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Chemical profiles of PM_{2.5} emitted from various anthropogenic sources of the Eastern Mediterranean: cooking, wood burning, and diesel generators

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11 <u>Abstract</u>

The chemical profiles of PM2.5 emitted from a non-road diesel generator, wood burning and 12 13 cooking activities including chicken and beef charcoal grilling and general cooking activities were determined. The characterization included the carbonaceous fraction (OC/EC), water-14 15 soluble ions, elements, and organic species comprising n-alkanes, polycyclic aromatic 16 hydrocarbons, carboxylic acids, levoglucosan, dioxins, furans, and dioxin-like polychlorinated biphenyls. The main component in the PM_{2.5} from the different sources was carbonaceous 17 matter with a mass contribution to PM2.5 of 49% for cooking activities, 53% for wood burning, 18 66% for beef grilling, 72% for chicken grilling, and 74% for diesel generator with different 19 OC/EC concentration ratios. The analysis of organic compounds contents using diagnostic 20 ratios and indexes showed differences between the sources and revealed specific source 21 22 markers. The water-soluble ions had the highest contribution in the cooking activities profile with 17% of $PM_{2.5}$ and the least in the chicken grilling profile (1.1%). Additionally, 29 analyzed 23 elements were identified, and their contribution varied with the sources (ranging from 1% to 24 11% of PM_{2.5}). These findings could be used to differentiate these sources and could assist in 25 26 the use of source apportionment methods.

<u>Keywords</u>: source profiles, PM_{2.5}, organic species, inorganic species, cooking, diesel
 generator, combustion.

30 Introduction

31 Source profiles or chemical fingerprints refer to the average relative chemical composition of the PM deriving from a pollution source, expressed as the mass ratio between each species to 32 the total PM or the total identified mass (Belis et al., 2019; Pernigotti et al., 2016). These 33 profiles are commonly used as input data for some receptor modeling approaches such as 34 35 Chemical Mass Balance (CMB) where the knowledge of the composition of the emissions is crucial (Viana et al., 2008). They are also used to attribute output factors to specific sources in 36 multivariate factor analysis methods such as Positive Matrix Factorization (PMF) (Bove et al., 37 2018). Additionally, source profiles contribute to the chemical speciation of emission 38 39 inventories whether to estimate emissions of hazardous and toxic pollutants or in source 40 oriented modeling for policy makers (Chow et al., 2004).

Several source profile databases have been created across the globe. Source profiles have been 41 gathered since 1988 in the United States Environmental Protection Agency (USEPA) 42 SPECIATE database (Simon et al., 2010). To date, the database contains more than 6700 PM, 43 gas and other profiles covering more than 2800 unique species. Recently, a European database, 44 SPECIEUROPE, was published in 2015 by the European Joint Research Centre consisting of 45 46 more than 280 profiles and reaching 250 species (Pernigotti et al., 2016). In 2017, researchers 47 from the Chinese Research Academy of Environmental Sciences (CRAES) developed a new database of emission source profiles for PM in Chinese environments (Liu et al., 2017). The 48 China Source Profile Shared Service contains more than 500 profiles in its first version (CSPSS 49 50 1.0) (Liu et al., 2017). These databases were built following the shortage of local source profiles that represented a true challenge for receptor modeling studies in terms of source identification 51 52 and comparability between studies (Pernigotti et al., 2016). Numerous source apportionment studies have been carried out using the American, European, and Chinese databases not only in 53 54 their countries of development but also for most of the source apportionment studies in developing countries despite the divergence in national circumstances (Chelani et al., 2008; 55 Gupta et al., 2007). Indeed, the chemical speciation of emissions from certain sources largely 56 depend on parameters such as geological substrate, local practices, emission control 57 technologies, as well as the fuel quality in the case of combustion sources and the combustion 58 59 efficiency, etc. which leads to higher uncertainty in source apportionment studies (Bove et al., 2018; Colombi et al., 2010; Salameh et al., 2014; Weber et al., 2019). Hopke (2016) stressed 60 on the idea that no efforts were deployed to develop source profiles especially for stationary 61

sources and for many others in developing countries. The main obstacle to achieve effectiveand accurate source apportionment remains in the lack of regional source profiles.

64 The Middle East is a vast region encompassing around 300 million inhabitants, different 65 countries including some of the East Mediterranean. Most of these countries are considered as 66 developing, with several cultures, traditions, and languages but mainly share common practices such as some cooking techniques, lack of law enforcement in many cases, etc. Very few source 67 profiles were established in this region and presented chemical profiles from vehicular 68 emissions (Daher et al., 2013; Gaga and Ari, 2019). However, other important sources of 69 pollution can be of interest among which cooking, power generation, and wood burning. The 70 composition of PM_{2.5} emitted from these typical anthropogenic sources might differ from those 71 72 observed in other regions due to local traditions observed in the East-Mediterranean-Middle Eastern region. The variety of products, seasoning, and cooking techniques make the 73 74 gastronomical rituals different in the Middle East from other regions. It is well established that cooking plays a major role in the Middle Eastern culture, unlike anywhere else (Essid, 2012) 75 76 especially during family gatherings on weekends, holidays, and special occasions with outdoor barbecue and several other cooking activities. Most of the literature studies related to emissions 77 from cooking focused on Indian (Bano et al., 2018), Chinese (He et al., 2004; Zhang et al., 78 2017; Zhao et al., 2019), and fast food (Rogge et al., 1991) that have different cooking practices 79 than the Middle East and focusing on certain species and classes of compounds. Additionally, 80 it has been demonstrated that the inhalation of PM2.5 emitted from different cooking styles could 81 result in adverse human health effects (Bandowe et al., 2021). 82

On the other hand, diesel generators are reciprocating engines widely used in the world in 83 temporary projects or as stand-by power in developed countries at power sensitive facilities or 84 even as continuous backup power in developing countries due to power supply instability 85 (Klimont et al., 2016). The literature mostly present PM_{2.5} profiles for regulated diesel engines 86 (Liang et al., 2005; Yilmaz and Davis, 2016) like Tier 1 to 4 in North America, Stage 1 and 87 above in Europe, etc. Even with these lean combustion conditions, experimental and 88 computational evidence showed important emission of pollutants from the fuel burning such as 89 PAHs (Yilmaz and Donaldson, 2007). However, many countries especially developing ones do 90 not always effectively enforce the law when it comes to stack emissions (Waked et al., 2012), 91 92 do not have regulations on the import of regulated engines, and mostly allow the installation of the generators in heavily populated areas without any pollution abatement. 93

Another combustion source commonly known in the region is the wood burning due to forest
fires but also used for cooking, residential heating, and outdoor activities such as camping. The
emission characterization of these sources in the region is still limited (Alves et al., 2010;
Kostenidou et al., 2013) and more focus should be given due to their impacts on air quality.

