

# Polar organic compounds in PM<sub>10</sub> and PM<sub>2.5</sub> atmospheric aerosols from a background Eastern Mediterranean site during the winter period: Secondary formation, distribution and source apportionment

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## HIGHLIGHTS

- BVOCs oxidation tracers and other related polar organic species at a background area of Eastern Mediterranean.
- Pinene SOA showed higher contribution to OC than Isoprene SOA in PM<sub>10</sub> samples but similar contribution in PM<sub>2.5</sub> samples.
- Phthalic acid is considered as a secondary product while its isomers found to be primarily emitted.
- Malic acid originated from a variety of sources.
- Dust episodes may affect secondary formation in PM<sub>10</sub> samples.

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## ABSTRACT

Atmospheric particle samples with aerodynamic diameter <10 μm (PM<sub>10</sub>) and <2.5 μm (PM<sub>2.5</sub>) were analyzed for elemental (EC), organic (OC) carbon and polar organic compounds. Samples were collected, on a daily basis, over 44 days during the winter period in Agia Maria Xyliatou, a background location of Cyprus. Polar organic compounds were determined using a 3-step derivatization method prior to analysis with GC/MS. Gas phase compounds and meteorological data were also measured. Secondary OC was estimated and found to be significantly higher in PM<sub>2.5</sub> than PM<sub>10</sub> fraction (mean of 0.81 ± 0.58 over 0.51 ± 0.66 μg m<sup>-3</sup>). Concentrations of biogenic secondary formation tracers, monocarboxylic acids, dicarboxylic acids and aromatic acids ranged from 7.3 to 29.0, 2.9–162, 7.6–82.0 and 1.9–19.6 ng m<sup>-3</sup> respectively, in all aerosol samples, accumulated mostly on PM<sub>2.5</sub> fraction. Molecular diagnostic ratios of selected carboxylic acids indicated influence of biogenic sources and aged aerosols. Source apportionment tools employed, including principal component analysis, demonstrated anthropogenic activity, biomass burning, biogenic volatile organic compounds oxidation and oxidation of unsaturated fatty acids as the basic sources of the studied analytes. Estimation of OC contribution from different sources was performed using tracer-based methods, such as “SOA tracer method” presenting biomass burning as a significant contributor (12.8 ± 14.8% in PM<sub>2.5</sub> and 5.8 ± 4.8% in PM<sub>10</sub>). Oxidation of biogenic volatile organic compounds accounted for 13.0 ± 8.9% and 5.6 ± 3.5% of OC in PM<sub>2.5</sub> and PM<sub>10</sub> samples respectively. Dust episodes that occurred during the sampling period, appear to enhance secondary formation mostly on PM<sub>10</sub> particles.

## 1. Introduction

Investigation of organic matter in atmospheric aerosols, also mentioned as organic aerosol (OA), is a continuing concern among scientists due to its severe consequences on human health (Kelly and

Fussell, 2012), air quality and climate (Kanakidou et al., 2005). Organic aerosols can be emitted in the atmosphere primarily from direct sources but also can be formed through numerous and complex reactions that occur in the gas and particle phase (Kroll & Seinfeld, 2008), the so called, secondary organic aerosol (SOA). An increasing interest has been

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observed about SOA formation (Volkamer et al., 2006; Shrivastava et al., 2017) and its possible effects on human health (Baltensperger et al., 2008). Recent studies, for example, have highlighted potential association of isoprene derived compounds with the expression of oxidative stress response genes in human lung and bronchial epithelial cells (Lin et al., 2016; Arashiro et al., 2018). SOA formation is the result of the reaction of atmospheric volatile organic compounds (VOCs), biogenic (BVOCs) (Williams et al., 2013) or anthropogenic (AVOCs) (Chen et al., 2010), with O<sub>3</sub>, NO<sub>3</sub>, OH radicals, chlorine atoms (Huang et al., 2012) or via photolysis. These reactions are greatly affected by the structure of each precursor and the ambient conditions, such as relative humidity, temperature, NO<sub>x</sub> and SO<sub>2</sub> concentration levels (Hallquist et al., 2009; Atkinson and Arey, 2003). The variety and diversity of the factors affecting the oxidation process of atmospheric VOCs leads to a great number of compounds constituting the SOA yields. The SOA yields include species with one or more oxygenated functional groups such as carbonyl (C=O), hydroxyl (OH) and carboxyl (HOC=O) groups (Hoffman et al., 1997; Liao et al., 2007; Hallquist et al., 2009).

Recent studies regarding the global emissions of VOCs indicate that the amount of BVOCs emitted in the atmosphere is greatly higher than the AVOCs (Ashworth et al., 2013). The most characteristic BVOCs that act as secondary organic aerosol precursors are isoprene, monoterpenes and sesquiterpenes (Williams et al., 2013). Their intense reactivity is due to the presence of C=C bonds in their molecules. Pinic acid (dicarboxylic acid) and pinonic acid (oxo carboxylic acid) are the main products of the reaction of α and β pinene with O<sub>3</sub> (Ma et al., 2007) while 3-hydroxyglutaric acid is considered as a marker of α-pinene photooxidation (Claeys et al., 2007). 2-Methyltetrols (sum of 2-methylerythritol and 2-methylthreitol) are major products of isoprene oxidation under low-NO<sub>x</sub> conditions (Claeys et al., 2004), while 2-methylglyceric acid is the basic product under high-NO<sub>x</sub> conditions, resulting from further oxidation of methacrolein and methacrylic acid which both are gas phase isoprene oxidation products (Surratt et al., 2006). The ratio of 2-methylerythritol/2-methylthreitol varies from 0.76 to 2.5 but in most cases 2-methylerythritol is more abundant than its diastereoisomer (Claeys et al., 2004; Fu et al., 2009, 2010). The variety of the above ratio suggests that formation procedures may differ by time and location (Fu et al., 2013).

Another group of compounds that can be formed via atmospheric photo-oxidation of volatile or semi volatile compounds are dicarboxylic acids (Zhang et al., 2010a). Their sources can be both biogenic and anthropogenic (Mochida et al., 2003); nevertheless their formation and chemical behavior remains a matter of concern (Zhao et al., 2014). The group includes straight chain dicarboxylic acids, unsaturated low molecular weight dicarboxylic acids, hydroxydicarboxylic acids and aromatic polyacids (Claeys et al., 2004; Kawamura and Bikkina, 2016, and references therein; He et al., 2018).

East Mediterranean (EM) is a region where the air quality receives increasing attention (Kanakidou et al., 2011; Achilleos et al., 2016; Iakovides et al., 2019). This area is characterized by excesses of the particulate matter and ozone limits, especially during the summer (Kanakidou et al., 2011). The intense solar radiation all year round, also enhances the photochemical processes (Dayan et al., 2017) making EM a favored place of expanded photochemical activity and thus formation of secondary pollutants.

Cyprus is located on the east side of the Mediterranean Sea. Its location between three continents, Europe, Africa and West Asia, makes Cyprus a receptor of air masses of different chemical composition. For example, Kleanthous et al. (2014) reported that high-ozone levels over the region are clear outcomes of long-range transport (Kleanthous et al., 2014). Moreover, transported dust is a significant contributor i.e. 33.6% of the yearly PM<sub>10</sub> levels measured in background stations (Pikridas et al., 2018). In addition, findings from the studies of Debevec et al. (2017, 2018), regarding the budget of AVOCs and BVOCs in the atmosphere of Cyprus, suggest that contributors of SOA exist in significant amounts in this region (Debevec et al., 2017, 2018).

In this study, we collected 132 samples, 44 PM<sub>10</sub>, 44 PM<sub>2.5</sub> and 44 gas phase samples from a background area of Cyprus, in order to study the formation, distribution and possible sources of BVOCs oxidation tracers and other related polar organic species, i.e. mono- and dicarboxylic acids (MCAs-DCAs), aromatic acids (AAs) and biomass burning tracers (levoglucosan) during the winter period. As far as we know, no previous research has investigated SOA in this region and this study is one of a few that have taken place in areas of the Mediterranean Sea (El-Haddad et al., 2011; Pietrogrande et al., 2014).

## 2. Experimental

### 2.1. Site description & sample collection

The sampling site is located at the Cyprus Atmospheric observatory (CAO) at Agia Marina Xyliatou, a remote location in the middle of the island (35.03° N, 33.05° E) (Fig. 1). CAO is at an altitude of 532 m ASL (above sea level), 1 km south of the village of Agia Marina (population about 630) and more than 35 km away from the major Cypriot cities with limited anthropogenic influences. The sampling location includes extensive plant life, such as the “maquis”, and is near the oak and pine forests covering the Troodos Mountain (Fall et al., 2012). The station is cooperated within the network of the European Monitoring and Evaluation Program (EMEP) by the Department of Labour Inspection (DLI).

Particulate phase samples (n = 44 for PM<sub>10</sub>, n = 44 for PM<sub>2.5</sub>) were collected daily (00:00–23:59), on pre-weighted filters (Whatman Quartz, 1851-150; Pall Tissuquartz 2500 QAT-UP) from 18 November 2017 to 31 December 2017. Two samplers (Leckel SEQ 47/50 and Digitel DHA-80) were used to collect the PM<sub>10</sub> (flow rate 30 m<sup>3</sup> h<sup>-1</sup>) and the PM<sub>2.5</sub> (flow rate 2.3 m<sup>3</sup> h<sup>-1</sup>) samples, respectively. Particle mass determination was carried out gravimetrically following the protocol of EN12341:2014 (EN12341, 2014). After collection, each filter was stored in a Petri dish in the freezer (−21 °C).

