Assessing anthropogenic contribution to PM$_{2.5}$ from an urban residential area of Lagos, Nigeria using aliphatic hydrocarbon compounds as indicators

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Abstract
Aliphatic hydrocarbons in PM$_{2.5}$ samples from a residential area of Lagos, Nigeria, were quantified using a Curie-point pyrolysis–gas chromatography–mass spectroscopy (CPPGC/MS). The total concentrations of $\sum n$-alkanes ($C_{20}-C_{34}$), hopanes ($\sum$ Hopanes), and steranes ($\sum$ Steranes) ranged from 1.8 to 146.6 ng m$^{-3}$ (avg. 43.6 ± 35.1 ng m$^{-3}$), 0.0 to 89.9 ng m$^{-3}$ (avg. 18.7 ± 25.9 ng m$^{-3}$), and 0.0 to 26.0 ng m$^{-3}$ (avg. 3.3 ± 6.7 ng m$^{-3}$), accounting for 0.2%, 0.1%, and 0.01% of the total PM$_{2.5}$ mass concentrations, respectively. They also accounted for, 1%, 0.4% and 0.1% of the organic matter content, respectively, making them non-negligible component of the organic matter in this region. An evaluation of the $n$-alkanes source diagnostic indices revealed that engines powered by gasoline and diesel were the main sources of particulate matter aliphatic hydrocarbons in this area of Lagos, consistent with the results obtained from steranes and hopanes profiles. Based on the air mass trajectories, both local and regional air mass transports showed a significant influence on the amounts of carbonaceous materials and aliphatic hydrocarbon compounds arriving at the study site. The results from this study established the occurrence of anthropogenic air pollution in Lagos residential area with a major contribution from petrogenic sources.

Keywords
ambient air quality, anthropogenic contaminants, n-alkanes, hopanes, and steranes

Introduction
Atmospheric particulate matter (PM) with an aerodynamic diameter of 2.5 μm or less (PM$_{2.5}$) is considered a major contributor to severe air pollution and has significant impacts on human health, atmospheric visibility and climate (Russell and Brunekeef, 2009; Javed et al., 2019; Tian et al., 2020; Sun et al., 2021). The composition of PM$_{2.5}$ is very complicated and includes organic carbon (OC) and elemental carbon (EC), often referred to as carbonaceous components, trace metals, inorganic salts and some specific organic compounds such as aliphatic hydrocarbons including $n$-alkanes, steranes and hopanes, n-alkanoic acids and polycyclic aromatic hydrocarbons (PAHs) (Mandalakis et al., 2002; Javed et al., 2019; Sun et al., 2021). However, the most prevalent and significant class of organic compounds in the atmosphere are the aliphatic hydrocarbons (Fu et al., 2008; Ren et al., 2016; Boreddy et al., 2018). Due to their specificity, hydrophobicity, and prolonged persistence in the environment, these aliphatic hydrocarbon compounds have been used as organic molecular markers for pollution source identification (Simoneit et al., 1991; Mudge and Duce, 2005; Andreou et al., 2007; Javed et al., 2019; Sun et al., 2021). For example, $n$-alkanes primarily come from both anthropogenic and biological sources, such as petroleum residue, diesel engine exhaust (Simoneit,1984), and biomass burning (Simoneit and Elias, 2000, 2001), and also from terrestrial plant wax, fungi, bacteria, algae, and plankton (Brown et al., 2002). Additionally, plant wax $n$-alkanes are employed directly as a proxy for both the atmospheric transport and genesis of organic aerosol (OA) in the atmosphere (Tang et al., 2006; Lyu et al., 2017). Hopanes and steranes are ubiquitous in crude petroleum and are enhanced in the lubricating oils used in diesel and gasoline-powered motor vehicles, and their existence in the environment confirms the contribution of the burning of fossil fuels in the area (Simoneit et al., 2004; Rushdi et al. 2017; Javed et al., 2019). EC is mainly emitted from anthropogenic combustion sources, whereas...
OC, as a complex mixture of many groups of compounds, has both primary and secondary origins. Primary organic carbon (POC) is generated during the combustion process, while secondary organic carbon (SOC) is produced in the atmosphere through the gas to particle conversion processes of volatile precursors. Exposure to high levels of these urban carbonaceous components has been linked with cardiovascular mortality and morbidity (Samara et al., 2013).

