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Anthropogenic and biogenic pollutants in a forested environment: SPRUCE-22 campaign overview

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Abstract

The SPRUCE-22 field campaign was conducted during July 2022 on a remote mountainous forested site in Greece to assess interactions of biogenic and anthropogenic pollutants in the Eastern Mediterranean. Particle chemical composition and size distributions along with concentrations of organic and inorganic gases were measured at high temporal resolution, while samples were collected and analyzed off-line. PM₁ had a surprisingly high average concentration of 13 μg m⁻³ consisting primarily of organics (57%), followed by sulfate (30%), ammonium (9%), and black carbon (2%). Nitrates (both inorganic and organic) were less than 1% of the PM₁ despite the relatively high NO_x emissions in the Balkans. The PM_{2.5} concentrations at this remote site were similar and even higher than those in major cities across Greece including Athens, indicating the importance of regional transport for summertime pollution in the Eastern Mediterranean. The relatively constant average diurnal profiles of major anthropogenic pollutants are consistent with only minimal effects from local sources.

36 Sulfates are not any more the dominant component of fine PM in Greece due to the reduction
37 of SO₂ emissions of coal-burning powerplants. The organic aerosol (OA) was quite oxidized
38 with an average oxygen to carbon ratio (O:C) equal to 0.83. The average concentration of
39 isoprene was 0.6 ppb, of monoterpenes 0.5 ppb, while the biogenic secondary organic aerosol
40 factor (obtained through source apportionment analysis) was estimated to contribute 22% of
41 the OA. Additional biogenic secondary organic aerosol (SOA) may be part of the two
42 oxygenated OA (OOA) factors that were also identified. Radiocarbon analysis indicated that
43 the non-fossil carbon was approximately equal to the sum of the biogenic and the more oxidized
44 oxygenated OA, implying that the less oxidized OOA in this study was mostly associated to
45 anthropogenic fossil fuel combustion. The biogenic SOA was quite aged (O:C equal to 0.63)
46 and was also mostly transported to the site. Nearby new particle formation events occurred
47 during 20 % of the days, with an average SO₂ concentration of 0.3 ppb. The oxidative potential
48 of the PM per unit of mass was quite high. The source attribution of the fine PM and the
49 interactions among its anthropogenic and biogenic components are also discussed.

51 **1. Introduction**

52 The airborne particulate matter (PM) effects on human health (Pope et al., 2006) and
53 climate have motivated investigations of the atmospheric processes that govern its formation
54 and evolution as well as its physical, chemical and toxicological properties. Field campaigns
55 that characterize the levels and variations of atmospheric pollutants at one or more sites, allow
56 the evaluation of atmospheric chemical transport models and help identify important processes
57 that can be further studied in laboratory experiments. The Mediterranean region is an
58 interesting study area due to the abundance of different sources (urban and biogenic continental
59 emissions, semi enclosed marine environment with influences from desert dust). During
60 summer, limited wet removal (due to low precipitation) and increased solar radiation promoting
61 oxidant formation (O₃, OH) lead to increased levels of secondary PM in the area (Bougiatioti
62 et al., 2014; Dayan et al., 2017; Cristofanelli et al., 2016).

63 A number of studies have focused on fine (PM₁) and coarse (PM₁₀) particle composition
64 and their sources on continental or regional background sites across the Mediterranean. Mallet
65 et al. (2019) gathered chemical composition observations for fine particulate matter (PM₁)
66 across the Mediterranean during spring and summer, where it can be noted that in the eastern
67 region sulfate was the dominant PM₁ component due to increased SO₂ emissions. In contrast,
68 the western part PM₁ was dominated by organics. A significant portion of the observed organic

69 aerosol is highly oxidized and is termed oxidized organic aerosol (OOA) creating a background
70 of PM for a broad area (Jimenez et al., 2009).

71 The remote background station of Finokalia has provided information about the regional
72 background of Eastern Mediterranean for 30 years (Gialesakis et al., 2023; Sciare et al. 2003).
73 Sciare et al. (2003) reported daily concentrations of non-sea salt sulfate up to more than 8 μg
74 m^{-3} during summertime. The bulk PM ammonium/non-sea salt sulfate equivalent ratio was on
75 an average 1.49, indicating strongly acidic particles. A year later, during the MINOS campaign
76 in August (Sciare et al., 2005) the fine PM measured was on average 17.4 $\mu\text{g m}^{-3}$ comprised
77 primarily of ammonium sulfate (45%) and organics (45%). In both summertime FAME
78 campaigns (May to June 2008 and 2016) (Pikridas et al., 2010; Florou et al. 2024) the sulfate
79 fraction of the PM_{10} was dominant at 50% and 45% respectively, while the organics contributed
80 28% and 35% respectively. In both cases the organics were primarily secondary and highly
81 aged. During the summer 2012, Bougiatioti et al. (2014) reported equal contributions of sulfate
82 and organics in Finokalia to the 12 $\mu\text{g m}^{-3}$ average PM_{10} levels. The organic aerosol was again
83 highly oxygenated and processed, with the study highlighting the influence of aged biomass
84 burning plumes reaching the site.

85 Summertime wildfires are a common occurrence in the Mediterranean region, influencing
86 air quality even far away, due to production of secondary OA, but also sulfates and nitrates
87 (Diapouli et al., 2014). PM components associated with biomass burning and used for source
88 attribution, like levoglucosan, are lost after atmospheric aging of a day under summertime
89 conditions in the Eastern Mediterranean (Bougiatioti et al., 2014; Vasilakopoulou et al., 2023).
90 In this way the organic chemical footprint of biomass burning PM is rapidly lost. Instead, aged
91 biomass burning plumes appear as highly oxidized organic material and correlate better with
92 inert species like fine K^+ and BC (Vasilakopoulou et al., 2023). Processed biomass burning
93 emissions make up a large fraction of the observed summertime OA in the Mediterranean with
94 Bougiatioti et al. (2014) reporting that 30% of organics in Finokalia were processed biomass
95 burning OA (bbOA). Bossioli et al. (2016) estimated that fires in Turkey led to a 95% increase
96 of the OA over the southeastern Aegean Sea under appropriate transport conditions.

97 Other studies have targeted the interactions of anthropogenic pollution with biogenic
98 components when mixed. The Southern Oxidant and Aerosol Study (SOAS) campaign
99 (Budisulistiorini et al., 2015) in a forested elevated site in Tennessee US, influenced by
100 anthropogenic emissions, focused on isoprene interaction with anthropogenic pollutants.
101 Approximately 10% of the observed OA was due to measured isoprene epoxydiol (IEPOX)
102 related secondary organic aerosol (SOA), while positive matrix factorization (PMF) analysis

103 attributed 32% of the OA to an IEPOX OA factor. The source apportionment yielded no
104 contribution from primary emissions, while one OOA factor was connected to biogenic
105 emissions. The total OA of that study was quite oxidized with an O:C of 0.77. A relationship
106 was found between anthropogenic sulfate and isoprene SOA, though no connection was
107 observed between isoprene SOA and acidity (Budisulistiorini et al., 2015).

108 The SPRUCE campaign (Summer PeRtoUli Campaign Emissions) was conducted in
109 2022, aiming at the characterization of air quality in a remote forested area in the Eastern
110 Mediterranean using an array of in-situ measurements and oxidation experiments as well as
111 offline analysis of collected samples. The present paper acts as an overview, presenting the
112 composition of the gas and particulate phase pollutants. Assessment of contributing sources to
113 the observed PM₁ is presented and the influence of anthropogenic activity on this forested site
114 is discussed. The magnitude of local organic production in this site, during summer was
115 estimated, along with the frequency of new particle formation events in this environment.
116 Finally, the air quality of this background site was related to the rest of the Greek mainland for
117 the period examined, with respect to their PM levels.

118 119 **2. Measurements**

120 **2.1 Site description**

121 The campaign took place in a mountainous area in the mainland of Greece. The selected
122 station was located at the chalet on top of the ski resort of Pertouli (39.545623, 21.498516) at
123 an elevation of 1300 m above sea level. The closest anthropogenic source was the nearest
124 village of Pertouli (80 inhabitants), located 3 km away and Trikala (81,400 inhabitants), the
125 largest town in the region, is 50 km from the site, while the nearest road is 1 km away. The
126 broad area includes a forest of fir trees (dominated by the *Abies borisii-regis* species), along
127 with beech, oak and pine trees. The forest is especially dense within a 2 km radius from the site
128 (Figure S1).

129 The majority of the instrumentation was placed inside the chalet. The sampling lines used
130 were either made of Teflon (for gas phase analyzers) or copper (for the particulates). Sampling
131 took place 8 m above ground. PM_{2.5} heads were used to cut off larger particles. The FORTH
132 mobile laboratory was used to house additional instruments. The inlet sampling lines protruded
133 from the front of the van at about 3 m above ground.

2.2 Instrumentation

The month-long campaign took place from July 2 to August 2, 2022. Information on instruments deployed is provided in Table 1.

Table 1. Pollutants measured during SPRUCE-22 and corresponding average concentrations.

Pollutant	Average Concentration	Time Resolution	Instrument
PM ₁	12.65±5.17 μg m ⁻³	3 min	HR-ToF-AMS (Aerodyne) *
PM ₁	13.19±5.27 μg m ⁻³	3 min	SMPS*
N ₄	3528±1615 cm ⁻³	3 min	SMPS
N ₇	2815±1517 cm ⁻³	1 min	WCPC (TSI model 3789)
OA (PM ₁)	7.44±3.19 μg m ⁻³	3 min	HR-ToF-AMS (Aerodyne) *
OC (PM _{2.5})	3.74±0.95 μg m ⁻³	1 d	Sunset OC/EC
BC (PM _{2.5})	0.26±0.12 μg m ⁻³	1 min	MAAP (Thermo Scientific Inc., 5012)
BC (PM _{2.5})	0.42±0.18 μg m ⁻³	1 min	Aethalometer (AE33, Magee Scientific)
BC (PM ₁)	0.15±0.07 μg m ⁻³	1 min	SP2-xr (Droplet measurement Technologies, DMT)
EC (PM _{2.5})	0.11±0.07 μg m ⁻³	1 d	Sunset Lab OCEC Analyzer
Sulfate (PM ₁)	3.84±1.74 μg m ⁻³	3 min	HR-ToF-AMS (Aerodyne) *
Ammonium (PM ₁)	1.23±0.55 μg m ⁻³	3 min	HR-ToF-AMS (Aerodyne) *
Ammonium (PM _{2.5})	1.73±0.56 μg m ⁻³	1 d	IC (Shimadzu, LC-20ADSP)
Nitrate (PM ₁)	0.12±0.05 μg m ⁻³	3 min	HR-ToF-AMS (Aerodyne) *
Nitrate (PM _{2.5})	0.51±0.14 μg m ⁻³	1 d	IC (Shimadzu, LC-20ADSP)
K ⁺ (PM ₁)**	0.08±0.09 μg m ⁻³	3 min	HR-ToF-AMS (Aerodyne) *
K ⁺ (PM _{2.5})	0.12±0.07 μg m ⁻³	1 d	XRF
Ca ²⁺ (PM _{2.5})	0.23±0.17 μg m ⁻³	1 d	XRF
Cl ⁻ (PM ₁)	0.025±0.005 μg m ⁻³	3 min	HR-ToF-AMS (Aerodyne) *
Cl ⁻ (PM _{2.5})	0.07±0.04 μg m ⁻³	1 d	XRF
Cu ²⁺ (PM _{2.5})	0.13±0.09 μg m ⁻³	1 d	XRF
O ₃	64.9±8.3 ppb	1 min	TELEDYNE API (T400) *
SO ₂	0.27±0.30 ppb	1 min	Pulsed Fluorescence Analyzer (Thermo, 43 i)
NO ₂	1.75±0.62 ppb	1 min	Serinus 40 (ECOTECH)
Acetonitrile	0.10±0.05 ppb	10 s	PTR-QMS (IONICON)*
Methylvinylketone (MVK)	0.49±0.40 ppb	10 s	PTR-QMS (IONICON)*
Acetone	2.07±0.66 ppb	10 s	PTR-QMS (IONICON)*
Toluene	0.002±0.055 ppb	10 s	PTR-QMS (IONICON)*
Monoterpenes	0.490±0.77 ppb	10 s	PTR-QMS (IONICON)*
Isoprene	0.62±1.09 ppb	10 s	PTR-QMS (IONICON)*
Methyl ethyl ketone (MEK)	0.16±0.10 ppb	10 s	PTR-QMS (IONICON)*
Benzene	0.04±0.03 ppb	10 s	PTR-QMS (IONICON)*
Acetone	2.13±0.75 ppb	10 s	PTR-QMS (IONICON)*
Acetic acid	0.51±0.39 ppb	10 s	PTR-QMS (IONICON)*

