PM$_{2.5}$ characterization of primary and secondary organic aerosols in two urban-industrial areas in the East Mediterranean

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**Abstract**

Primary and secondary organic aerosols in PM$_{2.5}$ were investigated over a one-year campaign at Zouk Mikael and Fiaa, Lebanon. The n-alkanes concentrations were quite similar at both sites (26-29 ng/m$^3$) and mainly explained by anthropogenic emissions rather than natural ones. The concentrations of total Polycyclic Aromatic Hydrocarbons (PAHs) were nearly three times higher at Zouk Mikael (2.56 ng/m$^3$) compared to Fiaa (0.95 ng/m$^3$), especially for indeno[1,2,3-c,d]pyrene linked to the presence of the power plant. A characteristic indeno[1,2,3-c,d]pyrene/(indeno[1,2,3-c,d]pyrene + benzo[g,h,i]perylene) ratio in the range 0.8-1.0 was determined for heavy fuel oil combustion from the power plant. Fatty acids and hopanes were also investigated and were assigned to cooking activities and vehicular emissions respectively. Phthalates were identified for the first time in Lebanon with high concentrations at Zouk and Fiaa (106.88 and 97.68 ng/m$^3$ respectively). Moreover, the biogenic secondary aerosols revealed higher concentrations in summer. The total terpene concentration varied between 131 ng/m$^3$ at Zouk Mikael in winter to 469 ng/m$^3$ at Fiaa in summer. Additionally, the concentrations of the dicarboxylic acids especially for adipic and phthalic acids were more influenced by anthropogenic sources. The analysis of molecular markers and diagnostic ratios indicated that the sites were strongly affected by anthropogenic sources such as waste open burning, diesel private generators, cooking activities, road transport, power plant, and industrial emissions. Moreover, results showed different pattern during winter and summer seasons. Whereas, higher concentrations of biogenic markers were clearly encountered during the summer period.

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Introduction

Atmospheric particulate matter (PM) which refers to a mixture of solid particles and liquid droplets suspended in air, is one of the most challenging issues in the environmental field nowadays due to its chemical complexity, its measurement, and its source apportionment leading to air quality management (Seinfeld and Pandis, 2016). Recent studies have shown that the premature mortality rate associated with exposure to ambient air pollution reached 8.8 million per year (Lelieveld et al., 2020) emphasizing on the seriousness of the human health hazards (Anderson et al., 2012; WHO, 2013; Zaheer et al., 2018).

Due to their very small size, PM$_{2.5}$ which are particles having an equivalent aerodynamic diameter less than 2.5 μm, have drawn much attention. Not only they can penetrate deeply into the lungs, but also they can be retained inside and induce respiratory (Xing et al., 2016) and cardiovascular diseases (Du et al., 2016).

The organic aerosol (OA) can contribute up to 50% to the total PM$_{2.5}$ dry mass (De Gouw and Jimenez, 2009) which can be divided into Primary (POA) and Secondary (SOA) Organic Aerosols. Primary organic compounds can serve as molecular markers of a specific source of pollution such as hopenes for vehicular emissions (Rogge et al., 1996), fatty acids for cooking activities (Robinson et al., 2006), PAHs for fossil and non-fossil fuel combustion (Mastral et al., 2003). In addition, products of oxidation of different terpenes (α-pinene, isoprene and β-caryophyllene) have been used to characterize and quantify the biogenic SOA (Kleindienst et al., 2007).

Lebanon, a Middle Eastern Mediterranean country, with a population of more than 6 million in the last few years, faces some important pollution events. Episodically, the country is affected by long range transport of dust from deserts (Borgie et al., 2016), but the main sources of pollution are local, specially in winter (Waked et al., 2013). Air quality in Lebanon is heavily affected by road transport emissions caused by the absence of the public transportation system. The road transport sector is the main source of CO, NOx and Non-Methane Volatile Organic Compounds (NMVOC) (Abdallah et al., 2020; Salameh et al., 2015; Waked and Afif, 2012). Moreover, since the national electricity company is unable to provide electricity 24/7, private diesel generators fill the gap with no law enforcement on stack emissions (Waked et al., 2012). On the other hand, based on the 2010 national inventory, the main emitter of PM is the industries followed by others like the transport and the power generation sectors. Finally, the population growth hypothesis along with the refugees displacement has led to an important residential solid waste generation that caused, in 2017, a substantial increase in open burning of waste in many parts of the country (Abbas et al., 2019).

Main air pollution studies conducted in Lebanon focused on the capital Beirut (Afif et al., 2008; Daher et al., 2013; Salameh et al., 2015). Studies on PM conducted in Lebanon generally focused on the inorganic composition (Jaafar et al., 2014; Kfouri et al., 2009; Yammine et al., 2010), and fewer examined certain organic families such as PAHs in urban areas (Badran et al., 2020; Borgie et al., 2016; Daher et al., 2013). Furthermore, Baalbaki et al. (2018) studied the PAH concentrations in PM$_{10}$ samples at a site in Zouk Mikael and showed higher values compared to two other urban sites in Beirut. Melki et al. (2017) presented the difference of PAHs and alkane concentrations and corresponding ratios between a site under industrial influence and a rural one in the Northern region of Lebanon. All the studies done on the PM$_{2.5}$ concentration reported values exceeding the WHO daily guideline (25 μg/m$^2$) and sometimes double or triple this value during dust storm events (Jaafar et al., 2014). A more complete study of the detailed organic characterization in summer and winter has also been performed in a semi-urban area in Beirut (Waked et al., 2013; Waked et al., 2014) measuring for the first time SOA in Lebanon.

Although these studies bring valuable information on air quality, they are limited to certain classes of organic compounds, and a short sampling period of few days to few weeks with a limited number of samples. In this context, this paper will bring a first detailed study of the organic compounds in PM$_{2.5}$ collected over almost one year period in Lebanon at a mixed industrial and heavy populated site in Zouk Mikael and an industrial-residential site in Chekka region, Fiaa. The present paper will focus on the composition and the seasonal variations of the POA including PAHs, alkanes, hopanes, fatty acids, and phthalates as well as the SOA including the oxidation products of α-pinene, isoprene and β-caryophyllene, and dicarboxylic acids. Some of these compounds, notably phthalates are reported for the first time in Lebanon. In order to identify the possible PM sources in the sampling areas, diagnostic ratios for different classes of compounds were also used. This first one-year study in the East Mediterranean region will help in assessing the impact of the industrial emissions on the organic aerosol composition.

1. Experimental

1.1. Sampling sites

PM$_{2.5}$ was collected at two sites in Lebanon: Zouk Mikael (33°57′57.07″N 35°37′09.46″E) – Mount Lebanon district, 14 km north-east of the capital Beirut, at the rooftop of a residential building (15 m above ground level), and in Chekka region, specifically Fiaa village (34°20′47.8″N 35°47′14.0″E)- Koura district, 60 km north-north-east of Beirut and 10 km southwest of Tripoli (Fig. 1).

Zouk Mikael area (ZK) is characterized by a high residential density (4,200 inhabitants/km$^2$), but also commercial and industrial activities. ZK has the biggest power plant in Lebanon of 1 GW$_{electrical}$ which runs on Heavy Fuel Oil (HFO). It encompasses 607 MW$_{electrical}$ of boilers with 2 common stacks releasing the emissions at 145 m, 198 MW$_{electrical}$ of reciprocating engines installed in 2017 with stack heights of around 40 m, and a power barge with 11 reciprocating engines with a total capacity of 198 MW$_{electrical}$ installed in 2012 with a stack height of around 50 m. Moreover, a high number of private generators along with small industries for plastic production, woodworks, steel construction, aluminum extrusion, marble, and granite production, etc. exist in this area. The Zouk Mikael highway and the thermal power plant are respectively 1.2 and 1.5 km away from the sampling site.
Fiaa area (FA) is far less populated than ZK (250 residents/km²). It is also influenced by private generators emissions. The main potential sources encompass chemical industries: two cement industries along with their corresponding quarries in Chekka, and a sulfuric acid and phosphate fertilizer industry few kilometers away (Fig. 1). In addition, the nearest highway is 4 km away from FA with moderate traffic. The two cement plants are 5 and 7 km away from the sampling site.

