.7
Pyr	84.7	3.1	3.6	83.7	4.0	4.8
BaA	84.7	3.5	4.1	84.3	4.2	4.9
Chr	84.7	3.8	4.5	78.3	1.5	2.0
BbF	78.3	3.1	3.9	76.3	3.5	4.6
BaP	81.7	3.5	4.3	68.0	2.0	2.9
IcdP	72.7	2.1	2.9	71.0	2.0	2.8
BghiP	76.0	3.6	4.7	71.0	2.0	2.8
DahA	78.0	2.0	2.6	71.3	3.2	4.5

23.) TDS desorption time vs weighing of beakers

TDS requires 11.5 min for thermal desorption of analytes hence it required more total analysis time compared to PASE analysis. In addition to the 2 min extraction time, PASE required approximately 2 min for the weighing procedure.

References:

1. Dragan, G.C., Kohlmeier, V., Breuer, D., Blaskowitz, M., Karg, E. and Zimmermann, R. On the challenges of measuring semi-volatile organic compound aerosols using personal samplers. *Gefahrstoffe Reinhaltung Luft*, 2017, **77:** p. 411-415.
2. Kohlmeier, V., Dragan, G. C., Karg, E. W., Schnelle-Kreis, J., Breuer, D., Forbes, P. B., Rohwer, E. R., & Zimmermann, R. Multi-channel silicone rubber traps as denuders for gas–particle partitioning of aerosols from semi-volatile organic compounds. *Environmental Science: Processes & Impacts,* 2017, **19(5)**: p. 676-686.

3. Strandberg, Bo, Anneli Julander, Mattias Sjöström, Marie Lewné, Hatice Koca Akdeva, and Carolina Bigert. "Evaluation of polyurethane foam passive air sampler (PUF) as a tool for occupational PAH measurements." *Chemosphere* 2018, **190**: p. 35-42.

Addendum to Chapter 4 (Paper 3)

1.) Field blanks and matrix matched blanks

Field blanks were taken to the sampling site but were not used for sampling (i.e. end-caps were not removed). They were similarly wrapped in aluminium foil and refrigerated before analysis as were the samples. Field blank samples were spiked with internal standard mix, extracted and analysed in the same manner as field samples. A blank trap was included in the matrix matched calibration and there were no targets analytes detected in the extracts therefore this was the first calibration point. A chromatogram of a field blank sample spiked with IS mix is given in Fig S2.

2.) Spiking amounts for matrix matched calibrations and LOD calculations

Spiking amounts: For matrix matched calibration curves, 5 to 150 ng (i.e. 1 µL of PAHs were spiked onto trap from concentration levels of 5 to 150 ng µL^{-1}). Considering 1 mL extraction volume this would theoretically give 0.005-0.15 ng µL^{-1}.

Extracts were blown down and reconstituted to 100 µL (x10 concentrating step). Therefore calibration amounts in vial were 0.05-1.5 ng µL^{-1} in 100 µL.

1 µL was drawn from the above mentioned vials and injected onto the column. (This implies that for 1 µL injection, column response was multiplied by 100 to get what is in the 100 µL extract. These amounts in 100 µL were used for calibration and quantification purposes). LODs and LOQs in Table S2 are also expressed based on a 100 µL as shown in **Table A7** below (i.e. LODs ranging from 0.01-0.15 ng µL^{-1} in 100 µL).

Table A7: Limits of detection (LODs) and limits of quantitation (LOQs) of PAHs based on SIM ions for the PASE method. The LOD was calculated based on a signal to noise (S/N) ratio of 3 and the LOQ on a S/N ratio of 10.

Analyte	LOD (ng µL^{-1})	Calculated air sample ^{a}LOD (ng m^{-3})	LOQ (ng µL^{-1})	Calculated air sample ^{a}LOQ (ng m^{-3})
Nap	0.01	2.09	0.03	6.07
2-mNap	0.01	1.93	0.03	5.60
Acy	0.01	2.30	0.03	6.67
Ace	0.02	4.18	0.06	12.14
Flu	0.02	3.55	0.05	10.32
Phe	0.02	3.98	0.05	11.53
Ant	0.03	5.23	0.08	15.17
FluAn	0.02	3.77	0.05	10.92
Pyr	0.02	4.81	0.07	13.96
BaA	0.06	12.76	0.19	37.01
Chr	0.10	19.67	0.29	57.04
BaF	0.11	21.97	0.32	63.71
BkF	0.13	25.05	0.36	72.64
BaP	0.14	27.20	0.39	78.88
IcdP	0.18	34.94	0.51	101.33
BghiP	0.16	31.38	0.46	91.02
DahA	0.15	30.34	0.44	87.98

^{a}LOD and ^{a}LOQ considering the airborne concentration obtained by sampling a volume of 5 L (0.005 m^{3}) and based on concentrations in final extract (100 µL).