98 The objective of this paper is to determine, for the first time in the Middle Eastern region, PM_{2.5} chemical source profiles for different anthropogenic sources such as cooking, wood burning, 99 and emissions from unregulated non-road diesel generator. While most of PM2.5 chemical 100 profiles found in the literature focus on specific chemical fractions or species, this study 101 presents for the first time, to the best of our knowledge, a full chemical characterization 102 including carbonaceous fraction, ionic, elemental, and organic species. The organic speciation 103 104 includes n-alkanes, Polycyclic Aromatic Hydrocarbons (PAHs), carboxylic acids, levoglucosan, dioxins (PCDD), furans (PCDF), and dioxin-like polychlorinated biphenyls (DL-105 106 PCBs). These exhaustive chemical profiles will be of utmost importance for future source apportionment studies in the region and will add additional components to the pre-existing 107 108 source profiles such as carboxylic acids, sugars, PCDD/Fs and DL-PCBs. Furthermore, source markers, diagnostic ratios, and indexes are presented in order to be used in source identification. 109 All of these results will be compared to available database in order to conclude whether the 110 differences are significant. Additionally, these results will provide valuable information for 111 source apportionment applications, speciated emission inventories, as well as for health impact 112 assessment studies. 113

114

115 1. <u>Materials and methods</u>

116 1.1 Sample collection

117 PM_{2.5} samples were collected onto 150 mm pure quartz microfibres filters (Fiorini, France) 118 using a high-volume sampler (CAV-A/mb, MCV S.A., Spain) operating at 30 m³/h in different 119 locations in Lebanon. Filters were pre-heated for 12 hours at 550°C before sampling to decrease 120 the level of organic impurities. The collected filters were sealed in aluminum foil and stored at 121 -20°C until analysis. It is worth noting that for combustion sources, the sampling was made at 122 a sufficient distance from the combustion process to let the plume cool down and to collect the 123 condensed fraction in the particulate phase.

125 1.2 Experimental design

The operating conditions, under which the sampling for the different anthropogenic sources 126 was conducted, were detailed in the sections below and were summarized in **Table 1**. All the 127 methods described below are representative of common practices in the East Mediterranean 128 region. Despite the limited number of samples, this paper will give an insight on the chemical 129 composition of PM_{2.5} emitted from these sources, especially for some species that are scarcely 130 presented in the literature. Variations between the replicates of the same source are related to 131 the fact that combustion and cooking sampling were done under real world conditions (variation 132 133 in humidity content, instantaneous variation of reciprocating engine load, etc.). High standard deviations were generally observed between the replicates of the same source (Akbari et al., 134 2021; Chantara et al., 2019; Salameh et al., 2014). 135

136

1.2.1 Wood burning (WB)

Hardwood combustion from different kinds of broad-leaved trees (oak, maple, beech trees, etc.) is commonly observed in the East Mediterranean for heating and outdoor activities. The wood combustion (open fire) experiment was conducted outdoor away from trees and other plant materials. Dry wood branches of hardwood broad-leaved trees (oak and fruit bearing trees) were added into the firepit in the shape of a pyramid, ignited using a lighter and burned with free air supply.

The sampler was placed directly in the smoke plume and 3 filters (sample label: WB) were exposed during the flaming combustion phase. Throughout the sampling, new pieces of wood were added to keep the fire going. The sampling duration varied between 10 and 15 minutes for each sample.

147

1.2.2 Diesel generator (DG)

The generator, with an engine capacity of 100 kVA, is placed in the basement of a residential building. This type is representative of the most used category (below 250 kVA) of diesel generators producing electricity for households in the region. The fuel type used is automotive diesel oil. The generator has an extended exhaust pipe of about 18 m to release emissions above the rooftop level. The sampler was placed at the same level as the top of the stack in order to collect the particulate sample with minimal influence by ambient PM. No sample was taken during the cold-start phase (the first 20 min of the engine operation). Four diesel generatorsamples (DG) were collected under the same operating conditions for 30 min each.

156

1.2.3 Cooking

In order to have exhaustive cooking source chemical profiles, 7 samples were collected from different cooking experiments: 2 for charcoal grilling and 5 for general cooking activities. The plumes emitted from the different cooking activities regroup mixed emissions released by food and the corresponding fuel used.

161

	Wood burning	Diesel generator	Cooking				
			Beef grilling	Chicken grilling	Cooking activities		
Abbreviation	WB	DG	BG	CG	GCA		
Main contents	Wood branches of broad- leaved trees (oak and fruit bearing trees)	Volvo Penta TAD531GE diesel generator, 100 kVA, four cylinders at 1500 rpm	Small pieces of beef grilled on both sides	Large pieces of skinned chicken grilled on both sides	Burger grilling, french fries frying, use of vegetables, daily dishes served		
Combustible	Biomass	Diesel fuel	Charcoal	Charcoal	Natural gas liquid (LPG)		
Sampling method		High volume sampler for PM _{2.5}					
Filter used		Quartz filters – 150 mm diameter					
Number of samples 4		3	1	1	5		
Sampling time	10-15 min	30 min	20 min	20 min	75 min		

Table 1: Operating conditions under which the different anthropogenic samples were obtained

163

164 1.2.3.1 Beef and chicken charcoaled experiments

The Mediterranean region is known for its tradition of charcoal grilling especially during weekends and holidays. The most commonly observed charcoal-grilled food in the region is mainly beef and chicken. The charcoal is made of oak wood. It was piled in a pyramid shape in the grill to help increase the contact between the charcoal and make the fire spread. A fire starter cube was inserted into the pyramid and lighted. After 20 min, the coal was covered in ash. It was then laid evenly in the grill and was ready to use. Two PM_{2.5} samples were taken during this procedure: the first one was sampled during beef grilling (BG) and the second one for chicken (CG). The sampling duration was 20 min for each sample. First, the meat (BG) was
cooked over charcoal for 20 min and turned several times during the total cooking time. The
distance between the meat and the charcoal was approximately 10 cm. The sampler was placed
directly in the grill smoke plume. Then, the chicken (CG) was grilled.