1.2. Sample collection

The sampling of fine particles (PM$_{2.5}$) was performed on a 24-hour basis every three days from 13th of December 2018 to 15th of October 2019. PM$_{2.5}$ was sampled using high-volume samplers (CAV-A/mb, MCV S.A., Spain) operating at 30 m$^3$/hr, onto 150 mm pure quartz microfibres filters (Fiorini, France). Filters were heated for 12 hr at 550°C before sampling to decrease the organic impurities content and kept at -20°C till sampling. Over the sampling period, 98 samples in ZK and 95 samples in FA have been collected. Field blanks (at least one/month) were also considered at each site by placing a blank filter in sampling conditions but without pumping. The collected filters were sealed in aluminum foil and stored at -20 °C until analysis. A wireless weather station (TFA-Dostmann 35.1112 OPUS) was installed at the ZK site to collect meteorological data. During the whole sampling period, 93% of the samples were collected under low windspeed (< 2 m/sec) indicating that the site was mainly under turbulent atmospheric conditions.

1.3. Organic compounds analysis

The method used for the organic compounds analysis was described elsewhere (Waked et al., 2013; 2014). In brief, a quarter of the filter was spiked with 50 μL of 2 internal standards (cis-ketopinic acid and bornylacetate) followed by an extraction by sonication for 30 min at 50°C using 30 mL of acetone/dichloromethane (50:50, V/V). After the extraction, the volume of the samples was reduced to 200 μL under a constant flow of nitrogen gas. The obtained solution was used to directly quantify non-polar compounds such as alkanes, PAHs, hopanes and some phthalates while polar compounds such as fatty acids and SOA compounds were quantified after derivatization. Derivatization was achieved with 50 μL of the extract treated using N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane and 10 μL of pyridine as a catalyst at 70°C for 2 hr.

A 2-μL of the derivatized and the non-derivatized extracts were injected using a gas chromatography coupled to a mass spectrometer (GC/MS) in the split mode with a split ratio of 1/25. The GC consisted of an ISQ 7000 (Thermo Scientific, United States of America) equipped with an HP 5MS UI capillary column (30 m x 0.25 mm x 0.25 μm, Agilent; United States of America). The column temperature program consisted of an injection at 65°C hold for 2 min, a ramp of temperature corresponding to 6°C/min up to 300°C followed by an isothermal hold step at 300°C for 20 min. The GC was interfaced to an ion trap MS with an external electron ionization (EI) source (220°C, 70 eV).

1.4. Identification and quantification of organic compounds

For compounds for which an authentic standard was available in the laboratory (around 50 compounds), the identification was made by comparing the retention time and the mass spectrum associated to the reference compound (full
scan mode, range 50-500 m/z). Additionally, this method permitted the identification of alkanes from C_{12} to C_{40}.

For other compounds, the identification was based on the retention time, and the reference mass spectrum from the literature (Claeys et al., 2004; El Haddad et al., 2011b; Jaoui et al., 2007). In this case, the quantification was done using the response factor (RF) of a surrogate compound. For α-pinene oxidation products: (i) the RF of malic acid was used for 3-hydroxyglutaric acid (A1), 3-acetylglutaric acid (A2) 3-isopropylglutaric acid (A3) and 3-methyl-1,2,3-butanetricarboxylic acid (A4); (ii) the RF of glyceric acid was assigned to 2-methylglyceric acid (2-MGA); (iii) the RF of threitol was used for 2-methylthreitol (MT1), 2-methylethreitol (MT2), and (iv) the RF of pinic acid was used for β-caryophyllinic acid (βC). For the hopane family, the RF of 17α(H)-21β(H)-hopane, an authentic standard, was used to quantify the concentrations of trisnorhopane, 17α(H)-trisnorhopane, 17α(H)-21β(H)-norhopane, 17α(H)-21β(H)-22S, and 22R-homohopane.

The field blanks were analyzed following the same procedure as the sampling filters. The concentrations of the species in the PM_{2.5} samples were corrected by subtracting the mean value obtained for the field blank filters.

The detection limit was evaluated for all the compounds and corresponds to the blank filter value plus 3 times the standard deviation calculated over 3 measurements. It ranged between 0.0003 and 0.08 ng/m^{3} for non-derivatized compounds and between 0.002 and 0.25 ng/m^{3} for derivatized compounds except for stearic acid with a higher detection limit (2.3 ng/m^{3}).

The coefficient of determination (R^{2}) of the calibration curves, determined several times during the analysis period, for compounds with authentic standards, ranged between 0.93 - 0.99 except for tetracosanoic acid (0.90). Repeatability was assessed by studying the variation in the RF of 5 consecutive injections of the authentic standards (DBI, 2003). The variations were less than 14%. The analytical uncertainty was calculated using the quantification limit of the compound, the repeatability, and the concentration of the compound. The total uncertainty including the analytical uncertainty and the uncertainty associated to the mass flow measurement of the sampler was in the range of 9%-30 % at 2σ.

Recoveries were determined by spiking blank filters by standard solutions. The values were estimated to be 80%, 82%, 92%, 90%, 85%, 82%, and 97% for alkanes, PAHs, fatty acids, phthalates, dicarboxylic acids, pinic acid, and hopanes respectively. For compounds with no authentic standard (i.e. some SOA markers), the recovery of the surrogate compound was determined to be 85% for glyceric acid and 95% for threitol.

1.5. Index and diagnostic ratios calculation

Statistical diagnostic methods were used in a quantitative and qualitative way in order to investigate the origin of the different organic species in the PM_{2.5}. The indexes for the n-alkanes were used to differentiate the anthropogenic and the biogenic origins. As for the PAHs, the ratios were used to separate pyrogenic and petrogenic sources with a focus on the type of combustion.

1.5.1. Ratios for the n-alkanes

Three methods were used to assess the contribution of the sources for the paraffins: the carbon number of the alkane having the maximum concentration (C_{max}), the carbon preference index (CPI), and the input of wax from plants (Wax ratio).

C_{max} is used in general to differentiate between two alkane sources: vegetation wax emissions for the high odd number of carbons, i.e. 27, 29, and 31, and anthropogenic source for the lower numbers (Andreou and Rapsomanikis, 2009).

The Carbon Preference Index (CPI) is a measure of odd to even alkanes predominance (Simoneit, 1999) and evaluates the contribution of the anthropogenic and the biogenic source. Two CPI parameters were adopted: the Overall CPI_{19-32} for all the alkanes and the High CPI_{25-32} for the biogenic n-alkanes and were calculated using Eq. 1 and Eq. 2 (Bray and Evans, 1961; Cooper and Bray, 1963).

\[
\text{Overall CPI}_{19-32} = \frac{\sum \text{odd } C_n - C_{31}}{\sum \text{even } C_n - C_{32}}
\]

\[
\text{High CPI}_{25-32} = \frac{\sum \text{odd } C_{25} - C_{31}}{\sum \text{even } C_{26} - C_{32}}
\]

An overall CPI value close to 1 indicates a petrogenic source, between 2 and 5 mainly biomass burning, while a value higher than 6 is characteristic of biogenic emissions (Simoneit, 2002). For the High CPI, a value less than 1.5 indicates an anthropogenic source while a value higher than 3 indicates a biogenic one (Melki et al., 2017). An intermediate value explains a mix of biogenic and anthropogenic sources.