3.) Additional information to Table S3 is provided in **Table A8** where standard deviations (SD) of the mean from duplicate injections and %RSDs are illustrated.

Table A8: PAH concentrations in µg m^{-3} in indoor and ambient air from rural and urban areas in coastal Kenya (average of duplicate injections). Note: Abbreviations are defined in Table 1 of Paper 3 in Chapter 4.

TAITA TAVETA RURAL SAMPLES															
	TTR-A	**SD**	**%RSD**	**TTR-H1**	**SD**	**%RSD**	**TTR-H2A**	**SD**	**%RSD**	**TTR-H2B**	**SD**	**%RSD**	**TTR-H3**	**SD**	**%RSD**
Nap	*	*	*	25.92	0.065	0.2	18.24	0.098	0.5	19.19	0.103	0.5	3.19	0.013	0.4
2-mNap	-	-	-	6.15	0.047	0.8	4.33	0.053	1.2	5.54	0.047	0.9	2.2	0.007	0.3
Acy	0.09	4E-06	4E-03	5.1	0.021	0.4	7.6	0.069	0.9	4.5	0.123	2.7	1.61	0.001	0.1
Ace	*	*	*	2.18	0.004	0.2	8.36	0.073	0.9	6.67	0.168	2.5	1.4	0.001	0.1
Flu	*	*	*	4.24	0.003	0.1	14.73	0.042	0.3	12.42	0.094	0.8	2.03	0.002	0.1
Phe	-	-	-	5.68	0.011	0.2	5.93	0.084	1.4	9.26	0.018	0.2	0.94	0.004	0.5
Ant	-	-	-	2.31	0.001	0.1	4.65	0.047	1.0	7.09	0.031	0.4	*	*	*
FluAn	-	-	-	1.25	0.008	0.7	5.39	0.036	0.7	4.61	0.018	0.4	*	*	*
Pyr	-	-	-	1.15	0.002	0.2	12.49	0.065	0.5	9.76	0.009	0.1	*	*	*
BaA	-	-	-	0.99	0.000	0.0	1.04	0.001	0.1	1	0.000	0.1	-	-	-
Chr	-	-	-	0.41	0.001	0.2	0.51	0.000	0.0	0.56	0.000	0.1	-	-	-
BaF	-	-	-	0.57	0.005	0.8	1.12	0.010	0.9	1.2	0.002	0.2	-	-	-
BkF	-	-	-	0.58	0.002	0.3	0.54	0.002	0.4	0.69	0.000	0.1	-	-	-
BaP	-	-	-	0.6	0.006	1.0	0.27	0.002	0.7	0.56	0.001	0.2	-	-	-

KILIFI RURAL SAMPLES															
	KR-A	**SD**	**%RSD**	**KR-H1**	**SD**	**%RSD**	**KR-H2A**	**SD**	**%RSD**	**KR-H2B**	**SD**	**%RSD**	**KR-H3**	**SD**	**%RSD**
Nap	0.12	0.015	12.5	8.54	0.386	4.5	10.58	0.050	0.5	11.01	0.360	3.3	4.16	0.206	4.9
2-mNap	*	*	*	2.21	0.317	14.3	5.2	0.336	6.5	5.05	0.173	3.4	1.73	0.270	15.6
Acy	0.36	0.014	3.8	3.43	0.003	0.1	2.83	0.078	2.8	2.62	0.091	3.5	1.89	0.044	2.3
Ace	*			1.64	0.209	12.8	3.66	0.257	7.0	2.17	0.149	6.9	1.67	0.247	14.8
Flu	0.39	0.005	1.3	2.54	0.014	0.6	3.84	0.271	7.1	2.75	0.133	4.8	2.31	0.002	0.1
Phe	0.35	0.008	2.3	2.41	0.018	0.8	2.27	0.068	3.0	2.34	0.048	2.0	1.22	0.111	9.1
Ant	*	*	*	1.68	0.001	0.1	3.45	0.142	4.1	2.87	0.159	5.5	1.44	0.033	2.3
FluAn	-	-	-	1.18	0.074	6.3	1.2	0.094	7.8	1.14	0.001	0.1	0.96	0.064	6.6
Pyr	-	-	-	1.08	0.111	10.3	2.69	0.294	10.9	2.59	0.162	6.3	0.78	0.018	2.3
BaA	-	-	-	*	*	*	-	-	-	-	-	-	-	-	-
Chr	-	-	-	*	*	*	*	*	*	*	*	*	*	*	*

