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Secondary organic aerosol tracers and related polar organic compounds between urban and rural areas in the Eastern Mediterranean region: source apportionment and the influence of atmospheric oxidants†

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Fine particle samples were collected during summer at an urban (LIM) and a rural/background (AGM) site of Cyprus. They were analyzed for pinene and isoprene secondary organic aerosol (PSOA–ISOA) tracers, linear dicarboxylic acids (DCAs), hydroxyacids (HAs), aromatic acids (AAs), monocarboxylic acids (MCAs) and levoglucosan by GC/MS with prior 3-step derivatization. DCAs, AAs, MCAs and levoglucosan exhibited significantly higher concentrations ($p < 0.05$) in LIM, PSOAs and ISOAs in AGM ($p < 0.05$), whereas mixed trends were found for HAs. Among DCAs, succinic was the most abundant in both sites, accounting for 42.5% and 36.5% of the total DCAs in LIM and AGM respectively, followed by adipic in LIM (20.1%) and azelaic in AGM (22.4%). Malic, phthalic and palmitic acids were the dominant HA, AA and MCA, respectively. Regarding PSOAs, significant differences were observed between the two sites, with the first-generation products accounting for 59.8% of the total measured PSOAs in AGM, but were remarkably lowered (10.3%) in LIM indicating that they were highly oxidized. 2-Methylerythritol was the dominant ISOA tracer in both sites; nevertheless the elevated relative abundance of 2-methylglyceric acid in LIM implies the influences of higher NO_x levels. The increased O_3 levels observed in AGM appear to have a significant impact on SOA formation. Source apportionment tools employed revealed factors related to secondary formation processes including oxidation of unsaturated fatty acids, pinene, isoprene and anthropogenic VOCs and factors associated with primary sources such as biomass burning, plant emissions and/or cooking and motor exhaust, with noteworthy differences observed between the two areas.

Environmental significance

Secondary organic aerosols (SOAs) are a significant component of airborne particulate matter. SOA yields consist of a great number of compounds formed by the reactions of biogenic and anthropogenic precursors with OH radicals, NO_3, and O_3 or *via* photolysis. Their formation is influenced by the type of each precursor and the ambient conditions. During the last decade, several studies have reported the impact of SOAs on global climate and human health. We present the spatial distribution of various SOA markers as well as other related polar compounds, in two Eastern Mediterranean sites, where photochemical processes are favored. The results provide useful insights into the sources and the formation pathways of SOA compounds under different atmospheric conditions.

1. Introduction

The organic fraction of airborne particulate matter (organic aerosol-OA) accounts for a significant portion of the total aerosol mass.[1,2] OAs can be released into the atmosphere from multiple sources in two main ways; primary OAs (POAs) include the directly emitted OAs from natural (*e.g.* plant emissions, fungi spores, and sea spray) and anthropogenic sources (*e.g.* traffic and industrial emissions and biomass and waste burning).[3–9] In contrast, secondary OAs (SOAs) are generated *in situ* in the atmosphere through multiple homogeneous or heterogeneous reactions, occurring in the gas or particle phase, of biogenic or anthropogenic volatile or semi-volatile organic compounds with O_3, NO_x, OH radicals, and chlorine atoms or *via* photolysis.[10–14] SOA yields contain a great number of compounds as a result of the multivariate and diverse factors that affect SOA formation such as the type of each precursor

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along with the different ambient conditions, including temperature, relative humidity and the type and abundance of atmospheric oxidants (O_3, NO_x, *etc.*).[11,15,16] SOAs are a remarkable component of atmospheric fine particles constituting a large to dominant (20–80%) percentage of their total organic mass;[17] hence a comprehensive understanding of SOA formation mechanisms under different atmospheric conditions is essential.[18,19]

SOA marker compounds generally contain one or more oxygenated functional groups including hydroxyl (OH), carboxyl (HOC=O) and carbonyl (C=O) groups, making them highly polar.[11] SOAs have direct effects on climate as they can absorb and scatter solar radiation and indirect effects as they affect the cloud condensation nuclei (CCN) particles either by forming new particles or by growing the preexisting ones.[16,20] SOA compounds can have adverse effects on human health. For example, short- and long-term exposure to dicarboxylic acids may lead to eye, nose and skin irritation, asthma and lung damage.[21] Moreover, recent studies have associated the expression of oxidative stress response genes in human lung and bronchial epithelial cells with isoprene-derived compounds.[22,23]

Several organic compounds are considered as tracers for specific atmospheric reactions involving biogenic volatile organic compounds and atmospheric oxidants. For example, 2-methylerythritol, 2-methylthreitol and 2-methylglyceric acid are specific tracers of isoprene oxidation derived from both laboratory and field studies.[24,25] In addition, pinic, pinonic, 3-hydroxyglutaric and 3-methylbutanetricarboxylic acids are known products from α/β pinene oxidation.[26,27] In contrast, other polar organic compounds have more than one possible formation source. Particularly, dicarboxylic acids can be formed from the oxidation of various unsaturated hydrocarbons, such as cyclopentene, cyclohexene, cycloheptene, 1-methylcyclohexe, α/β-farnesene, limonene[28–30] and fatty acids,[31,32] although contributions from primary sources, including biomass and plastic waste burning, have been reported.[33,34] Furthermore, the oxidation of aromatic volatile organic compounds and phthalates is a possible source of particle-bound aromatic carboxylic acids, such as phthalic and trimellitic acids.[33,35,36] However, primary emissions, such as motor exhaust and biomass burning, are also reported to increase to aromatic acids' ambient concentrations.[34,37,38]

Eastern Mediterranean (EM) is a basin sensitive to climate changes,[39,40] with increased levels of PM and ozone especially during summer.[41,42] High ozone levels combined with intense solar radiation all-year round[43] favor photochemical processes; hence causing SOA formation. For example, in Athens and Patra oxygenated organic aerosols were the dominant components of organic aerosols (65 and 78% respectively).[44] In addition, more than 80% of the organic fraction of fine particles in Athens, during summer, has been attributed to secondary formation.[45] In Cyprus, located on the east side of EM, significant amounts of SOA gas-phase precursors were presented in a recent study,[47,48] which, combined with the high-ozone levels especially during summer,[49] could lead to enhanced SOA yields. However, there are limited data about the individual SOA compounds and their levels in EM.[18,46]

This study focuses on the investigation of the abundance of SOA markers and other related polar organic compounds bound to fine particles, including seven biogenic SOA tracers, seven linear dicarboxylic acids, four monocarboxylic acids, four hydroxyacids, six aromatic acids and tracers of biomass burning (levoglucosan) in two Cypriot locations, representing an urban (Limassol) and a rural/background (Agia Marina Xyliatou) site during summer, while organic carbon and elemental carbon were also measured at the background area. For this purpose, a total of 88 samples were collected ($n = 44$ for each site) along with real time measurements of inorganic gases (O_3, NO_x and SO_2). The results are presented and discussed regarding the spatial variation of the analytes, the potentially different sources between the two sites and the influence of atmospheric oxidants on SOA formation. As SOA research is limited in EM, this work can provide useful information about the SOA yields and sources in this region.

2. Methods

2.1 Site description & sample collection

The urban site is located at the city of Limassol (LIM) (34°40′ N, 33°2′ E; 10 m ASL) (Fig. 1), the second largest Cypriot city (235 000 inhabitants, 2011 census). Samples were collected at a kerbside station with an approximate height of 4 m and at least 25 m from a major route. The rural/background site is located at the Cyprus Atmospheric Observatory (CAO) at Agia Marina Xyliatou (AGM), a remote location in the middle of the island (35.03°N, 33.05°E; 532 m ASL) (Fig. 1). CAO is 1 km south of the village of Agia Marina (population about 630) and more than 35 km away from the major Cypriot cities. The station is cooperated within the network of the European Monitoring and Evaluation Program (EMEP) by the Department of Labor Inspection (DLI). The AGM site is surrounded by extensive plant life, such as "maquis" and is also near oak and pine forests covering the Troodos mountain.[50] Fine aerosol samples ($n = 44$ for LIM; $n = 44$ for AGM) were collected daily (00:00–23:59), on pre-weighted filters, with a diameter of 47 mm (Pall Tissuquartz 2500 QAT-UP), from 16 July 2018 to 28 August 2018 in AGM and to 30 August 2018 in LIM (samples on the 26th and 27th of July were lost due to power loss). Two low volume samplers (Leckel SEQ 47/50) were used to collect the $PM_{2.5}$ (flow rate 2.3 m^3 h^{-1}) samples. Particle mass determination was carried out gravimetrically following the protocol of EN12341.[51] After collection, each filter was stored in a Petri dish in a freezer (−21 °C). Weather stations (Campbell Scientific Europe, Antony, France) were located on the rooftop of the sampling stations and were used for the monitoring of real time meteorological parameters, such as atmospheric pressure (AP), atmospheric temperature (AT), relative humidity (RH), wind speed (WS), wind direction (WD) and solar radiation (SR) (5 min time resolution). Moreover, inorganic gases, *i.e.* NO, NO_2, CO, SO_2 and O_3 (1 h time resolution) were measured in both sites for the whole sampling period. More details for the latter measurements are provided in Kleanthous *et al.* (2014).[49] Data reported in this work