At present, improving the ambient air quality is one of Lagos’s greatest environmental challenges. Studies relating to the PM$_{2.5}$ pollution status in Lagos have been reported by various authors (Ezeh et al., 2012; Obioh et al., 2013; Owoade et al., 2013; Ezeh et al., 2014; Alani et al., 2019; Zeng et al., 2019). However, reports have focused on the mass concentrations and elemental characterisation of PM$_{2.5}$, while information on specific organic compound classes such as aliphatic hydrocarbons in PM$_{2.5}$ that can be utilised as source markers in identifying the primary sources of organic aerosols (OA) are very scarce. For instance, Ezeh et al. (2012) and (2014) determined PM$_{2.5}$ mass concentrations at different locations in Lagos during the rainy season. Although their results showed that PM$_{2.5}$ mass concentrations were below the World Health Organization (WHO) limit of 25 µg m$^{-3}$, they argued on the basis of correlation and enrichment factor analyses that most trace elements in PM$_{2.5}$ originated from anthropogenic sources. Similarly, Owoade et al. (2013) determined the PM$_{2.5}$ mass concentrations from different classes of receptor sites in Lagos. They showed that some residential areas have higher PM$_{2.5}$ levels due to contributions from local sources and transport of pollutants from neighbouring sites more than industrial areas. Common anthropogenic sources for PM$_{2.5}$ in their study include traffic-related, traffic emissions, marine salt, and industrial emissions based on the principal component factor analysis (PCFA) of the detected elements. More recently, Zhen et al. (2019) reported the chemical characteristics of PM$_{2.5}$ based on PM$_{2.5}$ mass concentrations, OC, EC, water-soluble ions and elemental compositions. According to their results, PM$_{2.5}$ pollution was higher in Lagos than in Hong Kong. They also found that vehicular emissions contributed the most to PM$_{2.5}$ pollution.

Aliphatic hydrocarbon compounds have been used in other parts of the world to identify the main sources of PM$_{2.5}$ pollution and to understand the important impact of regional transport on the characterisation of PM$_{2.5}$ (Andreou et al., 2007; Javed et al., 2019; Sun et al., 2021). For instance, Andreou et al. (2007) investigated the organic chemical composition of PM$_{2.5}$ in Athens to determine the emission sources. They found that all samples in Athens contained n-alkanes, biomarkers for fossil fuels, and a mixed origin (petrogenic and biogenic) of Athenian PM$_{2.5}$. Vehicular emissions were the main source of aliphatic hydrocarbon compounds, with biogenic sources contributing less. Recently, Sun et al. (2021) determined the sources of PM$_{2.5}$-associated PAHs and n-alkanes in Changzhou, China. Their results showed that biogenic sources are the main source of n-alkanes and PAHs in PM$_{2.5}$. The authors also observed that variations in the concentration of n-alkanes and PAHs from different air mass transports were not consistent with the changes in PM$_{2.5}$ mass, and concluded that regional transport has important effects on the characterisation of PM$_{2.5}$. This study therefore aimed at determining the PM$_{2.5}$ mass concentration and characterising the chemical composition of PM$_{2.5}$ collected at a residential location in Agege area of Lagos, Nigeria. The chemical analysis included the elemental carbon (EC), organic carbon (OC), aliphatic hydrocarbon compounds comprising of n-alkanes, hopanes and steranes. The impact of local and regional air mass transports on the amount of PM$_{2.5}$ elemental carbon (EC), organic carbon (OC), and aliphatic hydrocarbon compounds arriving at the study site was also assessed using the air mass trajectory analysis. In addition, the sources of PM$_{2.5}$ pollution were identified based on the molecular diagnostic indices of n-alkanes, hopanes and steranes profiles. It is expected that this work will provide useful information on the characteristic nature of PM$_{2.5}$ and in particular the sources and profiles of aliphatic hydrocarbons in PM$_{2.5}$ in residential areas of Lagos, which is currently scarce.

Materials and methods

Description of sampling site

The sampling site was an urban residential area located at 3/5 Morenike Carena Close, Orile Agege, Lagos (6.635008N and 3.302543E). The site was located within the city, and thus the anthropogenic emissions from various sources was quite high. Lagos is the former administrative capital of Nigeria, and the biggest metropolis in West Africa with a population of over 21 million (Alani et al., 2019). It remains the economic and industrial hub of the nation, where a range of activities are taking place that might be detrimental to the city’s air quality. Lagos is susceptible to particulate matter pollution arising from vehicular traffic, diesel and gasoline generator emissions, open dumpsites, illegal waste burning, infrastructure construction, and household cooking using polluting fuel and stoves (Ibitayo 2012; Oseni 2016; Adegboye 2018; Adam 2018; Ozoh et al., 2018).

