

Article

Volatile Organic Compound Composition of Urban Air in Nairobi, Kenya and Lagos, Nigeria

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Abstract: Sub-Saharan Africa is seeing rapid urbanization, with the population of cities such as Lagos and Nairobi growing at a rate of 3–4% a year. The region is extremely under-sampled for all air pollutants, particularly VOCs, which are useful markers for source apportionment as well as toxic in their own right. There are many contributors to air pollution in the region, and studies examining fine particulate pollution implicate traffic as the primary source in urban areas. In this pilot study, VOCs were analysed at a selection of roadside and urban background locations in Nairobi and Lagos, and 74 VOCs were quantified. GC×GC–MS/FID analysis revealed all locations were dominated by hydrocarbons typical of vehicle emissions, with the aromatic hydrocarbons benzene and toluene among the most abundant VOCs. Typical personal exposure scenarios for citizens of the cities were calculated to far exceed those of a resident in a city in Europe/US. Finally, the calculated ozone forming potential of the VOCs measured was found to be similarly high to other large cities studied with similar air pollution problems. Further study is therefore essential to determine the full extent of VOC pollution in the region and its impact on tropospheric chemistry.

Keywords: volatile organic compounds; sub-Saharan Africa; ambient air pollution

1. Introduction

There are a number of contributors to poor air quality in sub-Saharan Africa (SSA), of both biogenic and anthropogenic origin. Firstly, seasonal biomass burning in Africa contributes to approximately 40% of global biomass burning [1,2]. Secondly, Saharan dust can contribute to the global burden of aerosol and can be transported worldwide [3,4]. Finally, local traffic emissions can have a major detrimental impact on air quality [5], particularly in cities, through the emission of primary particulate matter (PM), oxides of nitrogen (NO_x, i.e., NO and NO₂) and volatile organic compounds (VOCs). In addition, windblown and traffic re-suspended dust as well as waste burning are also well-known

contributors to the urban pollution mix [6–9]. Increasing urban populations, poorly maintained vehicles, inadequate air quality regulations and air pollution control polices have resulted in increased air pollution in major African cities [10]. Added to this, urbanization rates in Africa are among the highest in the world, where more than half the population is expected to reside in urban areas by 2035 [11]. Landrigan et al., (2018) [12] in their review of pollution and health observed air pollution as an important causative agent of many non-communicable diseases including cancer, asthma and chronic obstructive pulmonary disease, thus posing a major human health problem and sustainable socio-economic and economic development issue. Exposure to ambient air pollution (AAP) is a major threat to human health in Africa, with data indicating that deaths owing to AAP exposure increased by 57% over the period 1990 to 2017. Exposure to air pollutants is also reported to decrease the life expectancy of African children by 2 years [13]. According to the WHO, in 2012, exposure to AAP in the SSA regions resulted in as many as 176,000 deaths [14]. Finally, according to a recent study on the Global Burden of Disease, air pollution has an attributable burden percentage of 10–15% in SSA countries [15].

On a local scale, in densely populated SSA cities like Nairobi in Kenya and Lagos in Nigeria the major sources of air pollution are industry, burning of waste and traffic [16–21], with as much as 90% of air pollution attributable to motor vehicle emissions [22]. Currently there are no official urban air quality monitoring sites in Kenya producing validated, publicly accessible data [10,23]. The full extent of the problem is therefore poorly understood, making safeguarding the population from poor air quality almost impossible. From the information that is available, there are numerous locations with raised pollution, particularly roadside locations [9]. Whilst some air quality monitoring exists in Nigeria [24–26] infrastructure is limited, and the problem of increasing urbanization and a lack of regulation of pollutant levels has resulted in extremely poor air quality [27].

Previous studies on air quality in SSA have mostly focused on particulate matter [8,28–30]. There have also been some studies on black carbon and NO_x [8,18,31,32]. Ambient NO_x in urban environments primarily results from traffic processes; however, a wide range of VOCs are also co-emitted from motor vehicle exhaust, and despite the importance of their contribution to air quality in urban environments they have only been measured in a handful of studies within the region [33,34].

VOCs emitted from vehicles comprise a complex mixture of hydrocarbons, including benzene, toluene, ethyl benzene and *o,m,p*-xylene, known collectively as BTEX compounds, which are particularly hazardous to human health [35–38]. Huang et al., (2020) [39] identified 102 different VOCs from both diesel and gasoline fuelled vehicles in Wuhan, China, including acetylene, alkenes, olefins, aromatic hydrocarbons and oxygenated VOCs. The study demonstrated differing proportions of the same VOCs between the two fuel types with higher concentrations of aromatic hydrocarbons in gasoline vehicles in comparison to diesel vehicles, with the higher proportion of aromatic hydrocarbons being the main contributor to the increase in octane in gasoline. The identity of specific emitted VOCs can also provide information on their source; for example, benzene is a key indicator of vehicle emissions [40]. In addition to the emissions of VOCs, vehicles also emit semi-volatile organic compounds (SVOCs), including polycyclic aromatic hydrocarbons (PAHs), e.g., naphthalene, which also have numerous detrimental health affects [41,42].

VOCs also originate from other anthropogenic sources, notably industrial emissions and biomass burning. Liu et al., (2019) [43] measured VOC profiles at an industrial park in China and found that aromatic VOCs contributed to the highest percentage of the total VOCs (46%), followed by oxygenated VOCs (41%), alkenes (10%) and nitrogen containing VOCs (3%). In contrast Huang et al., (2020) [39] found that the contributors of total VOCs from diesel vehicles were alkenes (29%), OVOCs (27%), aromatics (18%), halo-hydrocarbons (14%), olefins (8%) and ethylene (1%). VOC emissions from biomass burning have been monitored by Wang et al., (2014) [44] in China, with the dominant VOCs being attributed to OVOCs (49%), alkenes (21%), aromatics (13%), alkenes (10%) and halogenated VOCs (5%). In addition to having a range of primary impacts on human health and the

environment, VOCs can also be oxidized via reactions with OH radicals, NO₃ and Cl atoms to form aerosol particles, which also have a range of negative impacts on human health and the natural and built environments. Such secondary products include excess ground level ozone (O₃) and other condensable organic species that can contribute to ultrafine (UFP) and fine particulate matter [45]. This process is not well understood in tropical Africa, where photolysis can be expected to drive tropospheric chemistry, due to scarce information on gaseous pollutants. Whilst there have been a small number of studies on roadside VOCs in Nigeria, there is little information on VOC levels or identity in Kenya. Furthermore, those studies that have been conducted on ambient VOCs in Lagos are limited in their scope and report a wide range of concentrations. Baumbach et al., (1995) [33] measured mean benzene and toluene concentrations of 250 µg m⁻³ and 750 µg m⁻³, respectively, at a roadside location in Lagos, and Olajire and Azeez (2014) [34] observed benzene and toluene concentrations of 3 µg m⁻³ and 1.9 µg m⁻³, respectively, at an industrial estate in Lagos. In the same study, Olajire and Azeez (2014) [34] measured concentrations of only 3.4 µg m⁻³ of benzene and 1.5 µg m⁻³ of toluene in an area where the authors have stated has large amounts of congested traffic.

Many commonly occurring VOCs are contributors to adverse health effects in humans [46], causing symptoms ranging from irritation of the eyes and skin (e.g., formaldehyde, acetaldehyde, toluene, limonene, styrene and alpha-pinene), the exacerbation of chronic diseases such as asthma and cardiovascular disease (e.g., various aromatics) and the development of cancer (e.g., trichloroethylene, benzene and naphthalene) [47]. Exposure to BTEX VOCs can be particularly harmful, causing damage to lung, kidney and liver tissue [48]. For example, Rumchev et al., (2004) [49] determined that the risk of children developing asthma increases with benzene and toluene concentrations in the indoor environment. With respect to health risks associated with human exposure to BTEX VOCs from vehicle emissions, Dehghani et al., (2018) [50] calculated an inhalation lifetime cancer risk for benzene at a bus terminal in Iran, and their results showed that exposure levels exceeded the levels recommended by the US EPA and the WHO. This elevated cancer risk owing to human exposure to benzene in air was also determined in another study by Zhou et al., (2011) [51]. In addition, Hoxha et al., (2009) [52] indicated a link between the shortening of leukocyte telomere and the exposure of traffic related VOCs, and Sørensen et al., (2003) [53] indicated that the exposure to benzene can result in DNA base oxidation, thus implying that hot spots where concentrations of BTEX VOCs are high can result in increased health problems.

Owing to the lack of available data regarding VOC concentrations in SSA cities, the aim of this pilot study was to examine the VOC composition of air in the cities of Nairobi and Lagos, both roadside and in residential/background areas. Multi-dimensional chromatography was applied to the analysis, offering easier identification and quantitation of VOCs from such complex mixtures by virtue of its increased peak capacity [54,55]. Whilst the technique has been increasingly applied to atmospheric studies, this is the first time this powerful analytical tool has been applied to examine the complex mixture of VOCs present in the urban air of African megacities.

Using the concentrations of VOCs determined, the personal exposure potential of residents of both cities to the health relevant BTEX compounds is investigated and compared to that experienced in other cities, and the potential for ozone formation from the quantified VOCs is also examined.

2. Materials and Methods

2.1. Sample Collection Sites

Nairobi is situated south of the equator at 1.3° S, 36.9° E and at approximately 1600 m above sea level. It experiences frequent temperature inversions and mild pressure variations at around 826 hPa [32]. Nairobi is the capital of Kenya and is typical of the fast-growing cities of sub-Saharan Africa. The City of Nairobi had a resident population of 3.1 million in 2009 which increased to 4.4 million in 2019 [56] representing a growth of 4.2% per year. VOC samples were collected at four sites (three roadside and one urban background) northwest of the centre of Nairobi and at the outskirts of the Nairobi Central Business District (CBD) (see Table 1). Samples were collected during a one-week period in June 2019 to avoid the two rainy seasons (March to May and October to December) at two sampling time points per day, i.e., one between 07:30 and 08:30 and one between 16:30 and 17:30. Thus, a total of 12 samples were taken per day.

Table 1. Description and locations of sampling sites in Nairobi CBD, and Lagos.