The Wax ratio was used to determine the distribution of the residual wax n-alkanes when the petroleum n-alkanes are subtracted (Simoneit et al., 1991). First, Wax_{C_n} is calculated by subtracting the odd average concentration C_{n} of the next higher C_{n+1} and lower C_{n-1} carbon (Eq. 3). Then, the Wax ratio (Wax%) corresponding to the percentage of Wax related n-alkanes, is calculated by dividing the ΣWax_{C_n} (the sum of Wax_{C_n} for odd alkanes, with negative values of Wax_{C_n} taken as a Zero) by the total concentration of all the n-alkanes in the sample (ΣA) (Eq. 4).

\[
\text{Wax}_{C_n} = \frac{1}{2} (C_{n-1} + C_{n+1}) \quad \text{with } n : \text{odd number}
\]

\[
\text{Wax} \% = \frac{\Sigma \text{Wax}_{C_n}}{\Sigma A} \times 100
\]

1.5.2. PAHs diagnostic ratios

PAHs diagnostic ratios have been used to determine the source of particle-containing PAHs. They can help to determine the different emission sources as well the different fuel types used in the combustion processes (Riffault et al., 2015). This methodology is based on the hypothesis that the PAH concentration ratios remain constant between the emission source and the measuring site. This is particularly true for isomers having similar photochemical properties considered to be affected in a similar manner by the different reactions occurring in the atmosphere (Borgie et al., 2016). Different ratios were calculated considering the concentrations of fluoranthene (Fla), pyrene (Pyr), indeno[1,2,3-c,d]pyrene (InPy), benzo[g,h,i]perylene (BghiPe), benzo[a]anthracene (B[a]An), chrysene (Chr), and benzo[a]pyrene (B[a]P), and com-
Table 1 – Atmospheric concentrations of identified n-alkanes and hopanes during the entire sampling period (Total: Dec 2018 - Nov 2019), winter (Dec 2018-March 2019), and summer (June 2019-September 2019) periods at Zouk (ZK) and Fiaa (FA) sites.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Average concentration (min-max) (ng/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZK site</td>
</tr>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td><strong>n-Alkanes</strong></td>
<td></td>
</tr>
<tr>
<td>Nonadecane (C19)</td>
<td>0.42 (0.11-0.97)</td>
</tr>
<tr>
<td>Heicosane (C20)</td>
<td>0.45 (0.01-1.50)</td>
</tr>
<tr>
<td>Heneicosane (C21)</td>
<td>0.56 (0.04-2.42)</td>
</tr>
<tr>
<td>Docosane (C22)</td>
<td>1.03 (0.11-3.61)</td>
</tr>
<tr>
<td>Tricosane (C23)</td>
<td>1.84 (0.09-6.49)</td>
</tr>
<tr>
<td>Tetracosane (C24)</td>
<td>2.55 (0.10-12.7)</td>
</tr>
<tr>
<td>Pentacosane (C25)</td>
<td>2.99 (0.45-13.2)</td>
</tr>
<tr>
<td>Hexacosane (C26)</td>
<td>2.90 (0.44-15.1)</td>
</tr>
<tr>
<td>Heptacosane (C27)</td>
<td>3.25 (0.73-16.9)</td>
</tr>
<tr>
<td>Octacosane (C28)</td>
<td>2.16 (0.21-11.6)</td>
</tr>
<tr>
<td>Nonacosane (C29)</td>
<td>2.94 (0.51-25.8)</td>
</tr>
<tr>
<td>Tricosane (C30)</td>
<td>1.65 (0.92-6.59)</td>
</tr>
<tr>
<td>Henrioanthane (C31)</td>
<td>2.66 (0.02-18.5)</td>
</tr>
<tr>
<td>Dotriacontane (C32)</td>
<td>1.27 (0.15-5.18)</td>
</tr>
<tr>
<td><strong>Total (ZA)</strong></td>
<td>26.70</td>
</tr>
<tr>
<td><strong>Hopanes</strong></td>
<td></td>
</tr>
<tr>
<td>Trinoroneohopane (H1)</td>
<td>0.28 (0.03-1.37)</td>
</tr>
<tr>
<td>17x(H)-Trinorohopane (H2)</td>
<td>0.37 (0.06-1.48)</td>
</tr>
<tr>
<td>17x(H)-21(H)-Norhopane (H3)</td>
<td>1.08 (0.24-3.51)</td>
</tr>
<tr>
<td>17x(H)-21(H)-Hopane (H4)</td>
<td>1.08 (0.28-3.39)</td>
</tr>
<tr>
<td>17x(H)-21(H)-22S-Homohopane (H5)</td>
<td>0.74 (0.13-3.19)</td>
</tr>
<tr>
<td>17x(H)-21(H)-22R-Homohopane (H6)</td>
<td>0.67 (0.10-3.74)</td>
</tr>
<tr>
<td><strong>Total (XHop)</strong></td>
<td>4.22</td>
</tr>
</tbody>
</table>

2. Results and discussions

This study was performed over almost a one-year period. We chose to discuss the average concentrations calculated for the overall period as well as the concentrations associated with the winter (December 2018 till March 2019) and the summer periods (June 2019 till September 2019) in order to assess seasonal trends. The corresponding concentrations for all studied compounds are given in Table 1, Table 2, and Table 4. Chronological evolutions are included in the supplementary material to support interpretations (Fig. S2, Fig. S3, Fig. S4).

2.1. Primary Organic Aerosols (POA)

Primary emissions from biogenic and anthropogenic sources include more than forty sources in urban areas (Rogge et al., 1996) such as road transport, road dust, tire wear, cooking operations, industrial boilers, fireplaces burning woods, plant leaf abrasion, etc.

2.1.1. n-Alkanes

The yearly average of n-alkanes concentrations at both sites is quite similar with 26.70 ng/m³ at ZK versus 29.12 ng/m³ at FA (Table 1). Nevertheless, the distribution of the n-alkanes concentration over the year was different: at ZK site, the winter period concentration (31.63 ng/m³) is much higher than the summer one (17.61 ng/m³) whereas it is similar for both seasons at FA (25.76 vs 28.11 ng/m³). The observed values are similar to those reported (23 ng/m³) for a coastal urban-industrial site at Dunkirk, France (Landkocz et al., 2017) and much lower than those presented for an industrial site in Tianjin, China (136-314 ng/m³) (Li et al., 2010). This difference gets more important with a big population in China and a site exposed to intensive coal burning emissions for industrial and domestic purposes.