Sample collection

Thirty-six (36) PM$_{2.5}$ samples (24-h samples) and blank samples (4) were taken between June and July 2021 during the peak of the rainy season to provide an overview of the extent of the impact of the rainy season on the PM$_{2.5}$ mass concentrations and aliphatic hydrocarbon compounds characteristics in PM$_{2.5}$. Samples were collected on high-purity quartz fibre filters (Φ = 47 mm) using a low-vol "Gent" stacked PM$_{2.5}$ air sampler (Maenhaut et al., 1994). The device was placed at a height of 4.65 m above the ground to minimise blockage of air parcels from surrounding buildings and was operated at a constant flow rate of 18 L/min. The samples were stored in a refrigerator at 5°C and subsequently cooled in a container packed with frozen ice packs and transported to TROPOS in Leipzig, Germany within 24 h. Upon arrival, the samples were stored in the freezer at -20 °C prior to laboratory analysis.
Gravimetric and organic/elemental carbon (OC/EC) analysis
The mass of the PM$_{2.5}$ samples were quantified using a microbalance (Mod. AT261 Delta Range, Mettler-Toledo) after being allowed to equilibrate in the weighing room for 72 h under a climate-controlled conditions (temperature: $20 \pm 1 ^\circ C$ and relative humidity: 50 $\pm$ 5%) before and after sampling. To determine the mass concentration, the weight difference of the filters before and after sampling was computed and divided by total sampling volume. Organic carbon and elemental carbon were analysed using a thermo-optical method (Sunset Laboratory Inc., USA) at a maximum temperature of 850 °C using the normalised temperature programme EUSAAR2 (European Supersites for Atmospheric Aerosol Research) as described in the literature (Cavalli et al., 2010; Yttri et al., 2019). The method is in accordance with the standard proposed by the European networks (ACTRIS, EMEP). Samples were thermally desorbed from the filter medium under an inert He atmosphere followed by an oxidising O$_2$-He atmosphere, under carefully controlled heating ramps. A flame ionisation detector was used to quantify methane after catalytic methanation of CO$_2$. With the EUSAAR2 protocol, different OC fractions in an inert atmosphere (He) were measured at 200°C for 120s, at 300°C for 150s, at 450°C for 180s and at 650°C for 180s. Subsequently, the EC fractions were measured in an oxidising atmosphere (O$_2$-He) at 500°C for 120s, at 550°C for 120s, at 700°C for 70s and at 850°C for 80s (Cavalli et al., 2010). Lower OC/EC ratios are usually the result of charring processes’ tendency to overestimate the EC and underestimate the OC. In order to adjust for the charring process, an optical correction was used. A laser with a wavelength of 678 nm was used to measure the sample’s transmission in order to calculate the optical correction for charring for pyrolytic carbon. For OC and EC measurements, the detection threshold was 0.2 µg cm$^{-2}$.

Turpin and Lim (2001) evaluated organic matter (OM) using the conversion factor fOM/OC. The organic matter was around twice as much as the organic carbon (OM = 2.1 × OC). Because the conversion factor varies depending on the specific conditions at each site, the factor fOM/OC = 2.1 is recommended as it also takes the age of the aerosol into account (Turpin and Lim, 2001). Thus, the OM in the present study was estimated accordingly. The POC content can be estimated using EC as a tracer by multiplying the minimum OC/EC ratio determined for the entire study period by the EC content as follows (Huang et al., 2012; Deabji et al., 2021):

$$\text{POC} = (\text{OC}/\text{EC})_{\text{min}} \times \text{EC}$$  \hspace{1cm} (1)

Consequently, the amount of SOC that contributes to total organic carbon can be determined as the difference between the concentrations of primary and secondary organic carbon using the following equation (Huang et al., 2012; Deabji et al., 2021):

$$\text{SOC} = \text{OC} - \text{POC}$$  \hspace{1cm} (2)