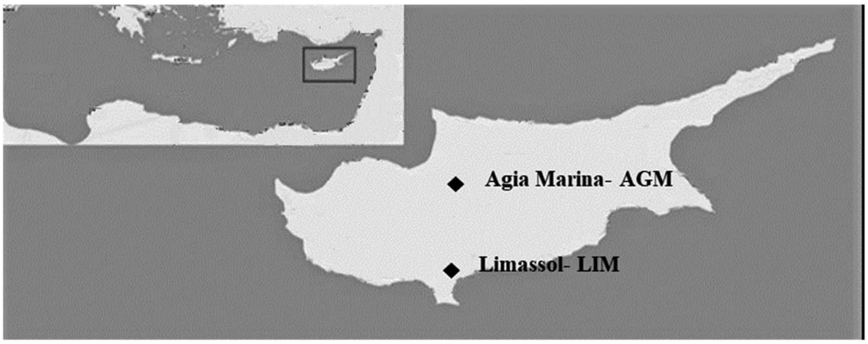

Fig. 1 Eastern Mediterranean and Cyprus maps. Sampling sites are displayed.

regarding the meteorological parameters and inorganic gases originate from the air quality network of Cyprus operated by the Department of Labor Inspection (https://www.airquality.dli.mlsi.gov.cy/).

2.2 Measurement of organic carbon and elemental carbon

Organic (OC) and elemental carbon (EC) were measured only for the samples collected at AGM. A 1 cm × 1.5 cm standard punch (1.5 cm^2) of the aerosol filter samples and the field blanks was cut and analyzed for organic carbon (OC) and elemental carbon using an OC/EC Lab Instrument (Model 5, Sunset Laboratory Inc., USA), following the EUSAAR 2 temperature program. More details of the analysis can be found elsewhere.[52] Secondary organic carbon (SOC) can't be measured directly, so it was measured using the method described by Castro *et al.* (1999).[53] In particular, the minimum OC/EC ratio, from the measured OC and EC concentrations, was used to calculate primary organic carbon (POC) and SOC by applying the following equations eqn (1) and (2).

$$\mathrm{POC} = \mathrm{EC} \times \frac{\mathrm{OC}}{(\mathrm{EC})_{\min}} \quad (1)$$

$$\mathrm{SOC} = \mathrm{OC} - \mathrm{POC} \quad (2)$$

This method for SOC estimation has already been used in many rural/background and urban locations.[19,54,55]

2.3 Extraction, derivatization and GC-EI-MS determination

Details about filter pretreatment and the 3-step derivatization procedures are discussed in depth elsewhere.[56] The rest of the filters collected at AGM, and the whole filters, collected at LIM, were subjected to a 30 mL extraction of (1 : 1) dichloromethane/methanol (Carlo Erba) in an ultrasonic bath for 20 min. Prior to the extraction, 5 μL of ketopinic acid (KPA) (Sigma Aldrich, 5 μg mL^{-1}, in MeOH) was added as a surrogate standard. The extraction procedure was performed in triplicate, and then the combined extracts were filtered through a Pasteur pipette and concentrated at nearly 4 mL with a rotary evaporator (Buchi). Further condensation was performed with a gentle steam of nitrogen until dryness. The first step of the derivatization procedure starts with the addition of 60 μL of heated *O*-methylhydroxylamine hydrochloride (MHA) solution (Sigma Aldrich, 1 mg mL^{-1}, in ACN). The reaction of carbonyl compounds with MHA took place for 60 minutes at 70 °C in a water bath. The second step includes the methylation of carboxylic acids to their methyl ester derivatives. This was achieved by adding 12 μL of (trimethylsilyl)diazomethane (TMSD) (Acros Organics) and 8 μL of methanol. Then, the vials were left in an ultrasonic bath for 20 minutes. Following this, 245 μL of *N*,*O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) (TCI Chemicals) and 50 μL of pyridine were added in order to convert the hydroxyl groups of the species to trimethylsilyl ethers. The reaction was carried out in an oven for 60 minutes at 70 °C. After cooling to room temperature, 50 μL of the internal standard, tetracosane d-50 (Sigma Aldrich, 30 μg mL^{-1}, in DCM), was added to each sample. A GC/MS system (6890N/5975B, Agilent Technologies, USA) was employed for both analyses. The GC instrument was equipped with a split/splitless injector and a HP-5ms [5%-(phenyl)-methylpolysiloxane] capillary column. High purity helium was the carrier gas with a velocity of 1.5 mL min^{-1}. Pulsed splitless mode was used for the injection and the injector's temperature was set at 280 °C. The GC oven temperature program was: 84 °C (hold for 1 min) to 200 °C at 4 °C min^{-1}, hold for 2 min, and then to 300 °C at 10 °C min^{-1} with final isothermal hold for 15 min. Inlet and MS source temperatures were 280 °C and 230 °C respectively. Selected ion monitoring (SIM) mode was used for the quantification of the analytes.

Most of the studied compounds were identified and quantified using available authentic standards. In particular, dicarboxylic acids including succinic (diC4), glutaric (diC5), adipic (diC6), pimelic (diC7), suberic (diC8), azelaic (diC9) and sebacic acid (diC10), monocarboxylic acids including palmitic (C16), margaric (C17), stearic (C18), and oleic (C18:1), and aromatic acids including benzoic (BEN), *p*-toluic (TOL), phthalic (PH), isophthalic (iPH), terephthalic (tPH) and trimellitic (TRIM) have been purchased from Sigma Aldrich. Pinene SOA tracers include pinonic acid (PNA), 3-hydroxyglutaric acid (3HGA) (Sigma Aldrich) and pinic acid (PA) (Chiron). The isoprene SOA tracer of 2-methylerythritol (MTL1) was purchased from Sigma Aldrich. Hydroxycarboxylic acids including malic (MAL), citric (CIT) and tartaric (TART) acids were obtained from TCI

Table 1 Mean concentrations and concentration ranges of PM, DCAs, AAs, HAs, PSOAs, ISOAs, MCAs, LEV, inorganic gases, mean values and value ranges of meteorological data in both sampling locations and mean concentrations and concentration ranges of OC, EC, TC and SOC in AGM

	LIM (urban) ($n = 44$)		AGM (background) ($n = 44$)		
Species	Range	Mean ± SD	Range	Mean ± SD	p Value
CPM$_{2.5}$ (μg m^{-3})	10.2–21.1	15.4 ± 2.6	4.5–21.9	13.8 ± 4.2	0.111
DCAs (ng m^{-3})					
diC4	6.1–88.2	31.9 ± 21.0	4.6–51.5	18.1 ± 11.5	0.001
diC5	3.0–30.5	6.8 ± 5.5	0.49–15.4	4.9 ± 3.7	0.102
diC6	3.1–56.1	15.1 ± 11.9	0.38–18.6	6.8 ± 4.6	0.000
diC7	0.69–16.1	3.1 ± 2.9	0.30–7.1	2.2 ± 1.3	0.253
diC8	3.3–10.1	5.0 ± 1.7	0.60–9.9	4.1 ± 2.5	0.048
diC9	6.2–41.6	12.9 ± 6.9	3.0–28.1	11.1 ± 5.5	0.841
diC10	0.64–9.7	2.2 ± 1.6	Nd^{a}-8.1	2.3 ± 2.0	0.783
ΣDCA	31.7–252	76.9 ± 45.7	14.0–111	49.6 ± 23.6	0.001
AAs (ng m^{-3})					
BEN	Nd-6.2	1.7 ± 1.6	Nd-2.9	0.96 ± 0.65	0.000
TOL	Nd-1.7	0.64 ± 0.35	Nd	Nd	—
PH	3.7–52.0	17.1 ± 11.7	1.8–19.0	5.9 ± 3.6	0.000
tPH	1.6–6.9	2.8 ± 1.2	Nd-3.7	1.5 ± 0.95	0.000
iPH	0.78–3.2	1.5 ± 0.65	Nd-1.5	0.63 ± 0.40	0.000
TRIM	1.7–24.7	4.2 ± 3.8	Nd-4.2	1.2 ± 0.82	0.000
ΣAA	9.3–87.5	28.0 ± 18.4	2.8–24.3	10.3 ± 5.1	0.000
HAs (ng m^{-3})					
MAL	2.6–58.7	22.3 ± 16.8	1.1–27.4	11.0 ± 6.4	0.009
2-HGA	1.4–13.8	4.8 ± 3.3	Nd-14.9	4.6 ± 2.8	0.894
TAR	Nd-6.8	2.1 ± 2.1	1.2–12.3	3.9 ± 2.1	0.000
CIT	1.9–9.6	2.9 ± 1.4	0.39–4.8	2.3 ± 1.3	0.010
ΣHCA	7.1–79.0	32.1 ± 21.2	5.6–46.3	21.8 ± 9.4	0.102
PSOA tracers (ng m^{-3})					
PA	Nd-4.7	0.72 ± 0.98	1.8–27.2	12.3 ± 5.8	0.000
PNA	0.32–2.5	1.1 ± 0.45	2.4–12.9	5.6 ± 2.3	0.000
3HGA	1.3–16.8	6.0 ± 4.1	1.6–20.0	8.6 ± 4.3	0.002
3MBTCA	1.9–31.2	10.2 ± 8.1	0.38–8.9	3.4 ± 2.1	0.000
ΣPSOA	3.9–49.2	18.0 ± 12.7	8.8–67.4	29.9 ± 13.3	0.000
ISOA tracers (ng m^{-3})					
MTL2	1.8–10.8	4.0 ± 2.0	4.3–20.8	7.3 ± 3.1	0.000
MTL1	5.8–31.1	11.4 ± 5.4	7.8–57.5	17.9 ± 9.8	0.000
2MGA	0.75–7.9	3.2 ± 2.4	0.53–3.9	0.93 ± 0.54	0.000
ΣISOA	9.1–49.9	18.6 ± 8.6	12.8–82.2	26.2 ± 13.2	0.000
ΣBSOA^{b}	13.7–85.5	36.6 ± 17.3	27.2–95.9	56.1 ± 18.9	0.000
MCAs (ng m^{-3})					
C16	10.7–161	56.1 ± 34.6	6.1–77.5	32.7 ± 16.0	0.001
C17	1.1–21.3	4.6 ± 4.2	Nd-8.8	2.7 ± 1.7	0.039
C18	3.9–130	40.8 ± 28.9	2.7–41.2	17.1 ± 8.0	0.000
C18:1	1.1–10.9	5.5 ± 2.5	0.82–3.2	1.6 ± 0.61	0.000
ΣMCAs	18.7–315	107 ± 67.0	9.8–126	54.1 ± 25.1	0.000
Biomass burning tracer (ng m^{-3})					
LEV	0.65–21.1	3.3 ± 3.5	Nd-8.6	1.3 ± 1.6	0.000
Meteorological parameters, inorganic gases OC and EC					
T(^{o}C)	26.7–30.6	27.9 ± 1.0	23.3–30.5	26.3 ± 1.9	0.000
RH (%)	39.5–64.5	53.1 ± 7.0	29.8–76.0	55.2 ± 14.1	0.226
O$_3$ (μg m^{-3})	40.9–70.6	53.8 ± 7.9	76.0–118	98.6 ± 10.3	0.000
NO (μg m^{-3})	1.6–13.0	4.4 ± 2.1	0.04–0.21	0.13 ± 0.04	0.000
NO$_2$ (μg m^{-3})	9.9–48.4	23.9 ± 9.7	0.53–1.7	1.0 ± 0.23	0.000
NO$_x$ (μg m^{-3})	12.3–68.3	31.0 ± 11.7	0.63–1.9	1.2 ± 0.39	0.000