A clear seasonal pattern for the n-alkanes distribution ranging from C19 to C32 was observed at ZK and FA with higher concentrations of C21-C27 during winter compared to summer.
Table 2 – Atmospheric concentrations of identified polycyclic aromatic hydrocarbons (PAHs), fatty acids, and phthalates during the entire sampling period (Total: Dec 2018-Nov 2019), winter (Dec 2018-March 2019), and summer (June 2019-September 2019) periods at Zouk (ZK) and Fiaa (FA) sites.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Average concentration (min-max) (ng/m³)</th>
<th>FA site</th>
<th>ZK site</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAHs</td>
<td></td>
<td>Total</td>
<td>Winter</td>
</tr>
<tr>
<td>Acenaphthylene (Acy)</td>
<td>0.02 (0.01-0.08)</td>
<td>0.02 (0.01-0.09)</td>
<td>0.03 (0.02-0.08)</td>
</tr>
<tr>
<td>Acenaphthene (Ace)</td>
<td>0.02 (0.01-0.09)</td>
<td>0.02 (0.01-0.09)</td>
<td>0.03 (0.01-0.09)</td>
</tr>
<tr>
<td>Fluorene (Flu)</td>
<td>0.02 (0.01-0.25)</td>
<td>0.02 (0.01-0.25)</td>
<td>0.02 (0.01-0.25)</td>
</tr>
<tr>
<td>Anthracene (Anth)</td>
<td>0.12 (0.01-0.42)</td>
<td>0.15 (0.05-0.42)</td>
<td>0.09 (0.01-0.21)</td>
</tr>
<tr>
<td>Phenanthrene (Phe)</td>
<td>0.03 (0.01-0.09)</td>
<td>0.04 (0.01-0.09)</td>
<td>0.02 (0.01-0.09)</td>
</tr>
<tr>
<td>Fluoranthene (Fla)</td>
<td>0.13 (0.01-0.68)</td>
<td>0.22 (0.05-0.68)</td>
<td>0.06 (0.01-0.19)</td>
</tr>
<tr>
<td>Pyrene (Pyr)</td>
<td>0.15 (0.01-0.76)</td>
<td>0.24 (0.05-0.76)</td>
<td>0.07 (0.01-0.19)</td>
</tr>
<tr>
<td>Benzo[a]anthracene (B[a]An)</td>
<td>0.15 (0.01-0.76)</td>
<td>0.25 (0.06-0.76)</td>
<td>0.07 (0.01-0.19)</td>
</tr>
<tr>
<td>Chrysene (Chr)</td>
<td>0.28 (0.02-1.17)</td>
<td>0.44 (0.11-1.17)</td>
<td>0.12 (0.02-0.30)</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene (B[b]Fl)</td>
<td>0.27 (0.04-1.07)</td>
<td>0.44 (0.12-1.05)</td>
<td>0.10 (0.04-0.22)</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene (B[k]Fl)</td>
<td>0.15 (0.07-0.75)</td>
<td>0.27 (0.04-0.75)</td>
<td>0.05 (0.01-0.13)</td>
</tr>
<tr>
<td>Benzo[a]pyrene (B[a]P)</td>
<td>0.20 (0.12-0.26)</td>
<td>0.38 (0.06-1.26)</td>
<td>0.05 (0.01-0.20)</td>
</tr>
<tr>
<td>Dibenz[a,h]anthracene (DB[a,h]An)</td>
<td>0.45 (0.21-0.86)</td>
<td>0.89 (0.20-1.86)</td>
<td>0.08 (0.01-0.26)</td>
</tr>
<tr>
<td>Benzo[g,h,i]perylene (BghiPe)</td>
<td>0.07 (0.01-0.40)</td>
<td>0.09 (0.02-0.38)</td>
<td>0.04 (0.01-0.13)</td>
</tr>
<tr>
<td>Indeno[1,2,3-c,d]pyrene (lnPy)</td>
<td>0.49 (0.03-3.11)</td>
<td>0.85 (0.03-3.11)</td>
<td>0.11 (0.03-0.50)</td>
</tr>
<tr>
<td>Total (ΣPAHs)</td>
<td>2.56</td>
<td>4.35</td>
<td>0.88</td>
</tr>
<tr>
<td>Fatty acids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dodecanoic acid (DDA)</td>
<td>5.35 (0.04-17.33)</td>
<td>7.00 (2.09-17.33)</td>
<td>3.98 (0.04-12.00)</td>
</tr>
<tr>
<td>Tetradecanoic acid (TDA)</td>
<td>8.05 (0.29-52.19)</td>
<td>7.15 (0.86-52.19)</td>
<td>8.21 (0.29-18.11)</td>
</tr>
<tr>
<td>Hexadecanoic acid (HDA)</td>
<td>259.47 (2.29-3197.75)</td>
<td>171.55 (20.25-1201.27)</td>
<td>423.99 (2.29-3197.72)</td>
</tr>
<tr>
<td>Octadecanoic acid (ODA)</td>
<td>175.32 (16.57-1508.02)</td>
<td>221.20 (16.57-730.00)</td>
<td>189.51 (18.00-1508.02)</td>
</tr>
<tr>
<td>Elcosanoic acid (EA)</td>
<td>8.50 (0.43-34.68)</td>
<td>12.08 (0.43-34.68)</td>
<td>7.07 (0.79-29.12)</td>
</tr>
<tr>
<td>Docosanoic acid (DA)</td>
<td>18.75 (0.10-124.74)</td>
<td>28.61 (4.96-107.34)</td>
<td>12.45 (0.10-124.74)</td>
</tr>
<tr>
<td>Tetracosanoic acid (TA)</td>
<td>15.79 (0.69-85.33)</td>
<td>26.84 (0.98-85.33)</td>
<td>10.89 (0.80-76.67)</td>
</tr>
<tr>
<td>Oleic acid (OA)</td>
<td>17.07 (0.13-80.26)</td>
<td>21.34 (3.19-80.26)</td>
<td>14.81 (0.13-71.59)</td>
</tr>
<tr>
<td>Total (ΣFA)</td>
<td>508.29</td>
<td>497.24</td>
<td>671.68</td>
</tr>
<tr>
<td>Phthalates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diisobutylphthalate (DiBP)</td>
<td>22.19 (2.12-102.10)</td>
<td>20.92 (3.41-102.10)</td>
<td>24.17 (2.12-53.75)</td>
</tr>
<tr>
<td>Dibutylphthalate (DnBP)</td>
<td>35.69 (3.86-126.93)</td>
<td>15.48 (3.86-60.06)</td>
<td>57.84 (20.09-114.06)</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl)phthalate (DEHP)</td>
<td>48.99 (4.93-124.05)</td>
<td>43.09 (4.93-104.01)</td>
<td>58.39 (0.13-124.05)</td>
</tr>
<tr>
<td>Total (ΣPAEs)</td>
<td>106.88</td>
<td>79.49</td>
<td>140.40</td>
</tr>
</tbody>
</table>

Number of rings for PAHs
1: 3 rings 2: 4 rings 3: 5 rings 4: 6 rings
especially for the ZK site (Fig. 2). This could be attributed to the higher contribution of the residential heating in the cold period. The larger difference observed for ZK reinforces this hypothesis since ZK is much more populated than FA. In the summer period, the n-alkanes distribution profile shifts to the highest carbon number, ≥ C27, ascribable to plant wax-derived alkanes (Rogge et al., 1993b). The concentrations of the high odd alkanes in FA are remarkably higher than those in ZK showing higher contribution of the natural source at FA. This can be explained by the fact that Chekka region, and Fiaa precisely are more densely surrounded by green lands and trees. In both sites in winter, Cmax was at C25 indicating the prevalence of the anthropogenic sources (Simoneit, 1989). In summer, the most abundant n-alkanes are C29 and C31 at ZK and C27 and C29 at FA suggesting a higher relative contribution of biogenic aerosols during the hot season (Li et al., 2006).

The CPI values were calculated as described in section 2.5.1 for each PM2.5 sample and presented in (Fig. 3). In the winter period, for both sites, the obtained High CPI values, below 1.5, indicate a quasi-exclusively anthropogenic origin for the n-alkanes. The Overall CPI close to 1 also indicates the contribution of a petrogenic source (petroleum residues). In the summer period, the High CPI shifted to values between 1.5 and 3 for most of the samples in ZK, indicating a mixed influence of natural and anthropogenic sources. Only few samples have the same tendency in FA site suggesting the higher impact of the anthropogenic sources during summer.

The contribution of the natural sources as the primary biogenic source can be assumed by calculating the Wax ratio (Wax%). Wax% values were similar for the whole period (13%) at both sites (Table 3). This ratio is in agreement with the value of 16% reported for a Lebanese site under industrial influence, Zakroun in Chekka region and lower than the one observed in a rural site (27%), Kaftoun in Chekka region too (Melki, 2017) due to the absence of primary sources near the site.

The Wax% increased in the summer period, 20% and 14% respectively in ZK and FA (compared to 7% and 9% during winter respectively) emphasizing on the increase of natural source contributions in the summer period. The winter Wax% at ZK and FA are in agreement with the value of 7% obtained in Sin El Fil, an urban site in Lebanon during a winter campaign in 2017 (Badran et al., 2020). The site was characterized by important road traffic, diesel generators, and waste incineration emissions. Additionnally, the values appear to be in the range of those measured at an industrial site in Tianjin of 10% in winter and 30% in summer (Li et al., 2010). A good correlation (R² > 0.90) was observed between the Wax% and the Overall CPI at both sites for the whole sampling period which is also noted in other urban areas (Andreou and Rapsomanikis, 2009; Kotianova et al., 2008).

Despite the fact that biogenic related alkanes have higher contributions in the hot season at both sites, low wax percentages and CPI values close to unity show that plant waxes are not the major source for these alkanes. Hence, anthropogenic combustion sources related to diesel generators, road traffic, industrial processes and to residential heating in winter can be assumed to account to the majority of emissions of n-alkanes in the studied areas.
2.1.2. Polycyclic aromatic hydrocarbons (PAHs)

The concentration of the 16 priority PAHs listed by the United States Environmental Protection Agency (US EPA) in relation with their toxicity, mutagenicity and/or carcinogenic properties has been investigated. The main source of emission of PAHs in the atmosphere is the combustion of fossil and non-fossil fuels (Mastral et al., 2003).

The total PAH concentration was higher in ZK (2.56 ng/m³) than in FA (0.95 ng/m³). The concentration of naphthalene was below the detection limit which has also been observed in other studies since the partitioning coefficient favors the gas phase of this compound (Waked et al., 2013; 2014). The total particulate phase PAHs measured values are in agreement with the 1.16 ng/m³ reported for a background urban site in Lebanon (Borgie et al., 2015) but are lower than those reported in both particulate and gaseous phases by Daher et al. (2013) near Jal el Dib freeeway, Lebanon for PM_{2.5} (12.2 ng/m³) and by Baalbaki et al. (2018) in Zouk Mikael (25.1 and 27.7 ng/m³ in winter and summer respectively for PM_{10}). Compared to other industrial urban sites, these values are higher than those observed (0.224 ng/m³) in the Czech Republic (Mikuška et al., 2015) but lower than those in Northern France (7.7 ng/m³) (Landkocz et al., 2017), and much lower than those measured at an industrial region in China (235 ng/m³) (Bi et al., 2020).