A weather station (Campbell Scientific Europe, Antony, France) located on the rooftop of CAO (5 m a.g.l) was 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<sub>2</sub>, CO, SO<sub>2</sub> and O<sub>3</sub> (1-hr time resolution) were measured at the CAO for the whole sampling period. More details for the latter measurements are provided in Kleanthous et al. (2014). During the sampling period, VOCs were also measured including 1 biogenic VOC (isoprene) and 6 anthropogenic (benzene, toluene, ethylbenzene, m + p xylene, o-xylene and 1,3-butadiene).

### 2.2. Measurement of organic carbon, elemental carbon and gas phase hydrocarbons

A 1 cm × 1.5 cm standard punch (1.5 cm<sup>2</sup>) 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) of Sunset Laboratory Inc., USA, following the EUSAAR 2 temperature program. More details for the analysis can be found elsewhere (Cavalli et al., 2010). Secondary organic carbon (OC<sub>sec</sub>) can't be measured directly, so it was calculated using the method described by (Castro et al., 1999). In particular, the minimum OC/EC ratio, from the measured OC and EC concentrations, was used to calculate primary organic carbon (OC<sub>pri</sub>) and OC<sub>sec</sub> by applying the following equations Eqs. (1) and (2).

$$OC_{pri} = EC \times \left(\frac{OC}{EC}\right)_{min} \quad (1)$$

$$OC_{sec} = OC - OC_{pri} \quad (2)$$

This equation has already been used for the estimation of OC<sub>sec</sub> in



samples ( $n = 3$  for  $PM_{10}$  and  $n = 3$  for  $PM_{2.5}$ ) were treated with the same procedure as the real samples and appropriate correction of the data took place when it was necessary.

## 2.6. Statistical analysis

Statistical analysis of the data was carried out using IBM SPSS statistics 23. Shapiro-Wilk test was used to check the normal distribution of the data and Mann Whitney test was selected to estimate the significance, using the 95% confidence level ( $p < 0.05$ ). Correlation analysis was applied with the use of Spearman test and Principal Component Analysis (PCA) was carried out in order to predict common sources between the analytes.

## 3. Results and discussion

### 3.1. PM, OC, EC and $OC_{sec}$ concentrations

Concentrations of PM, OC, EC, TC and  $OC_{sec}$  are summarized in Table 1. Meteorological data during the sampling period are also presented.

During the sampling period,  $PM_{10}$  and  $PM_{2.5}$  concentrations ranged from 5.3 to 268.9  $\mu\text{g m}^{-3}$  and from 2.0 to 71  $\mu\text{g m}^{-3}$ , respectively. Although the maximum concentrations are relatively high the average values were 25.0  $\mu\text{g m}^{-3}$  for  $PM_{10}$  and 10.0  $\mu\text{g m}^{-3}$  for  $PM_{2.5}$ . High PM concentrations can be explained by the dust episodes that occurred from 13 to 17 and on 27 of November 2017 and from 21 to 23 of December 2017.

(<https://www.airquality.dli.mlsi.gov.cy/news/archive/2017?page=0>)

During these days,  $PM_{10}$  concentrations exceeded the daily limit of 50  $\mu\text{g m}^{-3}$  (EU, 2008/50/EC) and thus five limit violations were observed. On 21 and 22 of December the threshold of 25  $\mu\text{g m}^{-3}$  for  $PM_{2.5}$  (WHO, 2006) was exceeded too. Mean concentrations of  $PM_{10}$  and  $PM_{2.5}$  appear to be consistent with the average November values measured at the same site during 2010–2015, although wintertime precipitation is responsible for the lower December values. (Pikridas et al., 2018). Additionally, a rural site near Brindisi (Italy) exhibited approximately same levels both for  $PM_{10}$ , i.e.  $22 \pm 14 \mu\text{g m}^{-3}$  and for  $PM_{2.5}$  i.e.  $11 \pm 6 \mu\text{g m}^{-3}$  (Siciliano et al., 2018). In contrast, in Chenhu qihao, a background location in Wuhan, China,  $PM_{10}$  and  $PM_{2.5}$  levels were significantly higher ranging from  $125 \pm 57$  and  $98 \pm 53 \mu\text{g m}^{-3}$  respectively, during the winter period (Xu et al., 2017). Significant good correlation ( $r = 0.98$ ,  $p < 0.05$ ) is observed for  $PM_{10}$  versus  $PM_{2.5}$  mass concentrations and the linear increase of their values reveals common emission sources (Fig. 2). Same trend was also noted at Brindisi (Siciliano et al., 2018).

In  $PM_{10}$  OC and EC values ranged from 0.43 to 9.1  $\mu\text{g m}^{-3}$  and from

0.03 to 1.4  $\mu\text{g m}^{-3}$  respectively, while in  $PM_{2.5}$  OC concentrations varied from 0.38 to 3.0  $\mu\text{g m}^{-3}$  and EC concentrations from 0.06 to 0.82  $\mu\text{g m}^{-3}$  (Fig. 3). Values noted in this work are comparable with results from other background locations in Greece (0.28–2.23  $\mu\text{g m}^{-3}$ ) (Bardouki et al., 2003) and lower than most rural sites of Italy (Sandrini et al., 2014). Interestingly,  $OC_{sec}$  in  $PM_{2.5}$  exhibited significant higher concentrations ( $p < 0.05$ ) (from 0.10 to 2.67 with median value 0.70  $\mu\text{g m}^{-3}$ ) than  $OC_{sec}$  in  $PM_{10}$  (from 0.11 to 4.39 with median value 0.35  $\mu\text{g m}^{-3}$ ), indicating that secondary organic carbon is mainly fine (Fig. 3). Comparing the concentration levels of  $OC_{sec}$ , measured with the same method, to those of other background locations, they appeared to be relatively lower than 2.9  $\mu\text{g m}^{-3}$  detected in Gongga Mountain, China (Li et al., 2018a), 3.31  $\mu\text{g m}^{-3}$  (heating season) and 1.46 (non-heating season) in Krynica Zdroj, Poland (Klejnowski et al., 2017) and 1.97  $\mu\text{g m}^{-3}$  ( $PM_{10}$ ) and 1.59 ( $PM_{2.5}$ ) in Brindisi, Italy (Siciliano et al., 2018). Daily variations of PM, OC, EC and  $OC_{sec}$  concentration are presented in (Figs. 4 and 5). As it is clear, dust episodes affect OC levels of both PM fractions, but higher diameter particles were more influenced, especially the 22<sup>nd</sup> of December 2017.

OC/EC ratios are an alternative way to estimate the contribution of primary and secondary sources to atmospheric aerosol. In particular, high ratios of OC/EC ( $>2$ ) refer to secondary processes as the main contributor to the organic aerosol (Kunwar and Kawamura, 2014; Haque et al., 2019). In this study, ratios of OC/EC were on average 4.8 and 5.2 for  $PM_{10}$  and  $PM_{2.5}$  respectively, suggesting that aerosols in Agia Marina Xyliatou are affected by secondary sources.

### 3.2. Gas and particle phase concentration of the analytes

#### 3.2.1. Overall results

Concentrations of inorganic gases and organic compounds of the gas phase are presented on Table 2, while particle phase concentrations of the analytes are illustrated on Table 3.

Anthropogenic aromatic compounds of gas phase exhibited low concentrations levels reinforcing the background typology of the location as firstly mentioned by (Debevec et al., 2017). Even lower concentrations were observed for benzene ( $0.18 \pm 0.07 \mu\text{g m}^{-3}$ ) and toluene ( $0.07 \pm 0.04 \mu\text{g m}^{-3}$ ), than those reported during March of 2015, i.e. 0.37  $\mu\text{g m}^{-3}$  and 0.19  $\mu\text{g m}^{-3}$  respectively (Debevec et al., 2017). 1, 3-Butadiene, an anthropogenic VOC with high reactivity and short lifetime, was measured at very low levels (in 12 out of 44 samples was measured above detection limits) compared to EU and US urban locations (RAR, 2002) but its gas/particle phase reaction products are receiving great attention (Jaoui et al., 2014). Isoprene ranges in our study were from 0.03 to 0.54  $\mu\text{g m}^{-3}$  with a median of 0.13  $\mu\text{g m}^{-3}$  showing comparable concentrations with those reported in Valderejo of Spain ( $0.14 \mu\text{g m}^{-3}$ ) (Navazo et al., 2008) and quite lower than those measured in the background location of Finokalia, Greece, during the

**Table 1**

Average, median concentrations and concentration ranges of PM, OC, EC,  $OC_{sec}$  and meteorological parameters of the sampling period.

| Species<br>( $\mu\text{g m}^{-3}$ ) | $PM_{10}$ (n = 44)                       |       |         |        |      | $PM_{2.5}$ (n = 44) |      |         |        |      |
|-------------------------------------|--|-------|---------|--------|------|---------------------|------|---------|--------|------|
|                                     | Min                                      | Max   | Average | Median | SD   | Min                 | Max  | Average | Median | SD   |
| C PM                                | 5.3                                      | 268.9 | 25.0    | 13.0   | 41.8 | 2.0                 | 71.0 | 10.0    | 7.4    | 11.0 |
| OC                                  | 0.43                                     | 9.1   | 1.6     | 1.1    | 1.4  | 0.38                | 3.0  | 1.3     | 1.0    | 0.80 |
| EC                                  | 0.03                                     | 1.4   | 0.33    | 0.19   | 0.29 | 0.06                | 0.82 | 0.24    | 0.19   | 0.28 |
| TC                                  | 0.48                                     | 10.5  | 1.9     | 1.2    | 1.7  | 0.44                | 3.65 | 1.5     | 1.1    | 0.90 |
| OC/EC                               | 3.3                                      | 20.9  | 5.7     | 4.8    | 2.8  | 1.96                | 17.6 | 5.7     | 5.2    | 2.8  |
| OC/PM (in %)                        | 3.3                                      | 12.8  | 8.5     | 8.9    | 2.6  | 3.7                 | 31.3 | 15.2    | 14.2   | 6.3  |
| $OC_{sec}$                          | 0.11                                     | 4.39  | 0.51    | 0.35   | 0.66 | 0.10                | 2.67 | 0.81    | 0.70   | 0.58 |
| <b>Parameter</b>                    | <b>Average Value <math>\pm</math> SD</b> |       |         |        |      |                     |      |         |        |      |
| AT ( $^{\circ}\text{C}$ )           | 13 $\pm$ 2                               |       |         |        |      |                     |      |         |        |      |
| RH (%)                              | 64 $\pm$ 7                               |       |         |        |      |                     |      |         |        |      |
| SR ( $\text{W m}^{-2}$ )            | 108 $\pm$ 30                             |       |         |        |      |                     |      |         |        |      |
| WD                                  | S/SW                                     |       |         |        |      |                     |      |         |        |      |