TAITA TAVETA URBAN SAMPLES

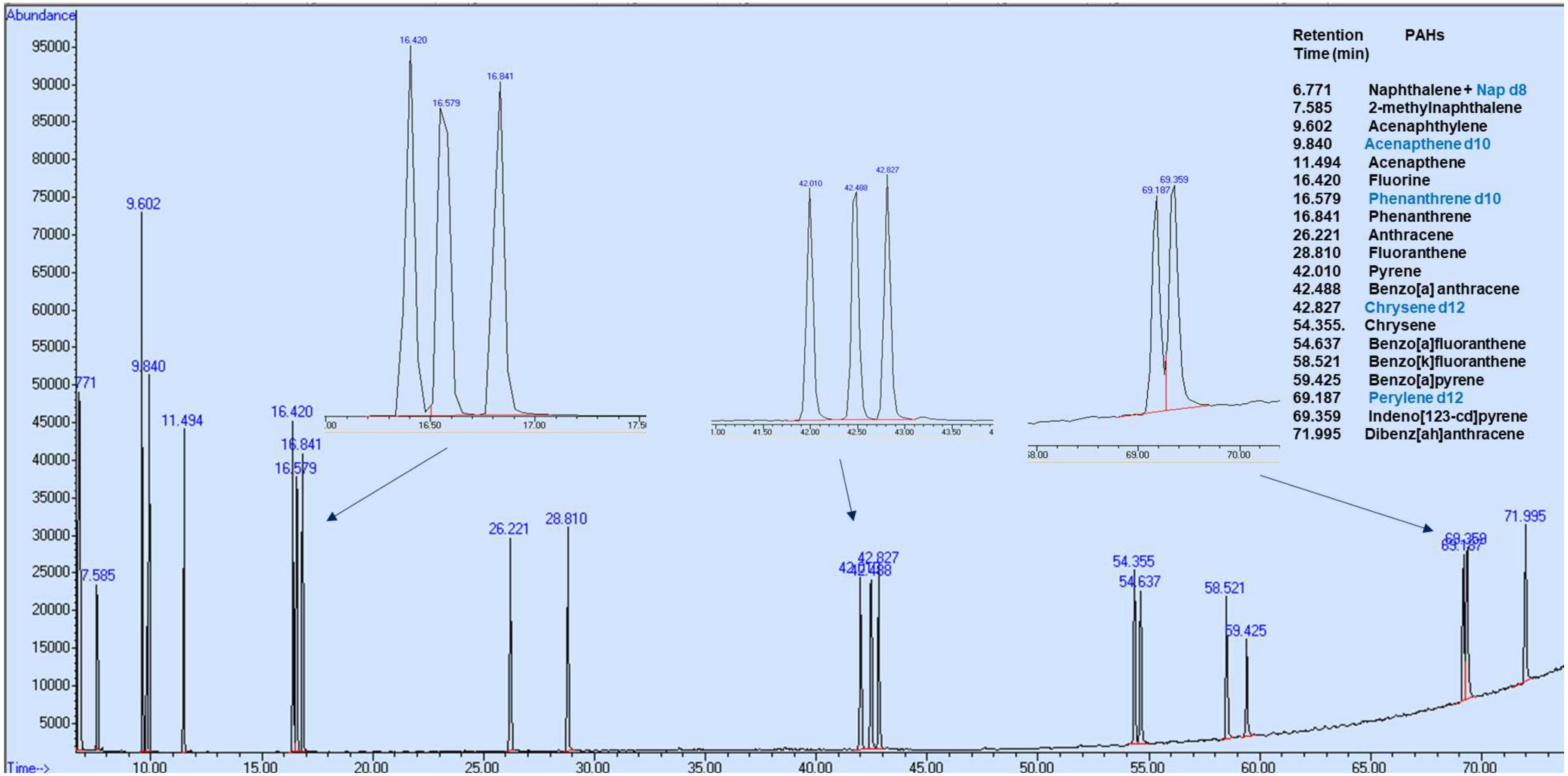
	TTU-A	SD	%RSD	TTU-H1	SD	%RSD	TTU-H2A	SD	%RSD	TTU-H2B	SD	%RSD	TTU-H3	SD	%RSD
Nap	0.21	0.000	0.2	*	*	*	12.01	0.281	2.3	13.01	0.502	3.9	1.71	0.008	0.5
2-mNap	0.59	0.000	0.0	*	*	*	3.82	0.090	2.3	3.89	0.036	0.9	1.08	0.002	0.2
Acy	0.99	0.001	0.1	*	*	*	2.71	0.005	0.2	2.56	0.076	3.0	1.42	0.001	0.1
Ace	*	*	*	-	-	-	*	*	*	*	*	*	0.9	0.001	0.1
Flu	-	-		-	-	-	3.39	0.014	0.4	2.93	0.233	8.0	1.91	0.001	0.0
Phe	*	*	*	-	-	-	2.78	0.073	2.6	2.62	0.081	3.1	0.87	0.008	0.9
Ant	*	*	*	-	-	-	2.79	0.394	14.1	3.34	0.275	8.2	1.48	0.003	0.2
FluAn	*	*	*	-	-	-	1.91	0.101	5.3	1.86	0.026	1.4	0.98	0.004	0.5
Pyr	*	*	*	-	-	-	2.49	0.074	3.0	2.32	0.084	3.6	5.59	0.011	0.2
Chr	-	-	-	-	-	-	0.48	0.008	1.7	0.45	0.014	3.1	0.46	0.002	0.4
BaF	-	-	-	-	-	-	0.16	0.004	2.4	0.2	0.021	10.7	-	-	-