Table 1 (*Contd.*)

Species	LIM (urban) ($n = 44$) Range	LIM (urban) ($n = 44$) Mean ± SD	AGM (background) ($n = 44$) Range	AGM (background) ($n = 44$) Mean ± SD	p Value
SO_2 (μg m^{-3})	0.43–2.66	1.5 ± 0.61	0.35–2.2	0.91 ± 0.39	0.000
OC (μg m^{-3})			0.6–3.1	1.9 ± 0.45	
EC (μg m^{-3})			0.08–0.46	0.19 ± 0.08	
TC (μg m^{-3})			0.67–3.4	2.1 ± 0.50	
OC/EC			5.5–18.8	11.0 ± 3.3	
SOC			0.06–2.0	0.91 ± 0.41	
SOC/OC (%)			2.9–70.9	46.8 ± 15.3	

[a] Not detected. [b] Sum of PSOAs and ISOAs.

Chemicals and Sigma Aldrich. Finally, levoglucosan (LEV) was purchased from Sigma Aldrich. Apart from the compounds mentioned above, another five compounds, for which authentic standards were unavailable, were identified using MS data from the literature and with the help of the NIST library.[57] Quantification was performed using the GC/MS response factors of the available standards. For example, 2-methylthreitol (MTL2), 2-methylglyceric acid (2MGA), 3-methyl-1,2,3-butanetricarboxylic acid (3MBTCA), and 2-hydroxyglutaric acid (2HGA) were quantified using the response factors of 2-methylerythritol, malic acid, suberic acid and 3-hydroxyglutaric acid, respectively. Detection limits ranged from 0.16 ng m^{-3} (suberic acid) to 0.62 ng m^{-3} (palmitic acid) and recoveries varied from 68% (pinonic acid) to 127% (stearic acid).

In Tables S1 and S2† the retention time and the ionic fragments used for the studied compounds are summarized. A total of six blank filters (three for each sampling site) were analyzed as real samples using the described procedure. If necessary, data were corrected appropriately for the field blanks but not for recoveries.

2.4 Statistical analysis

The Mann–Whitney test and principal component analysis (PCA) were applied to study the possible differences between sampling sites and for source apportionment purposes, respectively, using SPSS Software (IBM SPSS statistics, version 24). A value of $p < 0.05$ (95% confidence level) was considered to indicate a significant difference.

3. Results and discussion

In Table 1, the mean concentrations and concentration ranges of each individual analyte and inorganic gases are presented, as well as meteorological data values for both sampling sites. The measured OC and EC concentrations and the calculated SOC, regarding only the samples collected at AGM, are also shown in Table 1.

3.1 PM, OC, EC and SOC

Comparable levels of $PM_{2.5}$ were observed at both sites, with those of LIM being slightly higher (15.4 ± 2.6 *versus* 13.8 ± 4.2 μg m^{-3}) (Table 1). In general, in AGM, $PM_{2.5}$ levels reach their maximum average concentrations during summer (July–August) as a result of increased SOA formation, limited precipitation and the Etesian winds which transport rich in fine particle air masses from Turkey.[58] $PM_{2.5}$ levels in LIM are also comparable with those measured at the same site during 2012–2013 (13.1 ± 4.7 μg m^{-3}).[59] Similar and higher concentrations (>20 μg m^{-3}) have been reported in Akrotiri and Finokalia respectively, two sites of Crete, in Greece, during the summer months.[60,61] In contrast, quite higher concentrations have been observed in three urban sites in Lebanon (from 27.6 to 40.9 μg m^{-3}).[62]

In AGM OC presented a mean concentration of 1.9 ± 0.45 μg m^{-3} which is quite higher than that measured in Azores, Portugal (0.33 ± 0.26) and Sonnblick, Austria (0.90 ± 1.0),[63] but lower than 2.85 ± 1.63 μg m^{-3} measured in an urban-background site in Patra, Greece,[64] and also lower than 3.5 ± 2.8 μg m^{-3} in a rural site in Brindisi, Italy[55] and than 3.8 ± 3.7 μg m^{-3} found in Gongga Mountain, China.[19] The average OC/EC ratio, in AGM, was 11.0 ± 3.3 which is nearly ten times higher than the ratio calculated in Thessaloniki (1.9 ± 1.4), an urban area of Eastern Mediterranean,[65] and also higher than that at two urban-background Greek sites in Thessaloniki and Patra (8.1 and 7.5, respectively)[64,65] but lower than those reported in Azores (13.5 ± 17.4).[63] In general, the OC/EC ratio can be used to characterize the relative contribution of secondary *versus* primary sources, with values > 2 being indicative of significant SOA contributions.[66,67] As a result, it appears that aerosols in AGM are significantly influenced by secondary sources. This can be further supported by the calculated SOC which contributes to a significant portion of the total OC (46.8 ± 15.3%). Particularly, SOC mean concentration was 0.91 ± 0.41 μg m^{-3} which, compared with SOC from other studies, calculated with the same method, is lower than that in Toulouse (3.04 μg m^{-3} and 65.85% of OC, during summer),[68] and than 2.9 ± 3.4 μg m^{-3} in Gongga Mountain, China,[19] while being at the same levels as in Brindisi, Italy (1.9 ± 2.2 μg m^{-3}).[55] The daily variations of PM, OC, EC and SOC are presented in Fig. 2.