141 *Instruments in the FORTH mobile laboratory, also used in dual chamber experiments. During the periods of the smog
1 142 chamber experiments those did not collect ambient measurements, resulting in a partial deficit in the ambient dataset.

2 143 **The AMS measures only a fraction of the K^+

3
4 144 A High-Resolution Aerosol Mass Spectrometer (HR-Tof-AMS, Aerodyne) was operated
5
6 145 with no dryer, providing PM_{10} chemical composition measurements. The instrument
7
8 146 background was monitored daily with the use of a HEPA filter at the inlet for approximately
9
10 147 30 min. The AMS was calibrated with ammonium nitrate at the beginning of the campaign.

11 148 Three scanning mobility particle sizers (SMPS) were used, and their measurements were
12
13 149 combined to cover the size range from 4 to 710 nm. SMPS#1 complimented the measurements
14
15 150 of the AMS inside the FORTH mobile lab and was comprised by a TSI classifier (model 3080),
16
17 151 a differential mobility analyzer (DMA) measuring sizes of 14-710 nm (TSI 3081 model) and a
18
19 152 TSI 3775 butanol condensation particle counter (CPC). It operated on an aerosol flow rate of
20
21 153 0.6 L min^{-1} with a sheath flow of 3 L min^{-1} . SMPS#2, operating inside the chalet, differed from
22
23 154 SMPS#1 only in the use of a water CPC (TSI model 3787) instead of a butanol one. Finally,
24
25 155 SMPS#3 (classifier: 3080 TSI, CPC: TSI 3775) used the DMA model 3085 of TSI spanning
26
27 156 ranges of 4-118 nm and sampled with a flowrate of 1.5 L min^{-1} (sheath flow of 5 L min^{-1}) from
28
29 157 inside the chalet.

30 158 Black carbon was monitored by a Multi-Angle Absorption Photometer (MAAP model
31
32 159 5012, Thermo Scientific) and an Aethalometer (Model AE33, Magee Scientific), using a $PM_{2.5}$
33
34 160 cutoff head. Also, a Single Particle Soot Photometer (SP₂-xr, DMT) was operated on site. $PM_{2.5}$
35
36 161 mass concentrations were measured through a low-cost Purple Air monitor.

37 162 Concentrations of volatile organic compounds (VOCs) were measured by proton transfer
38
39 163 reaction mass spectrometry by a quadrupole PTR-MS (PTR-QMS 500, Ionicon Analytik).
40
41 164 Correcting for background instrument signal required sampling through an activated charcoal
42
43 165 filter (Supelco Analytics) each day for 30 min. The instrument was calibrated on site at the
44
45 166 beginning of the campaign with the use of a precision calibrator (model 702, Teledyne Inc.)
46
47 167 for dilution of a standard gas VOC mixture (15 compounds, Restek). Response factors can be
48
49 168 found in Table S1. The calibration mix had VOC concentrations of 1 ppm and was used with
50
51 169 a dilution factor of 40 (~25 ppb).

52 170 Measurements of inorganic trace gases included NO_2 (Ecotech, Serinus 40), SO_2 (Thermo
53
54 171 43 i) and O_3 (Teledyne, T400). The analyzers were zeroed using synthetic air at the beginning
55
56 172 of the campaign.

57 173 Along with the online instrumentation, particulate and gas phase samples were collected
58
59 174 daily for the duration of the campaign. Stainless steel sorbent tubes (3.5" x 0.25" packed with
60
61
62
63
64
65

175 Tenax^{TA}, Markes International[®]) were installed in a custom-made sampler operating at a flow
176 of 0.1 L min⁻¹. No scrubber was used prior to the sorbent tubes for the removal of oxidants.
177 The retained organic compounds were analyzed with the use of gas chromatography mass
178 spectrometry (GCMS, Shimadzu model QP2010) after a two-step desorption via a cold trap in
179 a thermal desorber (Markes International Ltd, UNITY–Air Server-xr).

180 For particulates, PM_{2.5} samples were collected on 101.6 mm Quartz filters (Pall
181 LifeSciences) on a medium flow sampler operating at 110 and 160 L min⁻¹ (Tisch
182 Environmental, TE-1000). The filters were subsequently cut into punches for use in different
183 analytical techniques.

184 Both the sorbent tubes and the filters were conditioned before deployment to minimize
185 artifacts (sorbent tubes at 300 °C for 10 min and filters for 4 h at 500 °C). To further minimize
186 potential artifacts, field blanks were used, and the samples were kept in a freezer to additionally
187 minimize loss of analytes.

188 A thermal optical method (protocol NIOSH 870, Panteliadis et al., 2015) was used by a
189 Sunset OC/EC analyzer (Sunset Laboratory Inc.) for the filter-based measurements of organic
190 carbon (OC). A solution of sucrose was applied into a filter punch and analyzed to verify the
191 calibration of the system.

192 The oxidative potential (OP) of the water-soluble fraction of the fine aerosol was measured
193 in an effort to assess its potential toxicity. The dithiothreitol (DTT) assay was used following
194 the approach described in Georgopoulou et al. (2024).

195 Radiocarbon measurements were conducted in Aix-en-Provence using an elemental
196 analyzer (EA) coupled to the gas interface system (GIS) of the AixMICADAS system (Bard et
197 al., 2015). In short, two filter punches (1.5 cm² each) were transferred into silver capsules (8 x
198 8 x 16 mm, Elementar Analysensysteme GmbH) previously prebaked at 800°C for 2 hours to
199 minimize contamination by extraneous carbon adsorbed at the surface of the vessels (Bonvalot
200 et al., 2016). The filters were then impregnated with 200 µL HCl (1 N) to eliminate potential
201 carbonates present in the aerosols. After the acidification step was carried out in a laminar flow
202 hood, the samples were immediately placed in a polypropylene glove box continuously fed
203 with nitrogen for a minimum of 1 hour before being dried at 80°C under a nitrogen stream
204 (Reacti-VapTM, Thermo Fisher Scientific Inc). Following decarbonation, the samples were
205 stored in 2 ml glass vials treated at 500°C for 2 hours and closed with screw caps with septa
206 silicon/PTFE. The samples were analysed within 2 weeks using the EA-GIS-AMS parameters
207 described elsewhere (Bonvalot et al., 2016; Tuna et al., 2018). The measurements were
208 normalized with OxA2 standard gas (≈100 µgC; CO₂ produced from NIST Oxalic Acid II,

209 NIST SRM4990C). A ¹⁴C free CO₂ gas canister (≈100 μgC) was used to correct the blanks for
210 OxA2 standard gas whereas samples were corrected for procedural blanks.

211

212 **2.3. Data Analysis**

213 The origin of the air masses arriving at the site was determined by the Single-Particle
214 Lagrangian Integrated Trajectory model HYSPLIT (Draxler and Hess, 1998) and the particle
215 dispersion model FLEXPART (Stohl et al., 2005) both in backward mode. HYSPLIT backward
216 trajectory analysis was conducted using meteorological input from the GFS model (0.25°
217 spatial resolution) with an endpoint 50 m above ground level. Categorization of the regional
218 sources was based on clustering analysis using the Openair R package (Carslaw and Ropkins,
219 2012), using as input the 48 h backward trajectories. The chosen method for grouping the data
220 employed 3 clusters and the angle distance matrix, clustering trajectories based on the angle of
221 their origin with respect to the site. Clusters were also tested with both the angle and Euclidean
222 distance methods (grouping based on distance of the trajectories' origin coordinates) and the
223 results were effectively similar.

224 The AMS dataset was analyzed using the SeQUential Igor data RetRiEvaL (SQUIRREL)
225 v1.57I and Peak Integration by Key Analysis (PIKA) v1.16I both written in Igor Pro
226 (WaveMetrics, Lake Oswego, OR). The Canagaratna et al. (2015) method was used to
227 determine the elemental ratios (e.g O:C, H:C) of the organic fraction of the aerosol. The AMS
228 measurements were corrected for the collection efficiency (CE) of the instrument with the use
229 of the Kostenidou et al. (2007) algorithm with an interval of 2-3 hours with the use of the
230 collocated SMPS size distribution measurements. The average CE was 0.80 ± 0.16. The density
231 of the OA was also estimated by the same algorithm. The fraction of the nitrate group that was
232 related to organic nitrates was determined as described by Kiendler-Scharr et al. (2016).
233 Positive matrix factorization (PMF, Paatero and Tapper, 1994) was applied to the high-
234 resolution mass spectra (*m/z* range of 12-200) of the organic aerosol (OA). The values of the
235 PM_{2.5} from the low-cost sensor were corrected following Kosmopoulos et al. (2022).