Organic compounds analysis
The analysis of aliphatic hydrocarbon compounds such as n-alkanes (C$_{2n}$-C$_{30}$), hopanes, and steranes were carried out using a Curie-point pyrolyser (JPS-350, JAI Inc., Japan) coupled to a gas chromatography-mass spectrometry system (6890 N GC, 5973 inert MSD, Agilent Technologies, CA, USA). A detailed description of the analytical procedures has been previously documented (Neusüss et al. 2000). Briefly, filter aliquots were spiked with a solution of internal standards, including perdeuterated tetracosane-d$_{25}$ (C$_{25}$-D$_{25}$) and dotriacontane-d$_{30}$ (C$_{30}$-D$_{30}$). Two circular filter punches (6 mm; 56.5 mm$^2$) from each sample were then coated with an alloy of iron and nickel (50% Fe; 50% Ni) and immediately evaporated in a pyrolysis chamber at 510 °C for 4 s in a helium environment. The compounds were separated using a capillary column coated with a stationary phase of 5 % phenyl-arylene and 95 % dimethylpolysiloxane (ZB-5MS, 30 m × 0.25 mm i.d. × 0.25 µm film thickness). The GC and MS conditions had been previously described by Khedidji et al. (2020). Individual compounds were identified by comparing the mass spectra with literature and library data and validated with standard compounds. Internal calibration was performed using the respective internal standards. The GC-MS data were acquired using dedicated software (ChemStation) from Agilent. For each compound analysed, the sample concentration was calculated by subtracting the average concentration of the blank filter from the measured concentration in the sample.

Molecular diagnostic ratios
To investigate the origin of the n-alkanes in the PM$_{2.5}$ samples, the following diagnostic ratios were used.

The carbon preference index (CPI): CPI is a diagnostic technique that depicts the relationship of proportionality between alkanes with odd and even carbon chains in a given sample. Based on several studies (Bray and Evans, 1961; Simonetti et al., 1991; Boreddy et al., 2018), the CPI for n-alkanes (odd to even ratio) in the PM$_{2.5}$ was calculated as follows:

$$\text{CPI} = \frac{\sum \text{odd} (C_{21} - C_{33})}{\sum \text{even} (C_{20} - C_{34})}$$  \hspace{1cm} (3)

The average chain length (ACL): ACL is based on the prevalence of odd high homologs. It is estimated as the mean number of carbon atoms per molecule (Caumo et al., 2020). ACL has been used to identify the origins of n-alkanes in a given sample (Kawamura et al., 2003; Boreddy et al., 2018; Caumo et al., 2020), and based on these studies, the ACL for n-alkanes in PM$_{2.5}$ was obtained according to the following equation:

$$\text{ACL} = \frac{[25(C_{25}) + 27(C_{27}) + 29(C_{29}) + 31(C_{31}) + 33(C_{33})]}{[C_{25} + C_{27} + C_{29} + C_{31} + C_{33}]}$$  \hspace{1cm} (4)

Odd-even predominance (OEP): The odd-even computation also known as the odd-even carbon number by dividing the concentration of odd-numbered n-alkanes by the concentration of even-numbered n-alkanes as follows:

$$\text{OEP} = \frac{C_{21} + 6(C_{23}) + C_{25}}{4(C_{22} + C_{24})}$$  \hspace{1cm} (5)
Air mass back trajectory
96-hour air mass back trajectories for each sample collection time interval were determined using the HYSPLIT model version 5 (www.ready.noaa.gov/HYSPLIT_traj.php, last use February 2023, Stein et al., 2015) to evaluate the origin of the PM$_{2.5}$ during the sampling period. The choice of using 96-h was to provide a representation for fine mode particles (PM$_{2.5}$) that have longer atmospheric lifetimes as coarse mode particles. The Global Data Assimilation System meteorological data set was used for the HYSPLIT trajectory calculations with a 1°-degree grid size. The obtained trajectories were further processed using the r studio software open-air package (https://davidcarslaw.github.io/openair) for graphical presentation. The computed trajectories also contained information of the air mass history, its residence time (average time the air parcel stays over a given grid cell or geographical landscape during its transport prior to arrival at the receptor site) over given geographical landscapes, different mixing depths (height at which the potential temperature of the air mass starts to change), radiation and general meteorology information that the air mass experienced during its transport. Using the trajCluster function of the open-air r package, a cluster analysis of the total determined trajectories was performed. Here, the trajectories were grouped according to the least Euclidian distance between the trajectory’s points. After several iterations amongst pairs of trajectories, the average trajectory representative of the minimum distance between the trajectories with a low total spatial variance (TSV) was determined and assigned as a cluster. The equation applied to determine the Euclidian distance (d(1,2)) between two points of two trajectories 1 and 2 at positions (X1, Y1) and (X2, Y2) respectively, is given as (Stein et al., 2015):

$$d_{1,2} = \left( \sum_{i=1}^{n} \left( X_{i1} - X_{i2} \right)^2 + \left( Y_{i1} - Y_{i2} \right)^2 \right)^{1/2} \quad (6)$$