3.2 Dicarboxylic acids (DCAs)

DCAs were abundant in both locations with LIM presenting significantly higher mean concentrations, 76.9 ± 45.7 ng m^{-3}

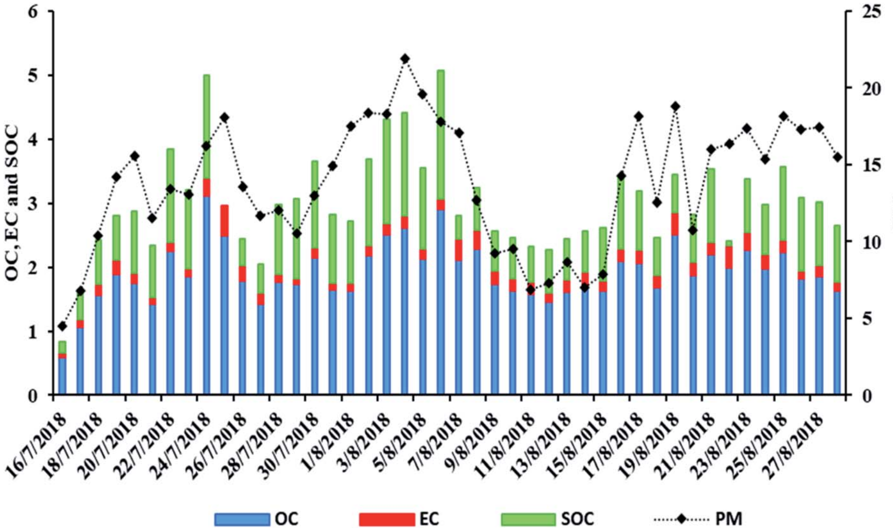

Fig. 2 Daily variations of $PM_{2.5}$, OC, EC and SOC ($\mu g\ m^{-3}$) of samples collected at AGM.

versus 49.6 ± 23.6 ng m^{-3} (Table 1, Fig. 3) measured in AGM. Considering that DCAs are formed by the oxidation of various precursors,[69] it is possible that in urban atmospheres, where VOCs are more abundant, the concentrations of DCAs are elevated. This is in agreement with Zhao *et al.* (2014)[70] and Guo *et al.* (2015),[71] where DCA values were higher in urban sites than those in rural. In general, it has been reported that DCAs in urban aerosols are mostly secondarily produced.[72] Although succinic acid was the dominant diacid in both sites, adipic acid presented the most intense difference as it was found over two times higher in LIM (15.1 ± 11.9 over 6.8 ± 4.6 ng m^{-3}). Significantly higher concentrations were also observed for succinic, adipic and suberic acids. Glutaric and azelaic acids were found at higher, but not significantly, ($p > 0.05$) concentrations, whereas only sebacic acid was found at higher levels in AGM although the difference was also not statistically significant. The DCA profile of the two sites is displayed in Fig. 4. As is obvious, low molecular weight diacids (diC4–diC6) contribute almost 71.6% of the total measured diacids in LIM, whereas in AGM the percentage is reduced to 60%. The increased relative abundance of higher molecular weight DCAs in AGM can be explained by the elevated influence of biogenic sources.[73] It is

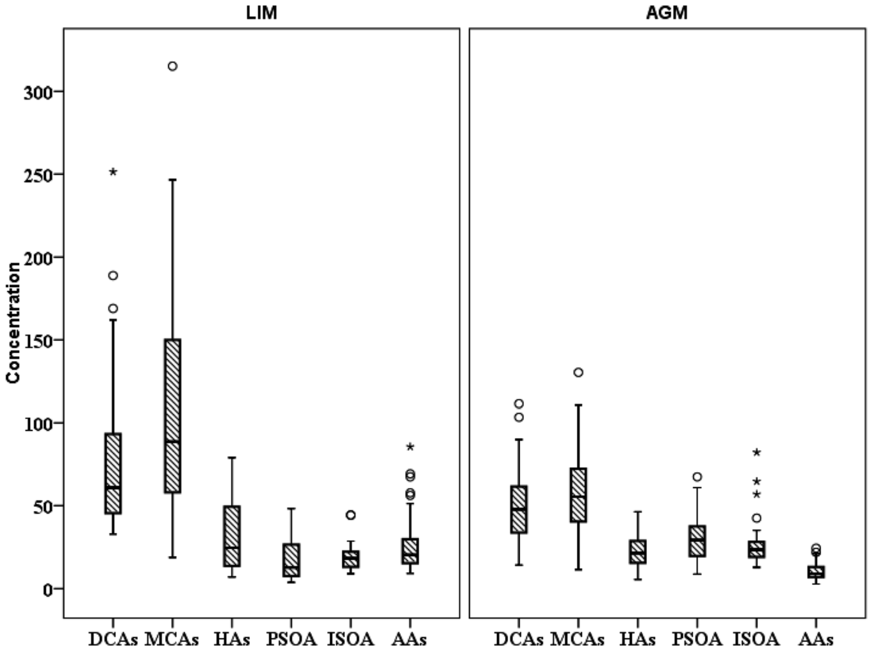

Fig. 3 Spatial distribution of the sum of studied polar organic compound groups (ng m^{-3}) (○ refers to values above the 3rd quartile and * to outliers).

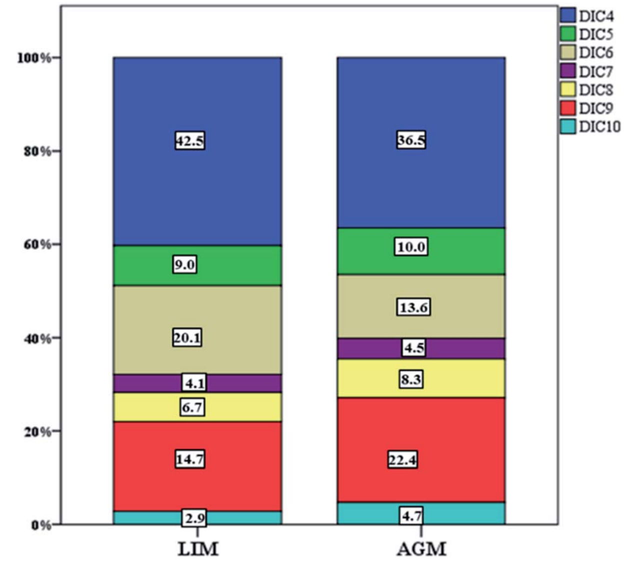

Fig. 4 Relative abundance of each individual DCA at both sampling sites.

known that higher molecular weight diacids are oxidation products of biogenic unsaturated fatty acids,[74,75] which are emitted from vegetation and the sea surface micro-layer as a result of phytoplankton activity,[76] although anthropogenic primary sources have been reported, including automobile engine exhaust and cooking.[77,78] A similar relative abundance was observed in six sites in the Pearl River Delta region of China, where in each site succinic acid was the most abundant DCA followed by azelaic acid,[70] and in 2 sites in Oporto, Portugal.[79] However, in other studies conducted at urban and background locations of China and Sweden, respectively, azelaic acid was the most abundant.[73,80] In order to differentiate the relative contribution of anthropogenic *versus* biogenic sources, the ratios of diC6/diC9 and PH/diC9 can be used.[81] Lower values indicate influence from biogenic sources, whereas higher values show the impact of anthropogenic sources. The mean ratio of diC6/diC9 for LIM (1.2 ± 0.79) was almost two times higher than that calculated for AGM (0.67 ± 0.42), while the mean ratios of PH/diC9 were respectively equal to 1.4 ± 0.94 and 0.57 ± 0.28 for LIM and AGM, revealing the stronger impact of anthropogenic sources in the urban site. However, in a study conducted at two sites in the Po Valley, Italy, during the deep-winter of 2013, slightly higher values of the mentioned ratios have been found for the rural/background site than those for the urban, indicating the impact of anthropogenic sources.[82] Moreover, in the Gosan site of Jeju Island, South Korea, the increase of the diC6/diC9 and Ph/diC9 ratios during wintertime was attributed to the greater amounts of transported air pollutants from East Asia.[83] A comparison with ratios from other studies around the world is presented in Table S3.†

Another possible source of low molecular weight DCAs is the oxidation of their higher homologues. According to Yang *et al.* (2008),[32] the photo-oxidation of azelaic acid can lead to the formation of lower homologues, including succinic and glutaric acids, as a result of the favorable cleavage of its C4–C5 bonds. Thus, such a relationship can be implied by the correlation of the diC4/diC6 ratio with the relative abundance of succinic acid (RdiC4%).[84] As is obvious from Fig. 5, in LIM the stronger correlations ($R^2 = 0.60$) between the aforementioned parameters could indicate another possible source of succinic acid, but in AGM such a relationship is much weaker ($R2 = 0.28$).

3.3 Aromatic acids (AAs) and levoglucosan (LEV)

Six aromatic acids were studied in both sites including compounds with one (BEN and TOL), two (PH, iPH, and tPH) and three (TRIM) carboxyl groups in their molecules. The sum of aromatic acids presented almost three-fold higher mean concentrations in LIM (28.0 ± 18.4 ng m^{-3}) than in AGM (10.3 ± 5.1 ng m^{-3}) ($p < 0.05$) (Table 1, Fig. 3). PH was the dominant AA in both sites, although it was found almost three times higher in LIM (mean of 17.1 ± 11.7 *versus* 5.9 ± 3.6 ng m^{-3}, $p < 0.05$). In other urban sites, PH was found at a considerably higher concentration such as in Thessaloniki (74 ± 55 ng m^{-3}), with an average summer value of over 30 ng m^{-3}.[18] In Guangzhou and Hok Tsui, two sites of the Pearl River Delta region with severe air pollution, PH was measured to be respectively equal to 215 ± 86.1 and 130 ± 75.0 ng m^{-3} during summer.[78] However, lower values have been measured on Jeju Island (4.9 ± 2.9 ng m^{-3}, during summer)[83] and in Vavihill, Sweden (2.4 ± 1.4 ng m^{-3}).[73] TRIM presented the biggest difference in concentration values between the two studied areas, as it was nearly 4 times higher in LIM than in AGM (4.2 ± 3.8 *versus* 1.2 ± 0.82 ng m^{-3}, respectively). Higher TRIM levels have been reported in six Chinese sites with average concentrations ranging from 5.6 ± 2.5 to 9.9 ± 4.9 ng m^{-3}.[70] Quite lower concentrations have been observed in both areas for monocarboxylic aromatic acids (BEN and TOL) and especially in AGM, TOL was detected in lower than 10% of the samples. This can be explained by their higher volatilities favoring their presence in the gas phase,[85,86] which can be further enhanced by the increased ambient temperature during the sampling period. However, significantly elevated concentrations of benzoic acid (>100 ng m^{-3}) have been measured in $PM_{2.5}$ samples at four different sites in the Pearl River Delta region.[78] AAs can be emitted or formed in the atmosphere from a variety of primary and secondary sources.[36,70,75,86,87] In our correlation