236 The concentrations of VOCs were measured by the PTRMS. For the 14 compounds
237 contained in the calibration mix their normalized (as to the hydronium ion) sensitivities were
238 calculated by:

$$239 S_m = \frac{C_{RH,cal} - C_{RH,zero}}{C_{H_3O^+,cal} 500 + 0.5 C_{H_3O^+(H_2O),cal}} 10^6 \text{ [ncps ppb}^{-1}\text{]} \quad (1)$$

240 where, C_{RH} , $C_{H_3O^+}$, $C_{H_3O+(H_2O)}$ the counts per second for the analyte and the primary ions for
241 either the zeroing or the calibration period. For the compounds included in the calibration mix,
242 the ambient concentrations were calculated with the use of this sensitivity factor. For the rest
243 of the monitored m/z values the operating conditions of the PTR drift tube were used for
244 estimation of ambient concentrations using a rate constant of $k=2.0 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ for all the
245 analytes (IONICON, 2020). Attribution of the signal m/z to compounds was made with use of
246 fragmentation tables taking into account the analysis of the Tenax tubes.

247 For the radiocarbon analysis, due to the small carbon amount contained in the processing
248 filters (around $0.3 \mu\text{gC}/\text{cm}^2$ were determined separately by EA measurement), approximately
249 $35 \mu\text{gC}$ of phthalic acid (^{14}C free blank) was added to the processing blanks. Because of
250 elevated analytical costs and the limited number of blank filters, the blank correction was
251 performed with a carbon mass representative of the aerosol samples (carbon masses ranging
252 from 23 to $70 \mu\text{gC}$ with an average of $38 \mu\text{gC}$ and a standard deviation of $12 \mu\text{gC}$). A relative
253 error of 50% based on the measurements of 12 procedural blanks from 3 sampling campaigns
254 was propagated to the procedural blank value obtained in this study ($F^{14}\text{C} = 0.0284$, $N=2$). An
255 additional uncertainty of 2.2‰ was propagated in the error calculation to account for the long-
256 term variability on OxA2 gas. Normalization and blank correction were performed using the
257 BATS software (Wacker et al., 2010) and all measurements are expressed in $F^{14}\text{C}$ as defined
258 by Reimer et al. (2004).

259 As a first approximation, we assume that the carbonaceous fraction is composed of two
260 endmembers: a fossil fraction free of ^{14}C , and a non-fossil fraction assumed to be isotopically
261 homogenous. To determine this non-fossil fraction (f_{NF}), the measured $F^{14}\text{C}$ has to be
262 normalized by a non-fossil reference value ($f_{NF,ref}$, expressed in $F^{14}\text{C}$) as described by:

$$f_{NF} = \frac{F^{14}\text{C}}{f_{NF,ref}} \quad (2)$$

264 In the present study, it is assumed that the non-fossil fraction can originate from biogenic
265 and/or wood burning emissions with slightly different ^{14}C signatures. Biogenic emission should
266 be close to the atmospheric ^{14}C level at the time of collection whereas wood burning emission
267 have higher ^{14}C content due to the uptake during tree growth of CO_2 contaminated by ^{14}C from
268 atmospheric thermonuclear tests that started in the late 1950s. Other source proxies may help
269 to discriminate between both processes. As a first approximation, we have estimated two end-
270 members for the non-fossil reference value: a lower bound ($f_{NF,ref} = 1.00$) for biogenic carbon
271 including modern (2022) atmospheric CO_2 and upper bound ($f_{NF,ref} = 1.04$) for wood burning
272 emission. This latter value was calculated by combining atmospheric data over the last decades

273 (Hua et al., 2022; Levin et al., 2022) and a tree-growth model (Lewis et al., 2004; Mohn et al.,
274 2008) assuming an average tree age of 30 years for forest wildfires.

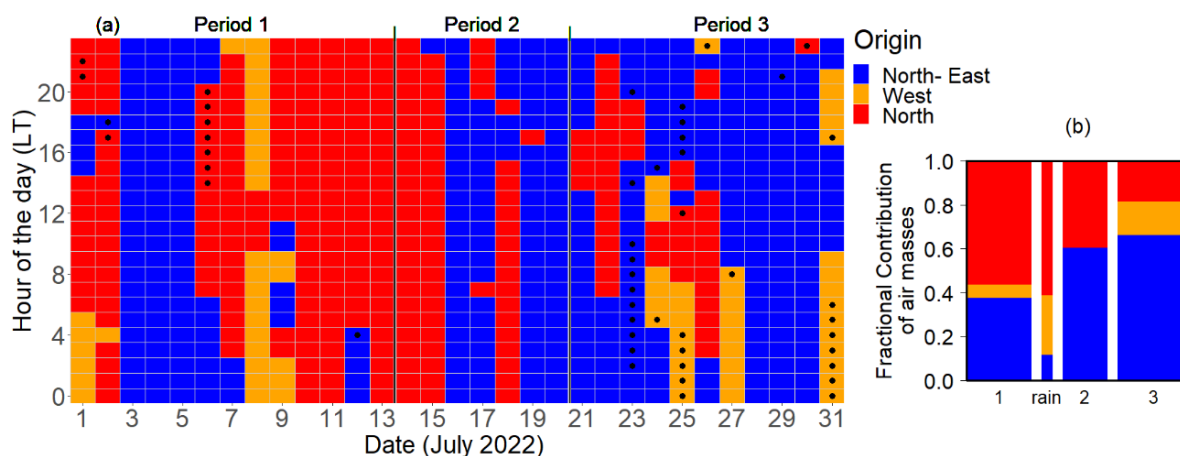
275

276 3. Results

277 3.1. Meteorology

278 The site was predominantly (51% of the time) affected by airmasses coming from the NE
279 Balkans (Figure 1), which reached the site from the east passing over the northern Aegean Sea
280 (Figure S2). Around 39% of the trajectories originated from the north passing over Serbia. The
281 remaining 10% of the air masses came from the west, had lower wind speeds, and passed over
282 the Ionian and the Adriatic Sea. Approximately, 6% of all the air masses are characterized as
283 stagnant, since for 2 d prior to reaching the site, they remained within 200 km from it.

284



285

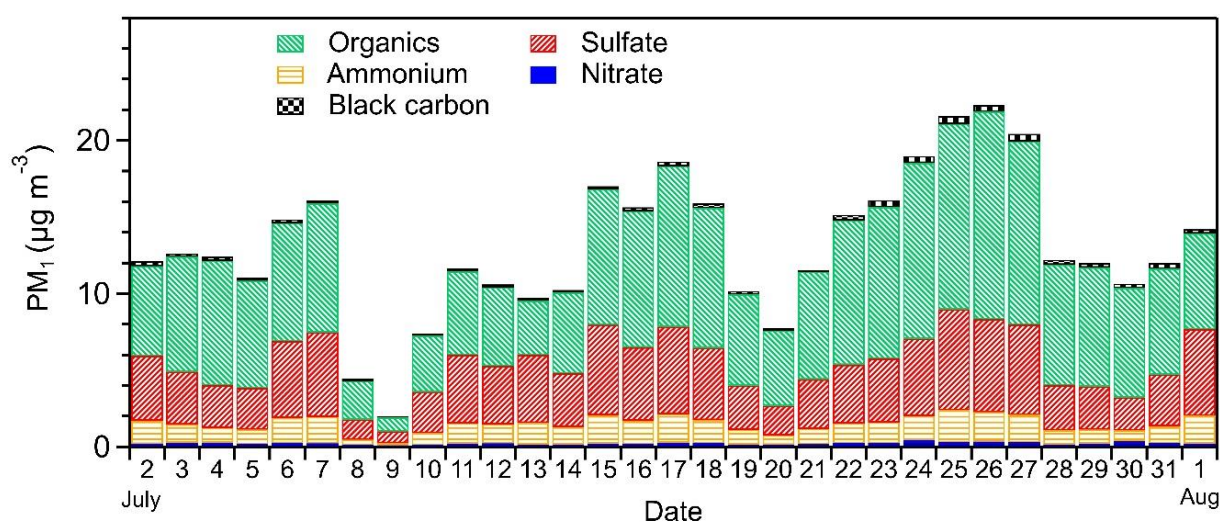
286 **Figure 1.** (a) Origin of air masses reaching the station at an elevation height of 50 m above the
287 ground based on HYSPLIT. Colors indicate the origin of the 48 h backward trajectories,
288 corresponding to three clusters coming from the North, the North-East and West. The black
289 dots indicate stagnant air masses, which for 2 days remained within 200 km from the site. The
290 black vertical lines define three subperiods in the campaign. (b) Fractional contribution of the
291 clusters in each sub period, with size proportional to their duration. The rain period involves
292 the period from July 8 midday to July 10 morning, when precipitation influenced pollutants'
293 levels at the site.

294 The temperature during the campaign was mild at 20 ± 5 °C (hourly average), with a relative
295 humidity of 57 ± 16 % (Figure S3). The average increase in temperature during the day was in
296 the order of 8 °C (maximum at 15:00 LT), with a corresponding decrease in the RH of 20 %.
297 There was one precipitation event accompanied by fog that lasted from midday of July 8 to
298 morning of July 10 and resulted in significant removal of pollutants.

299

300 3.2. Concentration, composition, and properties of particles

301 The hourly PM₁ concentrations (summing the AMS and the MAAP measurements) for the
302 entire campaign ranged from 0.7 (during the fog event) to 27 µg m⁻³ with an average value of
303 12.7±5.1 µg m⁻³ (Figure 2). The PM₁ was mostly comprised of organics (58.8%, with an
304 average of 7.4±3.2 µg m⁻³), whose density was 1.52 ± 0.29 g cm⁻³ as calculated from the
305 Kostenidou et al. (2007) algorithm, using the combined AMS-SMPS dataset. Sulfate
306 represented 30.3% of the PM₁ (average 3.8±1.7 µg m⁻³). Ammonium constituted 9.7 % (1.2
307 ±1.4 µg m⁻³), while PM₁ nitrate was <1% (0.12±0.05 µg m⁻³), with about 85% being
308 organonitrates (Figure S4). The PM_{2.5} black carbon was 0.26±0.12 µg m⁻³ (2.1 %). It is assumed
309 that most of the PM_{2.5} BC was in the PM₁ range. PM₁ ammonium displayed excellent
310 correlation to sulfate (R² = 0.98 for hourly averages, Figure S5).



311 **Figure 2.** Daily average PM₁ chemical composition during the SPRUCE campaign, based on
312 the AMS and the MAAP measurements.
313

314 The average mass distribution of all constituents peaked at a vacuum aerodynamic
315 diameter of approximately 480 nm (Figure 3). However, across the campaign there was some
316 differentiation in terms of the common peak of the mass distribution. During the period after
317 the rain event (July 12 to 15) the distributions shifted to smaller sizes (peak at 374 nm), from
318 the 460 nm that was the apex of the mass distribution at the beginning and during the
319 precipitation event (Figure S6). From then on, the mode diameter was steadily increasing
320 reaching 550 nm for after July 25. This variation could be the result of the wet removal of
321 particulates in a broad area of the Balkans (Figure S7) that resulted in smaller particles that
322 then progressively grew due to the formation of secondary PM.