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177 1.2.3.2 General Cooking activities (GCA)

The sampling was carried out in a university kitchen cafeteria during the peak hour of work for 178 5 consecutive days. The cooking equipment mainly consists of gas deep frying machines, free 179 180 standing griddles, and steam tables for the daily dishes. The main cooking technique is gas-181 grilling activity to make burgers or sandwiches (meat, chicken, etc.), and frying of French fries, 182 etc. The frying oils used are Canola and Soybean seed. There was no major outdoor ventilation 183 leading to the assumption that the PM_{2.5} mass collected was mainly due to the cooking activities. The sampler was placed next to the steam tables, deep-frying machine, and grill and 5 samples 184 185 (GCA) were taken for 75 min each.

186

187 1.3 Chemical analysis

The chemical characterization included the analysis of the carbonaceous matter (OC, EC),
water-soluble ions, major and trace elements, and organic species for the collected samples and
for blank filters.

1.3.1 Carbonaceous fraction

191 The organic carbon (OC) and the elemental carbon (EC) were quantified on a punch of the 192 quartz filter (1 cm^2) by a thermal optical transmission technique. It consists of a Sunset 193 Laboratory OC/EC analyzer implementing the EUSAAR2 protocol (Cavalli et al., 2010) with 194 a transmittance optical correction for pyrolysis.

195

1.3.2 Organic compounds

The organic compounds were quantified by gas chromatography (ISQ 7000, Thermo Scientific, United States of America) coupled to a mass spectrometer (GC-MS) following the method described in previous studies (Fadel et al., 2021; Waked et al., 2013; 2014). In brief, one quarter of each filter was extracted with acetone and dichloromethane (1:1, v/v) by sonication for 30 min at 50°C after spiking it with two internal standards (bornylacetate and ketopinic acid). The

extracts were concentrated to 200 µL under a gentle flow of nitrogen gas. An aliquot of the 201 202 sample is injected directly in the GC-MS to quantify non-polar compounds such as n-alkanes and PAHs while another aliquot was derivatized before injection to identify levoglucosan and 203 carboxylic acids. The detection limits (D.L) were evaluated for the different species and 204 correspond to the blank filter value plus 3 times the standard deviation calculated over 3 205 measurements. D.L. varied between 0.0003 and 0.25 ng/m³ except for stearic acid with higher 206 detection limit (2.3 ng/m³). Additionally, recoveries were determined by spiking blank filters 207 by standard solutions. The recovery values were estimated to be between 80 and 92% for the 208 209 different organic species.

210

1.3.3 Elements

Elements were analyzed by inductively coupled plasma (More detailed information on the 211 analysis are available in previous publications (Kfoury et al., 2016; Ledoux et al., 2006a). In 212 213 brief, for each sample, a 47 mm punch of the quartz filter was digested by an acid mixture of 4 mL nitric acid (HNO₃), 1 mL of hydrofluoric acid (HF), and 0.5 mL of perchloric acid (HClO₄) 214 in a PTFE flask at 120°C overnight. Then, the acid evaporation was made at 170°C to the last 215 drop followed by the addition of few milliliters of ultrapure water. The obtained solution was 216 then diluted to 15 mL by ultrapure water, acidified to 2% by HNO₃ and filtered on 0.45 µm 217 218 cellulose acetate filter prior to analysis. Mg, Mn, Al, Na, Ba, Ca, Fe, K, Ni, P, Pb, S, Sr, Ti, and Zn were quantified by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES, 219 iCAP 6000 series, Thermo Scientific, United Kingdom). V, Cr, Co, Cu, As, Rb, Nb, Ag, Cd, 220 Sn, Sb, La, Ce, and Bi were quantified by ICP-Mass Spectrometry (ICP-MS, Agilent 7900, 221 United States of America). The analytical procedure by ICP-AES and ICP-MS was validated 222 223 by considering standard reference material NIST-SRM 1648a (National Institute of Standards and Technology, United States of America). Recovery rates for all the elements varied between 224 89% and 103% with an exception for Cr (76%). The detection limits for the elements analyzed 225 by ICP-AES and ICP-MS corresponds to blank (water and acid blanks) values plus 3 times the 226 standard deviation calculated over 10 measurements. D.L. for the elements analyzed by ICP-227 AES varied between 0.004 and 0.45 ng/m³. As for the trace elements analyzed by ICP-MS, it 228 varied between 0.0003 and 0.01 ng/m^3 . 229

1.3.4 Water-soluble ions (WSI)

231 The protocol for water-soluble analysis was detailed elsewhere (Kfoury et al., 2016; Ledoux et al., 2006b). Briefly, three filter punches of 19 mm diameter each for every sample were 232 ultrasonically extracted by few milliliters of ultrapure water for 20 min. The obtained solution 233 is collected using a syringe, then filtered through a 0.45 µm porosity cellulose acetate 234 235 membrane previously rinsed with ultrapure water. The leachate containing the ions was placed in a polyethylene flask of 20 mL. The filters were submerged with ultrapure water prior to 2 236 237 additional ultrasonic extractions and filtrations and then stored at -20°C until analysis. The samples were analyzed by liquid ion chromatography (Dionex[™] ICS-900, Thermo Scientific, 238 United Kingdom) for the quantification of Cl⁻, SO₄²⁻, NO₃⁻, Ca²⁺, Mg²⁺, K⁺, Na⁺, and NH₄⁺. 239 D.L. varied between 0.17 and 0.78 ng/m^3 for the different WSI. 240

241

1.3.5 Dioxins, furans and dioxin-like polychlorobiphenyls

Dioxins, furans and dioxin-like polychlorobiphenyls were quantified by MicroPolluants
Technology SA (Saint Julien Les Metz, France). The PCDD/PCDF and DL-PCB analysis
method was based on the US EPA method 1613 and 1688 respectively using a high-resolution
gas chromatography coupled to a high-resolution mass spectrometer (HRGC/HRMS). Detailed
information are found in Borgie et al. (2015).