In this study, PAH concentrations tend to be 3 (at FA) to 5 (at ZK) times higher in the winter period (4.35 and 1.70 ng/m³ at ZK and FA respectively) compared with the summer period (0.88 and 0.50 ng/m³ respectively). This observation could be due to increasing primary source emissions specially combustion activities alongside the atmospheric stability in winter, partitioning between particulate and gaseous phases, and greater photochemical degradation during summer (Pindado et al., 2009). The ratio of (3+4 rings)/(5+6 rings) PAHs was calculated for both seasons and showed the same average of 0.76 at FA while a seasonal difference was evidenced in ZK (0.59 in winter and 1.21 in summer). The lower ratio in winter at ZK could indicate that the contribution of local sources to PAH concentration was higher in this period compared with the summer one (Tan et al., 2011).

Looking at the yearly average concentrations, and comparing the PAHs distribution, a specificity appears for the ZK site.
While no predominant compound is clearly evidenced at FA site, at ZK site InPy and DiB[a,h]An appear to be the main PAHs. Moreover, a strong correlation during the total sampling period exists for these latter only at ZK ($R^2 = 0.87$ at ZK versus $R^2 = 0.40$ at FA). This suggests that these compounds are locally emitted and are related to a common source of emission in the ZK study area.

To go further, the contribution of the different sources of PAHs was investigated by the study of the PAHs diagnostic ratios. Using the Fla/(Fla+Pyr) and the InPy/(InPy+B[ghi]Pe) isomer ratios makes possible the evidencing of the contribution of petrogenic, wood and coal combustion, fuel combustion, and also diesel and gasoline sources. According to the literature, the Fla/(Fla+Pyr) suggests a petrogenic source for a value lower than 0.2, a liquid fossil fuel combustion for 0.4-0.5, and wood or coal combustion for a value higher than 0.5 (Cazier et al., 2016; Ravindra et al., 2008). The InPy/(InPy+B[ghi]Pe) ranging between 0.2 and 0.5 is considered as a marker for gasoline source, 0.35-0.7 for diesel source, and wood and coal combustion for values higher than 0.5 (Bi et al., 2020; Riffault et al., 2015).

At ZK and in both seasons, Fla/(Fla+Pyr) ratio ranges between 0.4 and 0.5 indicating that fuel combustion emissions were predominant (Fig. 4). Moreover, InPy/(InPy + B[ghi]Pe) ratio shows values mainly above 0.8 and only few values in the 0.2-0.7 range. Hence, these observations allow to conclude that at ZK site (i) road traffic is not the predominant source of InPy and B[ghi]Pe since it has a characteristic InPy/(InPy+B[ghi]Pe) value of 0.31 in Lebanon (Daher et al., 2013) in line with Bi et al. (2020) and Riffault et al. (2015) as the traffic in Lebanon is dominated by gasoline (Abdallah et al., 2020), (ii) Diesel private generators are not the main source since the observed ratio values are higher than 0.8, and (iii) this source cannot be associated to biomass burning which has ratio values above 0.6 (Ravindra et al., 2008; Tobiszewski and Namieśnik, 2012) since it contradicts the observed Fla/(Fla+Pyr) values. Therefore, a deep interpretation of PAHs concentrations is needed to identify a potential source with a characteristic ratio above 0.8 specific to liquid fuel combustion.

High values of the InPy/(InPy+B[ghi]Pe) ratio were obtained by Manoli et al. (2004) for oil burning from residential heating appliance chimneys (0.82), cement plants (0.90-0.96) and diesel emissions from taxis and buses (0.96). However, none of these sources are present in the surroundings of the ZK site. Consequently, the thermal power plant located in ZK is a potential source since it uses a third type of liquid fuel; the Heavy Fuel Oil (HFO). To investigate this hypothesis, the samples when the site was predominantly down wind of the power plant encompassing wind speeds above 2 m/s were examined. Only two filters met clearly the selection criteria (Fig. S1) and showed InPy/(InPy+B[ghi]Pe) ratio values of 0.84 and 0.93 which are in line with our hypothesis. Ratio values varying around 0.9 were encountered in most of the samples which can be explained by the fact that HFO combustion emissions are released at 145 m of height by the 607 MW boilers resulting in an enhanced dispersion affecting a broader area like the surrounding cities ie. Jounieh, but also at around 50 m from the ground by the 396 MW reciprocating engines with consequently less enhanced dispersion impacting a smaller area concentrated on Zouk Mikael entirely and nearest surroundings. This observation results in affected air masses reaching the site from all directions.
Up to our knowledge, the literature is scarce regarding characteristic InPy/(InPy+B[ghi]Pe) ratio value for the heavy fuel oil combustion occurring in power plants. Cecinato et al. (2014) indicates a value of 0.35 based on the emission factors. This value won’t vary much for the particulate phase only since partitioning coefficients between particulate and gaseous phases for the two compounds are very close (Kim and Kim, 2015). Values of 0.35 and 0.5 can be also obtained from a study conducted by Yang and co-workers and from the US EPA AP-42 respectively (USEPA, 2010; Yang et al., 1998). However, the representativeness of these values is poor, as several authors in the literature stress on the idea that the PAH emissions strongly depend on the combustion conditions and quality of fuel that might change from a site to another (Masclet et al., 1987; Mastral and Callén, 2000; Ravindra et al., 2008; Tobiszewski and Namiešnik, 2012).

With the idea to better define this new characteristic ratio value, the “Source Profile by Unique Ratio” (SPUR) method was applied (Annegarn et al., 1992; Ledoux et al., 2017). This method consists to plot a ratio involving the characteristic species of the source versus the concentration of the characteristic species. The limit of the ratio obtained for the highest concentrations of the characteristic species can be assumed as the characteristic ratio of the source. It has been applied to the InPy/(InPy+B[ghi]Pe) ratio versus InPy concentrations (Fig. 5) as InPy shows particularly high concentrations at ZK site. The SPUR method allows to suggest an InPy/(InPy+B[ghi]Pe) characteristic ratio between 0.8 and 1 for the Heavy Fuel Oil combustion occurring in a thermal power plant.

At FA, the InPy/(InPy+B[ghi]Pe) ratio values appear mainly in the 0.2-0.7 range (diesel and gasoline combustion) and no value higher than 0.75. In addition, the Fla/(Fia+Pyr) ratio values indicate a mix of fuel combustion from vehicular emissions and diesel generators along with wood and coal combustion. The cement industries in Chekhha use coke as their primary combustion source which explains our results.

Then, the values of B[a]An/(B[a]An+Chr) ratios in ZK were 0.36 and 0.37 for winter and summer respectively with no significant difference between the seasons meaning that these compounds come from a constant activity throughout the sampling period. In addition to that, the B[a]P/(B[a]P+Chr) ratio was 0.46 in winter and 0.28 in summer. According to the literature, the ratio B[a]An/(B[a]An+Chr) refers to a pyrogenic source generated from the combustion of fossil fuel (coal and petroleum) and/or biomass for values higher than 0.35 and a petrogenic one from unburned crude oil and petroleum products for values lower than 0.2 (Boonyatumanond et al., 2007; Wu et al., 2014). On the other hand, the ratio B[a]P/(B[a]P+Chr) is generally used to assess the contribution of vehicular emissions. It was reported as 0.33 at an urban environment (Guo, 2003), 0.49 for gasoline emissions, and 0.73 for diesel emissions (Khalili et al., 1995). In Lebanon, the on-road fleet runs to a high extent gasoline (Abdallah et al., 2020). Consequently, these two ratios suggest that the road traffic is an important source of B[a]An, B[a]P, and Chr in ZK during both seasons. These ratios were not calculated in FA due to the values of Chr below quantitation limit.

Finally, the combustion PAHs (CPAHs) accounted for 71% and 77% during winter and 69% and 72% of the total PAH concentration (TPAH) during summer in ZK and FA, respectively. Despite the difference in the concentrations between the two sites, the combustion source impact is remarkably important and constant during both seasons suggesting that these PAHs are mainly emitted from sources that do not have any seasonal pattern such as diesel private generators, road traffic, and industrial emissions (HFO and coke combustion at ZK and FA, respectively) rather than unburned fossil fuels. These results are in agreement with the dominant anthropogenic origin of the alkanes emissions.