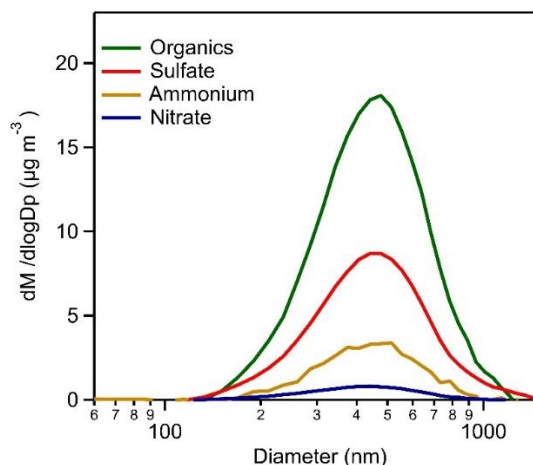
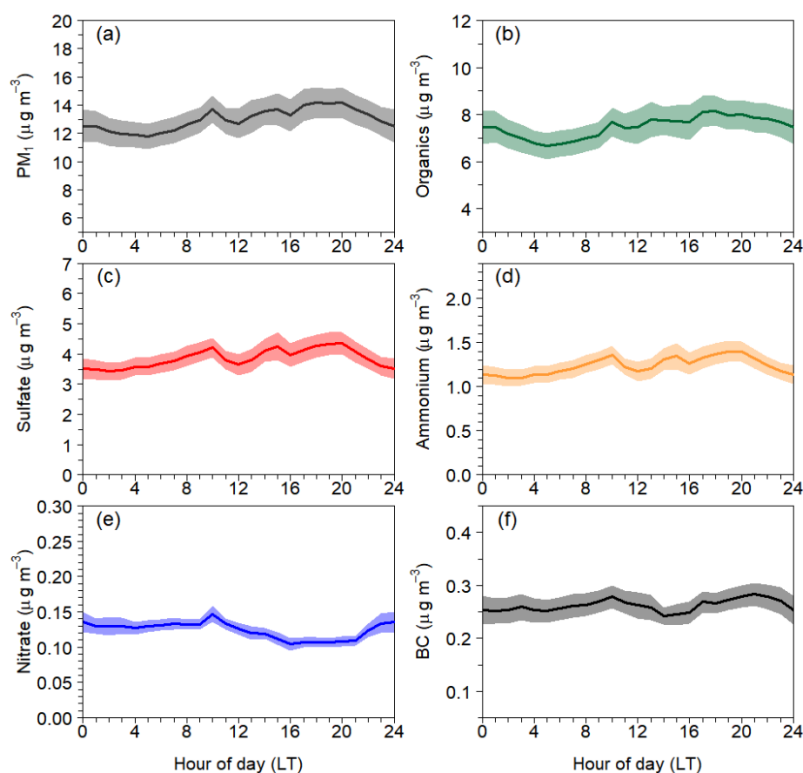


Figure 3. Average mass size distributions of major PM₁ constituents.

The OA was lowest when trajectories were coming from the North (median concentration of $6.6 \mu\text{g m}^{-3}$) and higher for the Western air masses (median equal to $9.3 \mu\text{g m}^{-3}$) (Figure S8). The differences were statistically significant. However, this variation in organics could be due to the progressive concentration increase during the campaign (with the first period dominated by the North air masses). On the other hand, sulfate was lower for the NE trajectories (median value of $3.50 \mu\text{g m}^{-3}$ as opposed to $4.35 \mu\text{g m}^{-3}$ for the western and $4.61 \mu\text{g m}^{-3}$ for the northern) but the difference in mean values was only statistically significant for the N-NE. This is probably due to the SO₂ emissions from major coal-fired power plants in northern Greece, Northern Macedonia, Bosnia/Herzegovina and Serbia (Figure S9). The Bulgarian power plants in the NE do not seem to contribute as much to the sulfate concentration observed at this site. Ammonium had similar behavior across all air masses as sulfate. Nitrate concentrations were low regardless of the air mass origin. Black carbon was slightly higher for the Western air masses (median of $0.38 \mu\text{g m}^{-3}$) than the other two (0.24 for the N and $0.29 \mu\text{g m}^{-3}$ for the NE) following the trend of the organics.

Organics and sulfate were moderately correlated with $R^2=0.51$ (0.39 with exclusion of the rain period) at an hourly resolution. The average OA/sulfate ratio was 2.1 ± 0.8 (Figure S10) and it exceeded 3 for several periods during the campaign, when the air masses had originated mainly from the NE and the W (Figure S11). The average OA/sulfate ratio from the NE and the W cluster was 2.8 and 2.6 respectively. The air masses from the north had the lowest mean OA/sulfate ratio of 1.6 as a result of the lower OA concentration and the slightly higher sulfates. There were very few hours (~ 30) during which the sulfate levels exceeded those of the OA (mainly on July 13).

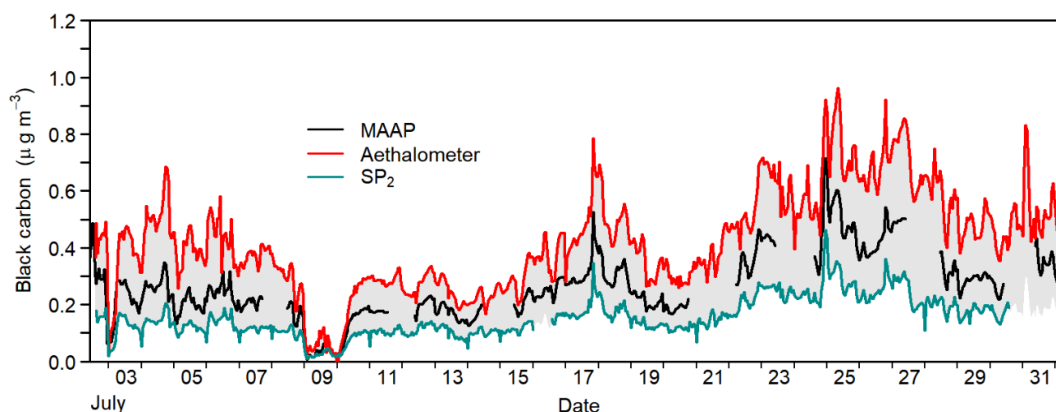
348 The diurnally averaged PM_{10} (Figure 4) increased from a minimum of $11.5 \mu g m^{-3}$ at 05:00
 349 LT to $14.1 \mu g m^{-3}$ at 19:00 LT. The same fractional increase was observed for OA, which
 350 peaked at 18:00 LT. Sulfate displayed a small peak at 10:00 LT (equal to $4.2 \mu g m^{-3}$) and a
 351 gradual increase peaking at 19:00 LT (from $3.6 \mu g m^{-3}$ at 12:00 LT to $4.3 \mu g m^{-3}$). Ammonium
 352 had the same behavior as sulfate increasing from $1.2 \mu g m^{-3}$ at 12:00 LT to $1.4 \mu g m^{-3}$. The
 353 concentration of nitrate slightly decreased during the day.



354
 355 **Figure 4.** Diurnal variation of PM_{10} concentrations and of major individual constituents. The
 356 shaded areas correspond to one standard deviation of the mean of the corresponding hourly
 357 values.

358 The black carbon (BC) concentration was relatively low throughout the campaign with
 359 hourly average values of $0.26 \mu g m^{-3}$ (Figure 5), as measured by the MAAP. Its concentration
 360 increased in the second part of the campaign along with the OA. The diurnal profile of BC was
 361 relatively flat with no more than $0.04 \mu g m^{-3}$ variation (13%) during the day (Figure 4f). This
 362 profile suggests negligible contributions from local sources. The measurements of the other
 363 two BC instruments (aethalometer and SP_2 -XR) had high correlations (R^2 from 0.88 to 0.95)
 364 with the MAAP values. The aethalometer measured higher BC by $0.16 \pm 0.08 \mu g m^{-3}$ compared
 365 to the MAAP (aethalometer average BC of $0.42 \pm 0.18 \mu g m^{-3}$), which is consistent with other
 366 studies (Tasoglou et al., 2018; Pikridas et al., 2019). The differences can probably be explained
 367 by the default mass absorption cross-section values used to derive the equivalent BC.

368 Significant coating effects on the BC absorption are expected in this environment in which the
369 aerosol is quite aged (Zhang et al., 2023). In turn, the SP₂, measured lower concentrations than
370 the MAAP by $0.10 \pm 0.08 \mu\text{g m}^{-3}$ (SP₂ average BC equal to $0.15 \pm 0.07 \mu\text{g m}^{-3}$). Lower values of
371 the refractive BC by about 50 % for aged PM have been also reported in past studies (Zhang et
372 al., 2023).



373
374 **Figure 5.** Hourly averaged concentrations of black carbon as measured by the various
375 instruments during the campaign.

376 The average diurnal variation of the OA to BC ratio is shown in Figure 6a. The fact that
377 the OA/BC increased by 22 % from 08:00 LT to 15:00 LT strongly suggests the presence of
378 regional photochemistry and SOA production. There is also another peak at 23:00 LT during
379 the nighttime.

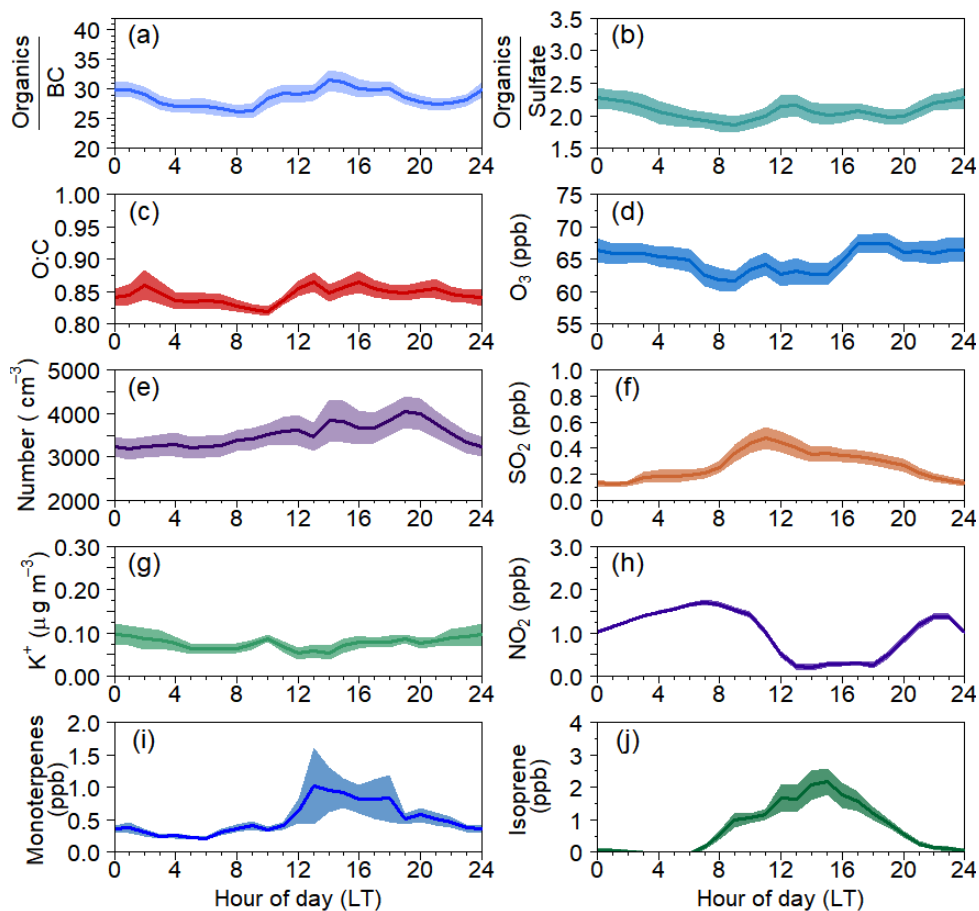


Figure 6. Diurnal variation of (a) organics to black carbon ratio (b) organics to sulfate ratio, (c) O:C ratio, (d) ozone, (e) N_4 , (f) SO_2 , (g) K^+ , (h) NO_2 , (i) monoterpenes, (j) isoprene. The shaded areas correspond to one standard deviation of the mean of the corresponding values.