247

248 1.4 Mass reconstruction of PM_{2.5}

The reconstructed mass of PM_{2.5} is calculated by summing the inorganic ions, elemental carbon,
 geological minerals, organic matter (OM) and other elements calculated as follows (Eq.1):

251 PM = OM + EC + [geological minerals] + [inorganic ions] + [other elements] (Eq. 1)

252

253 Organic matter (OM) is calculated by multiplying OC with an empirical coefficient (OM/OC) to account the mass of unmeasured oxygen and hydrogen in the organic matter (Turpin and 254 Lim, 2001). In this study, the OM/OC ratio was chosen to be 1.7 for the wood burning 255 experiment (Reff et al., 2009; Reid et al., 2005), 1.32 for beef grilling, 1.36 for chicken grilling, 256 1.42 for general cooking activities (Mohr et al., 2009; Zhao et al., 2007a), and 1.2 for diesel 257 generator emissions (Petzold et al., 2008; Sothea and Kim Oanh, 2019). Elemental carbon arises 258 from primary combustion sources and therefore no multiplication factor is needed, its mass is 259 260 used unchanged (Harrison et al., 2003). For the inorganic ions, a hydration factor of 1.29 was applied to convert the concentration of these species (Na⁺, Cl⁻, Mg²⁺, NO₃⁻, SO₄²⁻, and NH₄⁺) into hydrated ones to consider the bound water (Harrison et al., 2003; Sciare et al., 2005). The geological minerals concentration was estimated by assuming that these elements exist as oxides: Al₂O₃, SiO₂, K₂O, FeO and Fe₂O₃ in equal amounts, and TiO₂. The formula used to calculate the geological minerals concentration (Chow et al., 2015):

266 $[geological minerals] = 2.2 \times [Al] + 2.49 \times [Si] + 1.63 \times [Ca] + 2.42 \times [Fe] + 1.94 \times [Ti]$

Elemental Si was not analyzed by the ICP method used, it was estimated using the (Si/Al) ratio derived from Si and Al concentrations derived from field measurements near sources in other studies. The Si/Al ratio used was 2.4 for wood burning (Sun et al., 2019), 0.5 for beef and chicken grilling (Wang et al., 2020), 0.9 for general cooking activities (Sun et al., 2020), and 1.0 for diesel generators (Yayong et al., 2018). Other elements correspond to the sum of the remaining elements.

273

274 2 <u>Results and discussions</u>

The chemical relative abundance of the different species in the carbonaceous, ionic, and elemental fractions were calculated by dividing their mass by the reconstructed $PM_{2.5}$ mass. They were presented in **Fig. 1**, and in details in **Table S1** and **Figure S1**. The organic species were reported to the OM mass and were given in **Table S2**.

279 2.1 Carbonaceous fraction

In the different chemical profiles of $PM_{2.5}$, OC was the main component, ranging from 40% of PM_{2.5} for WB to 72% for CG (**Fig. 1**). EC ranged from 0.1% for CG to 20% for DG which presents the second most abundant share in WB and DG profiles.

High differences in the distribution of the carbonaceous fraction (OC+EC) occur between charcoal and general cooking activities profiles. GCA releases less carbonaceous matter (49% of $PM_{2.5}$) compared to BG (66%) and CG (72%). These differences were mainly attributed to the cooking process and ingredients (Abdullahi et al., 2013). Many studies have compared cooking styles and reported different chemical profiles for the emitted particulate matter.

The OC/EC ratio is an essential tool to differentiate combustion sources. This study determined a value of 3.4 for wood burning, comparable to the findings reported by Sun et al. (2019) for wood branches (2.69). As for cooking profiles, the highest ratio was found for CG (622), followed by BG (45) and GCA (18). This large difference between CG and BG could be attributed to the difference in fat content between the two types of food. Foods containing high
percentage of fat usually generate higher OC emission rates than those with a lower fat
percentage (Abdullahi et al., 2013).

The ratio for GCA was close to the value of 19.3 reported for samples collected form the exhaust stacks of a university canteen in Portugal (Alves et al., 2014). The lowest ratio was found for the diesel generator (2.9), slightly higher than 2.61 reported by Sothea and Kim Oanh (2019) for a 92 kW backup generator in Cambodia. For comparison, values of 0.37 were reported for tunnel studies (diesel and gasoline vehicles), 2.2-6.2 for urban areas, and 0.64 for diesel trucks (El Haddad et al., 2009; Waked et al., 2014).

301

302 2.2 Organic compounds

2.2.1 N-alkanes

303 C_{13} - C_{32} homologue series are presented for the different profiles in (**Fig. 2**). Total C_{13} - C_{32} 304 average contribution to OM were 11%, 0.8%, 0.6%, 0.6%, and 0.3% for DG, BG, WB, GCA, 305 and CG, respectively. The high contribution of n-alkanes in the DG profile is mainly due to the 306 composition of the diesel fuel that comprises a large fraction of n-alkanes (Liang et al., 2005).

Different methods can be used to characterize the alkanes profiles (Fadel et al., 2021). Briefly, 307 308 the overall carbon preference index (Overall CPI) for C_{13} - C_{31} is a measure of odd to even carbon 309 predominance with a value close to 1 for petrogenic sources, 2 to 5 for biomass and coal burning and values higher than 6 for biogenic emissions. The wax ratio (Wax%) can be used to assess 310 the contribution of wax n-alkanes from plants. The n-alkanes distribution pattern can be used 311 to identify alkanes with the highest concentrations. For wood burning, the profile pattern shows 312 a predominance of high molecular weight n-alkanes especially C₂₇, C₂₉, and C₃₁ with a 313 maximum at C_{29} (Fig. 2). This pattern is considered as a plant epicuticular wax signature 314 leading to a high Wax% of 58%. C₂₇, C₂₉, and C₃₁ are considered as n-alkanes tracers for 315 biomass burning (Simoneit, 2002). The CPI value for WB (CPI=4) is in the range reported for 316 biomass activities of 2 to 5 (Simoneit, 2002). A distinctive pattern was observed for DG where 317 the n-alkane homologues partitioning exhibited a smooth hump-like distribution with the 318 319 highest contribution for C_{20} - C_{21} (Fig. 2). A similar profile was observed for diesel powered engines (Rogge et al., 1993). 320



322

Fig. 1: Contribution of OC, EC, water-soluble ions (WSI), and elements to reconstructed PM_{2.5}
emitted from the different sources (BG: beef grilling, CG: chicken grilling, GCA: general
cooking activities, WB: wood burning, DG: diesel generator).