Site Location	Code	Site Designation	Description	Coordinates (Lat/lon)
Nairobi				
Waiyaki Way	W1&2	Roadside	Four lane highway (in each direction) to Mombasa average 3400 cars/hour at sampling times	−1.28095, 36.81481 −1.28024, 36.81449
University Way	UR1&2	Roadside	Three lane highway (in each direction) running past university 2700 cars/hour at sampling times	−1.28151, 36.81595 −1.28116, 36.81670
Roundabout on Waiyaki Way	R	Roadside	Roundabout joining University Way and Waiyaki Way	−1.28144, 36.81509
University of Nairobi Campus	INS	Urban Background	200 m from University Way, 400 m from Waiyaki Way, >60 m from nearest minor road	−1.27805, 36.81764
Total	6			
Lagos				
Ogba	OGB 1&2	Urban background/residential	Residential area 20m from road with traffic of 800 vehicles/hour	6.62558, 3.33510
Ikeja	IKE1	Urban background/residential	Mainly residential area >25m from minor road with ~500 vehicles/hour	6.44600, 3.42389
	IKE2		Residential area >50m from four lane urban road traversing residential and commercial catchments with traffic of 1450 vehicles/hour	6.44371, 3.43208
Victoria Island	VIS1	Urban background/residential	Residential area >50m from road with ~800 vehicles/hour	6.43037, 3.43109
	VIS2		Residential area >50m from roundabout of two four lane roads	6.43072, 3.42497
University of Lagos	UNI	Urban Background	>25 m nearest road intersection of three urban roads beside a mini open market and abattoir with traffic of 1150 vehicles/hour	6.54659, 3.39620
Oshodi	OSH 1&2	Roadside/commercial	On major route Oshodi–Oworonshoki Express way. Bus Terminal and commercial activities. Traffic of about 2800 vehicles/hour.	6.55608, 3.35266 6.55426,

				3.36280
Iyana Ipaja	IYA 1&2	Roadside/commercial	Next to six lane highway linking Lagos Eastern suburbs to Lagos Island with traffic of more than 5400 vehicles/hour.	6.54524, 3.39910 6.54533, 3.39850
Mushin	MUS 1&2	Roadside	Four lane urban road traversing residential and commercial areas	6.52646, 3.35546
Obalende	OBA 1&2	Roadside/commercial	Four lane urban road linking Lagos Island and Victoria Island with traffic of 3800 vehicle/hour	6.44845, 3.40588
Ojota	OJO1&2	Roadside/commercial	Six lane busy inter-state exchange road with traffic of 5800 vehicles/hour and road with 3200 vehicles/hour	6.58721, 3.37997 6.58843, 3.37945
Yaba	YAB 1&2	Roadside/commercial	Road with traffic of 3200 vehicles/hour at peak period.	6.51169, 3.37097
Ojuelegba	OJU 1 &2	Roadside/commercial	Intersection for major four lane urban road with traffic of 4800 vehicle/hour	6.50980, 3.36422 6.50972, 3.36364
Total	22			

Lagos is the commercial capital of Nigeria and one of the most densely populated and fast-growing cities in the world, with an estimated population of over 14 million [57] and an estimated growth rate of 3.3% [11]. Eleven sampling locations were selected to represent roadside and commercial environments (i.e., those areas with a high concentration of businesses dealing in the sale of goods and/or services) as well as urban background/residential areas. In Lagos, there are two main seasons: the rainy season from April to October and the dry season from October to March. The sampling period was between November and December 2019 in the dry season, and a total of 22 samples from 11 locations were taken (see Table 1).

2.2. Sample Collection

One litre of air was actively sampled onto pre-conditioned (for 2.5 hours at 330 °C in 50 mL/min CP grade N2, BOC) Tenax/TA with Carbograph 1TD sorbent tubes (Hydrophobic, Markes International Ltd., Llantrisant, UK) using a battery-operated pump (Escort Pump, Sigma Aldrich), operated at 250 mL/min at a height of 1.5 m above the ground. Sampled tubes, along with field control blank tubes, were immediately capped after sampling (brass caps, Markes International Ltd., Llantrisant, UK) and were shipped back to the UK with cool packs for analyses by GC–MS within 2 months of collection (field blanks stored over this time showed total integrated peak areas within 10% of the total peak areas of newly conditioned tubes). Nairobi samples were run in a single batch over one week in July, and the Lagos samples in a single batch in January 2020.

2.3. Internal Standard Addition

An internal standard solution was prepared from toluene-d8 and phenanthrene-d10 certified reference solutions (Sigma Aldrich, Dorset, UK) and n-octane-d18 (D, 99% Cambridge Isotope Laboratories, Tewksbury, US) to give a final concentration of 20 µg/mL (in methanol) per analyte. Before analysis, the samples were loaded with the internal standard solution using the calibration solution loading rig (CSLR, Markes International Ltd., Llantrisant, UK). A 0.6 µL aliquot of internal standard solution was injected onto the tube in a stream of nitrogen at a flow rate of 100 mL/min for 2 min, purging the excess solvent.

2.4. TD-GC×GC–MS Quality Control

A reference solution used to monitor retention behaviour was prepared in methanol (SupraSolv grade, Sigma Aldrich, Dorset, UK) to give final concentrations of 10 µg/mL and 20 µg/mL for L C₈–C₂₀ saturated alkanes certified reference material (Sigma Aldrich, Dorset, UK) and aromatic calibration standard (NJDEP EPH 10/08 Rev.2, Thames Restek, Saunderton, UK), respectively.

The multi-component air standard mix used for calibration was also used as a performance monitoring solution (1 µL at 10 µg/mL). A sample of retention monitoring solution was run at the beginning of each ten-sample sequence (loaded onto sorbent tubes as described above) alongside a trap blank, system blank and field blank to monitor potential interference, and the final sample of the sequence was the multi-component standard mix.

2.5. Calibration Standards and Compound Identification

A 100 µg/mL multi component air standard (47537-U Sigma Aldrich, Dorset, UK, Certified Reference Material (CRM) produced and certified in accordance with ISO 17034 and ISO/IEC 17025) was used for quantitation and identification of 52 components (to Metabolomics Standards Initiative (MSI) level 1) [58]. This consisted of a mixture of alkanes, aromatic hydrocarbons, halogenated compounds, carbonyls, alcohols, esters and terpenes commonly found in air. The solution was diluted in methanol to give final concentrations of 100, 50, 25, 10, 5, 2.5, 1 and 0.5 µg/mL. Standards (1 µL) were loaded into sorbent tubes into a stream of N₂ (zero grade, BOC) at 100 mL/min and purged for 2 minutes. FID data was used for compound quantitation of the 52 VOCs.

The retention monitoring mixture was also used to confirm the identities (to MSI level 1) of the alkanes and aromatic hydrocarbon absent in the multicomponent air standard (acenaphthene, acenaphthylene, eicosane, fluorene, heptadecane, naphthalene, nonadecane, octadecane, phenanthrene, pyrene). For these compounds, a response factor from the retention monitoring solution was used.

The additional compounds quantified that were not present in either standard (benzophenone; butane, 2,2-dimethyl-; butane, 2-methyl-; cyclohexane, methyl-; cyclopentane, methyl-; cyclopropane; 1,2-dimethyl-, trans-; dibenzofuran; hexane, 2 methyl-; hexane, 3-methyl-; naphthalene, 1-methyl-; naphthalene, 2-methyl-; pentane; pentane, 2-methyl- and pentane, 3-methyl-) were identified using library matching (MSI level 2) and their chromatographic location. Quantitation was carried out using the calibration data for the closest eluting proxy.

2.6. TD-GC–MS Analysis

Analysis by two-dimensional gas chromatography was carried out on an Agilent 7890 A gas chromatogram, with a G3486 A CFT flow modulator and three-way splitter plate coupled to a flame ionization detector and a HES 5977B quadrupole mass spectrometer with electron ionization (Agilent Technologies Ltd., Stockport, UK). Full details of the method and performance are given in Wilde et al., (2019) [59]. The column configuration was an Rxi-5Sil MS 30 m × 0.25 mm × 0.25 µm primary column (Thames Restek Ltd., Saunderton, UK) and a DB-WAX 4 m × 0.25 mm × 0.25 µm as the secondary column (Agilent Technologies Ltd., Stockport, UK). Helium (N6.0 BOC) was used as the carrier gas with the primary and secondary column flow rates of 0.6 and 23 mL/min, respectively. The modulation period was set to 3 s, with a fill and flush time of 2.799 s and 0.201 s, respectively. The restrictor from the first outlet port of the splitter plate to the flame ionization detector (FID) was 1.2 m × 0.25 mm deactivated fused silica, with a constant flow of 23 mL/min, and the restrictor from the splitter plate to the qMS was 0.76 m × 0.10 mm deactivated fused silica. The FID heater was set to 250 °C, and the make-up gas was nitrogen at 25 mL/min, with an air flow rate of 400 mL/min and 35 mL/min of hydrogen from a Peak Scientific hydrogen generator (Trace hydrogen, Peak Scientific Instruments Ltd., Inchinnan, UK). The FID collected data at 100 Hz. The transfer line to the qMS was kept

at 250 °C and the ion source and quadrupole at 230 °C and at 150 °C, respectively. The mass scan range was m/z 40–300 at 10,000 μs^{-1} , giving an acquisition rate of 21.5 Hz. The oven was programmed from 30 °C, held for 5 min, then heated to 80 °C at 3 °C/min, then at 5 °C/min to 250 °C and held for 10 min. Between each run a bake-out method was performed, the primary column flow was increased to 1.5 mL/min and the oven was held at 250 °C for 30 min.

The GC×GC was interfaced with a Markes TD-100xr thermal desorption autosampler (Markes International Ltd., Llantrisant, UK). Tubes were pre-purged with carrier gas for 1 min at 50 mL/min and then desorbed at 300 °C for 5 min with a flow of 50 mL/min onto a “hydrophobic general” trap (Markes International Ltd., Llantrisant, UK) held at −10 °C. The trap was then purged for 2 min at 2 mL/min before being heated at the maximum heating rate to 300 °C for 5 min with a split flow rate of 2 mL/min. Between each sample tube, a bake-out method was performed, which involved an empty tube (no sorbent) being loaded by the autosampler. Data was acquired in MassHunter GC–MS Acquisition B.07.04.2260 (Agilent Technologies Ltd., Stockport, UK) and the data processed using GC Image™ v2.6 along with Project and Image Investigator (JSB Ltd., Horsham, UK).

3. Results

3.1. Urban Air Visualization

Initial observation of the chromatograms obtained showed an extremely complex and chemically diverse mixture of VOCs for all locations, particularly in the roadside samples, an example of which can be seen in Figure 1 showing a GC×GC chromatogram of a roadside location in Nairobi. Multi-dimensional chromatography facilitates easier identification and quantitation of VOCs from such complex mixtures by virtue of its increased peak capacity [54,55]. The nature of GC×GC allows characterization of a sample by the regions in which compounds are eluting, as each region has a defined boiling point and polarity. The samples collected were dominated by the presence of large concentrations of aromatic compounds including several PAHs, and in particularly high concentrations, toluene and benzene followed by the C₈ and C₉ aromatics hydrocarbons. A complex mixture of many aliphatic hydrocarbons was also detected, with a clear n-alkane series present alongside a multitude of other unsaturated and branched hydrocarbons. This profile is typical of that seen at roadside locations [60,61] that are dominated by fresh vehicle emissions. Urban background sites within both cities were also dominated by the same VOCs despite the sampling sites being ≥ 20 m away from the roadside.