Fig. 5 – Source profile by unique ratio (SPUR) method applied to the InPy/(InPy+B[ghi]Pe) ratio considering ZK site data.
2.1.3. Hopanes

Hopanes are fossil fuel compounds present in unburned lubricating oils and are not found in diesel and gasoline because they belong to the higher boiling fraction of crude petroleum (Henry et al., 1984; Rogge et al., 1993a).

At ZK, the total concentration during the sampling period equals to 4.18 ng/m² (Table 1) and is close to that reported in Ostrava, Czech Republic equal to 3.79 ng/m² after smog episode (Mikuška et al., 2015). The average concentrations of hopanes were 4.66 and 3.91 ng/m² in PM2.5 for ZK in the winter and the summer periods respectively. The seasonal difference could be mainly due to the fact that the hopanes are more volatile during the hot season (Ruehl et al., 2011) as well as the lower average road traffic intensity in summer due to the closing of education institutions till September (Waked and Afif, 2012). These values are higher than 1.2 and 1.65 ng/m² reported for an urban area in Guangzhou, China for winter and summer, respectively (Wang et al., 2016).

The two most abundant hopanes were 17α(H)-21β(H)-norhopane and 17α(H)-21β(H)-hopane accounting for 50% of the total hopane concentration and exhibit a good correlation (R² = 0.85). The S/(S+R) epimers ratio for 17α(H)-21β(H)-homohopane could indicate that compounds are either emitted from road traffic or from coal combustion with 0.5 as the cutoff value between the two sources (Mikuška et al., 2015). At ZK site, higher concentrations for the S epimer compared with the R epimer were found (S/S + R > 0.5) showing the major influence of road traffic. All these findings were in agreement with El Haddad et al. (2009) who concluded that these compounds were emitted from vehicular emissions.

The observations also show a decrease of 25 % on average in hopanes concentration on Sundays (3.27 ng/m²) compared to weekdays (4.40 ng/m²) (Table S1). The weekend in general, but specially Sundays exhibit lower traffic related activities.

At the FA site, the PM2.5 hopane content was below the detection limit. This is in agreement with the fact that the vehicular emissions in Chekka region are much lower than those in ZK which is also highlighted by the chrysene concentrations which are below the detection limit at FA site.

2.1.4. Fatty acids

In this study, the fatty acids class were the most abundant detected organic compounds with average concentrations over the entire period of 508.29 and 717.63 ng/m³ at ZK and FA, respectively. The concentrations are in range of the 644 ng/m³ reported for the semi urban site in Beirut in summer (Waked et al., 2014) but much higher than the 234 ng/m³ reported in winter (Waked et al., 2013) for the same site and those reported for 3 urban Indian sites (234-583 ng/m³) (Gadi et al., 2019). Average concentrations of hexadecanoic acid (HDA) and octadecanoic acid (ODA) were 259.47 and 175.32 ng/m³ in ZK, and 415.19 and 247.14 ng/m³ in FA, respectively. Concentrations of these species accounted for 86 and 92% of the total alkanolic acids in ZK and FA, respectively. In addition to that, oleic acid which is an alkenolic acid was analyzed and showed concentrations of 17.07 ng/m³ at ZK and 14.61 ng/m³ at FA.

Generally, this class of compounds is the most abundant in the organic fraction (Rogge et al., 1991). The main components are hexadecanoic and octadecanoic acids as saturated fatty acids and oleic acid as unsaturated fatty acid. These compounds have multiple sources but are mostly emitted from cooking activities in urban areas (Rogge et al., 1991) when glycerides present in seed oils are pyrolyzed (Schauer et al., 2002).

HDA and ODA were well correlated in both sites (R² = 0.94 in ZK and R² = 0.96 in FA) but no correlation was found with oleic acid (R² = 0.15 in ZK and R² = 0.20 FA). These results are in agreement with Robinson et al. (2006) who concluded that saturated and unsaturated fatty acids have different cooking dominant sources with the assumption that these compounds are stable in the atmosphere.

The high concentrations observed for fatty acids are mainly due to the residential typology of the sites. The cooking activities are abundant especially with the usage of Canola and Soybean seed oil for frying. The concentrations for the fatty acids are higher in FA than in ZK due to the fact that the sampling site in FA was closer to houses. The seasonal variation in ZK show higher concentrations in summer mainly due to more outdoor cooking activities (i.e. charcoal grilling of meat and chicken) as well as for the restaurants that are more abundant in the area.

2.1.5. Phthalates

Phthalates are a group of man-made chemical compounds with esters of phthalic acid used as plasticizers in industrial final products and building materials (Lu et al., 2018).

To our knowledge, this study is the first dealing with the quantification of phthalates in Lebanon. The average concentration of phthalates was 106.88 and 97.68 ng/m³ respectively at ZK and FA. These values are lower than those reported in 3 Indian urban sites (211, 159, and 130 ng/m³) (Gadi et al., 2019) but similar to the 89 ng/m³ reported in an urban site in Northern Vietnam (Nguyen et al., 2016).

Bis(2-ethylhexylphthalate) (DEHP) has the highest concentration between the compounds during the different seasons at both sites and in all the samples. It is generally found in the particulate phase while other phthalates like diisobutylphthalate (DIBP) and dibutylphthalate (DnBP) are predominant in the gaseous fraction (Pei et al., 2013).

A particular attention was given to DIBP and DnBP at both sites because they show different time series (Fig. S2). At ZK site, similar values and trends were observed between the two species until the 15th of May after which the trend and values became different with higher concentrations of DIBP. While in FA, the contrary occurred with higher concentrations of DIBP than DnBP until the 1st of June 2019 after which concentrations became lower and similar. The comparison of the time series between the sites suggests that the emission sources were not the same and probably mainly related to local influence. Generally, it is known that these compounds are emitted during plastic burning (Simoneit et al., 2005). At FA, the high concentrations of these two phthalates were probably caused by the open waste burning in the North Governorate-which FA is part of- during the whole sampling time in several locations. This phenomenon increased during the March – May period (author field observation).

In order to further investigate this matter, DIBP and DnBP concentrations were plotted versus the sampling date (Fig. 6). Different correlation trends were observed at both sites. For the FA site, two separate trends with slopes of 1.36 (before June
17, 2019) and 1.01 (after June 17, 2019) can be distinguished. The difference might be explained by the different composition of waste that was burned.

A different scenario is shown in ZK between DIBP and DnBP, where the 15th of May 2019 is considered as the cutoff date between two trends for these 2 compounds. Before this date, the compounds are well correlated and show mostly a slope of 1.42 similar to those reported for Chekka region suggesting open waste burning with different waste composition. This activity might have been reduced in ZK after mid-May because the region is considered as a touristic destination in Lebanon during summer. However, a different slope value and higher DnBP concentrations were reported after this date suggesting higher production rates at the plastic industries located in ZK area and its surroundings in the south-west sector.

Considering the high concentrations of the phthalates in ZK and FA, further investigations should be focused on their emissions in the Lebanon and the middle eastern region. Whether they are emitted from municipal open waste burning or plastic industries, studies have shown that they might cause diverse health effects specially on the endocrine system, (Ji et al., 2014) the reproductive systems and children’s intelligence (Lu et al., 2018).

2.2. Secondary Organic Aerosols (SOA)

The secondary organic aerosols (SOA), an important fraction of the particulate matter, encompasses compounds produced from the transformation of organic species in the atmosphere in the gas or condensate phase (Kroll and Seinfeld, 2008). SOA from gas-phase reactions can result from oxidation of Volatile Organic Compounds (VOC) by atmospheric oxidants such as ozone O3, hydroxyl radicals OH and nitrate radicals NO3 (Atkinson, 2008). Isoprene, α-pinene, and β-caryophyllene are mainly emitted from deciduous trees, pine forests, and vegetation respectively as primary emissions. They can be oxidized through photochemical reactions to give Biogenic Secondary Organic Aerosol (BSOA). The formation of these compounds depend largely on temperature variations and photochemical processes of the precursors (Feng et al., 2013). In this part, we will focus on the BSOA as well as dicarboxylic acids which are generally produced by the gas phase photochemical reactions including a variety of anthropogenic and biogenic precursors.