The average O:C was 0.84 indicating highly oxygenated OA. The O:C was relatively stable throughout the campaign (Figure 7) with a notable decrease to a value of 0.62 at midnight of July 3, resulting from a general drop in PM concentrations (the OA decreased to $1.8 \mu\text{g m}^{-3}$ from $7 \mu\text{g m}^{-3}$) due to a shift in air mass origin from the north to passing over the Aegean within 2 days before reaching the site (Figure S12). These air masses were probably cleaned by rain that removed very aged organics and were enriched afterwards with fresher OA with lower O:C. The average diurnal behavior shows a small variation in the O:C which increased by 0.05 (6%) from 0.82 to 0.87 from 10:00 LT to 13:00 LT probably due to regional photochemistry (Figure 6.c). The OA:OC ratio was ~ 2.3 , similar to that observed at other Greek summer campaigns and indicative of aged aerosol (2.2 for Hildebrandt et al. (2010) in Finokalia).

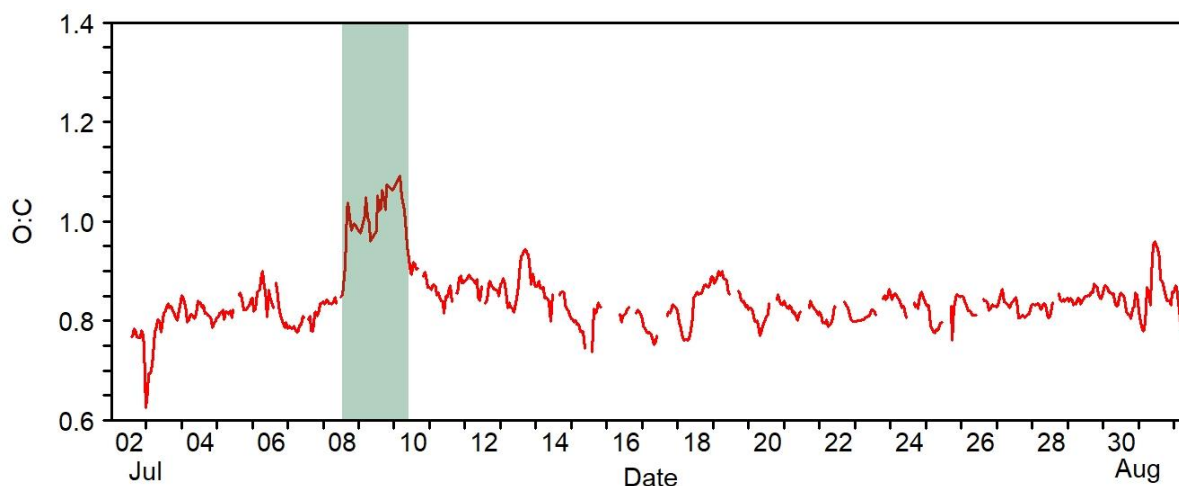


Figure 7. Hourly O:C ratio values of the PM₁ OA. The shaded area depicts the fog period.

The observed PM₁ composition is consistent with previous observations in the western Mediterranean for a similar period (Michoud et al., 2017; Minguillón et al., 2015). The decrease in the sulfate fraction that dominated PM₁ in past campaigns in the Eastern Mediterranean (for example Pikridas et al. (2010) reported that 50% of the PM₁ in Finokalia in 2008 was sulfate), stems from stricter regulations limiting SO₂ emissions and reducing the secondary sulfate (Urdiales-Flores et al., 2023). The low levels of nitrate (organic and inorganic) are mainly attributed to inorganic nitrate's volatilization under warm conditions (Voutsas et al., 2014; Ripoll et al., 2015) and to the dissociation of organic nitrates during aging (Kiendler-Scharr et al., 2016).

The PM_{2.5} potassium (based on the XRF analysis of the filter samples) was on average equal to $0.12 \pm 0.07 \mu\text{g m}^{-3}$ and it was correlated with BC ($R^2=0.65$) and the more aged part of the OA ($R^2=0.67$ with the more oxidized factor, further discussed in the next section), due to its connection to wildfire emissions (Vasilakopoulou et al., 2023). Calcium had an average concentration of $0.24 \pm 0.14 \mu\text{g m}^{-3}$, while copper and iron had $0.13 \pm 0.09 \mu\text{g m}^{-3}$ and $0.21 \pm 0.17 \mu\text{g m}^{-3}$ respectively.

The oxidative potential (OP), a known metric of aerosol toxicity, of the water-soluble components of the PM_{2.5} was analyzed by Vasilakopoulou et al. (2023). Briefly, the average OP per unit of mass (DDT_m at $84 \pm 27 \text{ pmol min}^{-1}$) was higher than literature-reported OP of oxidized OA in other Mediterranean sites. Expressed per volume of air the OP was $0.2 \pm 0.03 \text{ nmol min}^{-1} \text{ m}^{-3}$ a value consistent with other European sites.

3.3. Sources of PM₁ OA

The positive matrix factorization (PMF) of the OA spectra by Vasilakopoulou et al. (2023), yielded 3 highly aged factors (Figure S13). The O:C ratio for the factors ranged from 0.63 for the biogenic oxygenated OA factor (bOOA), to 0.92 for the more oxidized one (MO-OOA), while the less oxidized organic factor (LO-OOA) had an O:C=0.84. This high O:C for the biogenic factor along with an only 20% increase in its diurnal profile during daytime (Figure S28) suggest that a large portion of this factor is transported to the site. The contribution of the factors changed across the campaign (Figure 8), with initial dominance of the LO-OOA (58% contribution to OA, up to July 14). From July 21 to Aug 1 the MO-OOA (54%) and bOOA (27%) dominated, while the period in between had contributions from all factors. Along the campaign's progression the factors seemed to also be connected to different individual organic compounds (Figure S14). The overall contribution of the LO-OOA and MO-OOA factors were similar at around 40%, with the biogenic contributing 22% to the OA for the whole campaign.

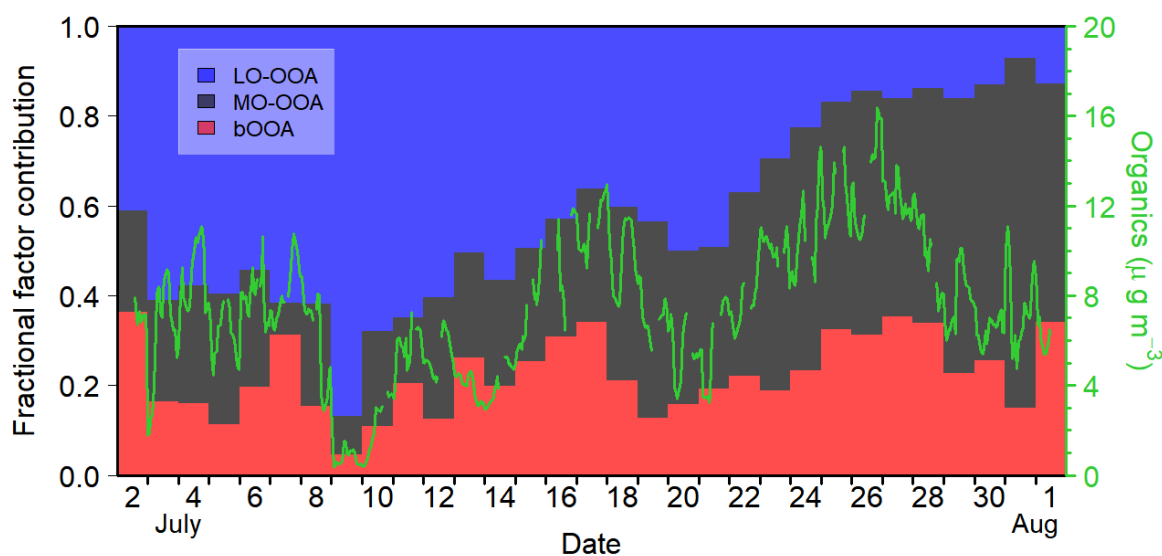
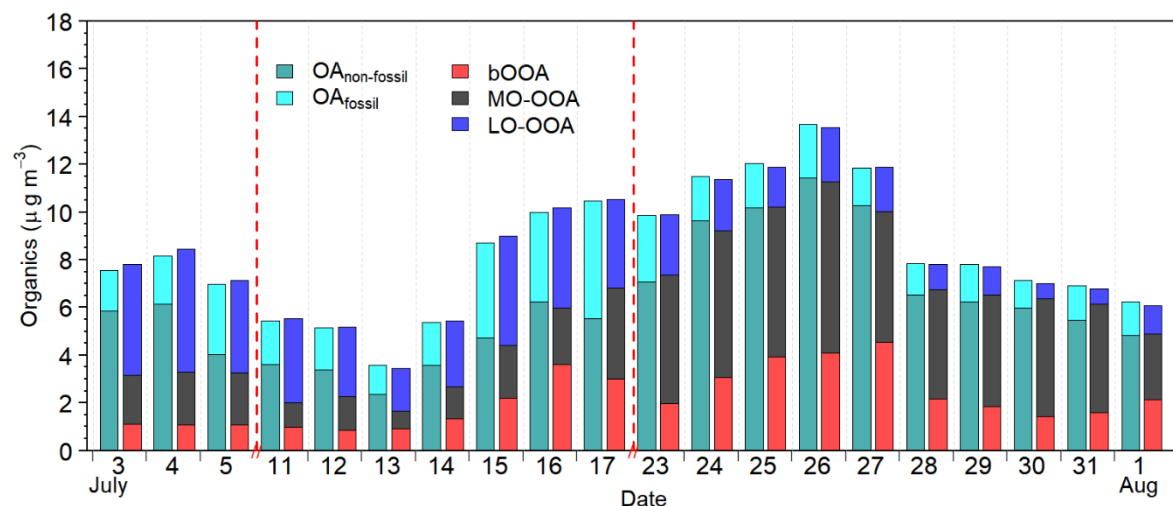


Figure 8. Daily fractional contribution of the factors to the observed OA for the SPRUCE campaign. The green line (right axis) depicts the hourly variations of the mass of the organics.