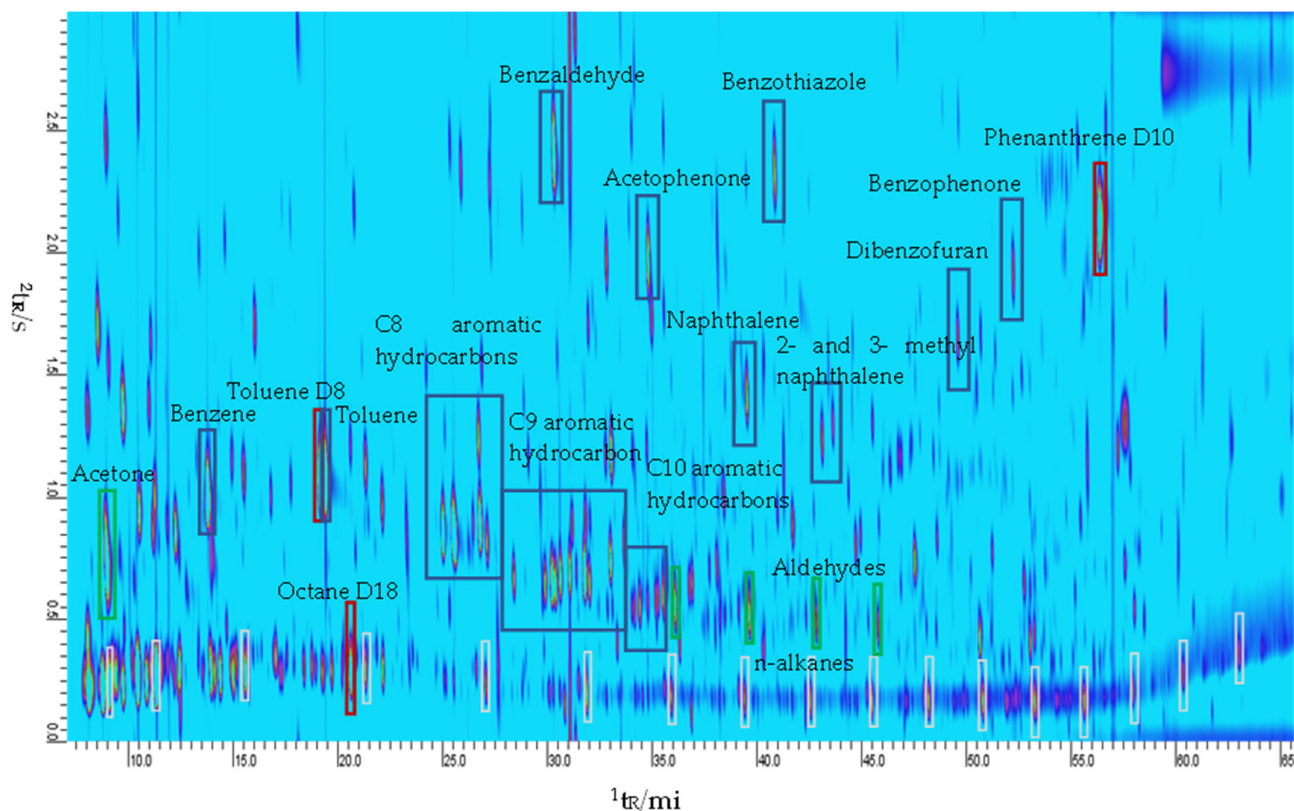


Figure 1. GCxGC-FID chromatogram of a roadside sample from Nairobi highlighting the dominant compounds observed in all samples. Added deuterated internal standards are shown in red boxes.

3.2. Total VOC by Site

Total VOC (TVOC) is a useful measurement to assess the overall contribution of VOCs to air quality across locations [62] and is defined in this study as the sum of the 74 definitively identified and quantified VOCs. An increasing TVOC was observed across the sites in Nairobi corresponding to the proximity to increasing traffic volumes (Figure 2). The roundabout on the Waiyaki Way and University Way is a particular VOC hotspot in the area; multiple lanes of traffic slow and queues form approaching the junction before vehicles accelerate away, and in doing so emit high levels of VOCs. TVOC levels drop significantly at the Institute of Nuclear Science and Technology (INS) building site measured 500 m from the junction, with average roadside levels being over a factor of 3 or higher.

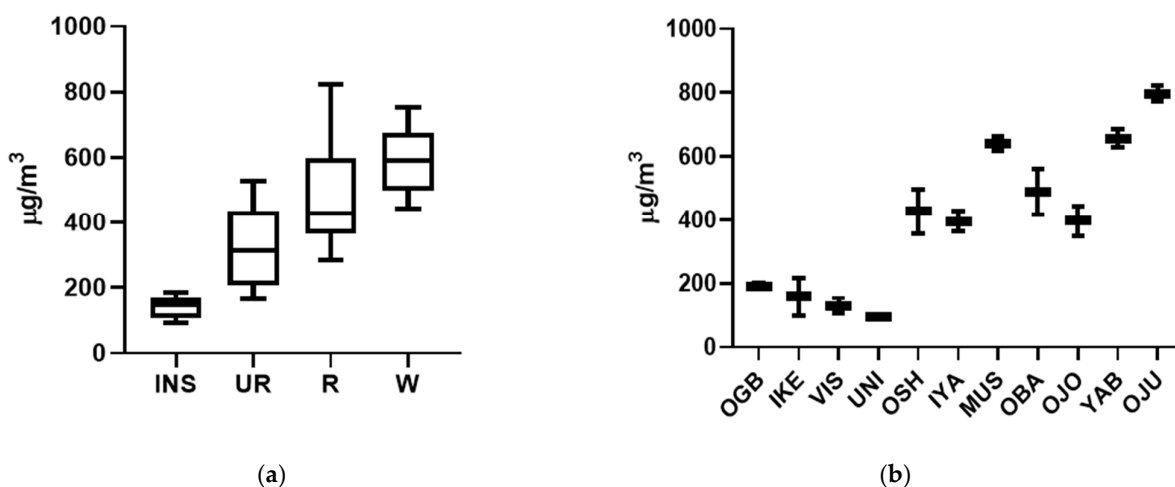


Figure 2. Concentration of TVOCs measured at individual sites in (a) Nairobi and (b) Lagos. Location name key can be found in Table 1.

Similarly, in Lagos, averaged roadside levels were more than a factor of 3 higher than the urban background locations (Figure 2). The mean roadside site TVOC level of $543 \pm 158 \mu\text{g}/\text{m}^3$ in Lagos was not significantly different ($p > 0.05$) from the averaged roadside site TVOC level in Nairobi, which was found to be $462 \pm 247 \mu\text{g}/\text{m}^3$. The average urban background TVOC levels were very similar between Lagos and Nairobi, at $143 \pm 51 \mu\text{g}/\text{m}^3$ and $142 \pm 34 \mu\text{g}/\text{m}^3$, respectively. Measurements were only made on a single day for each site in Lagos, explaining the reduced intra-site variation.

Ojuelegba had the highest TVOC concentration of all sites studied, at $800 \mu\text{g}/\text{m}^3$, most likely owing to its proximity to a major intersection of a main route (A1) out of the city and is one of the key transport nodes of Lagos that connects the city's mainland to Lagos Island. It also has a very high population density, high commerce and pockets of industrial activity. Mushin and Yaba had the next total highest VOC levels. Mushin is largely a congested residential area with high levels of commercial activities coupled with poor sanitary condition and lies at the intersection of major roads from Lagos, Shomolu and Ikeja. Yaba has one of the busiest market sites in Lagos and is a major transport hub. TVOC at Iyana Ipaja, Obalende, Ojoto and Oshodi ranged between 395 and $488 \mu\text{g}/\text{m}^3$, with these sites representing busy commercial areas with relatively high volumes of traffic, dumpsites and regular burning of refuse, particularly at the Olusosun refuse dump in Ojota. Oshodi has industrial activities and major motor parks (transportation hubs) contributing to the TVOC concentration. The four urban background sites were in quieter residential areas, away from major traffic routes, and have TVOC concentrations substantially lower, in the range of 95 – $191 \mu\text{g}/\text{m}^3$.

TVOC concentrations recorded in both cities were substantially higher than those normally recorded at European roadside locations, e.g., Ghent street = $54 \mu\text{g}/\text{m}^3$ [62], but in a similar range to roadside locations in cities in more developing countries, e.g., Hanoi, Vietnam = $507 \mu\text{g}/\text{m}^3$; Addis Ababa, Ethiopia = $318 \mu\text{g}/\text{m}^3$ [62]; and Delhi, India = 241 – $734 \mu\text{g}/\text{m}^3$ [63]. Whilst the measurement of TVOC allows an overall understanding of VOC pollution at a particular site, more detailed classification of the VOC composition is necessary to understand the potential detrimental health impacts.

3.3. Relative contribution TVOC

Despite having much lower TVOC concentrations at the urban background sites compared to roadside, the composition by chemical class was very similar for each given location (Figure 3). The ambient VOC loading at each location monitored for both cities

was dominated by hydrocarbons (57.1–7.1%) and aromatics (16.8–35.4%), demonstrating the ubiquitous significance of traffic emissions across the cities. The urban background site in Nairobi had a higher non-alcohol oxygenate contribution (13.3% compared to 3.9%) and slightly lower aromatic fraction (25.7% compared to 32.6%) than the nearby roadside locations, suggesting a higher contribution from non-traffic sources. A similar trend was seen at the Lagos urban background sites; the notable difference between the two cities is the presence of a considerable alcohol fraction observed in the Lagos air samples (6.2%), which was substantially less in the Nairobi samples (0.8%). Very few terpenes were seen in any of the Nairobi samples (all <0.3%) or in most of the Lagos samples (<0.5%). Mushin, Iyana Ipaja, Obalende and Ojota were the exception, where terpenes made up 4.1, 0.8, 1.2 and 1.5% of the total VOC pool, respectively.

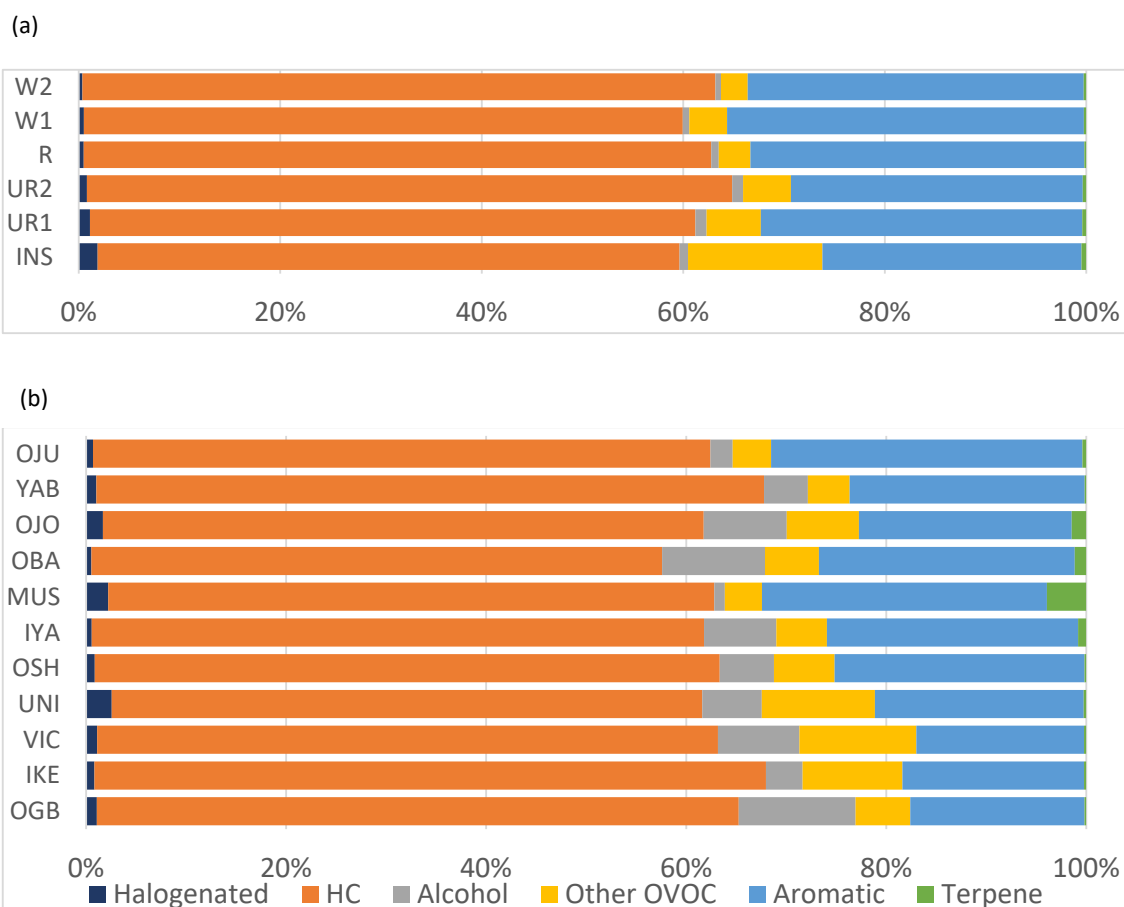


Figure 3. Total VOCs composition by chemical class across all measurement sites in (a) Nairobi and (b) Lagos.