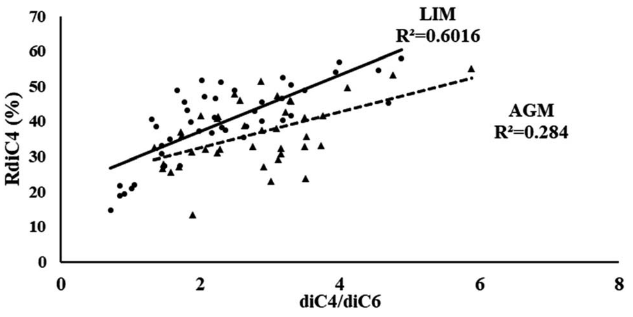

Fig. 5 Scatter plot of the diC4/diC6 ratio and the diC4 relative abundance (RdiC4%) in LIM (circle) and AGM (triangle).

analysis we have also included the biomass burning tracer of LEV. LEV is a definite tracer of biomass burning,[88] which is often correlated with aromatic acids. For example, in Thessaloniki PH was strongly correlated with biomass burning,[18] whereas, in Iowa, the secondary formation of PH was indicated as it was correlated with the toluene-SOA tracer, and tPH was associated mostly with biomass burning and iPH appeared to originate from mixed sources.[89] Despite the fact that LEV was found at low levels, its presence confirms the contribution of biomass burning to atmospheric aerosols in Eastern Mediterranean either from regional wildfires or long range transport.[90] In this study, the correlation analysis for LIM exported two groups of compounds that were strongly correlated (Table S4†). The first group includes PH, BEN, and TRIM ($r = 0.72–0.95$, $p < 0.05$) and is associated with secondary sources, while the second group includes LEV, tPH and TOL ($r = 0.69–0.72$, $p < 0.05$), which can be attributed to biomass burning. iPH presented moderate but significant correlations with PH ($r = 0.58$, $p < 0.05$) and BEN ($r = 0.54$, $p < 0.05$) suggesting contributions from secondary sources. Similar correlations were also observed in AGM (Table S5†) regarding BEN, PH and TRIM ($r = 0.56–0.84$, $p < 0.05$). However, iPH was strongly correlated with tPHA ($r = 0.84$, $p < 0.05$) indicating emissions from primary sources, which can be further supported by their significant correlations with LEV ($r = 0.51$ and 0.70, respectively, $p < 0.05$). Analogous correlations have been observed in a study conducted at Chinese urban and suburban sites, where tricarboxylic aromatic acids and PH were associated with secondary sources, whereas iPH and tPH with primary.[36]

3.4 Biogenic secondary organic aerosol (BSOA) tracers and hydroxyacids (HAs)

Seven BSOA tracer species were observed at both sites including four pinene oxidation products (PA, PNA, 3HGA and MBTCA) and three isoprene oxidation products (MTL1, MTL2 and 2MGA). Significantly higher BSOA concentrations were found in AGM, with a mean of 56.1 ± 18.9 ng m^{-3} compared with LIM, where BSOA average concentrations ranged from 13.7–85.5 ng m^{-3}, with a mean of 36.6 ± 17.3 ng m^{-3} (Table 1, Fig. 3). This difference is not surprising as there is widespread vegetation enclosing the background site of AGM (maquis, oak and pine forests). In AGM PSOA tracers exhibited slightly higher concentrations than ISOAs (29.9 ± 13.3 *versus* 26.2 ± 13.2 ng m^{-3}) which is in agreement with Debevec *et al.* (2018),[48] who found, in the same site during June–July 2015, α/β-pinene levels higher than those of isoprene. In LIM, similar concentrations between ISOAs, ranging from 9.1–49.9 ng m^{-3} with a mean of 18.6 ± 8.6, and PSOAs, from 3.9 to 49.2 ng m^{-3} with an average of 18.0 ± 12.7, have been observed. A comparison with BSOA data from other studies is presented in Table 2. Among PSOA tracers in AGM, PA was the most abundant (12.3 ± 5.8 ng m^{-3}), followed by 3HGA and PNA while MBTCA presented the lowest concentrations (3.4 ± 2.1 ng m^{-3}). PA and PNA are first generation oxidation products of pinenes, *via* O_3 or OH radicals, which can be further oxidized to 3HGA and MBTCA in the presence of NO_x.[91–93] Thus, the elevated relative abundance of PA and PNA (41.2 and 18.6%, respectively) (Fig. 6) can be explained by the increased O_3 along with the low NO_x levels favoring the formation of these products. However, PNA ambient concentrations are expected to be higher, as due to its volatility, it can be found in higher diameter particles[94] or in the gas phase.[95] In LIM, the PSOA profile was different as the most abundant tracer was MBTCA (10.2 ± 8.1 ng m^{-3} and 56.5% of the total PSOAs) followed by 3HGA (33.2%). PA and PNA contributed only 10.3% with PA being the least abundant (4.0%). It appears that the increased NO_x levels have a significant impact on PSOA formation, as higher NO_2 mixing ratios lead to a remarkable reduction in PA levels and to a moderate decrease of PNA;[96] hence the formation of second generation PSOA products may be prevailed.[19] This can be further supported by the ratios of MBTCA to PA plus PNA which are indicative of the aging degree of PSOAs.[97] In AGM the latter ratio

Table 2 Concentration ranges and mean concentrations of BSOA tracers in comparison with other studies. Each study refers to $PM_{2.5}$ samples

Species	Location, time	Concentration ng m^{-3} Mean ± SD	Reference
ΣPSOA	AGM/LIM Cyprus, July–August 2017	29.9 ± 13.3/18.0 ± 12.7	This study
	Mt Tai Mo Shan, Hong Kong, September–November 2010	26.3 ± 4.5	105
	Gongga Mountain, China, August 2011	3.6 ± 5.7	19
	Mt Wuyi, China, November 2015–July 2016	30.66 ± 24.44	97
	Marseille, France, July 2008	28.1	104
	Fairbanks, Alaska, June–September 2009	9.2 ± 8.7	106
	Beirut, Lebanon, winter 2012	19.3	46
	Yuen Long, Hong Kong, summer 2006	199 ± 291	107
ΣISOA	AGM/LIM Cyprus, July–August 2017	26.2 ± 13.2/18.6 ± 8.6	This study
	Mt Tai Mo Shan, Hong Kong, September–November 2010	54.7 ± 22.7	105
	Gongga Mountain, China, August 2011	88.6 ± 106.1	19
	Mt Wuyi, China, November 2015–July 2016	45.28 ± 65.52	97
	Marseille, France, July 2008	3.7	104
	Fairbanks, Alaska, June–September 2009	41 ± 43	106
	Beirut, Lebanon, winter 2012	0.79	46
	Yuen Long, Hong Kong, summer 2006	29.5 ± 33.0	107

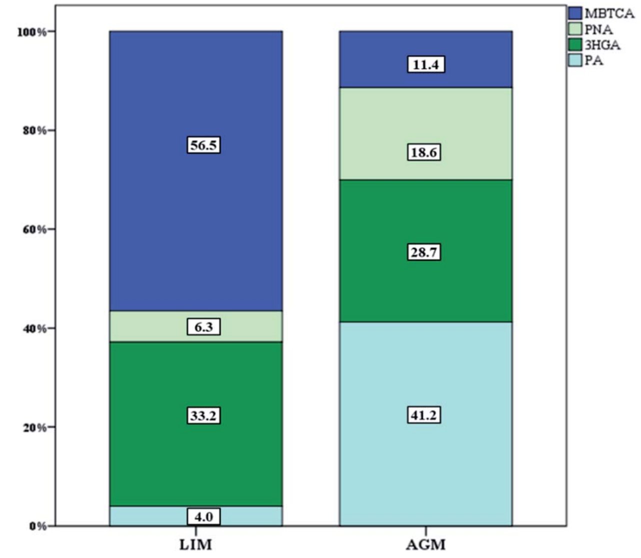

Fig. 6 Relative abundance of the individual PSOA tracer species.

presented mean values of 0.18 ± 0.07 which are quite lower than those observed in LIM 5.6 ± 3.6 implying that SOAs in AGM are freshly produced, whereas in LIM they are highly oxidized. Furthermore, the 3HGA/MBTCA ratio can be applied to discriminate the contribution of the individual monoterpenes as α-pinene SOA yields have been reported to be significantly more enriched in MBCTA relative to 3HGA compared with those of β-pinene or δ-limonene.[97–99] Our results suggest that β-pinene is a more important contributor in AGM (ratio of 0.67 ± 0.28) and α-pinene in LIM (3.2 ± 1.9), which is constant with the higher concentrations of β-pinene than α-pinene that were observed in AGM in a previous study.[48]