2.2.1. Isoprene oxidation products

Isoprene is mainly emitted by broadleaf vegetation (Guenther et al., 1995) and is considered as a highly reactive compound due to its two double bonds (Carlton et al., 2009). The major SOA tracers identified in the case of isoprene are mainly the 2-methylglyceric acid (2-MGA) and the two diastereoisomers 2-methylthreitol (MT1) and 2-methylerythritol (MT2).

The average concentrations of MT1 and MT2 in summer were respectively 2.64 and 6.53 ng/m³ at ZK and 3.68 and 10.40 ng/m³ at FA (Table 4). They were at least 5 times higher than those measured in winter. This phenomenon is mainly due to the fact that the emissions of the precursor depend largely on the temperature variation and solar radiation as it enhances the photochemical reactions in the atmosphere (Feng et al., 2013).

The concentrations of the 2-methyltetrols (MT) were in range of those reported by Feng et al. (2013) for an urban and a suburban sites in Shanghai and lower than those reported for
two industrial sites in Ohio for the summer since the authors could not identify these compounds during the cold season (Rutter et al., 2014). In ZK and FA, MT1 and MT2 showed a very good correlation ($R^2 = 0.94$ at ZK and $R^2 = 0.96$ at FA) along with an MT2/MT1 ratio equal to 2.8 at FA and 2.6 at ZK (Fig. 53). These values are consistent with the value of 2.77 reported by Ion et al. (2005) suggesting that the 2-methyltrials have the same photochemical reaction scheme, originating from the direct oxidation of isoprene, and their formation rate is relatively constant during the sampling period (Ding et al., 2011; Zhu et al., 2018).

The levels of 2-MGA averaging at 0.47 and 0.86 ng/m$^3$ at ZK and FA respectively were lower than the 2-methyltrials (Table 4) at both sites and through the seasons. They are in the range of the concentrations reported for a Mediterranean urban industrial site (0.027-5.9 ng/m$^3$) in Marseille (El Haddad et al., 2011a) and lower than the 1.29 ng/m$^3$ observed at an urban site in Shanghai, China (Zhu et al., 2018).

In addition to that, 2-MGA showed a different time series from the two diastereoisomers MT1 and MT2 at both sites (Fig. 54) but also higher concentrations during summer and a low correlation with their sum ($R^2 = 0.50$ in ZK and 0.57 in FA). Originating from the oxidation of an isoprene first-generation product methacrolein, the formation of 2-MGA in the atmosphere strongly depends among others on humidity, acidity, and NO$_x$ conditions. Oxidation of isoprene under low NO$_x$ conditions preferentially lead to the formation of the MT while high NO$_x$ conditions favors the 2-MGA formation (Hallquist et al., 2009). Thus, the MT/2-MGA ratio might give an insight on the variation of local conditions. At ZK and FA, the MT/2-MGA ratio increased respectively from 11.9 and 10.9 in winter to 16.7 and 13.5 in summer. The high MT/2-MGA ratio value at both sites let suggest a predominance of the MT formation pathway. The slight increase at both sites in the summer period might be associated to the change of conditions in aerosol acidity or the gas-phase partitioning of the precursors of these compounds (Fu et al., 2014).

### 2.2.2. $\alpha$-Pinene oxidation products

$\alpha$-Pinene is considered as the main species in the monoterpane class and is emitted from conifers (Guenther et al., 1995). The average total concentration of $\alpha$-pinene derived SOA were 2.92 and 11.41 ng/m$^3$ at ZK and 13.68 and 22.88 ng/m$^3$ at FA during winter and summer periods respectively. These values are higher than those presented for two urban sites in Shanghai (0.8-0.9 ng/m$^3$ in January and 8.0-10.0 ng/m$^3$ in July) (Feng et al., 2013). The concentrations in summer at FA are also higher than the 16.8 ng/m$^3$ found in a study conducted in July in western Germany while those at ZK are lower (Kourtchev et al., 2008). Generally, higher concentrations were

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Average concentration (min-max) (ng/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ZK site</td>
</tr>
<tr>
<td></td>
<td>Total Winter Summer</td>
</tr>
<tr>
<td>2-Methylglyceric acid (2-MGA)</td>
<td>0.47 (0.04-5.19) 0.22 (0.05-0.93) 0.77 (0.04-5.19)</td>
</tr>
<tr>
<td>2-Methylthreitol (MT1)</td>
<td>1.41 (0.10-5.81) 0.37 (0.10-1.13) 2.64 (0.73-5.81)</td>
</tr>
<tr>
<td>2-Methylerythritol (MT2)</td>
<td>3.78 (0.53-14.61) 1.43 (0.53-4.69) 6.53 (1.04-14.61)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>5.67</td>
</tr>
</tbody>
</table>

**Table 4 – Atmospheric concentrations of identified secondary organic compounds during the entire sampling period (Total: Dec 2018- Nov 2019), winter (Dec 2018-March 2019), and summer (June 2019-September 2019) periods at Zouk (ZK) and Flaa (FA) sites.**
recorded at FA at both seasons due a greater coverage of plants and vegetation in the Chekka region.

The oxidation of α-pinene by OH radicals or its ozonolysis leads to pinic acid (FA) and pinonic acid which are considered as lower -or first- generation oxidation products. The concentrations of FA (Table 4) at both sites were found lower than the 16 ng/m³ reported at a semi-urban site during summer (Waked et al., 2014) and winter (9.87 ng/m³) in Lebanon (Waked et al., 2013). It is also lower than 4.2 ng/m³ found in western Germany (Kourtech et al., 2008).

For A1, A2, A3, and A4, the average concentration in ZK PM2.5 were 0.65, 0.62, 0.74, and 0.41 ng/m³ respectively in winter and about 5 times higher in the summer period. The same observation was highlighted in FA with twice higher concentrations in the hot period (Table 4). Typically, higher temperature and more solar radiations during the summer period enhance photochemical reactions. In addition to that, A1, A2, A3 and A4 concentrations were highly inter-correlated (R² = 0.77-0.85 at ZK and 0.78-0.85 at FA) during the total sampling period (Table S2) emphasizing their origins as second generation oxidation products of α-pinene. It is well established that A1 and A4 are generated by further reaction of pinic acid including OH radical and NOx (Halquist et al., 2009). El Haddad et al. (2011a) reported a good correlation between these four compounds suggesting a similar formation process. However, even though belonging to the same class, these compounds did not show any correlation with pinic acid (R² = 0.10-0.25) probably due to the different formation pathway and the kinetics of the oxidation processes (El Haddad et al., 2011a).

2.2.3. β-Caryophyllene oxidation product

The β-caryophyllene (βC) is considered as the most abundant species in the sesquiterpene class emitted from plants. The sesquiterpenes are characterized by their high reactivity and their low vapor pressure (Fu et al., 2010). β-Caryophyllinic acid was first identified in smog chambers then in ambient samples (Jiaou et al., 2007). It is considered as the major oxidation product and the molecular marker of β-caryophyllene emitted by terrestrial vegetations.

In this study, the levels of β-caryophyllinic acid were higher in ZK (0.71 ng/m³) than FA (0.44 ng/m³). βC did not show any seasonal variations at both sites. The same observation was made during an aircraft campaign over central China (Fu et al., 2014) and in an urban and suburban site in Shanghai, China (Feng et al., 2013). The total average concentrations at both sites are slightly higher than the 0.27 ng/m³ reported in Marseille, France (El Haddad et al., 2011a) in summer 2008 and comparable with the 0.7 ng/m³ observed at an urban site in Shanghai (Fu et al., 2014). However, much higher concentrations were observed at a suburban site in Lebanon with 10.59 ng/m³ in the summer and 1.21 ng/m³ in the winter period (Waked et al., 2013; 2014). This difference might be explained by the biomass burning activities in the suburban site leading to higher β-caryophyllinic acid concentrations (Fu et al., 2014).

2.2.4. Contribution of biogenic sources to the secondary organic carbon

The apportionment of the Secondary Organic Carbon (SOC) to the different BSOA is based on the SOA tracer method proposed by Kleindienst et al. (2007) in order to determine the highest contributor to the the organic carbon (Waked et al., 2014) among the isoprene, α-pinene, and β-caryophyllene.