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A CPI value (0.9) close to unity usually attributed for petrogenic sources and a very negligible
Wax% characterizes the diesel emissions from non-road generators.

329 For charcoal cooking (BG and CG), the profiles are much alike with a maximum contribution for C₂₅. This observation can lead to the assumption that the n-alkanes are not predominantly 330 331 emitted from the food itself but from the charcoal combustion. This hypothesis can be supported 332 by CPI values of 2.5 and 4.5 for CG and BG respectively that are in the range of coal 333 combustion. However, a different pattern was observed for GCA. The CPI value for this GCA profile (1.3) and the Wax% (22%) were relatively low compared to various Chinese cooking 334 335 restaurants with calculated CPI and Wax% in the ranges of 2.3-4.6 and 40-64%, respectively 336 (He et al., 2004; Zhao et al., 2007a). These differences may be attributed to the different cooking methods and frying techniques without forgetting the large consumption of vegetables in the
Chinese cooking causing higher CPI and Wax% ratios (Zhao et al., 2007b).

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Fig. 2: N-alkanes profile patterns associated with PM_{2.5} for the different sources (WB: wood
burning, BG: beef grilling, CG: chicken grilling, DG: diesel generator, GCA: general cooking
activities).

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340

2.2.2 Polycyclic Aromatic Hydrocarbons

The relative concentration profiles of the different PAHs are presented in **Table S2** with the share (in mg/g of OM) of each one. Additionally, the distribution of these species with aromatic ring number was also shown in **Fig. 3** to further characterize them in the profiles.

The wood burning experiment emitted at least 5 times more PAHs normalized to OM than the other sources (2.64 mg/g for WB against 0.54 for BG, 0.35 for CG, 0.14 for GCA, and 0.44 for DG). The higher PAHs share for WB compared to CG and BG can be attributed to the more complete combustion of charcoal compared to wood. Furthermore, the volatilization and the pyrolysis of the volatile matter during the production of charcoal, and its low water content could also reduce the aromatic compounds formation (Oanh et al., 1999; Shen et al., 2011).

Low PAHs shares were observed for the different cooking profiles. McDonald et al. (2003) 354 suggested that the PAHs emitted during grilling activities were formed from the interaction 355 between the lipidic material in food and the cooking appliance since the temperature reached 356 on the surface of food was relatively low to form PAHs (maximum PAHs production occurs at 357 750 °C) and PAHs compounds were absent in the food chemical analysis. Furthermore, the 358 abundance of 4-rings PAHs in BG and CG profiles might be related to the coal combustion. 359 According to Vicente et al. (2018), fly ashes from charcoal combustion are rich in 4-rings PAHs 360 361 with fluoranthene and pyrene as the most abundant aromatics whereas raw charcoal is mainly 362 rich in 3-rings PAHs. As for GCA, several studies showed that 6-rings PAHs were rarely generated during cooking processes especially during deep frying activities because high 363 364 temperatures can decompose high molecular weight PAHs (Sun et al., 2020; Zhao et al., 2019). The most abundant PAHs for GCA were benzo[b]fluoranthene (B[b]Fl), pyrene (Pyr), and 365 366 chrysene (Chr).

Like BG, CG, and GCA, 4-rings PAHs predominated the total detected PM_{2.5}-bound PAHs emitted from WB with Fluoranthene (Fla), Pyr, benzo[a]anthracene (B[a]An) as the most abundant compounds. This distribution pattern along with the dominant PAHs were consistent with the data reported for the combustion of different types of biomass fuels (maize straw, wheat straw, and wood branches) (Sun et al., 2019). Pyrene was the most abundant PAH in the diesel generator profile, accounting for more than 50% of the sum of PAHs and highly contributing to the 4-rings category that is the most abundant.

PAHs diagnostic ratios were usually used for source apportionment in different environmental samples (Tobiszewski and Namieśnik, 2012). For every ratio, the species used should have similar reactivity in the atmosphere: Fla and Pyr (Molecular Weight =202 g/mol), B[a]An and Chr (MW = 228 g/mol), indeno[1,2,3-c,d]pyrene (InPy) and benzo[g,h,i]perylene (B[ghi]Pe) (MW= 278 g/mol), and anthracene (Anth) and phenanthrene (Phe) (MW= 178 g/mol). These ratios could serve as markers for the different source profiles presented in this paper and were reported in **Table 2**.

- 381 The values obtained for wood burning (0.49 for Fla/(Fla+Pyr), 0.57 for B[a]An/(B[a]An+Chr),
- 382 0.45 for InPy/(InPy+B[ghi]Pe), and 0.7 for Anth/(Anth+Phe)) are mostly in the ranges of ratios
- reported in other studies for biomass burning (Gong et al., 2019; Tobiszewski and Namieśnik,
- 384 2012; Vicente et al., 2012).



386

Fig. 3: Distribution of PAHs for the different sources (BG: beef grilling, CG: chicken grilling,
GCA: general cooking activities, WB: wood burning, DG: diesel generator) according to the
number of aromatic rings in mass percentages.

390

As for grilling activities, the similarity in the ratios and the closeness to the values reported in 391 the literature imply that these PAHs are mainly emitted from the charcoal combustion in the 392 393 barbecue grills (Gong et al., 2019; Vicente et al., 2018). For GCA, Fla/(Fla+Pyr) and 394 B[a]An/(B[a]An+Chr) ratio values are close to those reported for deep-frying activities and Chinese gas cooking (See and Balasubramanian, 2008; Wei See et al., 2006). A particular 395 396 attention was given to the ratios determined for diesel generators emissions. The values present 397 in the literature describe mostly diesel emissions from on-road vehicles (Gong et al., 2019; 398 Ravindra et al., 2008; Riffault et al., 2015; Shi et al., 2014). Although many similarities exist, the modes of operation are different. Non-road diesel generators run at a certain rpm 399 400 (revolutions per minute) and voltage and the amperage they produce can vary with the load while on-road diesel vehicles operate in transient conditions (Liang et al., 2005; Shah et al., 401 402 2006). These differences in the operation mode can potentially result in different emission characteristics and different diagnostic ratios for PAHs. On the other hand, Liang et al. (2005) 403 404 studied the organic composition of diesel particulate matter from a non-road diesel generator 405 and showed Fla/(Fla+Pyr) and B[a]An/(B[a]An+Chr) ratio values (0.28 and 0.5, respectively) close to the values obtained in this study (0.24 and 0.41, respectively) while values for
InPy/(InPy+B[ghi]Pe) and Anth/(Anth+Phe) were different (Table 2).