Of ISOA tracers, MTL1 was the most abundant in both sites followed by MTL2 and 2MGA (Table 1). Both MTLs were found at significantly ($p < 0.05$) higher concentrations in AGM. However, the concentrations of 2MGA were significantly increased in LIM (3.2 ± 2.4 *versus* 0.93 ± 0.54 ng m^{-3}). MTLs can be generated from the oxidation of isoprene through the HO_2 channel in the absence or at low levels of NO_x, whereas 2MGA is formed under rich-NO_x conditions by the oxidation of methacrolein, a gas phase first-generation product of isoprene's oxidation;[24,100–103] therefore the use of the MTLs/2MGA ratio could evaluate the effect of NO_x on ISOA formation, although factors including aerosol acidity, SO_2, RH and the ratio of NO_x/isoprene may also play an important role.[103] The aforementioned ratio was almost four times higher in AGM (29.0 ± 11.5) than that in LIM (7.5 ± 5.6) revealing the influence of NO_x on ISOA formation. Correspondingly, in a mountainous forest area of southeastern China, the winter-to-summer increase of MTLs/2MGA values was attributed to the higher NO_x levels during fall–winter.[97] Different formation mechanisms of ISOAs can also be implied as the excellent correlations observed between MTL1 and MTL2 (Fig. 7) at both sites indicate identical formation pathways, as also found in another Mediterranean site,[104] whereas MTLs were moderately to weakly correlated with 2MGA ($R2 = 0.36$ in AGM; $R^2 = 0.17$ in LIM).

HAs including MAL, 2HGA, TAR and CIT have been considered as secondary products of various precursors. Based on field studies, MAL, TAR and 2HGA have been associated with isoprene's oxidation in Amazonian aerosols.[108] In Alaskan aerosols TAR and CIT were considered, as well, to arise from isoprene's oxidation.[106] Apart from an isoprene product, MAL has been suggested as a transformation product of several other VOCs such as monoterpenes, β-caryophyllene, toluene, *etc.*[109] Recently, HAs including MAL, TAR, 2HGA and others were linked with photochemical oxidative chain reactions, as intermediates to the formation of oxalic acid from its higher homologues.[110] MAL was the dominant HA in both sites although its mean concentration was over two times higher in LIM (22.3 ± 16.8 ng m^{-3}) than in AGM (11.0 ± 6.4 ng m^{-3}) (Table 1), which can be explained by the increased levels of its possible precursors in the urban area. TAR was the only HA found in significantly ($p < 0.05$) higher concentrations in AGM, which may indicate a biogenic origin. This can be reinforced as in AGM TAR was correlated strong and significantly ($r = 0.77$, $p < 0.05$) with MTLs (Table S6†) supporting the findings of Claeys *et al.* (2004)[108] and Deshmukh *et al.* (2019).[106] Moreover, CIT was well correlated with TAR ($r = 0.72$, $p < 0.05$) and MTLs ($r = 65$, $p < 0.05$) suggesting isoprene's oxidation as a potential source. On the other hand, MAL can be associated with pinene SOA formation due to its high correlation with PSOA tracer species ($r = 0.72$, $p < 0.05$), which is in

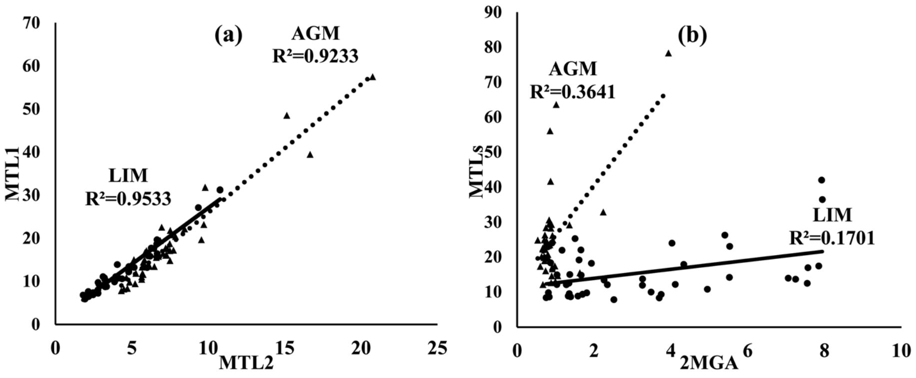

Fig. 7 Scatter plots of (a) MTL1 *versus* MTL2 and (b) MTLs (MTL1 + MTL2) *versus* 2MGA in AGM (triangle) and LIM (circle). Concentrations refer to ng m^{-3}.

accordance with Hu and Yu (2013),[109] where PSOAs and MAL, during summer, were satisfactorily correlated ($R^2 = 0.89$). Different sources can be indicated for 2HGA as it was mostly correlated with the sum of diC8-diC10, which is in agreement with the study of Gowda and Kawamura (2018),[110] although the moderate correlation with PSOAs ($r = 0.53$, $p < 0.05$) could show a minor boost from pinenes' oxidation. On the other hand, in LIM, a different trend was noticed (Table S7†). HA individual compounds were strongly correlated with each other ($r = 0.61$–0.83, $p < 0.05$) attributed to the same origin. Moderate to strong correlations were observed with ΣdiC4–diC6 and ΣdiC8–diC10 (from 0.55 to 0.78) indicating their formation from the oxidation of unsaturated fatty acids or higher homologous diacids, as intermediates, through photochemical oxidative chain reactions.[110] In this perspective, no significant associations have been found between HAs and BSOA except a moderate correlation of 2HGA with PSOA tracers ($r = 0.53$, $p < 0.05$).

3.5 Monocarboxylic acids (MCAs)

The group of MCAs is a remarkable component of atmospheric aerosols as it accounts for 46–80% of the total extractable organic compounds of urban $PM_{2.5}$ aerosols.[111] Several natural and anthropogenic sources have been reported for MCA emissions, including vehicular exhaust, cooking, biomass burning, fossil fuel combustion, and vegetative emissions and microbial activity.[71,77,79,112,113] MCAs in LIM presented significantly higher concentrations than those measured in AGM with mean concentrations respectively equal to 107 ± 67.0 and 54.1 ± 25.1 ng m^{-3} (Table 1, Fig. 3), suggesting that anthropogenic contributions are more important. Anthropogenic emissions are enhanced in LIM, as during summer, population is significantly elevated due to international and domestic tourism.[58] In both sites, C16 was the dominant MCA followed by C18, while C17 presented the lowest concentrations, which is consistent with the dominance of C16 over C18 measured in the Po Valley, Italy[82] and in 6 sites of the Pearl River Delta region.[70] In Beirut, Lebanon, MCAs were measured at quite higher concentrations, compared to our study, with C18 being the most abundant of the measured MCAs followed by C16.[46] Aerosol aging can be indicated through the value of the C18:1/C18 ratio, with higher values implying fresher aerosols.[34] C18:1 is more reactive than C18 due to the formers' double bond which makes it vulnerable to atmospheric oxidants including O_3 and OH radicals.[106] Fresher aerosols are indicated in LIM as mean C18:1/C18 values were significantly ($p < 0.05$) higher (0.19 ± 0.15) than those calculated in AGM (0.11 ± 0.05), probably because of (a) the increased anthropogenic emissions in the urban site and (b) the rapid degradation of C18:1 in AGM due to the almost two-fold higher concentrations of O_3. The latter hypothesis can be reinforced by the significantly higher ($p < 0.05$) ratio of diC9/C18:1 (mean of 7.3 ± 3.4) observed in AGM, where the respective mean value in LIM was 3.1 ± 2.7 suggesting that the photochemical process is enhanced in AGM.[114]

3.6 Influence of atmospheric oxidants on SOA formation

SOA formation and aging involve multiple and complex oxidation reactions, affected by the atmospheric abundance of OH radicals, O_3, NO_x, SO_2, aerosol acidity, *etc.*[11] Many laboratory studies have highlighted the influence of the aforementioned parameters on SOA formation.[10,11,115,116] Considering that mostly NO_x and SO_2 are of anthropogenic origin, several field studies in the US have revealed their impact on the increase of biogenic secondary organic aerosols.[117,118] As we mentioned above, the higher NO_x levels observed in LIM than in AGM possibly affect PSOAs with the dominance of MBTCA in LIM and ISOAs with the significantly higher relative abundance of 2MGA. This hypothesis can be further supported by the respectively positive and negative significant correlations observed between NO_x concentration values with 2MGA ($r = 0.67$, $p < 0.05$) and MTLs/2MGA ($r = -0.57$, $p < 0.05$) (Fig. 8a and b), indicating that isoprene's oxidation is influenced by NO_x in LIM. In another urban Mediterranean site, NO_x levels had a similar influence as a noticeable decrease of MTLs/2MGA was observed with the increase of NO_x,[104] which is also in accordance with the proposed pathway of isoprene's oxidation under high NO_x conditions.[24,102] The involvement of NO_x in PSOA formation could be suggested due to the significant correlations of NO_x with MBTCA ($r = 0.70$, $p < 0.05$) and HGA ($r = 0.56$, $p < 0.05$) (Fig. 8c and d). MBTCA was extensively detected in laboratory experiments from the ozonolysis and photo-oxidation of α-pinene under high NO_x levels, although several N-containing products have been also detected.[119] In addition, the increase of atmospheric oxidants including NO_2 and O_3 leads to elevated concentrations of 3HGA, other PSOA tracers.[103] In other studies, positive correlations were observed between NO and NO_2 with several other polar organic compounds including malic, maleic, succinic, phthalic acids, *etc.* indicating their secondary formation through various reactions.[18]