The selection of the final number of clusters involves a mathematical process wherein the total spatial variance is compared with the model estimated number of clusters. The level at which a change in the number of clusters significantly increases the TSV is considered as the point of the optimum number of clusters for the total evaluated back trajectories. In this study, 5-cluster solution provided a reasonable spatial representation of the entire computed trajectories and was considered the best solution of this analysis. The clusters were labelled C1 to C5 and were assigned to each sample. The samples chemical composition including their PM$_{2.5}$ mass was averaged according to their respective clusters and the relative contributions of the clusters to the chemical components were evaluated.

Results and discussion
PM$_{2.5}$ mass concentration and its carbonaceous components
Table 1 summarises the 24-h average PM$_{2.5}$ mass concentrations and its carbonaceous chemical components for the sampling period (June to July 2021). The 24-h PM$_{2.5}$ mass concentrations ranged from 8.7 to 56.5 µg m$^{-3}$ (avg. 27 ± 11.1 µg m$^{-3}$), surpassing the daily threshold of 15 µg m$^{-3}$ recommended by World Health Organisation (WHO, 2021). The OC concentration ranged from 1.0 to 4.9 µg m$^{-3}$ (avg. 2.2 ± 1.0 µg m$^{-3}$). On average, OC accounted for 8% of the total PM$_{2.5}$ mass and contributed 73% of the carbonaceous aerosol while the majority of OC consisted of POC (68%), indicating that the OC was a crucial component of PM$_{2.5}$ and the primary emission sources of OC in the study area need to be controlled. The EC concentration ranged from 0.4 to 1.8 µg m$^{-3}$ (avg. 0.8 ± 0.3 µg m$^{-3}$). On average, EC constituted about 3% of the total PM$_{2.5}$ mass. Though this value could be viewed as only a small portion of ambient PM$_{2.5}$, EC has been recognised as a crucial sign of unfavourable health impacts (Janssen et al., 2011). With a correlation value of $r^2 = 0.81$ (Fig. 1a), OC and EC demonstrate a strong relationship, indicating that the majority of the OC at the site was produced as a primary aerosol with EC. This revealed that EC and OC, as well as the precursor that resulted in SOC formation, could have an identical source. The positive bi-modal correlation ($r^2 = 0.76$ and 0.40) between SOC and EC indicated that the primary combustion sources have an influence on the generation of SOC (Fig. 1b), and also suggested two distinct associations such as sources or atmospheric processes linking the two different carbonaceous components. The OC/EC ratios ranged from 2 to 5.1 µg m$^{-3}$ (avg. 2.9 ± 0.7 µg m$^{-3}$). Hildemann et al. (1991), reported 2.2 µg m$^{-3}$ for light-duty gasoline vehicles while Cao et al. (2005) observed 4.1 µg m$^{-3}$ for vehicle exhaust. This suggested that the most probable common source of PM$_{2.5}$ emission in the area was gasoline-powered engines. Generally, OC/EC ratio > 2 is an indicator of SOC formation in the atmosphere (Javed et al., 2019).

<table>
<thead>
<tr>
<th>PM$_{2.5}$ mass</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM$_{2.5}$</td>
<td>8.7</td>
<td>56.5</td>
<td>27.0</td>
<td>11.1</td>
</tr>
<tr>
<td>EC</td>
<td>0.4</td>
<td>1.8</td>
<td>0.8</td>
<td>0.3</td>
</tr>
<tr>
<td>OC</td>
<td>1.0</td>
<td>4.9</td>
<td>2.2</td>
<td>1.0</td>
</tr>
<tr>
<td>OC/EC</td>
<td>2.0</td>
<td>5.1</td>
<td>2.9</td>
<td>0.7</td>
</tr>
<tr>
<td>POC</td>
<td>0.8</td>
<td>3.7</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td>SOC</td>
<td>0.0</td>
<td>1.7</td>
<td>0.6</td>
<td>0.5</td>
</tr>
<tr>
<td>OM</td>
<td>2.2</td>
<td>10.3</td>
<td>4.5</td>
<td>2.1</td>
</tr>
</tbody>
</table>