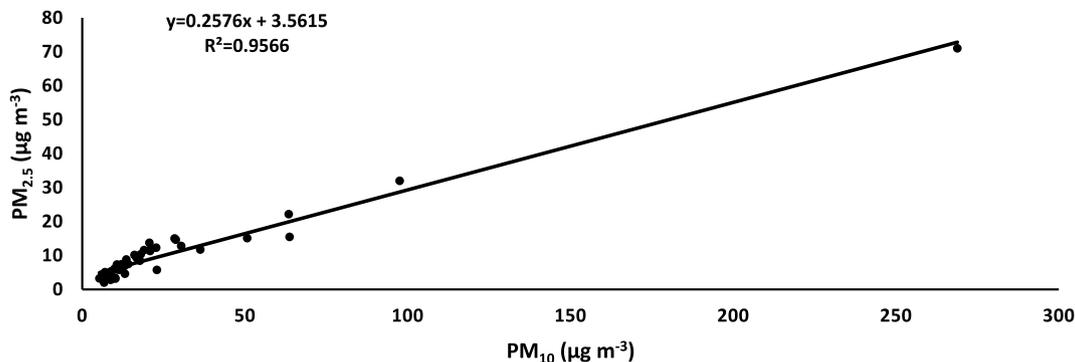


Fig. 2. PM<sub>10</sub> versus PM<sub>2.5</sub> mass concentrations.

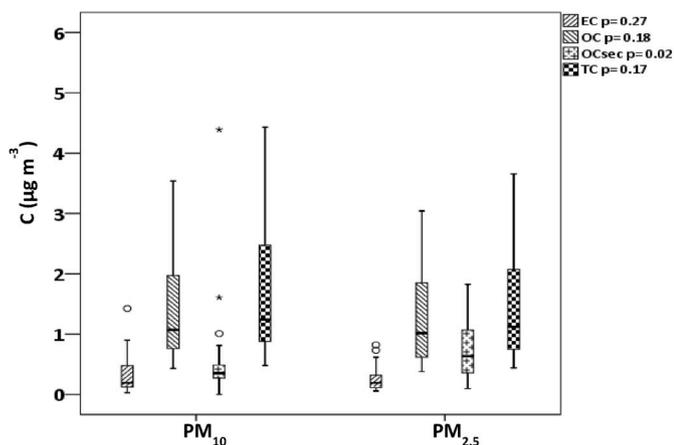


Fig. 3. Concentrations of elemental (EC), organic (OC), secondary organic (OC<sub>sec</sub>) and total carbon (TC) in PM<sub>10</sub> and PM<sub>2.5</sub> samples (° refers to values above the 3rd quartile and \* to outliers).

cold months of 2004–2006. (Liakakou et al., 2007 & 2009). The values are on the same levels with those reported for the same site in March 2015 (46 ppt) and lower than those of summer 2015 (121 ppt) (Debevec

et al., 2018).

Regarding the size distribution of the analytes, almost every one shows statistically significantly ( $p < 0.05$ ) higher concentration in PM<sub>2.5</sub>, except pinonic acid which presented higher but not significantly higher concentration ( $p = 0.053$ ). Dicarboxylic acids are found from 1.5 to 4.4 times higher in PM<sub>2.5</sub>. Similar size distribution of dicarboxylic acids is presented by Van Pinxteren et al. (2014) where dicarboxylic acids in particles with aerodynamic diameter of 0.14–1.2 µm having significantly higher concentrations ( $p < 0.05$ ) than in coarse particles (Van Pinxteren et al., 2014). Our results are also mostly comparable to those presented by Li et al. (2013) where most of their studied analytes showed higher concentrations in fine mode particles (<2.1 µm) (Li et al., 2013). Among pinene oxidation products pinic and 3-hydroxyglutaric acids were found mainly in fine particles (1.7- and 2.4-times higher concentration in PM<sub>2.5</sub>, respectively). However, pinonic acid didn't show significant difference regarding its concentration in PM<sub>10</sub> and PM<sub>2.5</sub> ( $p = 0.053$ ). A reason for this can be the high volatility of pinonic acid (Li et al., 2013). Secondary products from isoprene were from 2.2 to 2.9 times more abundant in PM<sub>2.5</sub>, as well as malic acid and levoglucosan are mainly associated with fine particles as also observed by (Graham et al., 2003). Aromatic acids presented 1.7–2.3 times higher concentrations in PM<sub>2.5</sub> as well. Monocarboxylic acids were found from 2.3 (oleic acid) to 3.6 times (stearic acid) higher in PM<sub>2.5</sub> indicating that these compounds are associated mostly with the fine mode.

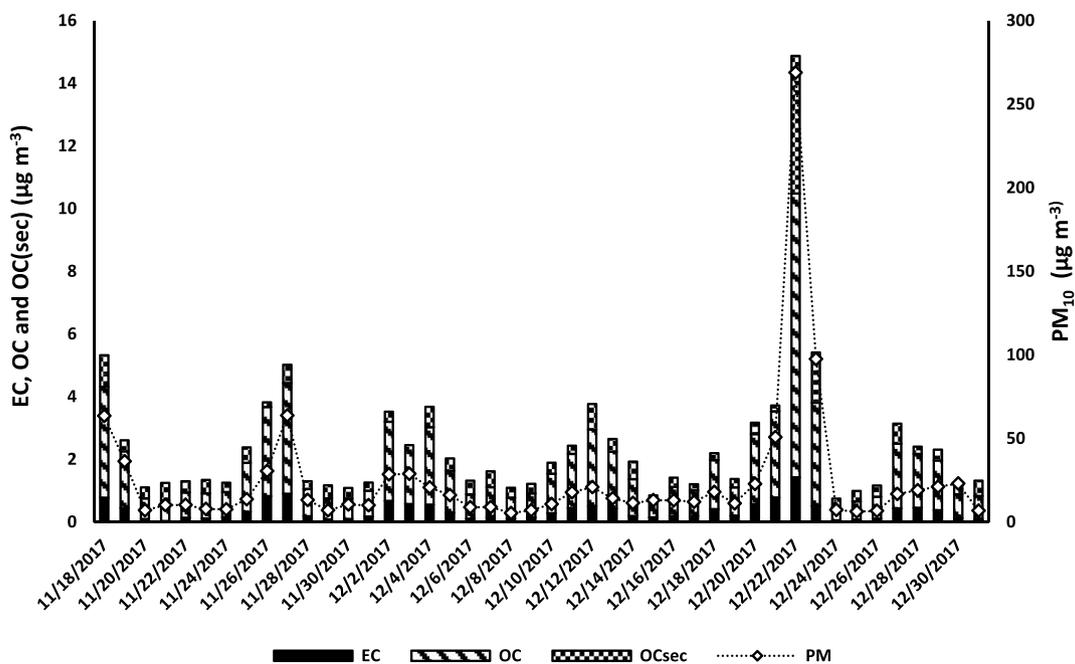


Fig. 4. Daily variation of PM<sub>10</sub>, OC, EC and OC<sub>sec</sub> concentrations.

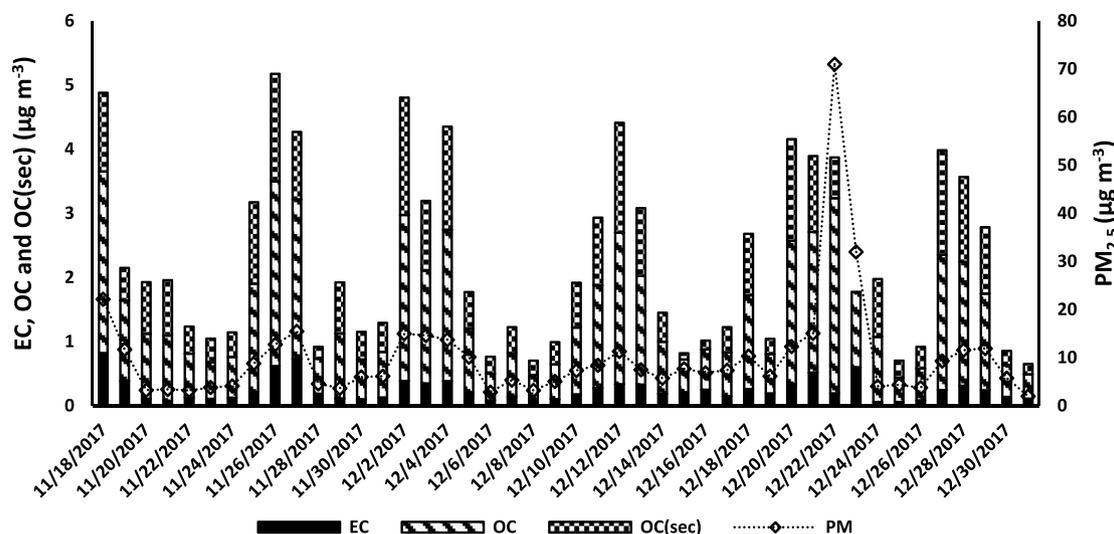


Fig. 5. Daily variation of  $PM_{2.5}$ , OC, EC and  $OC_{sec}$  concentrations.