Further examination of NO_x influence on BSOA was carried out through the results of the weekday–weekend variation on SOA tracer species for the reason that NO_x sources are mostly anthropogenic.[120] Weekday *versus* weekend variations in organic aerosol compositions and SOA tracers are limited.[121] As is clear from Fig. 9, NO_x concentrations were, unsurprisingly, significantly ($p < 0.05$) lower during weekends probably due to lower traffic emissions. Noteworthy differences were observed mostly for 2MGA as it was found almost two times lower during weekends than on weekdays (1.9 *versus* 3.7 ng m^{-3}). At the same approach, the MTLs/2MGA ratio was significantly higher during weekends (1.6 times higher than on weekdays) indicating the lower impact of NO_x to isoprene chemistry. Lower, but not significantly, concentrations were also found for MBTCA during weekends. However, due to the small number of weekend samples, this outcome should be further investigated with more samples.

On the other hand, in AGM no significant correlations between NO_x and the studied compounds have been observed. Nevertheless, the quite higher O_3 levels appear to have an impact on secondary formation (Fig. 8). In particular, a significant ($p < 0.05$) increase of PSOA first generation products (PA + PNA) was observed with the increase of O_3 (Fig. 8(i)), which is constant with the proposed α/β-pinene ozonolysis mechanisms.[92,122] Another noteworthy correlation was observed between O_3 and MTLs (Fig. 8(ii)) suggesting that the enhanced

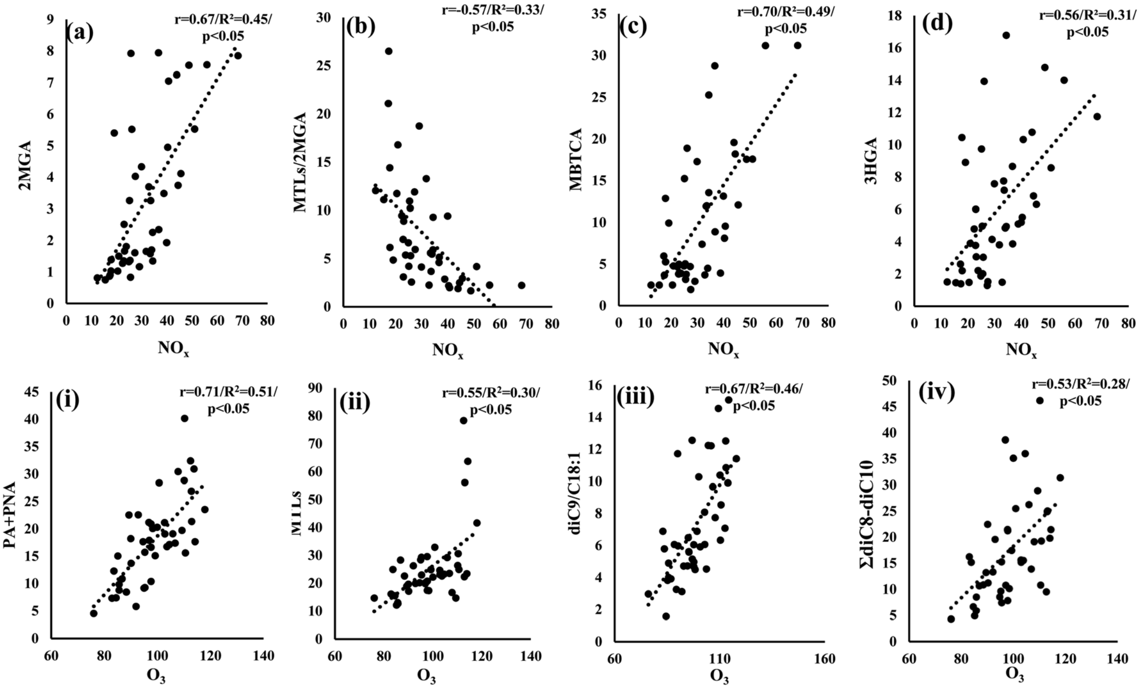

Fig. 8 Scatter plots of NO_x (μg m^{-3}) *versus* (a) 2MGA (ng m^{-3}), (b) MTLs/2MGA, (c) MBTCA (ng m^{-3}) and (d) 3HGA (ng m^{-3}) in LIM and scatter plots of O_3 (μg m^{-3}) *versus* (i) PA + PNA (ng m^{-3}), (ii) MTLs (ng m^{-3}), (iii) diC9/C18:1 and (iv) ΣdiC8–C10 (ng m^{-3}) in AGM.

O_3 levels could play an important role in isoprene's oxidation. Although isoprene's oxidation is initiated mostly by OH radicals, an ozonolysis pathway has been considered as a minor contributor to ISOAs in laboratory experiments.[123] Recently, Riva *et al.* (2016)[124] underlined the importance of ozonolysis on isoprene's transformation, as they found yields of MTLs and related isoprene organosulfates after the ozonolysis of isoprene in the presence of acidified sulfate aerosols. In addition to this, field studies have implied the impact of isoprene's ozonolysis through the moderate but significant correlations of O_3 with MTLs.[125,126] Our findings are in agreement with previous studies, as similar statistically significant correlations were observed, suggesting that isoprene's ozonolysis contributes to ISOA formation in AGM. Finally, high O_3 levels could possibly affect the oxidation of unsaturated fatty acids as the sum of diC8–diC10 diacids, *i.e.* known products of the formers' photooxidation,[31] was significantly ($r = 0.53$, $p < 0.05$) correlated with O_3 (Fig. 8(iv)). Besides this, the ratio of diC9/C18:1 significantly ($r = 0.67$, $p < 0.05$) increases as the O_3 concentration values increase (Fig. 8(iii)), indicating that higher molecular weight DCAs are formed by the oxidation of unsaturated fatty acids with O_3, such as C18:1, emitted from the local ecosystem. A similar correlation, between the ratio of diC9/(C18:1 + C18:2) and O_3, has been reported in a forest area, implying the

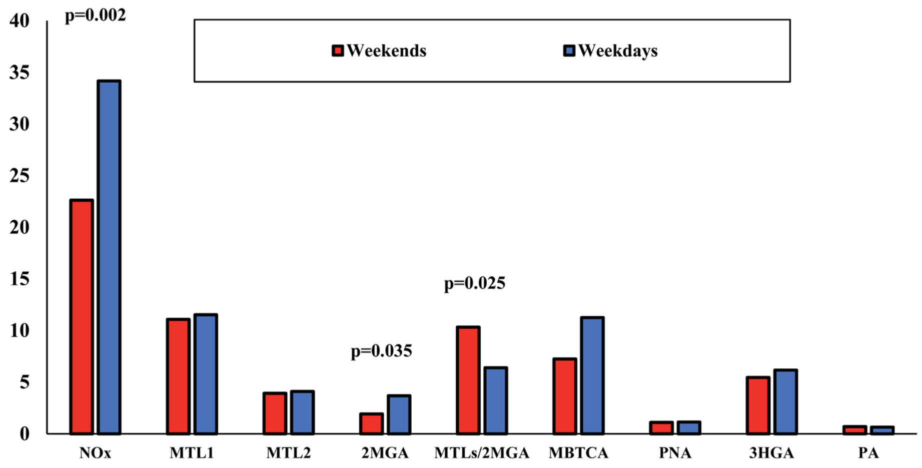

Fig. 9 Weekday ($n = 32$) *versus* weekend ($n = 12$) variations of NO_x (μg m^{-3}), BSOA tracers (μg m^{-3}) and the ratio of MTLs/2MGA in LIM.

secondary formation of diC9 from the forest's primary emissions.[127]