No significant link between the factors' concentration and the air mass origin was observed (Figure S15). The increased MO-OOA averages for the western sector are due to two fire plumes arriving within a couple of days to the site from Dadia, Greece (July 25) and Albania (July 31) (Vasilakopoulou et al., 2023, Figure S16). In general, the increased concentrations of MO-OOA for the period after July 22 were associated with aged fire plumes arriving from Portugal after a week of transport (Vasilakopoulou et al., 2023).

442 Radiocarbon analysis suggests that the non-fossil carbon fraction is quite close to the sum
 443 of the bOOA and the MO-OOA PMF factors (Figure 9). This observation strongly suggests
 444 that the more oxygenated factor observed on site does not include significant contributions
 445 from fossil fuel combustion, further supporting the hypothesis of Vasilakopoulou et al. (2023)
 446 that it consisted primarily of aged wildfire emissions.



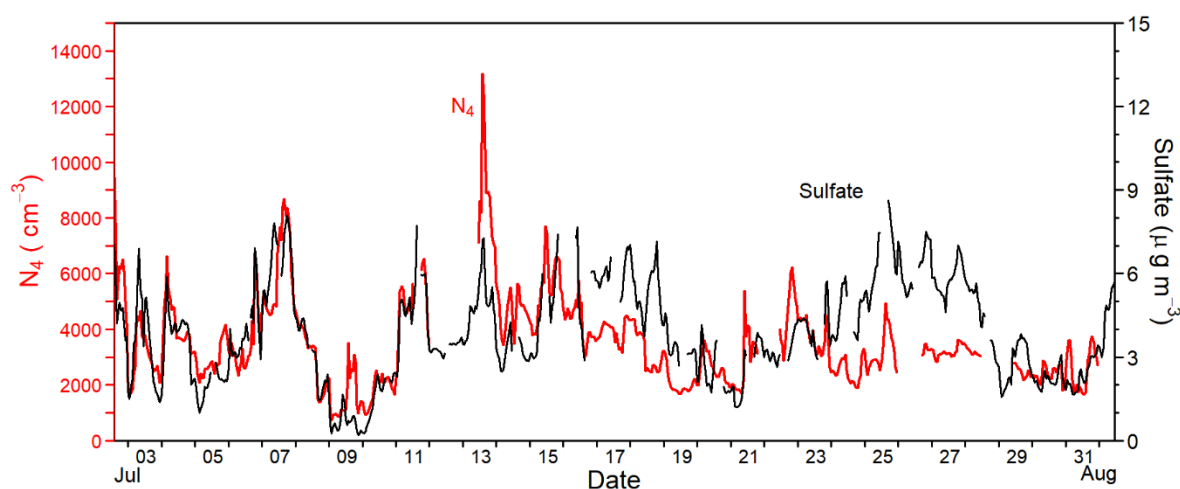
448 **Figure 9.** Comparison of the PMF factors with the fraction of the OA that is related to fossil
 449 fuel combustion. Only the days with available samples are depicted. The red dashed lines
 450 denote gaps in the collected sampling periods.
 451

452 In the first period, part of the dominant LO-OOA factor was also modern (unrelated to
 453 fossil fuel combustion). In the second part of the campaign the LO-OOA factor seems to be
 454 mostly due to anthropogenic fossil combustion sources. A sensitivity test of varying the non-
 455 fossil reference value resulted in only minor changes to the estimated fraction of modern carbon
 456 (Table S3).
 457

458 3.4. Particle number concentration and NPF frequency

459 The particle number N_4 had an average concentration of $3528 \pm 1615 \text{ cm}^{-3}$ (Figure 10),
 460 similar to particle number concentrations found in previous Greek campaigns in background
 461 sites. For example, Pikridas et al. (2010) observed around 2700 cm^{-3} in Finokalia in the summer
 462 of 2008 and Vratolis et al. (2019) around 3500 cm^{-3} during 2012. The maximum N_4
 463 concentration was around 13000 cm^{-3} (July 13) and the minimum 750 cm^{-3} (during the rain
 464 event), while there was a notable decrease with the campaign's progression. This reduction was
 465 accompanied by an increase in the accumulation mode diameter of the mass distribution along
 466 the campaign, indicating aged transported PM. The N_4 diurnal average profile suggests a subtle
 467 increase of 570 cm^{-3} in late afternoon (Figure 6e) that follows the afternoon increase of PM_{10}

468 mass. Days exhibiting sharp increases in number included July 7 (from 4,540 cm⁻³ to 8,590
 469 cm⁻³), July 11 (from about 2,000 cm⁻³ to more than 7,000 cm⁻³) and July 13 (~ 4,000 cm⁻³ up
 470 to more than 12,000 cm⁻³). These days had an increase in the number of particles in the smaller
 471 sizes (up to 25 nm), but most of the increase was in the Aitken range of 25-100 nm (Figure
 472 S17c). Since the major increases in number do not coincide with peaks in species like BC
 473 (Figure 5) or other primary anthropogenic pollutants (NO_x and anthropogenic VOCs) they are
 474 not related to local combustion sources. These particles are probably secondary in origin,
 475 potentially related to SO₂ oxidation and sulfate formation. Sulfate levels had a modest
 476 correlation (R²=0.34) with N₄ which increased during the high N₄ days (Figure 10), with an R²
 477 of 0.62 for the period up to July 14 (excluding the rain period). In the period after July 15 this
 478 correlation drops to R²=0.14. The OA showed a milder increase during July 7 and 11 when N₄
 479 increased, but on July 13 no increase was noted (Figure S18). This suggests a weaker link
 480 between the organics and these secondary particles. The number of larger particles (N₁₀₀)
 481 exhibited minimal variation during the day (Figure S17f) indicative of long-range transport.
 482 The particles smaller than 25 nm peaked at 10:00 LT on average during the campaign.

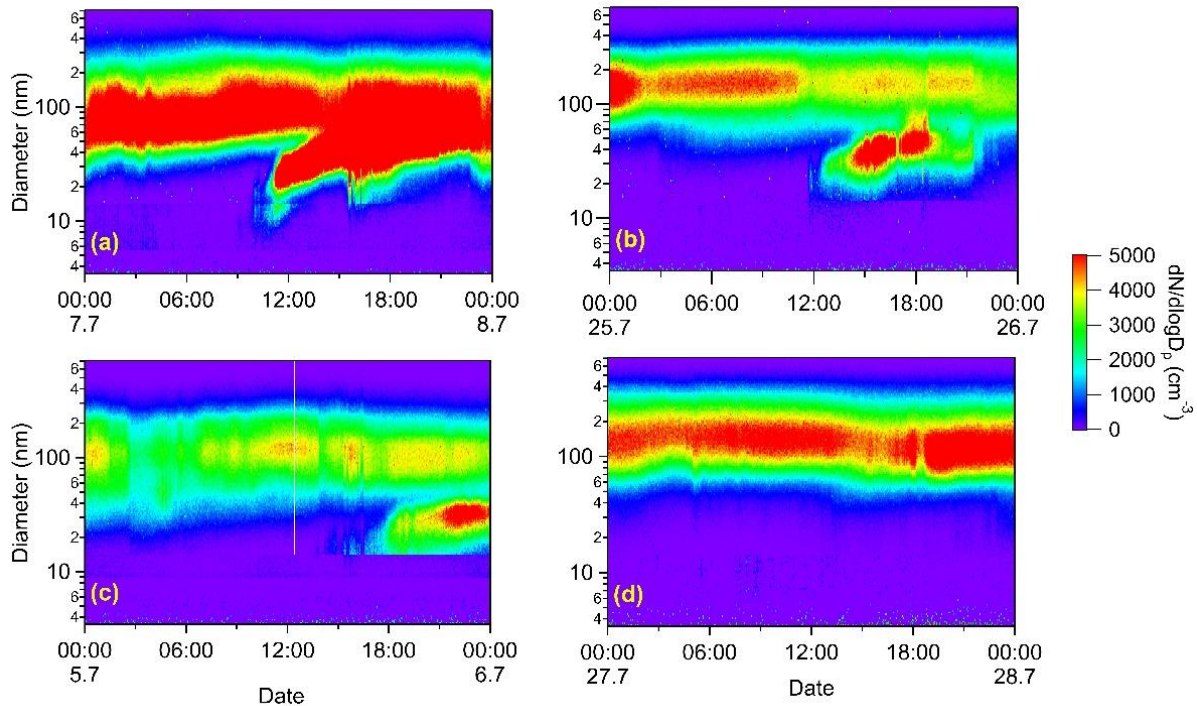


483
 484 **Figure 10.** Hourly values of N₄ number concentration (red line) and the sulfate mass hourly
 485 variation (black line) across the campaign.

486 The concentrations of N₄₋₇ particles remained negligible during the study, suggesting no
 487 local nucleation. However, growing particle modes starting from 8-10 nm were noted for 7
 488 days (July 7, 11, 13, 14, 20, 21, 22). These indicate new particle formation in another location
 489 relatively close to the site and subsequent transport there (Dada et al., 2018). Typical growth
 490 rates of particles in the region are 4-5 nm h⁻¹ (Aktypis et al., 2024), therefore the growth to 10
 491 nm would require nearly 2 hours. For typical morning wind speeds of 3-8 km h⁻¹ in the area
 492 during the study, this suggests that the particles were formed around 5-20 km away. These

493 particles were typically present at around 10-11:00 LT and grew to 30-50 nm during afternoon
1 494 hours. These 7 days of near-by new particle formation in a month-long period yield a frequency
2 495 of 22 %.

3 496 On July 15, 16 and 25 higher diameter modes of 20-30 nm appeared later in the day
4 497 (around or after midday, Figure 11), with lower growing rates. This suggests that these particles
5 498 were transported from more distant areas and arrived at the site already grown (Aktypis et al.
6 499 2023).



500
501 **Figure 11.** Typical examples of a) nearby NPF event, starting from 10 nm on July 7, b) event
502 with appearing modes above 20 nm on July 25, c) afternoon occurrence of particles in 10-20
503 nm range and d) non-event in Pertouli during July 2022.

504 Another worth mentioning group of events had appearing particle modes at 20-50 nm after
505 16:00 LT lasting for the rest of the day (observed on July 3, 5, 15 and 18). These could be
506 transported to the site from the nearby city of Trikala within a few hours (Figure S19). The
507 remaining 17 days were non-events.

508 For the near-by NPF events, SO₂ reached its daily maximum at approximately the same
509 hour as the new particles (9-11:00 LT) at levels of 0.1-1.7 ppb (Figure S20). The trajectories
510 for the three most intense cases of near-by NPF indicated air masses passing in the vicinity of
511 coal burning power plants in northern Greece and Northern Macedonia within a day (Figure
512 S21).