408

2.2.3 Carboxylic acids

According to Table S2, carboxylic acids were the most abundant organic species in the 409 410 chemical profiles of cooking activities. The highest contribution was observed for GCA explaining 24% of the OM mass followed by BG with 19% and CG with 11%. During high 411 temperature treatment of food, several chemical processes occur such as sugar degradation, 412 pyrolysis of proteins and amino-acids, and the degradation of fats. These mechanisms lead to 413 the production of free fatty acids, glycerol, and glycerides (Abdullahi et al., 2013). Additionally, 414 415 the use of oils in cafeteria cooking operations such as deep frying will increase fatty acids emissions being the major constituents of triglycerides in seed oils (Schauer et al., 2002; Zhao 416 417 et al., 2007a). From the saturated fatty acids presented in this paper, the most abundant are 418 palmitic (C_{16}) and stearic (C_{18}) acids accounting for more than 80% of the total mass of fatty acids in the three cooking profiles. These compounds are usually used as organic markers for 419 cooking activities in different source apportionment studies (Abdullahi et al., 2013). Carboxylic 420 421 acids were also found in biomass burning events and contribute to 5% of the OM mass. The highest concentration was observed for palmitic acid (C₁₆) accounting for 33% of the sum of 422 423 carboxylic acids. These findings were in accordance with the results obtained from wildfires 424 organic speciation in central Portugal (Vicente et al., 2012) and with the combustion of 425 hardwoods (Oros and Simoneit, 2001). Long-chain fatty acids are mainly considered as basic units of plant fats, oils, and phospholipids while short-chain species (C<16) are reported as 426 427 minor species of fungi and insects. As for the diesel generator, carboxylic acids contribute to 8% of the OM mass. Liang et al. (2005) determined the abundance of fatty acids in the engine 428 oil and the diesel particulate matter and found a strong similarity, bringing the conclusion that 429 fatty acids in diesel particles are not emitted from the combustion process itself but from the 430 evaporation of engine oil. 431

432

2.2.4 Levoglucosan

Levoglucosan or 1,6-anhydro-β-D-glucopyranose originates from the pyrolysis of cellulose and
hemicellulose at high temperature (Giannoni et al., 2012). It is considered as an organic
molecular marker for biomass burning due to its stability and its relatively high share in biomass

436 smoke (Chantara et al., 2019). This compound is the most abundant organic species in the WB 437 profile accounting for 17% of the OM mass. Levoglucosan/OC ratio is commonly used to 438 differentiate softwood and hardwood combustion. The value obtained in our study of 0.3 is in 439 the range of hardwood combustion (0.25-0.4) reported by Fine et al. (2004) compared to lower 440 ratios for softwood ranging between 0.1 and 0.23.

441

2.2.5 Dioxins, furans, and DL-PCBs

Table S3 shows congeners contribution to OM of PCDD/F and DL-PCBs for each source. The 442 BG and CG were combined in one factor and will be presented as "charcoal grilling". 443 1,2,3,4,6,7,8 HpCDD was identified in all emissions and was the only PCDD detected in GCA, 444 while OCDD contributed the most to the other profiles (73% of PCDD in WB, 76% in DG, and 445 70% in charcoal grilling, i.e., BG and CG). The DG emissions are 4.5, 3.7, and 2 more 446 concentrated in PCDD than GCA, charcoal grilling, and WB, respectively. However, charcoal 447 448 grilling showed the highest value when calculating the 2,3,7,8-TCDD equivalent (calculated by summing the multiplication results of each congener by its corresponding toxic equivalent 449 factor- WHO-TEF(Van den Berg et al., 2006). As for furans, 6 species out of 10 were identified 450 451 in the grilling sample mainly HxCDF and HpCDF.

The highest concentrations were recorded for PCDF emitted from the diesel generator with also the highest 2,3,7,8-TCDD equivalent. The PCDD/PCDF ratio is generally used to identify emission sources. It was calculated for the different profiles and values are presented in **Table 2.**

A similar observation was made by Lee et al. (2005) showing higher PCDD/PCDF emission factor ratio for domestic biomass burning (4.7) compared to coal combustion (2.1). Up to our knowledge, there is no PCDD/F data reported for oil cooking activities. The ratio in our study showed that the oil cooking source emits 2.4 times more PCDD than PCDF. The most abundant DL-PCB was PCB 118 accounting for 46%, 51%, 52%, and 52% of the total PCB in charcoal grilling, WB, GCA, and DG respectively followed by PCB 105. The total TEQ value expressed in pg/g of OM was the highest for DG, followed by charcoal grilling, GCA, and WB.

463

464

- **Table 2:** Experimental source diagnostics ratios and comparison with the literature (in brackets)
- 467 when available

	Wood	Diesel	Cooking					
	burning	generator	Beef grilling	Chicken grilling	General cooking activities			
OC/EC ratio	3.4	2.9	45	621	18			
n-alkanes diagnostic indexes								
Overall CPI	4.00	0.94	4.48	2.53	1.34			
Wax%	57.5%	1.4%	64.7%	46.1%	22.1%			
PAHs diagnostic ratios								
Fla/(Fla+Pyr)	0.49 (0.2-0.7) ^a	0.24 (0.28) ^b	0.51 (0.47) ^a	0.56 (0.47) ^a	0.47 (0.53) ^c			
B[a]An/(B[a]An+Chr)	0.57 (>0.37) ^e	0.41 (0.5) ^b	0.46 (0.47) ^a	0.43 (0.47) ^a	0.44 (0.28; 0.4) ^{c,f}			
InPy/(InPy+B[ghi]Pe)	0.45 (>0.5) ^d	0.18 (0.68) ^b	0.56 (0.50) ^a	$0.45 \\ (0.50)^{a}$	-			
Anth/(Anth+Phe)	0.70 (>0.1) ^e	0.85 (0.05) ^b	0.75 (>0.1) ^e	0.73 (>0.1) ^e	-			
PCDD/PCDF ratio	3.27	1.16	1.95		2.44			
Water-soluble ions ratios								
K ⁺ /EC	0.36	0.01	1.32	3.61	0.12			
K ⁺ /OC	0.12	0.003	0.03	0.01	0.007			
Cl ⁻ /SO ₄ ²⁻	3.96	-	1.34	0.4	-			