3.7 Principal component analysis (PCA)

Principal component analysis was applied to the dataset in order to assess any possible trends and to examine potential different sources between the two studied areas. PCA for AGM and LIM is illustrated in (Tables 3 and 4). TOL was not included in the PCA referring to AGM as it was detected in lower than 10% of the samples. Variable loadings >0.6 were considered as tightly clustered and are presented in bold.[128] Six factors explained 80.1% and 82.7% of the variance in AGM and LIM data, respectively. Although the number of exported factors is the same for both sites, there are some noteworthy differences regarding the compounds clustered in each factor and the relative variance coverage. Particularly, in AGM-PCA (Table 3) the first factor (19.5% of the variance) was loaded with diC4, diC5, diC6, diC7, PH, BEN and TRIM indicating secondary formation from anthropogenic precursors. The same factor has been found in a background area of Sweden, which correlated low molecular weight dicarboxylic acids with phthalic acid.[73] Factors 2 (14.1%) and 3 (13.3%) are associated with secondarily formed compounds from the oxidation of pinene and isoprene, respectively. Along with the PSOA tracer compounds (Factor 2), strong loadings of MAL were observed (0.76) indicating a possible biogenic source of MAL such as pinene oxidation, as also proposed by other studies.[107,109] Similarly, in the ISOA factor (Factor 3), TAR and CIT are tightly clustered suggesting their potential origin from isoprene's transformation.[106] Factor 4 (13.0%) is associated with the oxidation of unsaturated fatty acids due to the high positive values of diC8-diC10 and 2HGA, whereas Factors 5 and 6 (11.1 and 9.2%, respectively) are both linked with primary emissions local or regional, such as plant emissions, cooking and other anthropogenic sources[70] (Factor 5) and biomass burning, as Factor 6 is loaded with the biomass burning tracer of LEV, iPH and tPh, which can also be emitted from biomass burning.[89] In contrast, Factor 1 (26.4% of the variance) in LIM-PCA (Table 4) is heavily loaded with total DCAs and HAs attributed to the oxidation of unsaturated fatty acids or higher molecular weight DCAs with HAs as possible intermediates of these oxidative chain reactions leading to lower molecular weight DCAs.[110] Factor 2 (14.5%) is linked with primary emissions probably from anthropogenic activities (vehicle exhausts, cooking, *etc.*) due to the tight clusters of MCAs, while Factor 4 (11.4%) reveals secondarily formed compounds from anthropogenic precursors including BEN, PH,

Table 3 Varimax rotated component matrix of the studied compounds in AGM

Variance (%)	Component 19.5	14.1	13.3	13.0	11.1	9.2
Compound	1	2	3	4	5	6
DiC4	**0.866**	0.132	0.272	−0.018	−0.046	−0.080
DiC5	**0.891**	0.111	0.282	−0.087	0.082	0.067
DiC6	**0.886**	0.186	0.054	−0.007	0.092	−0.001
DiC7	**0.672**	0.012	0.174	0.130	−0.156	0.209
DiC8	0.083	0.184	0.018	**0.855**	0.158	0.244
DiC9	0.156	0.231	0.066	**0.833**	0.252	0.260
DiC10	0.269	0.344	0.008	**0.797**	0.107	0.093
MAL	0.096	**0.763**	0.138	0.241	0.109	0.112
2HGA	0.132	0.107	0.047	**0.783**	0.353	0.135
TAR	0.236	0.154	**0.825**	0.291	−0.136	0.022
CIT	0.459	0.154	**0.609**	0.270	0.037	0.205
LEV	0.020	0.182	0.017	0.330	0.026	**0.722**
MBTCA	0.057	**0.806**	0.342	0.240	−0.020	0.241
PNA	0.181	**0.849**	0.224	−0.037	−0.087	0.055
3HGA	0.161	**0.785**	0.324	0.331	−0.015	0.100
PA	0.290	**0.819**	0.082	0.204	−0.040	0.246
MTL2	0.293	0.220	**0.882**	0.011	0.015	0.018
MTL1	0.196	0.220	**0.892**	0.007	0.084	0.068
2MGA	0.088	0.232	**0.721**	−0.230	−0.058	−0.076
PH	**0.878**	0.051	0.105	0.330	0.000	0.122
TRIM	**0.659**	0.059	−0.055	0.221	−0.052	0.194
tPH	0.164	0.209	0.030	0.239	0.113	**0.881**
iPH	0.230	0.163	0.056	0.059	0.265	**0.837**
BEN	**0.842**	0.237	0.074	0.165	0.013	0.036
C16	−0.018	−0.101	0.091	0.167	**0.913**	0.015
C17	−0.027	0.053	−0.020	0.215	**0.814**	0.332
C18	0.012	−0.131	0.066	0.158	**0.889**	−0.035
C18:1	−0.038	0.135	−0.194	0.087	0.452	0.116

Table 4 Varimax rotated component matrix of the studied compounds in LIM

Variance (%)	Component 26.4	14.5	13.9	11.4	9.0	7.5
Compound	1	2	3	4	5	6
DiC4	**0.850**	−0.183	0.187	0.126	0.107	0.175
DiC5	**0.905**	−0.001	0.013	0.113	0.104	0.162
DiC6	**0.807**	−0.096	0.173	0.227	0.107	0.129
DiC7	**0.769**	0.485	−0.084	0.011	0.125	0.029
DiC8	**0.843**	0.287	0.146	0.256	0.145	−0.007
DiC9	**0.732**	0.591	−0.128	0.105	0.087	0.023
DiC10	**0.824**	0.455	−0.072	0.130	0.060	0.099
MAL	**0.683**	−0.009	0.242	0.160	0.141	−0.103
2HGA	**0.702**	0.208	0.513	0.123	0.043	0.042
TAR	**0.713**	0.185	0.398	0.199	0.098	−0.211
CIT	**0.890**	0.195	0.149	−0.084	0.035	−0.034
LEV	0.141	0.073	−0.019	0.222	**0.905**	0.022
MBTCA	0.132	−0.253	**0.835**	0.142	0.146	0.142
PNA	0.019	−0.260	**0.611**	0.157	0.345	−0.007
3HGA	0.330	−0.210	**0.848**	0.086	0.134	−0.058
PA	0.175	−0.143	**0.682**	0.084	0.219	0.037
MTL2	0.089	0.037	0.031	0.048	0.055	**0.975**
MTL1	0.057	−0.013	0.071	−0.009	0.081	**0.976**
2MGA	0.043	0.030	**0.721**	0.057	−0.116	0.035
PH	0.261	−0.097	0.087	**0.912**	0.164	−0.038
TRIM	0.233	−0.277	0.034	**0.691**	0.224	0.236
tPH	0.173	0.062	0.240	−0.033	**0.831**	0.210
iPH	0.015	0.228	0.145	**0.841**	−0.194	−0.010
BEN	0.254	−0.158	0.238	**0.869**	0.157	−0.060
TOL	0.263	−0.187	0.455	0.030	**0.764**	−0.071
C16	0.253	**0.860**	−0.170	−0.041	0.029	0.019
C17	0.322	**0.734**	−0.135	0.176	−0.154	0.066
C18	0.199	**0.882**	−0.273	−0.079	0.029	−0.042
C18:1	−0.097	**0.847**	−0.110	−0.322	0.001	−0.038

and TRIM, as well as iPH which is different with that observed in AGM. These three factors have many similarities with those derived from Zhao *et al.* (2014),[70] where MCAs, DCAs and polycarboxylic AAs were loaded in separate factors, connected with primary (MCAs) and secondary formation processes from different precursors (DCAs and AAs). Factor 5 (9.0%) is attributable to biomass burning through the strong loads of LEV. The presence of tPH in this factor confirms its primary origin although its other isomers (PH and iPH) are considered to be generated from secondary sources in LIM. Factors 3 and 6, with respective variance coverage of 13.9 and 7.5%, are associated with BVOC oxidation including pinene and isoprene respectively. Interestingly, although 2MGA is an isoprene's oxidation product, it is loaded in the pinene oxidation factor which may also reveal the influence of NO_x levels on BSOA formation from the fact that the other heavily clustered compounds (MBTCA and 3HGA) are significantly affected by the NO_X concentrations as already discussed in the previous section. Overall, the most interesting outcome exported from PCA is the significant contribution of the oxidation of unsaturated fatty acids in the urban site and the biogenic origin of hydroxyacids in the background site. In addition, the restriction on the application of iPH as an anthropogenic SOA tracer[89] is supported as it was considered as a secondary product in LIM but mostly correlated with primarily emitted compounds in AGM.

4. Conclusions

Twenty-eight polar organic species from six different compound classes and levoglucosan were studied in $PM_{2.5}$ aerosol samples from an urban and a rural/background site of Cyprus during summer. Total DCAs, MCAs and AAs presented significantly higher concentrations in the urban site, and PSOAs and ISOAs were significantly lower, whereas a mixed trend was found for HAs. The ratios of selected compounds showed that aerosols in LIM are fresher and quite more affected by anthropogenic sources while PSOAs were found highly oxidized. The higher NOx levels in LIM appear to affect BSOA formation as they were significantly correlated with MBTCA, 3HGA and 2MGA. In contrast, the higher O_3 observed in AGM enhances the formation of first-generation PSOAs and high molecular weight DCAs and contribute to ISOA formation as well. Correlation analysis revealed different potential sources or formation pathways for some of the studied compounds between the two sites, including MAL, TAR and CIT, which appear to be generated from BVOC oxidation in AGM, while in LIM they appear to be related to unsaturated fatty acids' or higher DCAs' oxidation, or iPH which was considered as a secondary product in LIM but associated with biomass burning in AGM. PCA analysis resulted in six factors for both studied areas with different, nevertheless, individual variance coverages and compounds loaded to each factor, including oxidation of unsaturated fatty acids, anthropogenic VOCs, isoprene and pinene along with primary emissions such as biomass burning, natural and anthropogenic related emissions (plant emissions, cooking, motor exhaust emissions, *etc.*)

Conflicts of interest

The authors declare no conflicts of interest.

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