MOMBASA URBAN SAMPLES

	MU-A	SD	%RSD	MU-H1	SD	%RSD	MU-H2A	SD	%RSD	MU-H2B	SD	%RSD	MU-H3	SD	%RSD
Nap	0.44	0.022	5.1	*	-	-	12.15	0.122	1.0	12.62	0.137	1.1	2.29	0.123	5.4
2-mNap	0.71	0.021	3.0	-	-	-	4.38	0.108	2.5	3.99	0.574	14.4	1.41	0.008	0.5
Acy	1.01	0.002	0.2	-	-	-	4.79	0.111	2.3	5.6	0.335	6.0	1.49	0.007	0.5
Ace	0.64	0.001	0.1	-	-	-	2.54	0.124	4.9	2.24	0.226	10.1	1.18	0.025	2.2
Flu	0.47	0.006	1.3	-	-	-	2.86	0.049	1.7	3.14	0.160	5.1	1.94	0.005	0.3
Phe	*	*	*	-	-	-	2.25	0.104	4.6	1.63	0.012	0.7	0.8	0.018	2.2
Ant	*	*	*	-	-	-	3.57	0.104	2.9	3.47	0.034	1.0	2.3	0.039	1.7
FluAn	*	*	*	-	-	-	1.32	0.042	3.2	1.07	0.013	1.2	0.79	0.001	0.1
Pyr	*	*	*	-	-	-	2.14	0.046	2.2	1.81	0.018	1.0	5.16	0.156	3.0
Chr	-	-	-	-	-	-	0.38	0.007	1.7	0.31	0.006	1.8	0.31	0.047	15.1
BaF	-	-	-	-	-	-	0.19	0.014	7.5	0.25	0.006	2.5	0.12	0.002	2.0

"*" indicates that the analyte was detected but was <LOQ

"-"means analyte was not detected



Retention Time (min)	PAHs
6.771	Naphthalene + Nap d8
7.585	2-methylnaphthalene
9.602	Acenaphthylene
9.840	Acenapthene d10
11.494	Acenapthene
16.420	Fluorine
16.579	Phenanthrene d10
16.841	Phenanthrene
26.221	Anthracene
28.810	Fluoranthene
42.010	Pyrene
42.488	Benzo[a] anthracene
42.827	Chrysene d12
54.355.	Chrysene
54.637	Benzo[a]fluoranthene
58.521	Benzo[k]fluoranthene
59.425	Benzo[a]pyrene
69.187	Perylene d12
69.359	Indeno[123-cd]pyrene
71.995	Dibenz[ah]anthracene

Fig. A4 Representative GC-MS-SIM chromatograms of PAHs and IS in a concentrated PASE extract (100 µL) from a spiked (100 ng PAHs onto trap to give 1 ng on column) PDMS trap. The IS mixture contained d8-naphthalene, d10-acenapthene, d10-phenanthrene, d12-chrysene and d12-perylene in toluene.