3.4. Quantification of VOC Pollutants in air

Figure 3 shows that roadside sites in both cities were dominated by saturated aliphatic hydrocarbons. Speciation of the fraction (Table 2) showed that the n-alkanes pentane and hexane were the most abundant VOCs, followed by 2-methyl butane and 2-methyl pentane. It is worth noting that the selected sorbent was not capable of trapping hydrocarbons lighter than pentane, so their detection was not possible in this study by the analytics used. However, their presence in substantial quantities in roadside air, as well as in combustive emissions from industrial sites, has been shown previously [64,65]. The dominant aromatics (the second largest contributing class) observed at all locations were toluene followed by benzene with lower, but still substantial, levels of xylenes, trimethyl

benzene isomers, ethylbenzene and ethyltoluene isomers. Both aliphatic and aromatic hydrocarbons are produced from diesel and petrol vehicles and are present in both exhaust and evaporative fuel emissions and are also formed during the incineration/electrification of biogas [62,64,66,67].

Table 2. Target VOCs averaged (\pm standard deviation) across urban background (UB) and roadside (RS) sites in Nairobi and Lagos, coloured by maximal value per sample group.

	Concentration ($\mu\text{g}\text{m}^{-3}$)			
	Nairobi		Lagos	
	Roadside ($\mu\text{g}\text{m}^{-3}$)	Urban Background ($\mu\text{g}\text{m}^{-3}$)	Roadside/commercial ($\mu\text{g}\text{m}^{-3}$)	Urban Background ($\mu\text{g}\text{m}^{-3}$)
1,2-dichloro propane	ND	ND	ND	ND
1-butanol	ND	ND	ND	ND
1-propanol	ND	ND	0.75 \pm 1.22	0.31 \pm 0.24
2-butanone	2.77 \pm 0.28	2.30 \pm 0.29	12.24 \pm 4.54	2.31 \pm 1.21
2-ethyltoluene	2.76 \pm 1.08	0.37 \pm 0.17	2.70 \pm 1.85	0.24 \pm 0.16
2-propanol	0.06 \pm 0.02	ND	ND	ND
3-ethyltoluene	8.87 \pm 3.60	0.91 \pm 0.39	7.77 \pm 4.43	1.14 \pm 0.51
4-ethyltoluene	1.89 \pm 0.74	0.31 \pm 0.13	2.94 \pm 1.87	0.47 \pm 0.30
4-methyl-2-pentanone	0.44 \pm 0.22	0.20 \pm 0.03	ND	ND
Acenaphthene	0.06 \pm 0.01	0.06 \pm 0.14	0.03 \pm 0.02	0.01 \pm 0.01
Acenaphthylene	0.09 \pm 0.07	0.02 \pm 0.06	0.06 \pm 0.04	0.01 \pm 0.00
Acetone	9.39 \pm 0.88	10.4 \pm 1.59	5.34 \pm 2.35	3.95 \pm 1.83
Alpha pinene	0.33 \pm 0.11	0.1 \pm 0.17	0.12 \pm 0.08	0.05 \pm 0.01
Benzene	21.60 \pm 7.09	4.95 \pm 1.74	24.23 \pm 7.29	4.20 \pm 2.20
Benzene, 1,2,3-trimethyl-	3.77 \pm 1.53	0.38 \pm 0.25	2.27 \pm 1.65	0.18 \pm 0.13
Benzene, 1,2,4-trimethyl-	12.24 \pm 5.02	1.22 \pm 0.58	9.17 \pm 5.26	1.03 \pm 0.65
Benzene, 1,3,5-trimethyl-	3.03 \pm 1.19	0.31 \pm 0.18	2.74 \pm 1.98	0.26 \pm 0.16
Benzene, 1,4-dichloro-	0.74 \pm 0.42	1.03 \pm 0.78	0.29 \pm 0.20	0.14 \pm 0.19
Benzophenone	0.51 \pm 0.07	0.45 \pm 0.20	0.33 \pm 0.34	0.27 \pm 0.22
Beta pinene	0.44 \pm 0.10	0.20 \pm 0.15	ND	ND
Butane, 2,2-dimethyl-	8.13 \pm 2.88	0.82 \pm 0.44	12.88 \pm 8.80	12.73 \pm 13.29
Butane, 2-methyl-	39.89 \pm 11.52	4.34 \pm 1.95	53.15 \pm 13.78	15.38 \pm 6.15
Butyl acetate	ND	ND	ND	ND
Carbon tetrachloride	ND	ND	ND	ND
Chloroform	ND	ND	ND	ND
Cyclohexane, methyl-	2.75 \pm 1.14	0.25 \pm 0.16	5.22 \pm 2.78	0.74 \pm 0.36
Cyclopentane, methyl-	7.54 \pm 2.95	1.48 \pm 1.00	27.69 \pm 13.15	4.26 \pm 2.15
Cyclopropane, 1,2-dimethyl-, trans-	6.99 \pm 2.27	0.56 \pm 0.49	10.13 \pm 7.79	0.48 \pm 0.22
Decanal	2.00 \pm 0.53	2.30 \pm 1.05	1.90 \pm 0.33	1.66 \pm 0.43
Decane	1.61 \pm 0.21	1.02 \pm 0.25	1.90 \pm 0.33	1.66 \pm 0.43
Dibenzofuran	0.17 \pm 0.05	0.45 \pm 0.49	0.13 \pm 0.09	0.05 \pm 0.03
Dodecane	0.92 \pm 0.16	0.27 \pm 0.10	1.25 \pm 1.18	0.25 \pm 0.10
Durene	1.61 \pm 0.64	0.15 \pm 0.09	0.63 \pm 0.54	0.01 \pm 0.02
Eicosane	0.38 \pm 0.10	0.27 \pm 0.28	0.10 \pm 0.06	0.04 \pm 0.05
Ethane, 1,1,1-trichloro	ND	ND	ND	ND
Ethane, 1,2-dichloro-	ND	ND	1.04 \pm 0.59	0.52 \pm 0.19
Ethanol	3.59 \pm 4.60	1.18 \pm 0.11	26.19 \pm 22.43	10.76 \pm 12.96
Ethyl acetate	ND	ND	3.22 \pm 2.40	2.45 \pm 1.58

Ethylbenzene	8.38 ± 3.25	1.10 ± 0.64	15.13 ± 6.71	1.84 ± 1.13
Fluorene	0.03 ± 0.04	0.09 ± 0.22	0.04 ± 0.02	0.01 ± 0.00
Heptadecane	2.90 ± 0.51	2.08 ± 0.95	0.27 ± 0.15	0.07 ± 0.04
Heptane	9.34 ± 3.89	1.06 ± 0.50	12.67 ± 6.61	1.74 ± 0.75
Hexadecane	2.01 ± 0.45	1.00 ± 0.34	0.33 ± 0.19	0.08 ± 0.05
Hexane	70.09 ± 22.46	36.48 ± 9.74	57.27 ± 22.16	10.81 ± 4.15
Hexane, 2 methyl-	11.37 ± 3.82	1.26 ± 0.39	5.87 ± 2.93	1.18 ± 0.49
Hexane, 3-methyl-	8.07 ± 3.30	0.68 ± 0.41	0.92 ± 0.46	0.13 ± 0.06
Limonene	0.47 ± 0.10	0.37 ± 0.11	6.24 ± 8.72	0.24 ± 0.15
m/p-xylene	14.73 ± 5.88	1.66 ± 1.06	25.01 ± 11.96	4.26 ± 1.71
Methane, dibromochloro-	ND	ND	ND	ND
Methylene chloride	0.05 ± 0.02	ND	4.26 ± 5.81	0.99 ± 0.78
Naphthalene	1.51 ± 0.48	0.64 ± 0.31	3.6 ± 1.49	0.83 ± 0.54
Naphthalene, 1-methyl-	0.48 ± 0.13	0.38 ± 0.30	0.49 ± 0.27	0.07 ± 0.02
Naphthalene, 2-methyl-	0.33 ± 0.08	0.23 ± 0.14	0.95 ± 1.15	0.18 ± 0.11
Nonadecane	0.77 ± 0.19	0.53 ± 0.37	0.07 ± 0.04	0.02 ± 0.03
Nonanal	1.85 ± 0.35	2.98 ± 2.45	2.92 ± 1.51	2.32 ± 1.81
Nonane	0.85 ± 0.22	0.37 ± 0.24	4.54 ± 2.72	1.24 ± 0.25
Octadecane	1.42 ± 0.29	1.01 ± 0.54	0.17 ± 0.09	0.05 ± 0.04
Octane	2.06 ± 0.78	0.55 ± 0.21	5.76 ± 3.27	0.94 ± 0.28
o-xylene	10.72 ± 4.33	1.15 ± 0.72	8.86 ± 5.08	1.54 ± 0.47
pentadecane	1.39 ± 0.38	0.43 ± 0.12	0.53 ± 0.49	0.09 ± 0.04
Pentane	54.18 ± 16.86	7.29 ± 3.03	90.38 ± 17.69	32.93 ± 11.8
Pentane, 2,2,4-trimethyl-	7.55 ± 3.24	0.51 ± 0.20	1.79 ± 0.97	0.32 ± 0.10
Pentane, 2,4-dimethyl-	ND	ND	ND	ND
Pentane, 2-methyl-	33.37 ± 9.14	17.94 ± 18.01	10.36 ± 4.40	1.73 ± 0.77
Pentane, 3-methyl-	10.39 ± 3.84	1.14 ± 0.61	28.18 ± 14.11	4.03 ± 1.80
Phenanthrene	14.67 ± 0.62	0.02 ± 0.02	0.24 ± 0.15	0.09 ± 0.05
Pyrene	0.18 ± 0.09	0.23 ± 0.32	0.07 ± 0.02	0.03 ± 0.01
Styrene	2.18 ± 0.75	0.54 ± 0.28	3.05 ± 2.16	0.36 ± 0.32
Tetrachloroethylene	ND	ND	0.33 ± 0.60	0.16 ± 0.05
Tetradecane	1.25 ± 0.27	0.48 ± 0.14	0.55 ± 0.66	0.02 ± 0.03
Toluene	44.5 ± 17.14	5.94 ± 3.86	32.89 ± 8.27	9.10 ± 3.40
Trichloroethylene	2.00 ± 0.26	1.64 ± 0.25	ND	ND
Tridecane	1.00 ± 0.20	0.32 ± 0.08	1.17 ± 1.05	0.17 ± 0.06
Undecane	1.24 ± 0.21	0.5 ± 0.20	1.77 ± 2.03	0.14 ± 0.20

The exact composition of VOC emissions from vehicles is dependent on a number of factors, including the age of the vehicles, the way in which they are driven and maintained and the type and quality of fuel used. In developing countries such as Kenya and Nigeria, vehicles tend to be older and have fewer modern adaptations such as catalytic converters [68,69]. Old cars are often shipped to Africa from Europe [70], leading to higher VOC pollution for a given traffic volume.