Table 2

Minimum, maximum, median concentrations and concentration ranges of volatile organic compounds and inorganic gases during the sampling period ( $n = 44$ ).

| Organic Compounds                                   | Min   | Max   | Median | SD   |
|---|-------|-------|--------|------|
| Benzene ( $ng\ m^{-3}$ )                            | 84.8  | 320   | 178    | 69.1 |
| Toluene   | 15.8  | 200   | 74.1   | 43.8 |
| m + p Xylene  | 1.3   | 38.3  | 4.7    | 9.7  |
| o- Xylene   | 1.1   | 20.0  | 5.4    | 5.3  |
| Ethylbenzene  | 1.0   | 13.8  | 1.5    | 3.1  |
| Isoprene  | 24.6  | 543   | 115    | 95.1 |
| 1,3-Butadiene                                       | 2.8   | 46    | 2.3    | 10.3 |
| <b>Inorganic gases (<math>\mu g\ m^{-3}</math>)</b> |       |       |        |      |
| $NO_x$  | 1.9   | 6.6   | 3.3    | 1.2  |
| $SO_2$  | 0.18  | 3.2   | 0.89   | 1.3  |
| $O_3$   | 71.8  | 102.9 | 82.7   | 0.84 |
| CO  | 111.8 | 82.7  | 156.8  | 8.0  |

Comparison of the concentration levels of studied analytes with those of other studies is presented in Table S3.

### 3.2.2. BVOCs oxidation products

In this study, six compounds known as oxidation products of BVOCs such as isoprene and pinenes have been detected. Pinic and pinonic acids are the major reaction products of the oxidation of  $\alpha/\beta$ -pinene with  $O_3$  or OH radicals in a  $NO_x$  free environment (Eddingsaas et al., 2012), whereas 3-hydroxyglutaric acid is generated from monoterpene oxidation in a  $NO_x$ -present atmosphere (Claeys et al., 2007; Lyu et al., 2017). The most representative isoprene SOA tracers include the 2-methyltetrol isomers (2-methylerythritol and 2-methylthreitol) (Claeys et al., 2004; Surratt et al., 2006) and 2-methylglyceric acid which is mostly formed in  $NO_x$  rich atmosphere (Surratt et al., 2006). Pinene SOA tracers exhibited higher concentrations than isoprene SOA tracers in both PM fractions (Table 3). In  $PM_{2.5}$  samples, the median concentration of the total pinene SOA tracers was approximately 1.6 times higher than the sum of isoprene SOA tracers ( $12.9 \pm 3.2$  versus  $8.1 \pm 2.0\ ng\ m^{-3}$ ). Same trend was observed in  $PM_{10}$  fraction where concentrations of pinene SOA tracers were 1.9 higher those of isoprene ( $7.1 \pm 3.8$  versus  $3.7 \pm 0.80\ ng\ m^{-3}$ ). This difference is in agreement with (Debevec et al., 2018) who found in the same site,  $\alpha+\beta$  pinene levels over 2 times higher than isoprene levels on June–July of 2015 approximately 5 times higher on winter of 2015 (Debevec et al., 2017, 2018). This indicates that

pinene oxidation is the main biogenic source of SOA in this region. In other studies, in three China sites isoprene oxidation dominates pinene oxidation (Lyu et al., 2017; Li et al., 2018a; Hong et al., 2019). On the contrary, in Marseille and Los Angeles pinene oxidation is a more important source of SOA (Stone et al., 2009; El Haddad et al., 2011). Among the pinene SOA tracers, the most abundant was pinic acid with median concentration  $6.9 \pm 1.8\ ng\ m^{-3}$  for  $PM_{2.5}$  and  $4.1 \pm 1.8\ ng\ m^{-3}$  for  $PM_{10}$  samples, followed by 3-hydroxyglutaric acid in  $PM_{2.5}$  ( $3.4 \pm 0.83\ ng\ m^{-3}$ ) and by pinonic acid in  $PM_{10}$  ( $1.9 \pm 1.3\ ng\ m^{-3}$ ). The dominance of pinic over pinonic acid can be attributed to low vapor pressure of the former, as also described by (Deshmukh et al., 2019) in summer time aerosols in Alaska and by (Hong et al., 2019) in all-year round aerosols, but especially during the fall-winter period, pinic acid was found about 5 times higher than pinonic acid. On the other hand, in two mountainous sites in China 3-hydroxyglutaric acid was greatly higher than the sum of pinic and pinonic acids indicating that different formation pathways are favored (Lyu et al., 2017; Ren et al., 2019).

Of isoprene SOA tracers, 2-methylerythritol was the most abundant ( $4.9 \pm 0.92$  for  $PM_{2.5}$  and  $2.2 \pm 0.47\ ng\ m^{-3}$  for  $PM_{10}$ ) followed by 2-methylthreitol. The least abundant isoprene SOA tracer was 2-methylglyceric acid with median values of  $1.1 \pm 0.38$  and  $0.43 \pm 0.19\ ng\ m^{-3}$  in  $PM_{2.5}$  and  $PM_{10}$  samples respectively. Furthermore, the low concentrations of 2-methylglyceric acid (approximately 4.5 times than 2-methylerythritol) can be explained by the low  $NO_x$  levels of the sampling site meaning that other processes of isoprene oxidation are favored. In contrast, in the North China Plain, where  $NO_x$  levels are close to 20 ppb, 2-methylglyceric acid was observed higher than 2-methylthreitol and close to 2-methylerythritol (Li et al., 2018b). The ratios of 2-methylerythritol/2-methylthreitol, in our study, were  $2.1 \pm 0.60$  in  $PM_{2.5}$  and  $2.2 \pm 0.5$  in  $PM_{10}$  fraction, values that are in agreement with the most studies in the literature (Fu et al., 2009, 2010; Ding et al., 2012; Li et al., 2018b).

Concerning the potential associations among the BVOCs oxidation products we observed strong and significant correlations between pinene oxidation products ( $r = 0.70\text{--}0.84$ ,  $p < 0.01$  in  $PM_{2.5}$  and  $r = 0.68\text{--}0.86$ ,  $p < 0.01$  in  $PM_{10}$  aerosol samples, Tables S4 and S5) potentially confirming their same source and possible same formation pathways. Similarly, regarding the isoprene oxidation products, very strong correlations were observed between 2-methylerythritol and 2-methylthreitol in both PM fractions ( $r = 0.92$ ,  $p < 0.01$  in  $PM_{2.5}$  and  $r = 0.91$  in  $PM_{10}$  particles), revealing identical formation pathways. However, lower but significant correlations were found between 2-

**Table 3**Minimum, maximum, median concentrations and concentration ranges of polar organic compounds in PM<sub>10</sub> and PM<sub>2.5</sub> during the sampling period.