n-alkanes in PM$_{2.5}$
The concentrations of aliphatic hydrocarbons detected in the PM$_{2.5}$ samples from the residential area in Lagos and the molecular diagnostic indices are presented in Table 2. The aliphatic fraction of the PM$_{2.5}$ was dominated by n-alkanes from C$_{20}$ to C$_{34}$, and maximizing at C$_{28}$, followed by C$_{32}$ and C$_{34}$ respectively (Fig. 2). The total concentrations of the n-alkanes $\Sigma(C_{20}-C_{34})$ in the samples ranged from 1.8 to 146.6 ng m$^{-3}$ (avg. 43.6 ± 35.1 ng m$^{-3}$) (Table 2). On average, n-alkane contributed 0.2% and 1.0% of the total PM$_{2.5}$ mass and OM budget,
respectively, indicating a sizeable portion of the ambient PM$_{2.5}$ and organic matter concentration in the area. A comparable range of total n-alkanes concentrations in PM$_{2.5}$ were recently found in densely populated and traffic-intensive city of Beijing, China (4.51-153 ng m$^{-3}$) (Yang et al., 2023), but higher than the average total concentrations recorded in PM$_{2.5}$ in a residential/commercial area in Doha, Qatar (8.04 ± 7.74 ng m$^{-3}$) (Javed et al., 2019), an urban residential area (Aglantizia) in Nicosia, Cyprus (13 ± 12 ng m$^{-3}$) (Iakovides et al., 2021), and roadsides in Lisbon, Portugal (22.4 ± 17.9 ng m$^{-3}$ in winter and 23.3 ± 2.83 ng m$^{-3}$ in summer) (Alves et al., 2016). In contrast, the average total concentration of n-alkanes obtained in this work was lower than some urban cities in China (Changzhou: 252.37 ± 184.02 ng m$^{-3}$; Nanjing: 205 ng m$^{-3}$; Changchun: 209 ng m$^{-3}$; Shanghai: 259 ng m$^{-3}$ in PM$_{2.5}$) (Wang et al., 2006; Haque et al., 2019; Sun et al., 2021) and Hong Kong (195 ng m$^{-3}$) (Wang et al., 2006). The prevalence of low carbon number (C$_{20}$-C$_{26}$) in the aerosol particles showed a predominance of anthropogenic sources, such as incomplete combustion of fossil fuels (Zhang et al., 2018). Fossil fuel-derived n-alkanes with the dominant of C$_{25}$ and C$_{20}$ homologs are considered to be from gasoline engines while C$_{20}$-dominated n-alkanes are regarded as from heavy and medium-duty diesel engines (Rogge et al., 1993; Schauer et al., 1999). The preponderance of C$_{25}$ and C$_{20}$ in the samples (Fig. 2) showed that anthropogenic emissions resulting from gasoline and diesel engines were probably the dominant sources of n-alkanes in the area under study.

The carbon preference index (CPI) values calculated from n-alkane distribution have been extensively employed as

Table 2: Aliphatic hydrocarbon concentrations (ng m$^{-3}$) and molecular indices of n-alkanes in PM$_{2.5}$ from a residential area in Lagos, Nigeria

<table>
<thead>
<tr>
<th>Compound</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>∑n-alkanes (C$<em>{20}$-C$</em>{34}$)</td>
<td>1.8</td>
<td>146.6</td>
<td>43.6</td>
<td>35.1</td>
</tr>
<tr>
<td>Indices</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CPI</td>
<td>0.0</td>
<td>2.3</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>ACL</td>
<td>25.0</td>
<td>30.8</td>
<td>25.7</td>
<td>1.6</td>
</tr>
<tr>
<td>OEP</td>
<td>0.0</td>
<td>1.9</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Hopanes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17α(H), 21β(H)-30-Norhopane</td>
<td>0.0</td>
<td>22.1</td>
<td>4.4</td>
<td>7.0</td>
</tr>
<tr>
<td>17α(H), 21β(H)-Hopane</td>
<td>0.0</td>
<td>31.7</td>
<td>5.6</td>
<td>8.9</td>
</tr>
<tr>
<td>17α(H), 21β(H)-22S-Homohopane</td>
<td>0.0</td>
<td>89.9</td>
<td>2.9</td>
<td>15.1</td>
</tr>
<tr>
<td>17α(H), 21β(H)-22R-Homohopane</td>
<td>0.0</td>
<td>14.1</td>
<td>1.9</td>
<td>3.7</td>
</tr>
<tr>
<td>∑Hopanes</td>
<td>0.0</td>
<td>89.9</td>
<td>18.7</td>
<td>25.9</td>
</tr>
<tr>
<td>Steranes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α, α, α 20R-Cholestane</td>
<td>0.0</td>
<td>3.1</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>α, β, β (20R 24S)-24-Ethylcholestane</td>
<td>0.0</td>
<td>15.1</td>
<td>1.7</td>
<td>3.9</td>
</tr>
<tr>
<td>α, α, α (20R 24S)-24-Ethylcholestane</td>
<td>0.0</td>
<td>7.9</td>
<td>1.3</td>
<td>2.1</td>
</tr>
<tr>
<td>∑Steranes</td>
<td>0.0</td>
<td>26.0</td>
<td>3.3</td>
<td>6.7</td>
</tr>
</tbody>
</table>
Hopanes and steranes in PM$_{2.5}$