Oxygenate concentrations were more variable between the cities. Acetone ($9.3 \mu\text{g}\cdot\text{m}^{-3}$) was the most prominent OVOC at Nairobi roadside locations (compared to $5.3 \mu\text{g}\cdot\text{m}^{-3}$ Lagos $\mu\text{g}\cdot\text{m}^{-3}$), whereas ethanol was the highest OVOC in Lagos, at $26.2 \mu\text{g}\cdot\text{m}^{-3}$, but considerably lower in Nairobi, at $3.6 \mu\text{g}\cdot\text{m}^{-3}$. Anthropogenic sources of acetone include vehicular emissions and secondary production by the oxidation of anthropogenic hydrocarbons; however, the levels were not significantly raised in the measurements taken later in the day, as primary emissions would appear to dominate. Solvent use, biomass burning and vegetation can also contribute [71–73].

Ethanol, the most abundant OVOC in Lagos, has multiple sources, including vegetation, biomass combustion and release from various industrial processes, and there are several ethanol distilleries in the city [74] which are known local sources of ethanol [75]. Ethanol is also increasingly being used as a biofuel across the globe [76]. Whilst there are plans to introduce a proportion of ethanol into fuel in Lagos [77], this has not yet been implemented. There also exists a scheme to replace solid fuel cookers in homes with ethanol burning, which could also be a potential source [78]. 2-butanone was also abundant in Lagos roadside air, found at concentrations of $12.2 \mu\text{g m}^{-3}$, compared to 2.3 in residential areas, the most likely source of which is car exhaust butane oxidation [79]; however, this large increase from urban background was not seen in Nairobi ($2.8 \mu\text{g m}^{-3}$ roadside, $2.3 \mu\text{g m}^{-3}$ urban background).

Limonene was responsible for the higher terpene levels measured in Mushin; as biogenic sources are unlikely in this area, other potential sources include various industrial processes, where it is becoming increasingly used as a “green alternative” industrial solvent [80].

The VOCs measured at the urban background sites in both cities were still dominated by the vehicle-derived pentane, hexane, methyl butane and methyl pentane, as well as the aromatics, benzene and toluene. Acetone was the next highest contributor and had a larger contribution to TVOC in the urban background locations than roadside. It was higher in absolute concentration in Nairobi urban background compared to roadside ($10.4 \mu\text{g m}^{-3}$ compared to $9.4 \mu\text{g m}^{-3}$), and only slightly lower at the Lagos urban background sites ($5.3 \mu\text{g m}^{-3}$ compared to $4.0 \mu\text{g m}^{-3}$), suggesting that traffic is not major source. Ethanol was lower in absolute concentration in the urban background ($10.8 \mu\text{g m}^{-3}$ vs. $26.2 \mu\text{g m}^{-3}$) in Lagos but on average had a higher contribution to TVOC of 7.1% (range 5.9–11.6%), compared to 5.4% (range 1.0–10.2%) at the roadside.

The ratio of toluene to benzene (T:B) can be a useful indicator of emission age, owing to the shorter tropospheric lifetime of toluene compared to benzene (ca. 225 h for benzene, 50 h for toluene [81]; as the distance from the emission source increases, the T:B decreases. This is reflected in the ratios measured across the sites in Nairobi (Figure 4); a decrease in ratio was seen as the sampling moved away from the road sites to the urban background site, as can be seen in Figure 4 (range of T:B was 2.4–2). In Lagos, the opposite trend was observed (T:B 1.31), which was potentially caused by alternative sources of toluene further from roads, such as industrial emissions. The ranges for the ratios were similar to those reported previously, with ratios between 0.36 and 3 measured in several Chinese cities [60,65,82], 3.22 in Antwerp, Belgium [83] and values of 2.92 to 3.91 in Canadian cities [84], over similar geographic scales.

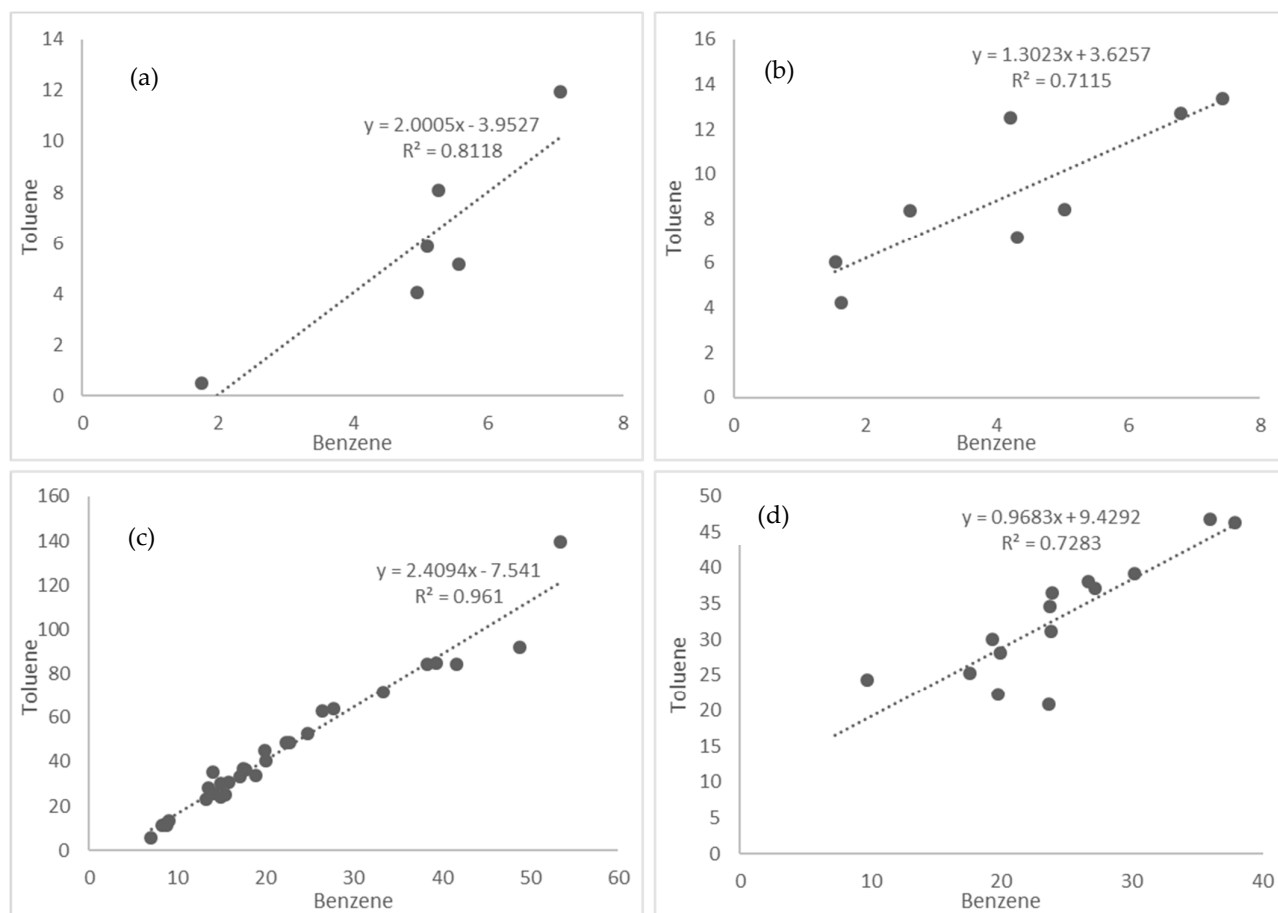
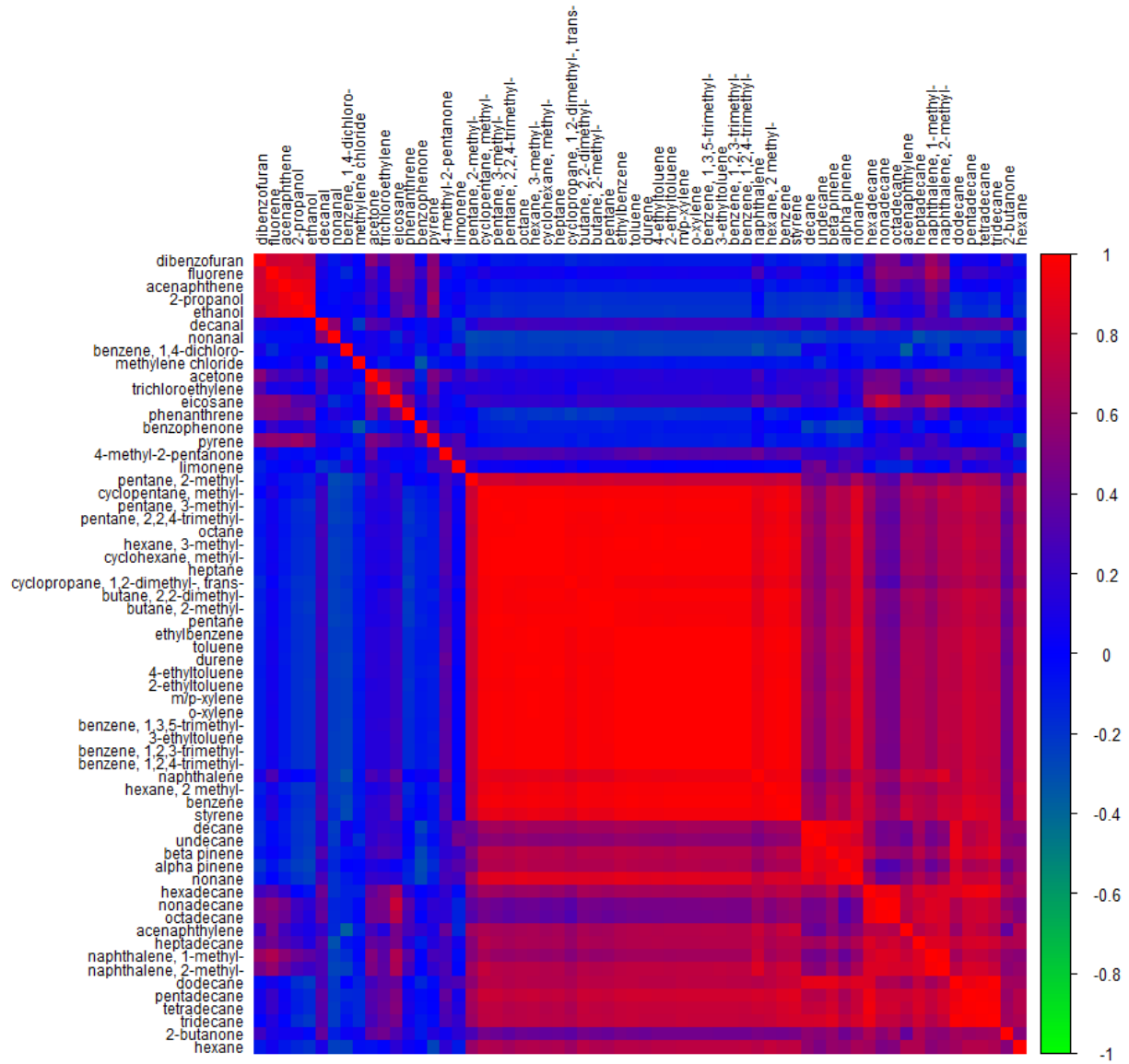


Figure 4. Ratio of toluene to benzene measurements at (a) urban background site, Nairobi; (b) urban background/residential sites, Lagos; (c) roadside, Nairobi; and (d) roadside, Lagos.