| Species<br>(ng m <sup>-3</sup> ) | PM <sub>10</sub> (n = 44) |      |        |      | PM <sub>2.5</sub> (n = 44) |      |        |      | p-value |
|----------------------------------|---------------------------|------|--------|------|----------------------------|------|--------|------|---------|
|                                  | Min                       | Max  | Median | SD   | Min                        | Max  | Median | SD   |         |
| <b>Linear dicarboxylic acids</b> |                           |      |        |      |                            |      |        |      |         |
| Succinic (diC <sub>4</sub> )     | 1.0                       | 13.2 | 5.5    | 3.3  | 2.0                        | 22.9 | 8.1    | 5.9  | 0.008   |
| Malic (dihC <sub>4</sub> )       | 1.1                       | 4.3  | 2.0    | 0.88 | 3.1                        | 13.9 | 4.8    | 2.5  | 0.000   |
| Glutaric (diC <sub>5</sub> )     | 0.25                      | 3.0  | 1.0    | 0.63 | 0.64                       | 12.8 | 3.2    | 3.3  | 0.015   |
| Adipic (diC <sub>6</sub> )       | 0.15                      | 8.6  | 2.2    | 1.8  | 1.1                        | 12.6 | 3.2    | 2.9  | 0.015   |
| Pimelic (diC <sub>7</sub> )      | 0.15                      | 2.8  | 0.40   | 0.66 | 0.38                       | 3.9  | 0.98   | 0.88 | 0.000   |
| Suberic (diC <sub>8</sub> )      | 0.09                      | 9.4  | 1.3    | 1.7  | 1.1                        | 12.9 | 2.4    | 2.9  | 0.000   |
| Azelaic (diC <sub>9</sub> )      | 0.55                      | 10.3 | 2.4    | 2.2  | 0.74                       | 14.8 | 5.8    | 3.5  | 0.000   |
| Sebacic (diC <sub>10</sub> )     | 0.11                      | 2.6  | 0.80   | 0.67 | 0.58                       | 10.7 | 3.5    | 2.2  | 0.000   |
| Σdicarboxylic acids              | 7.6                       | 37.4 | 18.0   | 7.1  | 8.7                        | 82.0 | 35.3   | 16.1 | 0.000   |
| <b>BVOCs oxidation products</b>  |                           |      |        |      |                            |      |        |      |         |
| Pinic acid                       | 1.6                       | 10.1 | 4.1    | 1.8  | 2.6                        | 11.8 | 6.9    | 1.8  | 0.000   |
| Pinonic acid                     | 0.18                      | 5.3  | 1.9    | 1.3  | 0.86                       | 4.8  | 2.7    | 0.77 | 0.053   |
| 3-Hydroxyglutaric acid           | 0.92                      | 5.5  | 1.4    | 1.1  | 1.3                        | 5.7  | 3.4    | 0.83 | 0.000   |
| 2-Methylglyceric acid            | 0.20                      | 1.1  | 0.43   | 0.19 | 0.32                       | 2.0  | 1.1    | 0.38 | 0.000   |
| 2-Methylthreitol                 | 0.69                      | 0.95 | 0.80   | 0.67 | 0.78                       | 5.6  | 2.3    | 0.90 | 0.000   |
| 2-Methylerythritol               | 1.9                       | 4.1  | 2.2    | 0.47 | 3.2                        | 8.5  | 4.9    | 0.92 | 0.000   |
| ΣPinene SOA tracers              | 2.9                       | 20.8 | 7.1    | 3.8  | 5.1                        | 21.2 | 12.9   | 3.2  | 0.000   |
| ΣIsoprene SOA tracers            | 3.0                       | 6.5  | 3.7    | 0.80 | 4.4                        | 16.1 | 8.1    | 2.0  | 0.000   |
| ΣBVOCs SOA tracers               | 7.3                       | 25.3 | 11.0   | 3.9  | 12.9                       | 29.0 | 21.1   | 3.7  | 0.000   |
| <b>Aromatic acids</b>            |                           |      |        |      |                            |      |        |      |         |
| Phthalic                         | 0.20                      | 4.7  | 2.0    | 0.77 | 0.22                       | 8.9  | 4.4    | 2.1  | 0.000   |
| Isophthalic                      | 0.18                      | 0.54 | 0.39   | 0.08 | 0.20                       | 1.3  | 0.70   | 0.38 | 0.037   |
| Terephthalic                     | 0.24                      | 4.0  | 1.0    | 0.90 | 1.1                        | 7.8  | 2.3    | 1.7  | 0.000   |
| Trimellitic                      | 0.28                      | 4.1  | 1.2    | 1.1  | 0.45                       | 5.9  | 2.4    | 1.2  | 0.000   |
| Σaromatic acids                  | 2.7                       | 9.6  | 5.1    | 1.7  | 1.9                        | 19.6 | 9.9    | 4.3  | 0.000   |
| <b>Monocarboxylic acids</b>      |                           |      |        |      |                            |      |        |      |         |
| Palmitic (C16)                   | 0.33                      | 16.1 | 5.5    | 4.7  | 2.3                        | 64.5 | 16.6   | 18.1 | 0.000   |
| Margaric (C17)                   | 0.57                      | 4.1  | 0.94   | 0.78 | 0.60                       | 9.8  | 2.4    | 2.1  | 0.000   |
| Stearic acid (C18)               | 0.60                      | 17.3 | 4.1    | 4.0  | 1.4                        | 58.3 | 14.6   | 14.3 | 0.000   |
| Oleic (C18:1)                    | 0.22                      | 5.9  | 1.4    | 1.5  | 0.57                       | 11.3 | 3.3    | 2.7  | 0.000   |
| Linoleic acid (C18:2)            | 0.16                      | 5.4  | 0.79   | 1.4  | 0.49                       | 7.64 | 2.0    | 1.9  | 0.000   |
| Σmonocarboxylic acids            | 2.9                       | 39.2 | 13.4   | 9.5  | 14.0                       | 162  | 55.7   | 36.5 | 0.000   |
| <b>Biomass burning tracer</b>    |                           |      |        |      |                            |      |        |      |         |
| Levoglucosan                     | 0.54                      | 34.0 | 4.0    | 5.8  | 1.0                        | 30.8 | 7.1    | 5.4  | 0.014   |

methylglyceric acid and the two methyltetrols (MTL2:  $r = 0.48$ ,  $p < 0.01$  in PM<sub>2.5</sub> and  $r = 0.54$ ,  $p < 0.01$  in PM<sub>10</sub>) (MTL1:  $r = 0.54$ ,  $p < 0.01$  in PM<sub>2.5</sub> and  $r = 0.47$ ,  $p < 0.01$  in PM<sub>10</sub>) suggesting that their formation procedures may differ (Tables S4 and S5). Similar correlations of 2-methylglyceric acid were noticed in an urban site of Marseille (El Haddad et al., 2011). Ratios of the sum of methyltetrols to 2-methylglyceric acid appear to be affected by the NO<sub>x</sub> (NO + NO<sub>2</sub>) levels even in this low NO<sub>x</sub> atmosphere. In particular, in PM<sub>2.5</sub> samples the above ratio correlated significantly with NO<sub>x</sub> ( $r = |0.64|$ ,  $p < 0.01$ ) (Fig. 6). Same trend was found also in PM<sub>10</sub> samples ( $r = |0.60|$ ,  $p < 0.01$ ) suggesting that the increase in NO<sub>x</sub> concentrations could affect the isoprene SOA formation.

Interestingly, isoprene levels are poorly correlated with 2-methyltetrols values of the same day ( $R^2 = 0.001$  for PM<sub>2.5</sub>,  $R^2 = 0.02$  for PM<sub>10</sub>)

(Fig. 7), but the correlation significantly increases with the next day values of 2-methyltetrols ( $R^2 = 0.55$  for PM<sub>2.5</sub>,  $R^2 = 0.54$  for PM<sub>10</sub>) indicating the reaction time between isoprene and O<sub>3</sub>. This outcome is in accordance with the calculated atmospheric lifetime of isoprene with O<sub>3</sub> (1.3 days) (Atkinson and Arey, 2003). Although the OH-initiated oxidation of isoprene is favored, isoprene ozonolysis was suggested as an important contributor to SOA formation in urban and rural areas (Rattanavara et al., 2016; Li et al., 2018b).

### 3.2.3. Linear dicarboxylic acids

A homologous series of linear dicarboxylic acids, from 4 to 10 carbon atoms as well as malic acid (2-hydroxybutanedioic acid) were detected in both PM<sub>10</sub> and PM<sub>2.5</sub> samples during the sampling period. In general, linear dicarboxylic acids can be emitted into the atmosphere by both

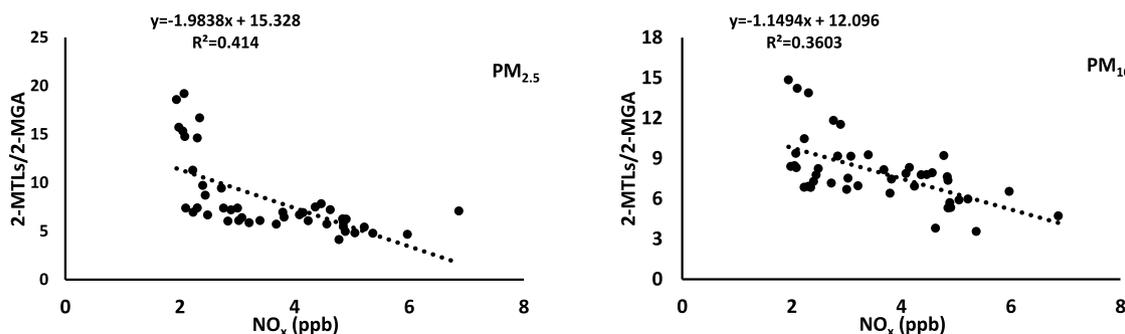


Fig. 6. Scatter plot of NO<sub>x</sub> versus the ratio of MTLs (sum of 2-methylerythritol+2-methylthreitol) to 2-methylglyceric acid in PM<sub>2.5</sub> (left) and PM<sub>10</sub> (right) samples.

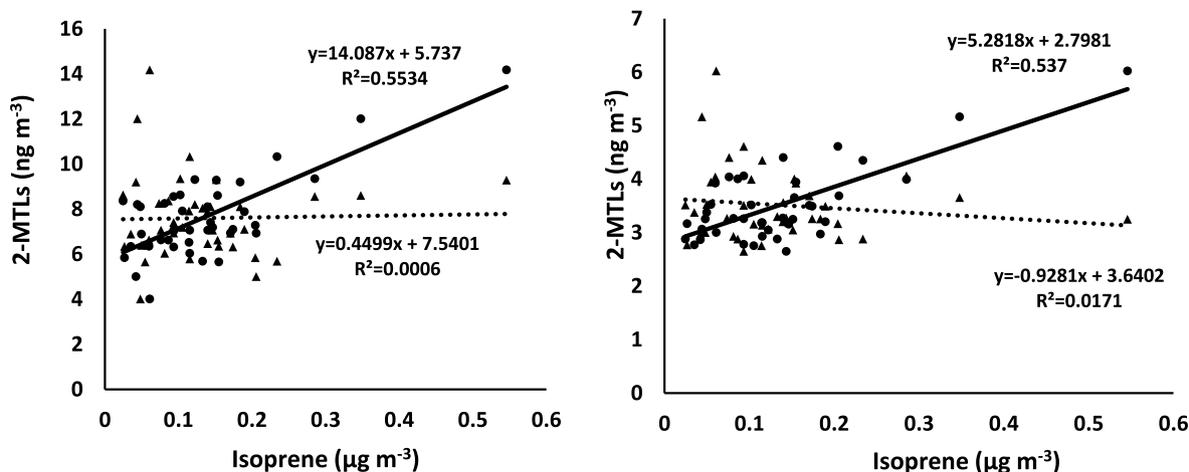


Fig. 7. Scatter plot of isoprene versus MLTs (sum of 2-methylerythritol+2-methylthreitol) in the same (triangle) and next day (circle) in PM<sub>2.5</sub> (left) and PM<sub>10</sub> (right) samples.