Briefly, the measured concentrations of tracer compounds derived from a given hydrocarbon precursor were converted into SOC concentrations by using laboratory generated mass fractions of the same tracers (ratio of the tracers/SOC determined in smog chambers). The considered values for the mass fractions were 0.155 ± 0.039 for isoprene, 0.231 ± 0.111 for α-pinene and 0.023 ± 0.005 for β-caryophyllene (Kleindienst et al., 2007). In addition to that, to assess the SOC contribution of monoterpenes and sesquiterpenes, the SOC estimates of α-pinene and β-caryophyllene were multiplied by 3.2 and 3.6 respectively (Geron and Arnts, 2010; Ormeño et al., 2007; Waked et al., 2014). This method holds high uncertainties due to limiting the complex chemistry behind the SOA formation to a simplified single value for each precursor. This replacement cannot cover neither the whole range of compounds emitted from the precursor nor the meteorological conditions (Kleindienst et al., 2007; Waked et al., 2014). However, the method remains a valuable approach to give insights into apportioning BSOC fractions.

Fig. 7 shows the contribution of isoprene, monoterpenes, and sesquiterpenes to the SOC at both sites. A clear seasonal pattern is evidenced for the SOC concentrations and could be related to the higher concentrations of the precursors in summer. The total SOC concentrations in FA account for 469 ng/m³ in the summer period and 255 ng/m³ in winter. These values are higher than ZK (305 ng/m³ in summer and 131 ng/m³ in winter) but lower than those reported for a suburban site in Lebanon (3408 ng/m³ in summer 2011 and 462 ng/m³ in winter 2012) (Waked et al., 2013; 2014). In the latter study, the site was located in the suburb of the capital Beirut and was mainly characterized by a high residential density, commercial activities and by forested trees surrounding the sampling site.

As discussed before, the anthropogenic contribution of all the primary species is more important than the biogenic ones in ZK and FA due to the industrial typology of the sites while the Chekka area is more affected by forested pine lands. Monoterpenes are found to be the largest contributors to SOC especially in summer accounting for 47% and 63% in ZK and FA respectively.

2.2.5. Dicarboxylic acids

Dicarboxylic acids are part of the water-soluble organic compounds. Due to their low vapor pressures, they are mainly present in the particulate phase (Li et al., 2006). The concentrations of oxalic acid recorded at both sites were 1.33 ng/m³ and 2.33 ng/m³ in winter, 2.05 ng/m³ and 5.34 ng/m³ in summer at ZK and FA respectively. The higher concentrations in summer could be due, as for other SOA, to enhanced photochemical reactions by more intense solar radiations, and favoring the decomposition of succinic acid to malonic and oxalic acid (Hsieh et al., 2007). Waked et al. (2013; 2014) reported much higher concentrations of this compound in summer (67.8 ng/m³) and in winter (14.1 ng/m³) in Mansourieh, Lebanon: a suburban site located in the suburbs of Beirut. Generally, oxalic acid is considered as the dominant species between the dicarboxylic acids because of its stability and its production by atmospheric oxidation of other dicarboxylic acids with higher number of carbons (Yu et al., 2019).
In this study, Azelaic acid (diC9) is the most abundant dicarboxylic acid at ZK with concentrations of 12.9 and 8.03 ng/m³ and the second most abundant with 6.64 and 5.36 ng/m³ at FA in the winter and the summer periods respectively. The summer values are higher than the 4.2 ng/m³ observed at central Alaska during the hot season (Deshmukh et al., 2018). Azelaic acid is generated by the oxidation process of biogenic unsaturated fatty acids such as oleic acid. The high concentrations might be explained by the intense cooking activities in ZK and FA as mentioned in Section 3.1.4.

As for the adipic acid (diC6), higher concentrations (Table 4) were found compared to the value of 2 ng/m³ reported in the city of Philadelphia (Ray and McDow, 2005) except for 1.04 ng/m³ observed in ZK during winter. Adipic acid (diC6) is produced by the photooxidation of cyclohexene via ozone and OH reactions (Kawamura and Yasui, 2005). Cyclohexene can be found in motor exhausts revealing the anthropogenic nature of the compound (Grosjean and Fung, 1984).

Additionally, the average concentrations of phthalic acid (PhA) were 3.41 and 6.65 ng/m³ at ZK and FA respectively. These values are higher than the 2.4 ng/m³ reported for a site in southern Sweden (Hyder et al., 2012). PhA is generally produced by secondary photochemical reaction with PAHs, specifically naphthalene, but can also be emitted directly from combustion sources (Nguyen et al., 2016).

As mentioned earlier, PhA and diC6 are known to be the oxidation products of compounds emitted by anthropogenic sources while diC9 is mainly from biogenic activities. In order to qualitatively evaluate the evolution of the strength of the anthropogenic versus the biogenic sources of the diacids, the diC6/diC9 and the PhA/diC9 ratios can be used (Kunwar et al., 2019; Meng et al., 2013). Higher ratios will be observed for samples that are more influenced by anthropogenic sources.

The average values of the diC6/diC9 and the PhA/diC9 ratios increased in ZK from 0.09 and 0.38 respectively in winter samples to 0.44 and 0.54 in summer samples. The higher PhA/diC9 ratio is explained by the lower concentrations of diC9 in the summer period which might be related to the lower concentrations of one of its precursors such as oleic acid (Table 2) in ZK. This assumption can also stand for the diC6/diC9 ratio with also higher diC6 concentrations that might be caused by an increase in the vehicular emissions during this period.

On the contrary, the ratios decreased in FA from 1.28 and 2.91 in winter to 0.52 and 0.71 in summer for diC6/diC9 and PhA/diC9, respectively. This might be due to a decrease in anthropogenic emissions due to the shutdown of the cement factories in this period (lower PhA and diC9 concentrations in summer while diC6 is almost constant).

All of these findings regarding SOA showed firstly the complexity of the atmospheric processes and secondly that the composition of this part of the aerosol strongly depend on local and seasonal factors affecting the primary emissions and photooxidation conditions. Thus, trees, plants, and vegetation around the site affect the emissions of the Biogenic Volatile Organic Compounds leading to variations in the concentrations of their oxidation products. In addition to that, meteorological factors and local atmospheric chemistry (aerosol acidity, NOx conditions, solar radiation intensity…) influence the formation of the SOA to a high extent.

3. Conclusions

The analysis of the organic fraction in PM2.5 collected over a one year period in Lebanon in the urban-industrial areas of Zouk Mikael and Chekka region, in particular Fiaa, revealed significant variations between the sites on the concentration...
levels, the potential sources, and the seasonal variations of the organic compounds. The most abundant class of compounds was the fatty acids, that is part of the primary organic aerosols (POA), emitted mainly from cooking activities.

For most of the POA, ZK recorded higher concentrations due to the more urbanized, residential and industrial influence than FA. The petrogenic source at both sites was highlighted considering the concentrations of the n-alkanes, CPI, Wax% and C$_{max}$ with a low contribution of the primary biogenic emissions especially in winter. The fuel combustion in ZK might be assigned to vehicular emissions, diesel generators and most importantly the HFO combustion from the power plant by observing the PAHs concentrations and their corresponding diagnostic ratios. In addition to the PAHs and n-alkanes, the hopanes identified in ZK underline the importance of the road traffic in the region. On the other hand, the main sources highlighted in Chekka region were a mix of coke and fuel burning. The variation in the concentrations of phthalates at ZK and FA suggests plastic incineration near the study areas alongside a contribution from the plastic production industries in ZK during summer.

For the secondary organic aerosols (SOA), higher concentrations were reported during summer at both sites due to the enhancement of the photochemical reactions and high temperatures. The α-pinene oxidation products were the most abundant class in the secondary biogenic organic aerosols. Even with low concentrations, BSOA compounds can largely contribute to the SOC. Due to higher vegetation and forests in the Chekka region, higher concentrations of the BSOA were noted during both seasons. In addition, industrial activities have an important influence on the SOA formation especially for compounds having their precursors emitted from anthropogenic sources such as phthalic and adipic acids.

Finally, following the high concentrations of the different organic compounds classes of which some are of particular interest to the health field due to their high toxicity, further investigation would be needed specially source apportionment studies and health risk assessment for a better air quality management planning.

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Appendix A. Supplementary data


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