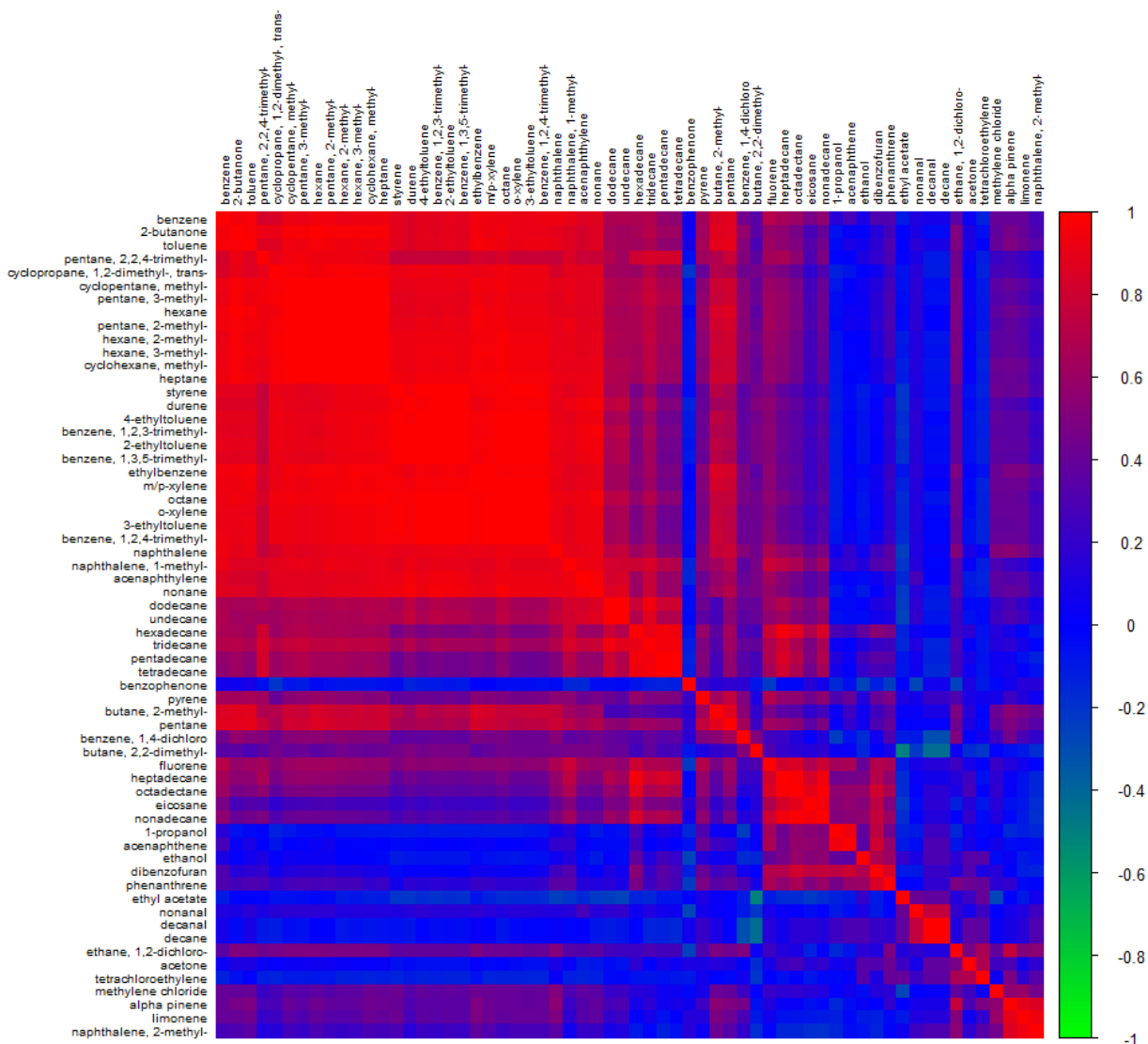
The overall lower T:B ratio values recorded in Lagos possibly result from the greater fraction of diesel vehicles in the city compared to Nairobi and hence greater contributions from diesel combustion emissions, as the car fleet in west Africa is dominated by vehicles with diesel engines [31]. Diesel engines are known to produce lower T:B ratios than petrol equivalents, particularly for older vehicles with worn and high millage engines, such as those found in many developing cities [68,85]. Both pollutants have alternate sources; benzene has a considerable contribution from domestic biomass burning, which could explain the raised background levels in Nairobi, and industry-sourced toluene the background level in Lagos.

3.5. Classification of Sources of VOCs

By examining correlations between concentrations of different VOCs, information can be determined regarding sources of the pollutants, with strong positive correlations being indicative of common sources [86] and weak correlations being associated with different or multiple emission sources [87]. Figure 5 shows the correlation between the quantified VOCs across all sample sites in (a) Nairobi and (b) Lagos to determine common atmospheric sources. It has been previously reported that good correlations between the aromatic species can be found in areas where traffic is the dominant source [88]. Indeed, the largest cluster of high correlations for both cities is seen for the aromatics, alongside the smaller alkanes. Additionally, part of this cluster, albeit with weaker correlations, are the larger $\geq C_{10}$ n-alkanes and butanone.



(a)



(b)

Figure 5. Pearson correlation coefficients for target VOCs measured that were above LOD in (a) Nairobi air and (b) Lagos air, displayed with hierarchical clustering.

In Nairobi air, a smaller cluster with strong correlations was seen for pyrene and some other PAHs, which had little correlation with the vehicle exhaust VOCs, so these were likely derived from other sources, such as biomass burning and solid waste combustion. Acetone could also be seen to have some correlation within this cluster and has also been documented to be present in biomass burning emissions [89]. Furthermore, there was moderate correlation with some of the larger alkanes and methyl naphthalenes, which are also products of combustion [90].

In Lagos, ethanol was clustered with larger alkanes and had a moderate strength correlation with PAHs (>0.6) but had poor correlation with the vehicle emission cluster of aromatics and small alkanes, this suggesting an alternative combustion source than vehicle emission. Acetone in Lagos had no correlation with roadside emissions, suggesting alternate sources most likely of industrial origin.

3.6. Ozone Forming Potential

In the presence of sunlight, the reactions of VOCs and NO_x emitted from vehicle exhausts can form ozone, which has the potential to have significant detrimental effects on health [91,92]. The ozone forming potential (OFP) of the targeted VOCs monitored at the roadside, commercial and urban background sites in Nairobi and Lagos (Table 2) was calculated and can be seen in Table 3. Calculations were made using the following determination:

$$OFP (\mu\text{gm}^{-3}) = MIR (\text{g O}_3/\text{g VOC}) * \text{concentration of VOC } (\mu\text{gm}^{-3})$$

where maximum incremental reactivity (MIR) is defined as the maximum amount of ozone formed per unit of VOC added to a system [93].

The total OFPs for the roadside locations in both Nairobi and Lagos were 1055.4 μgm^{-3} and 1184.1 μgm^{-3} , respectively, and were larger than their respective background sites, by a factor of 5.3 and 4.8, respectively. Individually, aromatic compounds were the largest contributors to the total OFP at roadside locations in Nairobi, with the three largest being toluene (178.0 μgm^{-3}), m/p-xylene (114.8 μgm^{-3}) and 1,2,4-trimethylbenzene (108.6 μgm^{-3}) at 16.8%, 10.8% and 10.2% of the total OFP, respectively. At the background location in Nairobi, however, the three largest contributors to the total OFP were hexane (45.1 μgm^{-3}), 2-methylpentane (26.9 μgm^{-3}) and toluene (23.8 μgm^{-3}) at 45%, 26% and 23% of the total OFP, respectively; these VOCs are typical vehicle emissions, indicating that whilst the OFP of VOCs detected at the background site was lower than that calculated at the roadside, the sources of VOCs are still traffic dominated [94,95].

In Lagos, m/p-xylene (195.0 μgm^{-3}), toluene (131.6 μgm^{-3}) and pentane (118.4 μgm^{-3}) were the three largest contributors to the total OFP at roadside/commercial locations, at 16.4%, 11.1% and 10.0%, respectively. As per the background location in Nairobi, the highest contributing VOCs and the respective OFP at the background location in Lagos could be attributed to traffic-based VOCs pentane (43.1 μgm^{-3}), toluene (36.4 μgm^{-3}) and m/p-xylene (33.2 μgm^{-3}).

Previous studies have shown a wide range of OFP values, owing to discrepancies between the number of VOCs monitored, the types of vehicles used in the respective cities, the vehicle fuel type and ambient conditions. Olajire and Azeez (2014) [34] previously measured a smaller number of VOCs in Lagos, specifically focusing on BTEX compounds, along with trichloroethylene. For these VOCs, a total OFP of 12,760 μgm^{-3} was calculated across three sites, with o-xylene having the largest OFP, ranging from 2949 to 4241 μgm^{-3} . For the same BTEX VOCs monitored in this study, we calculated a total OFP of 457.64 μgm^{-3} at roadside/commercial areas in Lagos. This difference in total OFP between these studies is due to considerably larger concentrations of xylenes measured by Olajire and Azeez (2014), by a factor of 35.9 and 3.1 for o-xylene and m/p-xylene, respectively, measured across all sites. Olajire and Azeez (2014) noted that high concentrations of xylene isomers in their study could be attributed to industrial sources as well as vehicle exhaust emissions, possibly explaining the discrepancy.

Other measurements of VOC concentrations in Lagos have been made by Olumayede (2014) [96]. They determined a lower OFP in Benin City, Nigeria than determined in this study for Lagos roadside sites (1184 μgm^{-3}) (although also monitoring fewer species) at a total of 281.1 μgm^{-3} , with the largest contributor being m,p-xylene at 25.7 μgm^{-3} . This difference in the calculated OFPs between the two cities was due to significantly larger concentrations of VOCs measured in our study compared to that by Olumayede (2014) with concentrations ranging from 10.5 times lower for m,p-xylene to 4.3 times lower for ethylbenzene. This is likely due to the wider range of site locations used in our study, ranging from background sites to road intersections.