primary and secondary sources. Primary sources include biomass burning (Kundu et al., 2010a; Cao et al., 2017) and fossil fuel combustion (Kawamura and Kaplan, 1987). Dicarboxylic acids can also be formed by the oxidation of biogenic and anthropogenic olefins (Hatakeyama et al., 1987; Stephanou and Stratigakis, 1993; Gao et al., 2004; Jaoui et al., 2017). Another formation pathway of lower molecular weight dicarboxylic acids might be the oxidation of their higher homologues (Yang et al., 2008). As far as malic acid is concerned, until now, there has been no reliable evidence about its primary sources (Hu and Yu, 2013). Malic acid can be formed by the ozonolysis of some olefins i.e. cyclopentene, cyclohexene and 1-methylcyclopentene (Gao et al., 2004), isoprene (Claeys et al., 2004) and is also believed to be an intermediate of the oxidation of unsaturated fatty acids (Kawamura and Ikushima, 1993). In PM<sub>2.5</sub> aerosol samples of our study, succinic acid was the most abundant dicarboxylic acid with median concentration  $8.1 \pm 5.9 \text{ ng m}^{-3}$  (Table 3), followed by azelaic acid with a median of  $5.8 \pm 3.5 \text{ ng m}^{-3}$ . Lower concentrations have been observed for malic acid (from  $3.1$  to  $13.9 \text{ ng m}^{-3}$ , with a median of  $4.8 \text{ ng m}^{-3}$ ). The two C<sub>4</sub> diacids accounted for  $37.8 \pm 18.3\%$  of the total measured linear dicarboxylic acids (Table 4). Glutaric and adipic acids exhibited almost the same concentration in PM<sub>2.5</sub> samples i.e.  $3.2 \pm 3.3$  and  $3.2 \pm 2.9 \text{ ng m}^{-3}$  respectively. Pimelic acid was the least abundant dicarboxylic acid in our study with median concentration  $0.98 \pm 0.88 \text{ ng m}^{-3}$  accounting for  $3.3 \pm 3.3\%$  of the total diacids. Among low molecular weight dicarboxylic acids, good correlations were observed (Table S4). Particularly, correlation coefficients among succinic, glutaric and adipic acid ranged from 0.73 to 0.77 ( $p < 0.01$ ) attributing to the same source. In addition, each of the mentioned dicarboxylic acids exhibits strong correlation with phthalic acid ( $r = 0.72\text{--}0.77$ ,  $p < 0.01$ ) indicating common anthropogenic sources (see below). Comparable correlations were observed in a background location in Sweden (Hyder et al., 2012), during a one-year study, and in Pearl River Delta region of south China (Zhao et al., 2014).

Table 4  
Relative abundance (%) of linear dicarboxylic acids in PM<sub>10</sub> and PM<sub>2.5</sub> samples.

| Linear dicarboxylic acids    | PM <sub>10</sub> (n = 44) |      |      |        | PM <sub>2.5</sub> (n = 44) |      |      |        |
|------------------------------|---------------------------|------|------|--------|----------------------------|------|------|--------|
|                              | Relative abundance %      | Min  | Max  | Median | SD                         | Min  | Max  | Median |
| Succinic (diC <sub>4</sub> ) | 12.2                      | 55.0 | 30.0 | 10.5   | 1.0                        | 51.2 | 22.9 | 10.8   |
| Malic (dihC <sub>4</sub> )   | 5.3                       | 20.8 | 11.5 | 3.5    | 5.3                        | 38.2 | 14.9 | 7.5    |
| Glutaric (diC <sub>5</sub> ) | 1.6                       | 14.1 | 6.1  | 3.1    | 0.96                       | 25.9 | 9.6  | 6.6    |
| Adipic (diC <sub>6</sub> )   | 1.1                       | 34.6 | 12.8 | 7.8    | 1.5                        | 22.7 | 9.7  | 4.4    |
| Pimelic (diC <sub>7</sub> )  | 0.08                      | 23.2 | 2.1  | 4.9    | 0.82                       | 17.0 | 3.3  | 3.3    |
| Suberic (diC <sub>8</sub> )  | 0.55                      | 28.5 | 7.7  | 6.0    | 3.0                        | 23.2 | 7.6  | 4.9    |
| Azelaic (diC <sub>9</sub> )  | 5.9                       | 34.7 | 17.9 | 8.1    | 3.0                        | 41.0 | 15.4 | 8.7    |
| Sebacic (diC <sub>10</sub> ) | 0.13                      | 11.4 | 4.6  | 2.9    | 0.86                       | 28.2 | 9.1  | 6.3    |

High molecular weight dicarboxylic acids (diC<sub>8</sub>–diC<sub>10</sub>) are considered as photooxidation products of unsaturated fatty acids (Kawamura and Gagosian, 1987; Stephanou and Stratigakis, 1993; Ho et al., 2010). Suberic and sebacic acids are significantly correlated ( $r = 0.68$ ,  $p < 0.01$ ) suggesting that they have common source. However, azelaic acid isn't as strong correlated with the previous acids ( $r = 0.30$  and  $0.36$  respectively,  $p < 0.05$ ) but shows interesting relationship with biomass burning as it highly correlated with levoglucosan ( $r = 0.69$ ,  $p < 0.01$ ). The main source of diC<sub>8</sub> and diC<sub>10</sub> acids may be the oxidation of fatty acids as both are satisfactorily correlated with the sum of oleic ( $r = 0.83$ ) and linoleic ( $r = 0.69$ ) acids. However, biomass burning might also enhance the formation of suberic and sebacic acids as they are significantly ( $p < 0.01$ ) but moderately correlated with levoglucosan ( $r = 0.47$ ,  $0.45$  respectively). Biomass burning has already reported to enrich the aerosols with dicarboxylic acids (Kawamura et al., 2013; Cao et al., 2017). Malic acid in PM<sub>2.5</sub> samples is strongly correlated ( $r = 0.64$ ,  $p < 0.01$ ) (Fig. 8) with the sum of pinene oxidation tracers indicating that pinene oxidation might be the source of malic acid. Same correlation is observed as well in PM<sub>2.5</sub> samples in Hong Kong during both summer and winter periods (Hu and Yu, 2013). Lately, 1,3-butadiene was proposed as a precursor of malic acid following similar reaction pathways with isoprene (Jaoui et al., 2014), though such relationship is most likely to occur at urban aerosols. However, in this study, concentrations of 1,3-butadiene, which were measured above the detection limits, were correlated with malic acid suggesting another possible formation pathway of the latter (Fig. 9).

In PM<sub>10</sub> samples, dicarboxylic acids with 4 carbon atoms, likewise PM<sub>2.5</sub> samples, were abundant accounting together for  $41.5 \pm 14.0\%$  (Table 4.) of the total measured dicarboxylic acids. In particular, succinic acid showed the highest concentrations from  $1.0$  to  $13 \text{ ng m}^{-3}$  (median concentration,  $5.5 \text{ ng m}^{-3}$ ). Corresponding concentrations of malic acid varied from  $1.1$  to  $4.3 \text{ ng m}^{-3}$  (median value,  $2.0 \text{ ng m}^{-3}$ ).

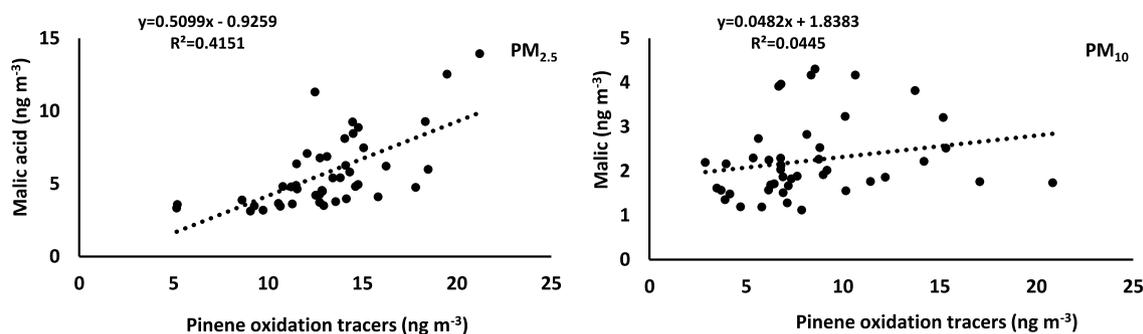


Fig. 8. Scatter plot of pinene oxidation tracers versus malic acid in  $PM_{2.5}$  and  $PM_{10}$  samples.

Adipic and azelaic acids were more relatively abundant in  $PM_{10}$  samples accounting for  $12.8 \pm 7.8\%$  and  $17.9 \pm 8.1\%$  respectively, of the total measured linear diacids. Glutaric acid exhibited lower relative abundance ( $6.1 \pm 3.1\%$ ) in  $PM_{10}$  samples and pimelic acid was found again with the lowest concentrations ( $0.40 \pm 0.66 \text{ ng m}^{-3}$ ). Differently from  $PM_{2.5}$  samples, sebacic acid presented lower concentrations than suberic acid (median concentration of 1.3 versus  $0.80 \text{ ng m}^{-3}$ ). The profile of dicarboxylic acids observed in this work is in agreement with that presented in a rural site of China where succinic acid was dominant followed by azelaic acid (Zhao et al., 2014) (Table S3). However, in other studies azelaic acid was found to be the most abundant diacid followed by succinic and suberic acids (Hyder et al., 2012; Yin et al., 2014).