4.) Error bars have been added to **Fig 3** which is now illustrated as **Fig. A5** below:

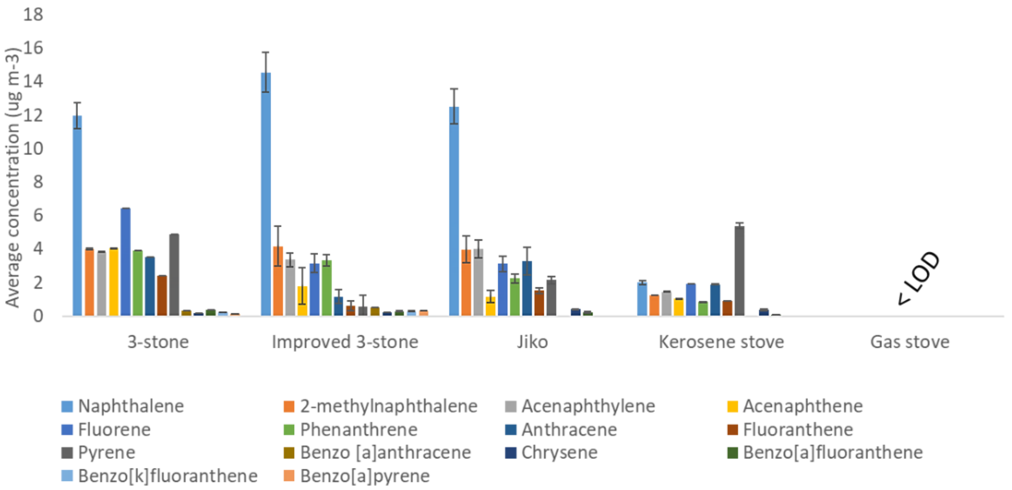


Fig A5: Average polycyclic aromatic hydrocarbon concentrations for various combustion devices. Ace = acenaphthene; Acy = acenaphthylene; Ant = anthracene; BaA = benzo[a]anthracene; BaF = benzo[a]fluoranthene; BaP = benzo[a]pyrene; BkF = benzo[k]fluoranthene; Chr = chrysene; Flu = fluorene; FluAn = fluoranthene; LOD = limit of detection; 2-mNap = 2-methylnaphthalene; Nap = naphthalene; Phe = phenanthrene; Pyr = pyrene. Error bars show standard deviations associated with mean concentration for each type of combustion device. Combustion devices included were 3-stone (n=4), improved 3-stone (n=2), Jiko (n=2) and kerosene stove (n=2), where n=number of devices.

5.) Calculation of TEQs/ BaPeq:

Table A9: Calculation of TEQs/BaPeq using concentrations from Taita Taveta rural household 1 (TTR-H1) as an example.

Compound	**[1]TEF**	**TTR-H1 (μg m^{-3})**	**[2]BaPeq/ TEQ**
Naphthalene	0.001	25.919	0.026
2-methylnaphthalene	0.001	6.149	0.006
Acenaphthylene	0.001	5.098	0.005
Acenaphthene	0.001	2.175	0.002
Fluorene	0.001	4.242	0.004
Phenanthrene	0.001	5.678	0.006
Anthracene	0.01	2.307	0.023
Fluoranthene	0.001	1.246	0.001
Pyrene	0.001	1.150	0.001
Benzo [a]anthracene	0.1	0.994	0.099
Chrysene	0.01	0.409	0.004
Benzo[a]fluoranthene	0.1	0.574	0.057
Benzo[k]fluoranthene	0.1	0.585	0.058
Benzo[a]pyrene	1	0.602	0.602
Total TEQ			0.894

[1] TEF = Toxic Equivalency Factors proposed by Nisbet & Lagoy (1992) [1]

[2] TEQs/BaPeq were used interchangeably in the text as explained under 'Toxic assessment of gaseous PAHs' in the article.

References

1. Nisbet IC, Lagoy PK. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul Toxicol Pharmacol,*1992 **16**: p. 290-300.