^a(Vicente et al., 2012), ^b(Liang et al., 2005), ^c(See and Balasubramanian, 2008), ^d(Tobiszewski
and Namieśnik, 2012), ^e(Gong et al., 2019), ^f(Wei See et al., 2006)

470

471 2.3 Water-soluble ions (WSI) composition

472 Water-soluble ions have the highest share of $PM_{2.5}$ in the GCA profile (17%), then WB (14%),

473 then DG and BG (6%), and finally CG (1%) (**Fig. 2**).

474 GCA profile showed more than 85% of the ionic mass for SO_4^{2-} , NO_3^{-} , and NH_4^+ . This result 475 was also observed by See and Balasubramanian (2008) for oil deep-frying activities. Although 476 WSI contributed more to the total $PM_{2.5}$ mass in BG compared to CG, they have a similar 477 distribution in ions with K⁺, SO_4^{2-} , and Cl⁻ having the highest contribution and accounting for 478 more than 70% of the total WSI mass. McDonald et al. (2003) also reported these ions as the 479 most abundant in the fumes of meat charbroiling. The high amounts of K⁺ and Cl⁻ in both 480 charcoal and wood burning are mainly due to their abundance in the fluid of plants ; they 481 volatilize during the combustion process and, after condensation or nucleation reaction (Alves 482 et al., 2010), become in the particulate phase. In the three cooking profiles, Ca^{2+} ions could 483 mainly be emitted from the cooking utensils and raw materials (Sun et al., 2020).

As for wood burning, K^+ and Cl^- have the highest share of WSI (74%) followed by SO_4^{2-} and Ca²⁺. These ions account for nearly 92% of the total soluble ions in the profile. Our results are consistent with those reported for other biomass burning experiments (86-94%) (Chantara et al., 2019; Sun et al., 2019).

The main water-soluble ions in diesel particulate matter were Ca^{2+} , SO_4^{2-} , and NO_3^{-} . SO_4^{2-} only 488 accounted for 27% of the total WSI mass which is lower than the 80% value reported by Sothea 489 and Kim Oanh (2019) for a 25 kVA and a 110 kVA diesel backup generators. However, the 490 main difference between the two experiments remains in the diesel sulfur content. The diesel 491 used by the latter study was assumed to have the same quality as the diesel oil used for 492 transportation and thus a sulfur content of 0.2% (2,000 ppm). On the other hand, since 2017, 493 Lebanon implemented stricter laws on the quality of the imported automotive diesel by 494 495 decreasing the sulfur content to 10 ppm and allowing higher sulfur content diesel to be delivered only to the big industries (ex. cement plants, fertilizer industry, etc.) and power plants. Despite 496 497 that law enforcement is not always guaranteed, the sulfur content in automotive diesel did not exceed the 200-300 ppm since 2014-2015. This difference in the fuel oil sulfur content might 498 499 explain the chemical composition differences since it has been established that sulfate in diesel particulate matter is function of the engine operating mode and the fuel sulfur content 500 501 (Saiyasitpanich et al., 2005).

502 Different diagnostic ratios including water-soluble ions are used to distinguish emission 503 sources. For instance, K⁺/EC and K⁺/OC ratios can be used to distinguish biomass burning from 504 fossil fuel combustion. The ratios calculated from this study can be used as marker values for 505 the sources and are reported in **Table 2.**

506 DG exhibited low K⁺/EC and K⁺/OC (0.01 and 0.003, respectively) compared to WB (0.36 and 507 0.12, respectively). These findings were also reported by Benetello et al. (2017) that assigned 508 a range of K⁺/EC and K⁺/OC at the source of 0.025-0.09 and 0.01 for fuel burning, respectively 509 and 0.21-0.46 and 0.1 for biomass burning, respectively. Additionally, the Cl⁻/SO₄²⁻ ratio might 510 be used to differentiate wood and coal combustion. In this study, higher values were observed for biomass burning (3.96) compared to coal combustion (0.4-1.34) and indicate that SO_4^{2-} is less emitted from WB compared to CG and BG.

513

514 2.4 Elemental composition

Twenty-nine analyzed elements in the profiles present different fractions of $PM_{2.5}$: the lowest total contribution of the considered elements was observed for CG which accounted to 1.2%, followed by DG (6%), then BG (7%), WB (8%), and GCA (11%) (**Figure S1**).

518 Ca is the most abundant element in the DG profile contributing to 56% of the sum of elements and is classified as the third most abundant species after OC and EC contributing to 3.3% of 519 PM_{2.5}. Other elements such as Fe, Al, Mg, K, and Zn were also abundant in the profile sharing 520 25% of their sum. These results are consistent with the ones from the composition of particles 521 emitted by a lab-designed engine (Mg, Na, Al, K, Ca, Fe, Zn) (Kerminen et al., 1997), and in 522 diesel PM composition reported by Yang et al. (1998) including Fe, Al, Ca, Na, Cr, Ba, Ni, Mg, 523 and K. However, some differences exist between the three profiles that might be caused by the 524 presence of organometallic additives in the diesel, the lubricating oil quality, and the operating 525 526 conditions. For instance, elements such as Ca and Zn can be used as markers of total lubrication oil consumption and their contribution to the total mass of elements may vary depending on its 527 quality (Sippula et al., 2014). 528

529 In the WB profile, K shares 50% of the mass of the 29 analyzed elements and is identified as a major metal in biomass burning since it is a major constituent of plants (Adam et al., 2021). 530 The other abundant elements in descending order were Ca, Al, S, Na, Fe, and Mg. These 531 findings were also observed during biomass burning events and in ash samples in a simulated 532 open combustion chamber (Akbari et al., 2021). Fe is considered as an important component in 533 vegetation and intervenes in physiological processes while Mg and Na play a major role in the 534 metabolism and the structure of the plant respectively (Alves, 2008; Brownell, 1979). Other 535 536 elements accumulated by trees were also present in WB such as Cu, Pb, Ti, Zn, and Mn.