Low molecular weight dicarboxylic acids in  $PM_{10}$  show different correlations compared to those in  $PM_{2.5}$ . For example, succinic acid isn't strongly correlated with glutaric ( $r = 0.55$ ,  $p < 0.01$ ) and adipic ( $r = 0.57$ ,  $p < 0.01$ ) acids (Table S5.) but is more associated with malic acid ( $r = 0.61$ ,  $p < 0.01$ ) meaning that succinic acid possibly has different origin in higher diameter particles. On the other hand, glutaric and adipic acids are significantly correlated with each other ( $r = 0.74$ ,  $p < 0.01$ ) and both of them with phthalic acid ( $r = 0.65$  and  $0.74$ ,  $p < 0.01$  respectively) revealing anthropogenic sources of the former acids. Another interesting difference between  $PM_{10}$  and  $PM_{2.5}$  samples is that malic acid is stronger correlated with succinic acid ( $r = 0.61$ ,  $p < 0.01$ ) than with pinene oxidation tracers ( $r = 0.21$ ,  $p < 0.05$ ) (Fig. 8) which means that pinene oxidation isn't the main source of malic acid. In addition, malic acid didn't show significant correlation with 1,3-butadiene as it was observed in  $PM_{2.5}$  samples (Fig. 9). Furthermore, significant ( $p < 0.01$ ) correlations were observed between suberic, azelaic and sebacic acids ( $r = 0.69$ – $0.76$ ) (Table S5) suggesting that they are generated from the same source, such as the oxidation of unsaturated fatty acids. This hypothesis can be reinforced by the strong correlations between each individual diacid (diC8–diC10) with linoleic and oleic acids.

### 3.2.4. Aromatic acids

Three aromatic dicarboxylic acids (phthalic, terephthalic and

isophthalic) and one aromatic tricarboxylic acid (trimellitic acid) were detected in this study. Although phthalic acids are reported to be primarily emitted by motor exhaust (Kawamura and Kaplan, 1987) or through plastic burning (Simoneit et al., 2005) they have been observed as oxidation products of naphthalene and methyl naphthalene in both high and zero  $NO_x$  levels (Kleindienst et al., 2012; Kautzman et al., 2010). Recently, phthalic acid was proposed for the first time as SOA tracer for naphthalene photooxidation (Al-Naiema and Stone, 2017). Additionally, polycarboxylic aromatic compounds such as trimellitic acid have been used as SOA tracer (Sheesley et al., 2004; Stone et al., 2011), though primary sources are reported as well (Simoneit, 1985). Therefore, it is clear that there are many contributors of aromatic acids into the atmosphere and thus field studies need to predict the fate and sources of these acids (Al-Naiema and Stone, 2017). In this study, phthalic acid was the most abundant among aromatic carboxylic acids both in  $PM_{2.5}$  (median concentration  $4.4 \pm 2.1 \text{ ng m}^{-3}$ ) and  $PM_{10}$  (median of  $2.0 \pm 0.77 \text{ ng m}^{-3}$ ) aerosol samples. Trimellitic and terephthalic acids presented lower and comparable median concentrations in both PM fractions, respectively equal to  $2.4 \pm 1.2$  and  $2.3 \pm 1.7 \text{ ng m}^{-3}$  in  $PM_{2.5}$  and equal to  $1.2 \pm 1.1$  and  $1.0 \pm 0.90$  in  $PM_{10}$ . Isophthalic acid presented the lowest levels in both  $PM_{2.5}$  ( $0.70 \pm 0.38 \text{ ng m}^{-3}$ ) and  $PM_{10}$  ( $0.39 \pm 0.08 \text{ ng m}^{-3}$ ) (Table 3). Comparable levels of phthalic acid isomers have been measured in mountainous aerosols in China (Li et al., 2013) (Table S3) but in urban/rural aerosols those are significantly increased (Ho et al., 2007; Zhao et al., 2014; Zhu et al., 2017).

As described above (3.2.3), phthalic acid showed high correlation with low molecular weight dicarboxylic acids in  $PM_{2.5}$  ( $r = 0.72$ – $0.77$ ,  $p < 0.01$ ), but weaker association with the other aromatic acids. For example, the correlation coefficient of phthalic acid with isophthalic, terephthalic and trimellitic acids was 0.46, 0.46 ( $p < 0.05$ ) and 0.55 ( $p < 0.01$ ) respectively. The weak relationship between phthalic and its other isomers combined with the strong correlation of terephthalic and isophthalic acids with levoglucosan ( $r = 0.63$  &  $0.62$ ,  $p < 0.01$ ) (see below) indicates that secondary transformation may be the source of phthalic acid and biomass burning the source of its isomers, although association between phthalic acid and biomass burning has been

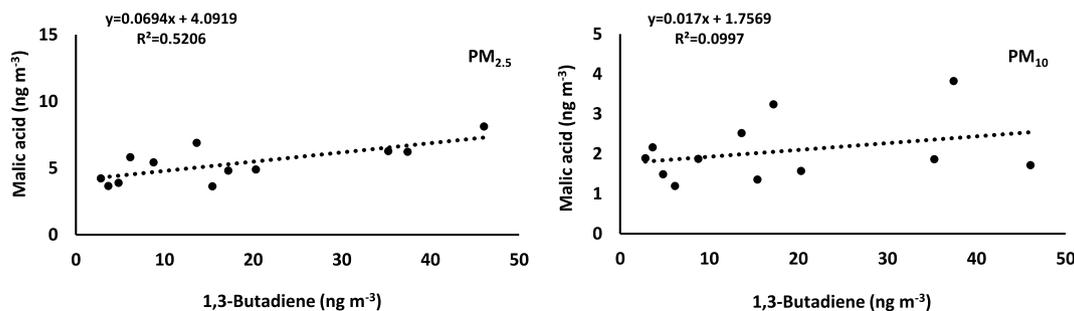


Fig. 9. Scatter plot of 1,3-Butadiene versus malic acid in  $PM_{2.5}$  (left) and  $PM_{10}$  (right) samples.

**Table 5**

Diagnostic mass ratios of Ph/diC<sub>9</sub> and diC<sub>6</sub>/diC<sub>9</sub> in comparison with other studies.

| Location                     | Ph/diC <sub>9</sub> | diC <sub>6</sub> /diC <sub>9</sub> | Particle size     | Time                   | Reference                  |
|------------------------------|---------------------|------------------------------------|-------------------|------------------------|----------------------------|
| Agia Marina Xyliatou, Cyprus | 0.52                | 0.70                               | PM <sub>10</sub>  | November–December 2018 | This study                 |
| Agia Marina Xyliatou, Cyprus | 0.71                | 0.63                               | PM <sub>2.5</sub> | November–December 2018 | This study                 |
| San Pietro, Italy            | 0.96                | 0.38                               | PM <sub>2.5</sub> | Winter 2013            | Pietrogrande et al. (2014) |
| Mainz, Germany               | 3.13                | 0.65                               | PM <sub>3</sub>   | June 2006–May 2007     | Zhang et al. (2010a)       |
| Vavihill, Sweden             | 0.40                | 0.54                               | PM <sub>10</sub>  | April 2008–March 2009  | Hyder et al. (2012)        |
| Hong Kong, roadside          | 6.50                | 0.90                               | PM <sub>2.5</sub> | Summer, winter 2003    | Ho et al. (2006)           |
| Wuhan, China                 |                     | 1.89                               | PM <sub>2.5</sub> | Winter 2011–2012       | Guo et al. (2015)          |

reported in urban aerosols in Thessaloniki, Greece (Balla et al., 2018). Also, iso- and terephthalic acids correlated strongly and significantly with each other ( $r = 0.68$ ,  $p < 0.01$ ) enhancing the hypothesis of their common origin (Table S4). Same relationship about isophthalic and terephthalic acids with biomass burning is also observed in Iowa during winter (Al-Naiema and Stone, 2017). Additionally, Zhao et al. (2014) provided evidence that terephthalic acid is primarily emitted into the atmosphere in contrast with its other isomers, which are mostly secondary products, in PRD region of China, during the cold months (Zhao et al., 2014). In PM<sub>10</sub> samples, phthalic acid is well correlated with glutaric and adipic acids ( $r = 0.59$  and  $0.72$ ,  $p < 0.01$ ) but again poorly correlated with the other aromatic acids ( $r = 0.05$  with terephthalic,  $0.11$  with isophthalic and  $0.03$  with trimellitic acids) suggesting same origin as in PM<sub>2.5</sub>. Terephthalic and isophthalic acids are well correlated ( $r = 0.73$ ,  $p < 0.01$ ), as in PM<sub>2.5</sub>, leading to the conclusion that they have similar origin. Both the latter acids as well as trimellitic are moderately but significantly correlated with levoglucosan, ( $r = 0.42$ – $0.55$ ,  $p < 0.01$ , respectively) indicating possible enhances from biomass burning (Table S5).

### 3.2.5. Monocarboxylic acids

Monocarboxylic acids are ubiquitous compounds of the atmosphere and they have been detected in rural, marine and urban aerosols (Mochida et al., 2002; Shannigrahi et al., 2014; Guo et al., 2015). In this work, three saturated monocarboxylic acids have been detected including palmitic, margaric and stearic and two unsaturated including oleic and linoleic. All of them are considered Low molecular weight Fatty Acids (LFAs  $C \leq 20$ ) and they can be emitted into the atmosphere from plenty of sources such as vegetation, phytoplankton, biomass burning emissions and microbial activity; (Simoneit and Mazurek, 1982; Kawamura et al., 2003; Oliveira et al., 2007). For example, oleic and linoleic acids can be issued into the atmosphere from the leaf surface of terrestrial plants (Yokouchi and Ambe, 1986). Emissions from cooking operations is an additional source of monocarboxylic acids and especially of palmitic acid and stearic acid (Schauer et al., 1999).