OFP has been calculated for a range of locations around the world; for example, Do et al., (2013) [62] previously measured VOCs in Ghent, Belgium; Hanoi, Vietnam; and Jimma and Addis Ababa, Ethiopia. Whilst only 28 VOCs were monitored in their study,

the OFP calculations made for Hanoi were on a similar level to those calculated for roadside locations in Nairobi and Lagos in this study at $1308 \mu\text{gm}^{-3}$. The OFP calculated for BTEX VOCs measured by Do et al., (2013) in Hanoi ($928.83 \mu\text{gm}^{-3}$) was higher than that calculated for the same VOCs at the roadside locations in Nairobi and Lagos ($333.85 \mu\text{gm}^{-3}$ and $389.95 \mu\text{gm}^{-3}$). However, the BTEX related OFP calculated in Ghent was lower ($64.42 \mu\text{gm}^{-3}$) than that calculated at the roadside Nairobi and Lagos sites and also lower than the Lagos urban background site ($78.22 \mu\text{gm}^{-3}$). Finally, BTEX OFP calculated at Addis Ababa ($368 \mu\text{gm}^{-3}$) was lower than that calculated at the Lagos roadside site, but larger than the Nairobi roadside site.

Duan et al., (2008) [97] monitored VOC concentrations and calculated the respective OFPs ($937 \mu\text{gm}^{-3}$) during an ozone episode in Beijing, with formaldehyde, xylenes, trimethylbenzene, acetaldehyde and propene being the largest contributors to total OFP. However, it is important to note that within their measurements, Duan et al., (2008) monitored a number of short chained alkanes and alkenes as well as formaldehyde and acetaldehyde, which could not be monitored within this study, that could contribute to the total OFP and will be considered in future campaigns in order to fully constrain the OFP. The calculated OFP from VOCs measured at roadside locations in this study were also larger than that made in a previous study at roadside locations in Hong Kong by Huang et al., (2015) [65], in which the total OFP was calculated as $567.3 \mu\text{gm}^{-3}$ in 2003 and proceeded to decrease to $300 \mu\text{gm}^{-3}$ by 2011.

The concentrations of VOCs detected, and the resultant OFP, depends upon the fuel type. Chang et al., (2001) [98] studied the tailpipe emission factors of gasoline and liquefied petroleum gas (LPG) powered vehicles in Taiwan and calculated a larger OFP per kilometre for gasoline powered vehicles compared to that running on LPG (1828 mg/km compared to 965 mg/km). In addition, Wang et al., (2020) [99] monitored VOC emission factors and calculated the respective OFPs per kilometre for a number of vehicle types: light duty gasoline vehicles, light duty diesel trucks, heavy duty diesel trucks and liquefied petroleum gas electric hybrid buses. They determined that VOCs emitted from heavy duty diesel truck vehicles had the largest OFP of all vehicles tested (2489.4 mg/km), with liquefied petroleum gas electric vehicles having the lowest OFP at 124.7 mg/km .

NO_x emissions and ambient NO_x concentrations also determine the rate and concentration of ozone formed. When the concentrations of NO_x are high, the formation of ozone is limited by peroxy radicals formed through the reactions of VOCs, whereas when NO_x concentrations are low, ozone formation is NO_x limited [97,100]; during this field campaign, the concentration of NO_x was not measured.

Table 3. Calculated ozone forming potential for targeted VOCs across roadside and urban background sites in Nairobi and Lagos coloured by maximal value per sample group. Maximum incremental reactivity (MIR) determined from Carter (2010) [93] unless stated otherwise. NA indicates that an MIR value for the compound could not be found, and ND indicates that the target compound was not detected in the sample.

	OFP (μgm^{-3})			
	Nairobi		Lagos	
	Roadside	Urban Background	Roadside/ commercial	Urban Background
1,2-dichloro propane	ND	ND	ND	ND
1-butanol	ND	ND	ND	ND
1-propanol ^a	ND	ND	2.06	0.85
2-butanone ^b	4.10	3.40	18.12	3.42
2-ethyltoluene	15.43	2.07	15.09	1.34
2-propanol	ND	ND	ND	ND
3-ethyltoluene	65.55	6.72	57.42	8.42
4-ethyltoluene	8.39	1.38	13.05	2.09
4-methyl-2-pentanone	1.71	0.78	ND	ND

Acenaphthene	NA	NA	NA	NA
Acenaphthylene	NA	NA	NA	NA
Acetone	3.38	3.74	1.92	1.42
Alpha pinene	1.49	0.45	0.54	0.23
Benzene	15.55	3.56	17.45	3.02
Benzene, 1,2,3-trimethyl-	45.13	4.55	27.17	2.15
Benzene, 1,2,4-trimethyl-	108.57	10.82	81.34	9.14
Benzene, 1,3,5-trimethyl-	35.63	3.65	32.22	3.06
Benzene, 1,4-dichloro-	0.13	0.18	0.05	0.02
Benzophenone	1.80	1.58	1.16	0.95
Beta pinene	0.04	0.02	ND	ND
Bromodichloro-methane	ND	ND	ND	ND
Butane, 2,2-dimethyl-	9.51	0.96	15.07	14.86
Butane, 2-methyl-	NA	NA	NA	NA
Butyl acetate	ND	ND	ND	ND
Carbon tetrachloride	ND	ND	ND	ND
Chloroform	ND	ND	ND	ND
Cyclohexane, methyl-	4.68	0.43	8.87	1.26
Cyclopentane, methyl-	16.51	3.24	60.64	9.33
Cyclopropane, 1,2-dimethyl-, trans-	NA	NA	NA	NA
Decanal	NA	NA	NA	NA
Decane	1.09	0.69	1.29	1.13
Dibenzofuran	NA	NA	NA	NA
Dodecane	0.51	0.15	0.69	0.14
Durene	14.91	1.39	5.83	0.09
Eicosane	0.14	0.10	0.04	0.01
Ethane, 1,1,1-trichloro	ND	ND	ND	ND
Ethane, 1,2-dichloro-	ND	ND	0.22	0.11
Ethanol	5.49	1.81	40.07	16.37
Ethyl acetate	ND	ND	2.03	1.54
Ethylbenzene	25.48	3.34	46.00	5.59
Fluorene	NA	NA	NA	NA
Heptadecane	1.22	0.87	0.11	0.03
Heptane	9.99	1.13	13.56	1.86
Hexadecane	0.90	0.45	0.15	0.04
Hexane	86.91	45.14	71.01	13.39
Hexane, 2 methyl-	13.53	1.50	6.99	1.40
Hexane, 3-methyl-	12.99	1.09	1.48	0.21
Limonene	2.14	1.68	28.39	1.09
m/p-xylene (average)	114.82	12.94	194.95	33.21
Methane, dibromochloro-	ND	ND	ND	ND
Methylene chloride	ND	ND	0.17	0.04
Naphthalene	5.04	2.14	12.02	2.77
Naphthalene, 1-methyl-	1.47	1.16	1.50	0.21
Naphthalene, 2-methyl-	1.01	0.70	2.91	0.55
Nonadecane	0.29	0.20	0.03	0.01
Nonanal	NA	NA	NA	NA
Nonane	0.66	0.29	3.54	0.97
Octadecane	0.57	0.40	0.07	0.02
Octane	1.85	0.50	5.18	0.85
o-Xylene	81.90	8.79	67.69	11.77

pentadecane	0.70	0.22	0.27	0.05
Pentane	70.98	9.55	118.40	43.1
Pentane, 2,2,4-trimethyl-	9.51	0.64	2.26	0.40
Pentane, 2,4-dimethyl-	ND	ND	ND	ND
Pentane, 2-methyl-	50.06	26.85	15.54	2.6
Pentane, 3-methyl-	18.70	2.05	50.72	7.25
Phenanthrene	NA	NA	NA	NA
Pyrene	NA	NA	NA	NA
Styrene	3.77	0.93	5.28	0.62
Tetrachloroethylene	ND	ND	0.01	0
Tetradecane	0.64	0.24	0.28	0.01
Toluene	178.00	23.76	131.56	36.4
Trichloroethylene	1.28	1.05	ND	ND
Tridecane	0.53	0.17	0.62	0.09
Undecane	0.76	0.31	1.08	0.09
Total	1055.44	199.78	1184.11	245.58

MIR values from Carter (2010) [93] unless stated otherwise. ^a MIR value from (EPA) [101] ^b MIR value from Do et al., (2013) [62].

3.7. BTEX Concentrations in Air

BTEX compounds in general are an important class of compounds to consider when examining the composition of the troposphere. They are abundant in ambient air, have high ozone forming potential [102] and have well documented harmful effects on human health [50], falling within the classification of the World Health Organization's hazardous air pollutants.

Benzene in particular is of interest owing to its effects on human health, being a known carcinogen [103], which has resulted in the production of guideline values for benzene concentrations for indoor and ambient air in various countries. According to WHO guidelines, the concentrations of airborne benzene that are associated with an excess lifetime risk of leukaemia of 1/10,000, 1/100,000 and 1/1,000,000 are 17, 1.7 and 0.17 $\mu\text{g}\text{m}^{-3}$, respectively [104]. In Europe, the ambient benzene concentration is restricted by the EU 2000/69/EC directive to 5 $\mu\text{g}\text{m}^{-3}$ as an annual average. Aside from the acute health effects of BTEX compounds, they are also important compounds in the photochemical formation of ozone and as such can have health and environmental impacts far from the primary emission source [40,105].

Figure 6 shows the concentrations of BTEX compounds across the sites monitored. The dominance of these compounds in the ambient VOC matrix, produced primarily by motor vehicles, shows the major influence of traffic sources even at locations several hundred meters away from busy roads. In Nairobi as expected, levels were lowest at the urban background site, with levels of benzene, toluene and total BTEX recorded at 4.9 $\mu\text{g}\text{m}^{-3}$, 5.9 $\mu\text{g}\text{m}^{-3}$ and 14.8 $\mu\text{g}\text{m}^{-3}$, respectively. At Waiyaki Way, the site with greatest traffic intensity in Nairobi, average benzene concentrations were 28.5 $\mu\text{g}\text{m}^{-3}$, toluene 60.8 $\mu\text{g}\text{m}^{-3}$ and BTEX 135.8 $\mu\text{g}\text{m}^{-3}$. At the residential/urban background sites in Lagos, benzene ranged from 2.1 to 6.2 $\mu\text{g}\text{m}^{-3}$, toluene 7.2 to 10.9 $\mu\text{g}\text{m}^{-3}$ and total BTEX 16.1 to 26.7 $\mu\text{g}\text{m}^{-3}$, and the most polluted site for BTEX (and TVOC) was Ojuelegba, which saw average concentrations of benzene of 36.5 $\mu\text{g}\text{m}^{-3}$, toluene 46.5 $\mu\text{g}\text{m}^{-3}$ and total BTEX 172 $\mu\text{g}\text{m}^{-3}$. Gasoline fuels contain mainly paraffinic and aromatic fractions [106]; in an analysis of neat gasoline and diesel by Chin and Batterman (2012), concentrations of 6140 mg L⁻¹ and 64 mg L⁻¹ have been detected. Whilst benzene may be present within the fuel before combustion, it can also be continuously formed from other fractions in fuel through a series of reactions [106] and can also form in the catalytic converter [107].