Even though the total mass fraction of elements differs between BG, CG, and GCA, the most abundant elements observed are S, Ca, Na, K, Al, Mg, and Fe. They account for about 98% of the measured elements despite the cooking method used. Similar observations were made by See and Balasubramanian (2008) showing high content in Ca, Na, Fe, Mg, and Al for different cooking styles. This study showed sulfur as the dominant element for GCA in agreement with other residential cooking experiments (Wang et al., 2015; Zhao et al., 2019). This might be due to the addition of organic sulfur compounds such as ethyl mercaptan to liquid natural gas usedfor the detection of leak.

545 As for the other elements, Na is attributed to the salts and seasoning added to the food while Ca which has an important contribution in the three cooking profiles could be released from raw 546 547 materials (Zhang et al., 2017). K showed a considerable abundance in BG and CG and is mainly associated with charcoal combustion (Zhao et al., 2019). Although their contribution is 548 negligible to the total mass of the profile, trace elements are known to have harmful effects on 549 the human health. The GCA profile shows the presence of Pb and Mn that could be emitted 550 from cooking oil (peanut and canola oil) (Zhao et al., 2019). Other trace elements such as Cr, 551 Ni, Cu along with Fe are released from the interaction between the heating source and the 552 553 stainless steel wok used as cooking utensils in the different cooking profiles (Sun et al., 2020).

554

555 2.5 Organic and inorganic source markers

The knowledge of chemical profiles is an important tool to be used by receptor model users in the source apportionment exercise. According to Galvão et al. (2020), for a better separation between sources, the chemical speciation should include carbonaceous fraction, ions, elements, and organic compounds with a focus on chemical markers. The latter are considered as fingerprints that link the chemical profiles to the sources.

561 The markers of hardwood burning were OC, EC (with an OC/EC ratio of 3.4), potassium in its ionic and elemental form, and Cl⁻, accounting for 68% of the PM_{2.5}. Levoglucosan was the 562 major contributor to organic compounds along with the predominance of high molecular weight 563 n-alkanes, higher PAHs mass per gram of OM compared to the other profiles especially for 564 fluoranthene, pyrene, and benz[a]anthracene. The values of the characteristic PAHs ratios were 565 0.49 for fluoranthene/ (fluoranthene + pyrene) and 0.57 for benz[a]anthracene 566 /(benz[a]anthracene +chrysene). The K⁺/EC and K⁺/OC ratios were used to differentiate wood 567 from fuel combustion and were reported as 0.36 and 0.12 for wood burning, respectively. The 568 569 ratio between levoglucosan and OC for the hardwood combustion was equal to 0.3 in this study.

570 The major contributors to diesel generators profile were OC and EC accounting for more than

571 74% of PM_{2.5} with an OC/EC ratio of 2.9, followed by SO_4^{2-} , NO_3^{-} , Ca, Ca^{2+} , and S. N-alkanes

showed a high contribution to OC in this profile with a profile pattern maximizing at C_{20} - C_{21} ,

573 a carbon preference index value close to unity (0.9) and very low wax percentage (1.4%).

574 Pyrene was the most abundant compound between PAHs. The PAHs ratios reported for the

diesel combustion in our study were 0.24 for fluoranthene/(fluoranthene + pyrene), 0.41 for
benz[a]anthracene /(benz[a]anthracene +chrysene), and 0.18 for indeno[1,2,3-c,d]pyrene /
(indeno[1,2,3-c,d]pyrene + benzo[g,h,i]perylene). The profile also recorded the highest relative
share of PCDD/F and DL-PCBs compared to the other profiles. The K⁺/EC and K⁺/OC ratios
were 0.01 and 0.003, respectively.

The three cooking profiles showed similarities with a high contribution of carboxylic acids, 580 581 especially palmitic and stearic acids, high OC contribution and low EC share. The presence of food with different fat content and composition might increase the share of OC in the chemical 582 profile. Chicken grilling profile recorded the highest OC contribution of 72% of PM_{2.5} with an 583 OC/EC ratio of 622. Beef grilling profile markers were OC, EC (with an OC/EC ratio of 45), 584 Cl^{-} , K, NO₃⁻, and SO₄²⁻. For both profiles, C₂₅ having the highest contribution to n-alkanes, 585 carbon preference index values between 2 and 5, and high abundance of 4-rings PAHs with 586 587 fluoranthene/(fluoranthene + pyrene), benz[a]anthracene /(benz[a]anthracene +chrysene), and (indeno[1,2,3-c,d]pyrene + benzo[g,h,i]perylene) close to 0.5 were attributed to the charcoal 588 combustion. The general cooking activity profile presented an OC/EC ratio of 18, an important 589 contribution of $SO_4^{2^-}$, $NO_3^{-^-}$, and NH_4^+ (85% of WSI), and a high abundance of Al, Na, and Ca. 590 The n-alkanes pattern maximized at C₂₉, and the major emitted PAHs were 591 benzo[b]fluoranthene, pyrene, and chrysene. 592

593

594 3 <u>Conclusions</u>

595 This study is a first in the East Mediterranean and Middle East region presenting a full chemical characterization of 5 PM_{2.5} sources in the East Mediterranean region: hardwood burning, diesel 596 597 generator, beef and chicken charcoal grilling and general cooking activities. This characterization included the analysis of the carbonaceous fraction, ions, elements, and organic 598 599 species comprising n-alkanes, polycyclic aromatic hydrocarbons, carboxylic acids, levoglucosan, dioxins, furans, and dioxin-like polychlorobiphenyls. The markers for the 600 601 profiles along with the different ratios will be of utmost importance for future source 602 apportionment and modeling studies It would be also important for further studies to consider 603 other sources such as waste incineration, tire burning, etc. The results of this work will contribute to further broaden our knowledge of the PM sources in the region by expanding the 604 605 database for the East Mediterranean - Middle Eastern region. It might be also interesting to 606 evaluate the impact of using these local profiles on the policy making in the region.

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