The concentrations of hopanes and steranes detected in the PM$_{2.5}$ samples during the entire campaign period are listed in Table 2. Four (4) hopanes including 17α(H),21β(H)-30-norhopane, 17α(H),21β(H)-hopane, 17α(H),21β(H)-22S-homohopane, and 17α(H),21β(H)-22R-homohopane and three (3) steranes including α, α, α 20R-Cholestane, α, β, β (20R 24S)-24-Ethylcholestane and α, α, α (20R 24S)-24-Ethylcholestane, were detected in the PM$_{2.5}$ samples (Table 2). The total concentrations of hopanes (Σ4 hopanes) and steranes (Σ3 steranes) varied from 0.0 to 89.9 ng m$^{-3}$ (avg. 18.7 ± 25.9 ng m$^{-3}$) and 0.0 to 26.0 ng m$^{-3}$ (avg. 3.3 ± 6.7 ng m$^{-3}$), respectively, in PM$_{2.5}$. On average, hopanes accounted for 0.1% and 0.4% of the total PM$_{2.5}$ and OM, while steranes contributed 0.01% and 0.1% of the total PM$_{2.5}$ and OM, respectively, making them a non-negligible part of the organic matter content in the study area. The average total hopanes and steranes concentrations in this study were higher than those reported in PM$_{2.5}$ in a residential/commercial area in Doha, Qatar (0.521 ± 0.677 ng m$^{-3}$) and (0.162 ± 0.25 ng m$^{-3}$), respectively (Javed et al., 2019). Similarly, lower average hopanes and steranes concentrations were observed in an urban residential area in Nicosia, Cyprus (0.83 ± 1.04 ng m$^{-3}$) and (0.27 ± 0.39 ng m$^{-3}$), respectively. The average hopanes level in this study was likewise higher than those observed in roadside areas in Lisbon, Portugal in winter (1.71 ± 1.55 ng m$^{-3}$), but comparable to those observed in roadside areas in Lisbon, Portugal in summer (3.23 ± 1.15 ng m$^{-3}$) (Alves et al., 2016). The presence of hopanes and steranes in PM$_{2.5}$ samples suggested fossil fuels combustion in the area (Simoneit et al., 2004; Javed et al., 2019). The steranes were dominated by α, β, β (20R 24S)-24-Ethylcholestane (Table 2). The stereocchemistry of the C17 and C21 positions of hopanes are frequently used to assess the thermal maturity levels of fossil fuels, and have proved useful in evaluating the source of hopanes in aerosols (Simoneit et al., 2004; Barakat, 2002; Mikuška, Křůmal, and Večeřa 2015; Javed et al., 2019). Hopanes with configurations of 17β(H), 21β(H) are considered immature; 17β(H), 21α(H) are of low maturity while 17α(H), 21β(H) are fully mature (Mikuška, Křůmal, and Večeřa 2015; Javed et al., 2019). The main homologs of hopanes detected in the samples were the thermodynamically more stable 17α(H), 21β(H) configurations, with a preponderance of the 17α(H), 21β(H)-hopane compound (C30αβ; 36% of total hopanes). This was followed by 17α(H), 21β(H)-norhopane (C29αβ; 28%) (Fig. 3), a fingerprint for vehicle emissions (Mikuška, Křůmal, and Večeřa 2015; Javed et al., 2019). The dominance of αβ configuration indicated that atmospheric contamination in the study area emanated from matured petroleum. Again, the higher concentration of the 22S hopane relative to the corresponding 22R epimer (Table 2; Fig. 3), further supported the fact that the hopanes were primarily derived from gasoline and diesel engine exhaust (Rushdi et al. 2017; Javed et al., 2019). The enhanced levels of these petroleum biomarkers (Barakat, 2002; Mikuška, Křůmal, and Večeřa 2015; Javed et al., 2019), indicated a significant impact of petrogenic source emission in the study area.
Two strong positive correlations ($r^2 = 0.96$ and 0.90) were observed between hopanes and steranes (Fig. 4a), indicating two separate associations such as sources or atmospheric processes linking the two different types of compounds. Hopanes and EC have been used to allocate gasoline and diesel emissions (Yu et al., 2011). Diesel engines are strong contributors to both EC and hopanes, whereas gasoline engines are huge sources of hopanes but only contribute moderate amounts of EC. As a result, diesel-powered engines have substantially lower hopanes to EC ratios than engines that run on gasoline (Yu et al., 2011). The ratio-ratio plot of hopane ($17\alpha$($H$),$21\beta$($H$)-hopane) and norhopane ($17\alpha$($H$),$21\beta$($H$)-30-norhopane) obtained for PM$_{2.5}$ in this study, normalised by EC is shown in Fig. 4b, modified from Yu et al. (2011). The plot corroborated the sources of hopanes as being from diesel and gasoline engines due to the strong correlation between the groups of compounds, which might have emanated from vehicle emissions, motorbikes, and fumes emitted by diesel and gasoline engines.