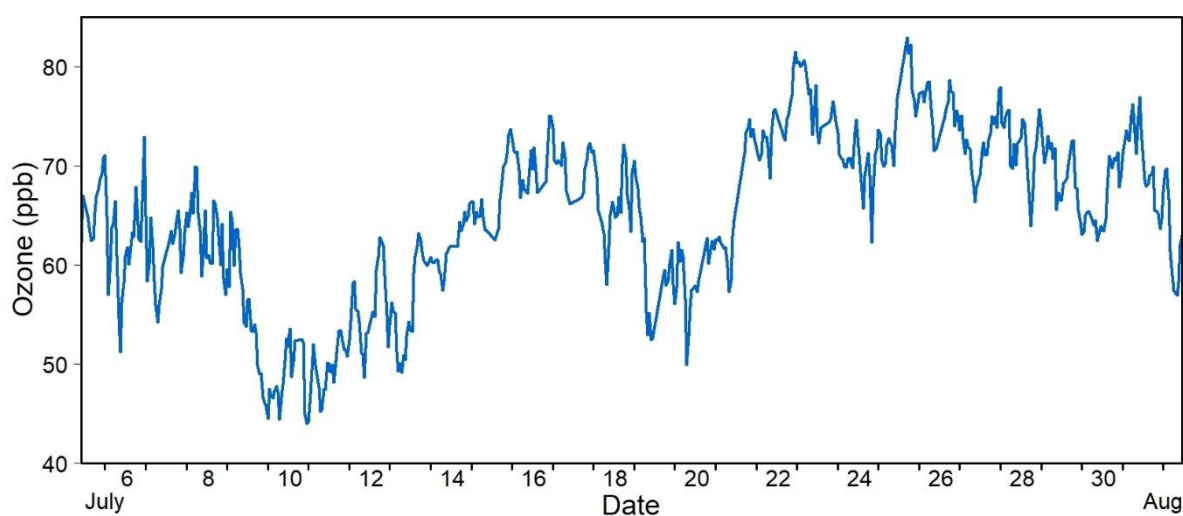
513 In the event on July 20, SO₂ levels reached hourly concentrations of only 0.3 ppb, but this
514 time the air masses came from the East (arriving locally from the NE) and the number of

515 particles present was smaller compared to other events (Figure S22). For the events with the
516 20-30 nm modes SO₂ concentrations were also elevated (1.3, 0.6 and 1.6 ppb for July 15, 16
517 and 25 respectively).

518

519 3.5. Concentrations of organic and inorganic gas-phase pollutants

520 The average ozone concentration during the campaign was at 64.8 ± 8.3 ppb with small
521 diurnal variation of 6 ppb or 9% (Figure 6d). The variation was more noticeable across the
522 campaign with a minimum of 44 ppb (during the precipitation event) and a maximum of 83
523 ppb (Figure 12). It had a moderate correlation with PM₁ ($R^2 = 0.37$) and was better correlated
524 with the OA ($R^2 = 0.51$).



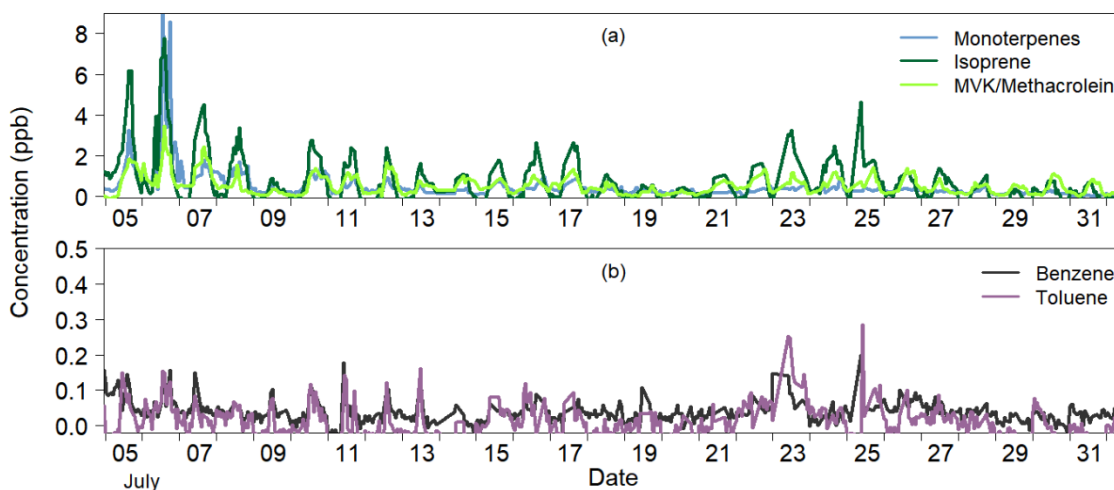
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526 **Figure 12.** Hourly O₃ levels for the campaign's duration.

527 The average SO₂ concentration was 0.27 ± 0.30 ppb, but there were periods when it
528 exceeded 1 ppb (Figure S20). There was no correlation ($R^2 = 0.09$) between the PM₁ sulfate
529 and sulfur dioxide. The average SO₂/Sulfate molar ratio was low at 0.3, (Figure S23). NO₂
530 levels were consistently below 3 ppb, with low average levels in midday and afternoon hours
531 (Figure 6h).

532 The concentrations of individual anthropogenic VOCs such as toluene (derived from m/z
533 93) and benzene (m/z 79) never exceeded 0.3 ppb throughout the campaign (Figure 13).
534 However, their diurnal variation included a small peak at noon (Figure S24). This small
535 increase (0.05 ppb for toluene, 0.03 ppb for benzene) could be due to transport from below as
536 the boundary layer height increases. It shows that the site may have some small effects from
537 medium distance sources. This variation was not related to air mass origin. Toluene and
538 benzene exhibited moderate correlation with other VOCs like phenol or vinyl furan (attributed

539 to m/z 95, $R^2=0.49$ for benzene) and octene (m/z 113, $R^2=0.43$ for toluene, 0.46 for benzene).
540 Other aromatics such as xylenes/ethylbenzene and benzaldehyde represented by m/z 107 also
541 exhibited a peak at noon of the order of 0.1 ppb. Other aromatic compounds like benzene
542 acetaldehyde/acetophenone/trimethyl benzenes detected on m/z 121 also reached 0.1 ppb
543 during midday. Other analytes (at m/z of 129, 139, 155, 169 and 105) with similar diurnal
544 profile are depicted in Figure S25.



545
546 **Figure 13.** (a) Biogenic and (b) anthropogenic VOC hourly variation for the campaign.

547 Compounds of predominantly biogenic origin had higher levels during the first days of the
548 campaign (5-7 July) (Figure 13a). The highest levels were observed in a period of lower
549 velocity air masses at midday of July 6, when the air masses had stayed for some time in the
550 forested areas north of the site. Isoprene (at m/z 69) was on average 0.65 ± 1.12 ppb, while
551 monoterpenes (added m/z 81 and 137) were 0.5 ± 0.78 ppb. Known products of the photo
552 oxidation of isoprene like methyl-vinyl-ketone and methacrolein (measured in m/z 71) had
553 average levels equal to 0.51 ± 0.46 ppb. Isoprene's correlation with temperature was low
554 $R^2=0.25$. Methyl-ethyl-ketone, also of biogenic origin at m/z 73, was 0.17 ± 0.15 ppb. After the
555 rain event isoprene did not exceed 5 ppb. There was a general drop in the observed
556 concentrations of the biogenics which were significantly lower after the first days of the
557 campaign.

558 Identified aldehydes such as hexanal (m/z 101) and pentanal (m/z 87), methylfuran (m/z
559 83) and 1-heptene (m/z 99) increased by about 0.1 ppb starting at 07:00 LT and peaking at
560 14:00 LT (Figure S26). Their levels slowly returned to their initial values at around 20:00. They
561 could be either directly emitted or produced by photochemical processes.

562 Acetone had a modest correlation with BC ($R^2=0.5$) and its average concentration during
563 the campaign was 2.13 ± 0.75 ppb (Figure S27). Its diurnal average level increased by 0.55 ppb

564 (22%) during the day (from a minimum of 1.86 ppb at 05:00 to 2.41 at 15:00 LT), which could
1 565 be a result of regional production. Acetic acid ($R^2=0.52$ with acetone) had an average level of
2 566 0.51 ± 0.39 ppb and had a correlation of around 0.2 with the major PM_1 constituents.
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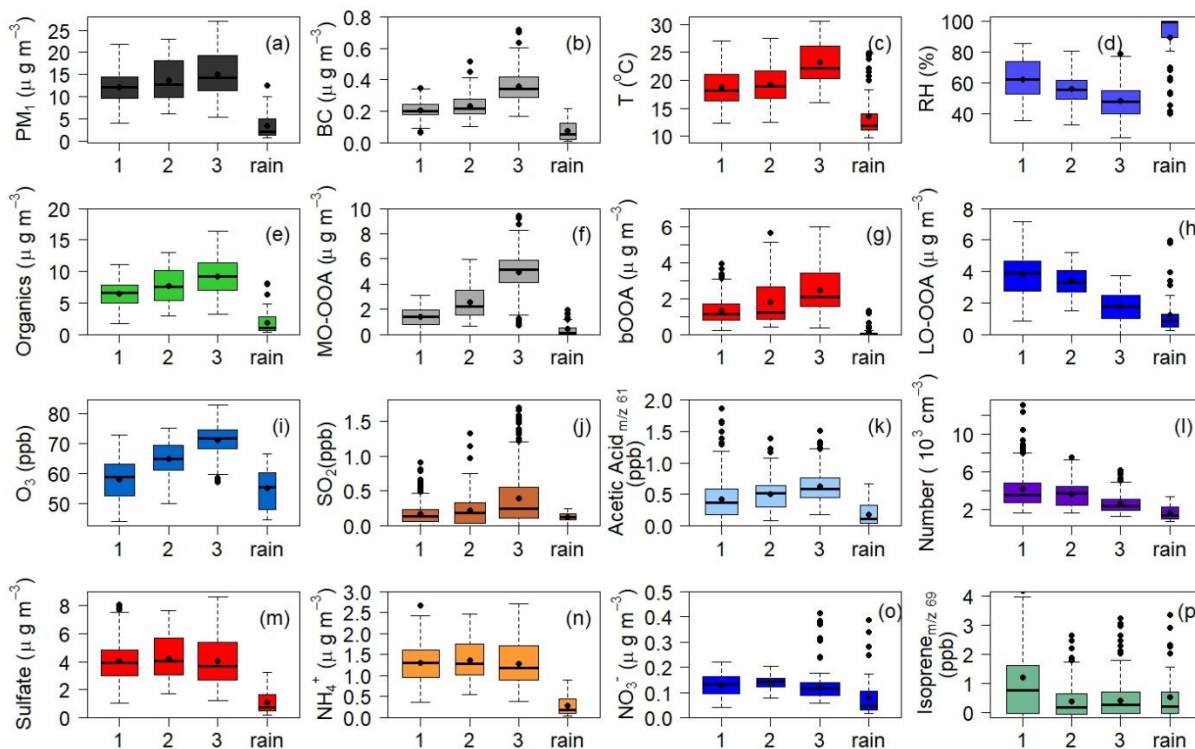
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568 3.7. Air quality variation across sub-periods