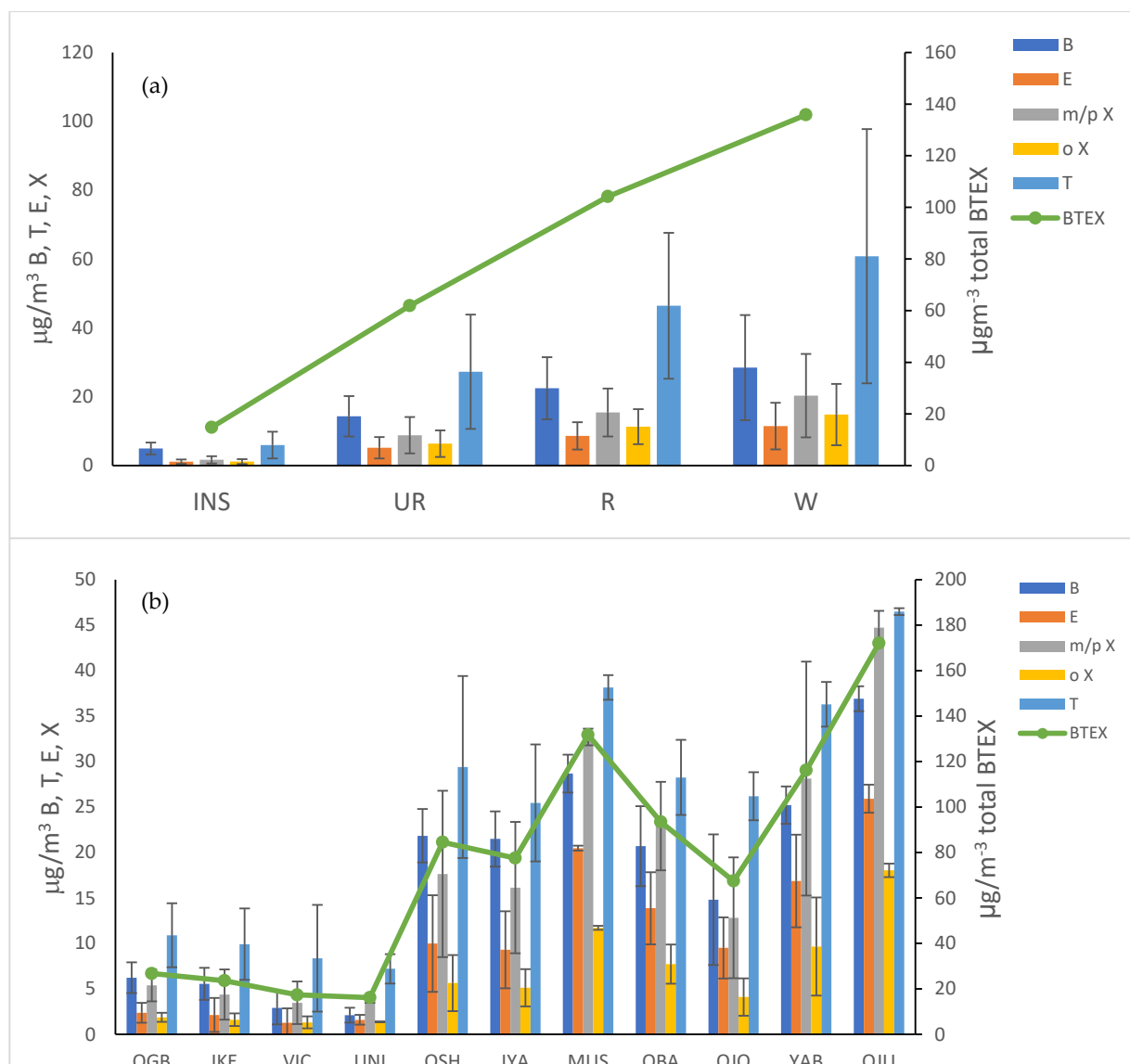


Figure 6. Concentrations of BTEX compounds across site measured in (a) Nairobi and (b) Lagos.

All roadside/commercial sites investigated in this study exceeded the EU limit value for benzene by between 3 and 7.5 times. In the urban background, Victoria Island and the University of Lagos were the only sites below the limit, levels in Nairobi were close to the limit and all other sites in Lagos exceeded it. The results here are, however, temporally limited and restricted to a few measurements, and it should be noted that the EU regulatory limit is averaged over a one year period. Whilst levels of benzene in cities in the US and Europe are normally below the EU limit of $5 \mu\text{g}/\text{m}^3$ even at roadside locations [62,108,109], this is often not the case in large developing cities. Whilst regulations have resulted in lower benzene content in fuels [66], in many African countries, where the limits are less regulated, gasoline can contain up to 5% benzene [110]. The Do et al. study [62] measured BTEX at roadside location in Hanoi, Vietnam, and Addis Ababa and Jimma in Ethiopia, where benzene concentrations were $5.4\text{--}49.4 \mu\text{g}/\text{m}^3$, and Dehghani et al. [50] took roadside measurements in Shiraz, Iran and recorded concentrations in the range of $26.2\text{--}34.4 \mu\text{g}/\text{m}^3$ [50], which are in a similar range to those observed in this study.

Unlike much of Africa, China has been the focus of several VOC studies in recent years [51,60,86,95,97,111]. These have demonstrated BTEX levels to be high, particularly

in roadside locations. For example, Wang et al., (2002) [86] demonstrated mean roadside levels of benzene between 20 and 51.5, toluene between 39.1 and 85.9, ethylbenzene between 3 and 24.1 and xylene between 14.2 and 95.65 μgm^{-3} . These exceed the highest levels observed in Nairobi and Lagos in this study, and China, along with India [112] and SE Asia [113], has some of the highest recorded BTEX pollution in the world.

3.8. Exposure Calculations

The health effects of airborne pollutants are dependent not only on their concentration but on the length of exposure time and the inhalation rate of the exposed individual. An average inhalation rate of 20 m^3 air/day is widely used to determine the inhaled dose for a given air pollutant for adults [103,114]. Table 4 shows the average BTEX absorption typical of an adult who is exposed to the air measured at the roadside in both cities for 8 hours, as a typical informal market seller or hawker would be exposed to, for a typical commute time for both cities, and for working an outdoor job in the urban background for 8 hours. Salau et al., (2013) [115] found that a significant proportion of residents of peri-urban area of Ota in Ogun State, north of Lagos, commute to Lagos for work using mostly the public transport network, private cars, commercial motorcycles and tricycles, and residents reported to spend an average of 2–3 hours commuting daily. In urban Nairobi, 89% of adult commuting is by walking and/or matatus (privately-operated paratransit), with typical total daily commute times of around an hour [116].

Table 4. Potential exposure doses of workers in Nairobi and Lagos.

	Inhaled Dose (μg)					
	Nairobi			Lagos		
Average daily commute driving/walking roadside (1 hour)	Working outside in the urban background (8 hours)	Working roadside (8 hours)	Average daily commute driving (2.5 hours)	Working outside in the urban background (8 hours)	Working roadside (8 hours)	
B	18	33	144	50	28	161
T	38	39	297	69	61	219
E	7	7	56	31	12	101
X	12	11	98	52	29	167

Benzene is carcinogenic to humans, and no level of exposure can be deemed safe [104]; thus, measurement of personal exposure to benzene is important to consider. From the measurements carried out in this pilot study, an 8-hour exposure (a typical working day) to benzene was 4.4 times higher (144 μg compared to 33 μg) at the roadside in Nairobi and 5.7 times higher in Lagos (161 μg compared to 28 μg) when compared to the local urban background (Table 4). Exposure between the cities was similar within scenarios; however, the extended commute time experienced in Lagos inevitable leads to a higher (2.7 times) exposure that in Nairobi. There are a limited number of studies on personal exposure to benzene to relate these figures to. One example is the Duarte-Davidson et al., (2001) [103] study to estimate total daily exposure in the UK to benzene for various populations (using 1995 benzene air quality measurements). In this study an urban living individual could expect a daily exposure of 89–95 μg , so an individual working at the roadside in Nairobi or Lagos will exceed this dose by >50% with the roadside exposure alone. Benzene levels in the UK have also decreased from 1995 to present with annual mean concentrations of benzene now consistently below 2 μgm^{-3} due to the introduction of catalytic converters on car exhausts in the 1990s [117].

To further put this into perspective, the inhaled dose of benzene from a cigarette is on average 40 μg per cigarette [118], so working a roadside job in one of these cities can be equated to smoking 3–4 cigarettes a day. Whilst not investigated in this study, indoor exposure to BTEX when using solid fuel for heating and cooking is likely to far exceed the

exposure from outdoors, as has been observed previously for particulate pollution in the region [119]. The total daily exposure of a citizen of Nairobi or Lagos is therefore likely to greatly exceed that of a citizen in a city in a developed country such as the UK, and this high exposure will be disproportionately affecting the most deprived residents of the cities, who live and work in the busiest most polluted areas.

3.9. Key Messages and Recommendations

- This study revealed very high levels of traffic-related VOCs in both Nairobi and Lagos and highlights that exposure to VOCs should be investigated alongside exposure to the more commonly measured air pollutants (NO_x, O₃, PM and SO₂).
- Key similarities between the two cities were the high levels of aliphatic and aromatic hydrocarbons, including the carcinogen benzene, from vehicle exhausts and fuel evaporation, showing the dominance of traffic as a pollution source in such environments.
- Other emissions differed between the cities, particularly the OVOCs. These had a higher contribution to TVOC in Lagos, mostly due to the high abundance of ethanol, likely from the ethanol refining industry.
- While studies from China show an even more severe problem, exposures in these two major African cities are greater than those typical in European and North American cities.
- In terms of burden of disease estimates, VOCs should not be prioritized over PM_{2.5}, but for air quality policy in the two cities, targeted VOC sampling such as that in this study can reveal a wealth of information regarding air pollution sources and determining the photo-chemical age of air masses in complex urban environments and providing evidence to motivate targeted interventions to improve air quality.

4. Conclusions

VOCs were measured at selected sites in Nairobi and Lagos to examine the extent of VOC pollution in the cities. Whilst there are a handful of other VOC studies in Lagos, these are the first measurements we are aware of examining VOCs in Nairobi. The preliminary results demonstrated in this study show that compared to European and US cities, VOC pollution concentrations and the ozone forming potential of the VOCs in the two SSA cities is high, but in a similar range to other developing cities both within the continent and beyond. Consequently, exposure levels of outdoor workers in these cities to harmful VOCs, such as benzene, and their secondary reaction products, are substantially higher. This pilot study represents a useful snapshot into VOC pollution in SSA, a region with huge challenges to overcome in air quality and shows that studies like this one are crucial to raise awareness in the scientific community to the exposure to air pollution of millions of vulnerable people. It also highlights how more VOC measurements are needed, alongside measurements of other pollutants, including radicals, to determine which species limit ozone production and therefore where future mitigation strategies can be best focused.

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