**Air mass source regions**

As shown in Fig. 5, air masses originated from different regions of the Atlantic Ocean crossing through various densely populated areas in the coastal settlements in Lagos at different altitudes before arriving at the site. The clusters C1 and C2, represent 44% and 25%, respectively, of the total air mass inflow during the sampling period and were characterised by their different origins, but with a similar profile in the mixing depth and trajectory heights (air masses altitudes) close to their arrival at the sampling site. C3 (13%) and C4 (15%) were representative of air masses that spent more time over the Atlantic Ocean and little time over terrain with C4 passing closer to the coast of neighbouring Benin republic while C3 was confined within the coast of Nigeria and originated from the Gulf of Guinea region. C5 made up only about 2% of the trajectories but represented air masses originating from the coastal area of Nigeria with higher residence time over land and vegetation regions with low mixing depth. These characteristics made it contributed significantly to the composition of the particles at the sampling site.

**Influence of source regions on PM$_{2.5}$ mass and carbonaceous components**

Fig. 6 gives the quantified contributions of the different directions of air masses to the PM$_{2.5}$ mass and its carbonaceous components. Interestingly, air mass for cluster 5 (C5) with few episodes of air transports contributed more to PM$_{2.5}$ mass (22%), EC (21.4%), OC (24.7%), OC/EC (23%), POC (21.4%), SOC (32%), and OM (24.7%) (Fig. 6a), as compared to air masses for clusters 1 to 4 (C1 to C4) which passed mainly through the Atlantic Ocean before crossing the mainland to the sampling site. Cluster 5 after emerging from the sea has a relatively long residence time in the continental coastal areas of the Atlantic Ocean before returning to the marine area and eventually crossing the mainland to the sampling site. The relatively low mixing depth of the air mass, high exposure to different continental environments and natural vegetation during transports may have raised the levels of the PM$_{2.5}$ mass and its chemical components in the C5 trajectory (Fig. 6b).

**Influence of source regions on aliphatic hydrocarbon compounds**

The contributions of the different direction of air mass to aliphatic hydrocarbon compounds are shown in Fig. 6. As previously observed in the carbonaceous materials and PM$_{2.5}$ mass
Assessing anthropogenic contribution to PM$_{2.5}$ from an urban residential area of Lagos

Based on the air mass trajectories, the levels of PM$_{2.5}$, carbonaceous materials, and aliphatic hydrocarbon compounds arriving at the study site have been considerably impacted by both local and regional air transports. This study could help decision-makers and environmental stakeholders to develop specific, focused, and efficient management strategies for mitigating local air pollution challenges in Lagos, Nigeria.

Author contribution
OLF: Conceptualisation, Performed the fieldwork, Formal analysis, and interpretation, Writing - original draft. HH and KWF: Methodology, Resources, Supervision, Writing – review & editing. GCE: Resources. All the authors contributed to the final version of this paper.

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