569 The campaign was segregated into three periods in an attempt to infer additional
10 570 information about the pollutants observed and their sources. The subperiods were selected
11 571 based on the fractional contribution of the PMF factors (initial LO-OOA dominance and
12 572 subsequent MO-OOA dominance), as well as based on absolute concentrations (organics and
13 573 BC increased during July 14-20). The first period was from July 2 up to 13 excluding the rain
14 574 period, July 14 to 20 was the second sub-period. Finally, from July 21 up to the end was the
15 575 third subperiod of the campaign. The concentration distributions of the major pollutants across
16 576 the three subperiods are shown in Figure 14. The biggest differences are observed for the first
17 577 and third period, while the second seems to act as a transitioning period. The third subperiod
18 578 had higher temperatures (by about 4 °C), with an increase of PM_1 by $2.7 \mu g m^{-3}$ (compared to
19 579 the first subperiod), mainly due to an increase in organics (and a slight increase in BC).
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29 580 The LO-OOA concentration decreased by about $2 \mu g m^{-3}$ (from the first to the third
30 581 subperiod). Based on the average diurnal profiles during the sub periods, the LO-OOA in the
31 582 first and second period had a roughly 20% contributions from regional photochemistry (Figure
32 583 S28). The mostly fossil related LO-OOA of the third period had a flat diurnal profile indicative
33 584 of long-range transport.
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38 585 Ozone levels increased by 13 ppb (from 58 ppb in the first period to 71 ppb for the third
39 586 (Figure 14i). The diurnal variation also changed between the periods (Figure S29). In the first
40 587 period there is an increase of 10 ppb across the day from a minimum at 09:00 LT (when VOCs
41 588 start increasing), to a maximum at 18:00 LT. The corresponding diurnal variation for the third
42 589 period was halved to 5.3 ppb. There was a moderate correlation of O_3 with both the MO-OOA
43 590 ($R^2 = 0.53$) and the bOOA factor ($R^2 = 0.34$), but none with the LO-OOA ($R^2 = 0.01$). This O_3
44 591 variation suggests that it was formed upwind by reactions that contributed also to the MO-OOA
45 592 (e.g. wildfire aging). No sudden ozone changes were observed suggesting no major intrusions
46 593 from the stratosphere.
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595 **Figure 14.** Boxplots of hourly pollutant distribution during different periods of the campaign.
 596 Median values are denoted by the black line (average by the dots in the box which corresponds
 597 to the interquartile range). The width of the boxes is proportional to the size of the subperiods.
 598 Period 1 is from July 2 to 13 excluding the rain period (midday of July 8 to morning of July
 599 10). The second period covered July 14 up to July 20 and the last one went up to the end of the
 600 campaign (1st of August).

601 The acetone average diurnal profile in the first period showed an increase of 0.76 ppb from
 602 06:00 LT to 14:00 LT, whereas in the third period it was flatter. Excluding the first period there
 603 was a moderate correlation of around 0.45 of acetone with both the MO-OOA and the bOOA
 604 factors, suggesting also that the observed acetone during that time was a result of transport
 605 rather than locally produced.

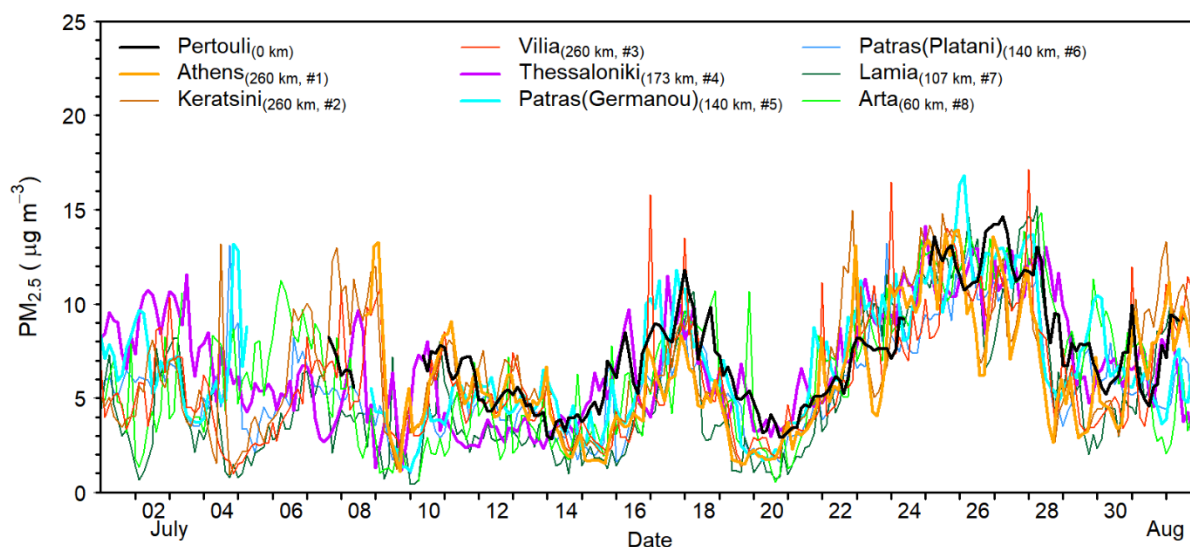
606 N_4 was lower in the third subperiod of the campaign with average hourly values of 2600
 607 cm^{-3} after July 21, as opposed to 4200 cm^{-3} in the first subperiod and 3700 cm^{-3} in the second
 608 (Figure 14). For sulfur dioxide, higher concentrations were observed in the last subperiod.

609

610 3.8. PM_{2.5} variability across Greece

611 The PM_{2.5} values by the PANACEA low-cost sensor network (Stavroulas et al., 2020)
 612 were used to relate the PM_{2.5} levels in Pertouli to those in the rest of the country (Figure S30,
 613 Table S2). Figure 15 depicts the relative homogeneity of PM_{2.5} across Greece during SPRUCE-
 614 22. The local sources are apparent spikes especially in the case of urban stations but there is

615 clear dominance of long-range transport. It is worth noting that the center of the densely
 616 populated Athens (4 million inhabitants) had similar or even lower levels of PM_{2.5} than this
 617 isolated Pertouli background site 260 km away.



618 **Figure 15.** Background concentrations for PM_{2.5} in Greece. The panel displays 3 h average
 619 concentrations of all sensors for the campaign period with the parenthesis denoting the distance
 620 to the campaign’s site and the ID of the sensors in relation to the map in Figure S30.
 621

622 The three stations located in and close to Athens had little variability in daily
 623 concentrations (average of 1.3 µg m⁻³) and a maximum daily variability of 3.5 µg m⁻³. The
 624 average daily PM_{2.5} concentration reported in Athens was around 1 µg m⁻³ lower than the
 625 corresponding one in Pertouli. The corresponding variability for the sensors in the city of Patras
 626 was on average 1 µg m⁻³ and their mean about 1 µg m⁻³ lower than the concentrations in
 627 Pertouli. Thessaloniki, a major city in the north of the Pertouli site had a mean difference of
 628 just 0.6 µg m⁻³ with Pertouli, while Arta the nearest station (~60 km) to the southwest reported
 629 about 0.9 µg m⁻³ less.

631 4. Conclusions

632 The campaign conducted in Pertouli aimed at the characterization of a mountainous
 633 background site under summertime conditions. PM₁ concentrations had an average of close to
 634 13 µg m⁻³, relatively high for a remote site. Most of the PM₁ was transported pollution rather
 635 than locally produced material, or nearby anthropogenic influences. The fact that a remote site
 636 had daily PM₁ concentrations that surpassed the 24-h PM_{2.5} air quality guidelines of 15 µg m⁻³
 637 (WHO global air quality guidelines, 2021) for 10 days out of a month indicates the significance
 638 of background aerosol in the Eastern Mediterranean during summer. PM_{2.5} was homogeneously

639 distributed across the Greek mainland during the campaign. Local sources played a minor role
640 in the overall fine PM levels even for large cities like Athens.

641 Fine particles mostly consisted of organics (~60%). The once dominant sulfate in the
642 Eastern Mediterranean represented only 30% of the PM₁ due to stricter regulations of SO₂
643 emissions. The aerosol on the site was fairly processed with a high oxygen content (average
644 O:C of 0.85) and PMF attribution showed 3 secondary oxidized factors. The highly aged
645 particulates were well mixed with the size distribution of the PM₁ components' mass peaking
646 at approximately the same diameter (480 nm).

647 The MO-OOA and bOOA levels were consistent with measured modern carbon. This
648 supports their attribution to mostly oxidized biomass burning and aged biogenic SOA,
649 respectively. The LO-OOA was mostly associated to fossil fuel combustion. The biogenic SOA
650 was highly oxidized and to its majority was produced away from the site, despite its location
651 in the middle of the forest. The chemistry has progressed past the first-generation products of
652 the major biogenic VOCs towards highly oxidized organic molecules, during the whole
653 campaign.

654 The first campaign period had higher regional photochemical activity, with higher particle
655 number (connected to regional sulfate formation) and higher concentrations of biogenic VOCs.
656 The dominant OA factor was the LO-OOA (with contributions from both fossil fuel related
657 and modern carbon sources). With the campaign's progression the site was affected mostly by
658 long range transport. The OA became mostly MO-OOA, with fewer particles but higher PM₁
659 concentrations. The sum of the MO-OOA and the bOOA was consistent with the non-fossil
660 organic aerosol. Ozone levels increased and together with acetone were also related to transport
661 during this period.

662 NPF did not occur directly in this site. Seven days with nearby (5-20 km away) NPF events
663 were found. In most cases they coincided with increased SO₂ concentrations and with
664 trajectories passing near coal burning power plants north of the site.

665

666 **Authorship contribution statement**

667 **A.M.:** Investigation, Methodology, Data Curation, Visualization, Writing - Original Draft.

668 **C.N.V. K.F., A.A.:** Investigation, Data Curation, Writing - Review & Editing. **C.K.**

669 Investigation, Methodology, Project administration, Writing - Review & Editing. **A.B. D.P.,**

670 **E.K., K.B. Y.F., T.T., C.P., E.B. A.N., K.SK.:** Investigation, Writing - Review & Editing.

671 **K.SE.:** Project administration, Writing - Review & Editing. **S.N.P.:** Conceptualization,

672 Investigation, Methodology, Supervision, Writing - Review & Editing.

673 **Declaration of interests**

674 The authors declare that they have no known competing financial interests or personal
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