In this study, palmitic and stearic acids were dominant in both aerodynamic diameter fractions with median concentrations respectively equal to  $16.6 \pm 18.1$  and  $14.6 \pm 14.3$  ng m<sup>-3</sup> in PM<sub>2.5</sub> and equal to  $5.5 \pm 4.7$  and  $4.1 \pm 4.0$  ng m<sup>-3</sup> in PM<sub>10</sub> which are higher than those measured in Mt Tai, China (Zhu et al., 2017) (Table S3) but over 10 times lower than those measured in Beijing (Ren et al., 2016). Margaric acid was detected in quite lower concentrations for both fractions i.e. median of  $2.4 \pm 2.1$  ng m<sup>-3</sup> in PM<sub>2.5</sub> and  $0.94 \pm 0.78$  ng m<sup>-3</sup> in PM<sub>10</sub>. The predominance of even carbon number monocarboxylic acids is

generally observed in many studies (Guo et al., 2015; Kang et al., 2016). Unsaturated fatty acids (sum of oleic and linoleic) presented median concentrations of  $5.1 \pm 4.5$  ng m<sup>-3</sup> in PM<sub>2.5</sub> and  $2.0 \pm 2.9$  ng m<sup>-3</sup> in PM<sub>10</sub> which are quite higher than those reported in a background marine aerosol site in Greece but lower than those measured in forest sites (Kavouras and Stephanou, 2002).

Oleic and linoleic were greatly correlated with each other in both aerodynamic diameter aerosol samples ( $r = 0.94$  for PM<sub>2.5</sub>,  $r = 0.99$  for PM<sub>10</sub>,  $p < 0.01$ ) confirming their common origin. Comparably strong correlations were observed for palmitic versus stearic acids ( $r = 0.81$  for PM<sub>2.5</sub>,  $r = 0.93$  for PM<sub>10</sub>,  $p < 0.01$ ), proposing that they have similar source. Margaric acid showed a significant association with levoglucosan ( $r = 0.55$ ,  $p < 0.01$ ) only in PM<sub>2.5</sub> samples suggesting probably enhancement from biomass burning.

### 3.2.6. Biomass burning tracer

The tracer of biomass burning (levoglucosan) was also determined. Levoglucosan is the thermal decomposition product of carbohydrates such as cellulose (Simoneit, 2002). Levoglucosan, in this study, ranged from  $1.0$  to  $30.8$  ng m<sup>-3</sup> in fine mode (median of  $7.1$  ng m<sup>-3</sup>) and from  $0.54$  to  $34.0$  in PM<sub>10</sub> samples (median of  $4.0$  ng m<sup>-3</sup>). Levels reported here are comparable with the wintertime levels in Okinawa, Japan ( $5.3 \pm 4.9$  ng m<sup>-3</sup>) (Zhu et al., 2015), a little lower than those reported in Finokalia, Greece (mean of  $12.6$ ,  $0.89$ – $142$  ng m<sup>-3</sup>) (Theodosi et al., 2018) during two campaigns and quite lower than Belgrade, Serbia (average of  $424.9$  ng m<sup>-3</sup>) (Zangrando et al., 2016). As already discussed (3.2.4), levoglucosan was mostly correlated with terephthalic, azelaic and margaric acids in PM<sub>2.5</sub>. Significant ( $p < 0.01$ ) but moderate correlation was also observed with the following acids: trimellitic ( $r = 0.50$ ), sebacic ( $r = 0.45$ ), suberic ( $r = 0.47$ ), pinic ( $r = 0.47$ ), isophthalic ( $r = 0.47$ ) phthalic ( $r = 0.43$ ), oleic ( $r = 0.41$ ) and linoleic ( $r = 0.37$ ). In PM<sub>10</sub> the only moderate but significant correlations observed were with terephthalic acid ( $r = 0.55$ ,  $p < 0.01$ ), isophthalic acid ( $r = 0.48$ ,  $p < 0.01$ ), trimellitic acid ( $r = 0.42$ ,  $p < 0.01$ ), pinonic acid ( $r = 0.38$ ,  $p < 0.05$ ) and oleic acid ( $r = 0.31$ ,  $p < 0.05$ ) (Tables S4 and S5).

### 3.3. Diagnostic mass ratios of carboxylic acids

Investigation of the potential anthropogenic or biogenic sources of organic aerosol can be performed by calculating the ratios of phthalic acid (Ph) and adipic (diC<sub>6</sub>) acid to azelaic acid (diC<sub>9</sub>) (Ho et al., 2006). In general, lower values of the above ratios show that aerosols are influenced by biogenic sources. In contrast, higher values indicate influences from anthropogenic emissions. In the present study, Ph/diC<sub>9</sub> ratio ranged from  $0.04$  to  $2.8$  (mean

Value  $0.71 \pm 0.81$ ) in PM<sub>2.5</sub>, whereas in PM<sub>10</sub> from  $0.01$  to  $4.2$  (mean value  $0.52 \pm 0.75$ ). Respectively, diC<sub>6</sub>/diC<sub>9</sub> value ranged from  $0.02$  to  $2.8$  (mean value  $0.63 \pm 0.64$ ) in PM<sub>2.5</sub> samples while in PM<sub>10</sub>, the same ratio ranged from  $0.04$  to  $4.7$  (mean value  $0.70 \pm 0.90$ ). The values of Ph/diC<sub>9</sub> determined in this work are considerably lower than those reported in Mainz ( $3.13$ ) (Zhang et al., 2010a) and Hong Kong ( $6.50$ ) (Ho et al., 2006) which are rural/urban and urban sites respectively, lower than San Pietro (rural site) ( $0.93$ ) during the wintertime of 2013 (Pietrogrande et al., 2014) and higher than Vavihill (background site) ( $0.40$ ) during a one-year study (Hyder et al., 2012). Furthermore, diC<sub>6</sub>/diC<sub>9</sub> value was quite lower than Wuhan ( $1.89$ ) (Guo et al., 2015), lower than Hong Kong ( $0.90$ ) (Ho et al., 2006) and on the same levels with those reported in the rural/urban site in Mainz (Zhang et al., 2010a).

The calculated ratio levels in Agia Marina Xyliatou, show that aerosols are mainly impacted by biogenic sources but anthropogenic emissions are not negligible. Comparison of the mentioned mass ratios with ratios of other studies can be observed in Table 5.

Apart from source estimation, aerosol aging can be additionally assessed from the ratio of oleic (C<sub>18:1</sub>) to stearic acid (C<sub>18</sub>). Oleic acid with its C=C bond is considered unstable and reacts promptly with the

atmospheric oxidants ( $O_3$  and OH radicals) (Kawamura and Gagosian, 1987). Therefore, higher values refer to lower aging processes and thus fresher aerosols (Bendle et al., 2007). For example, Cao et al. (2017) found the latter ratio during intensive field burning days equal to 5.2 (Cao et al., 2017). In our study, the mean value of  $C_{18:1}/C_{18}$  was  $0.27 \pm 0.46$  for  $PM_{2.5}$  and  $0.37 \pm 1.0$  for  $PM_{10}$  showing that aerosols were aged. However, during the dust episode days ( $n = 4$ ) (Fig. 10) an increase of the average ratio regarding the  $PM_{10}$  samples has been observed to  $3.0 \pm 1.1$ , approximately 5.4 times higher than the average ratio of normal days ( $0.56 \pm 0.74$ ). Additionally, OC levels exhibited about 3.6 time higher average concentrations during dust episode days ( $4.7 \pm 3.0 \mu g m^{-3}$ ) than normal days ( $1.3 \pm 0.74$ ). For  $PM_{2.5}$  samples,

$$\text{Contribution of isoprene oxidation products: } \frac{C2 - methylerythritol + C2 - methylthreitol + C2 - methylglyceric acid}{OC \times 0.155} \times 100\% \quad (4)$$

during dust episode days the average  $C_{18:1}/C_{18}$  ratio was increased approximately 2.6 times ( $1.0 \pm 0.46$  on dust episode days,  $0.38 \pm 0.42$  on normal days) and OC levels increased almost 1.9 times ( $1.2 \pm 0.75$  on dust episode days,  $2.2 \pm 0.78$  on normal days). In  $PM_{10}$  samples, apart from the  $C_{18:1}/C_{18}$  ratio and OC levels, we observed an increase in the concentrations of azelaic, suberic and sebacic acids, known photo-oxidation products of oleic and linoleic acid, hinting that dust episodes boost the atmosphere with fresh particles which might also enhance SOA formation on  $PM_{10}$ . This is also supported from Kang et al. (2016) where fresher particulate matters were observed on dust storm days and were mainly associated with coarse mode (Kang et al., 2016). However, with a small sampling size ( $n = 4$ ) concerning the dust episode days, caution must be applied as the findings might not be representative and more samples from dust episode days are needed.

### 3.4. Contribution to OC from different sources

Contribution towards OC of biogenic SOA precursors can be estimated from a tracer-based method, called ‘‘SOA tracer method’’. In particular, contributions of  $\alpha$ -pinene and isoprene oxidation products can be quantified with the values of their concentrations divided by the conversion factor ( $f_{soc}$ ),  $0.231 \pm 0.111$  for  $\alpha$ -pinene and  $0.155 \pm 0.039$  for isoprene (Eqs. (3 and (4), Kleindienst et al., 2007). The aforementioned  $f_{soc}$  values, were derived from smog chamber experiments, under high  $NO_x$  conditions. However, it was shown that mass fractions of isoprene are comparable with those of zero  $NO_x$  levels. Consequently, the above method can be applied to low  $NO_x$  level atmospheres and has been also used in previous studies (Kleindienst et al., 2007; Zhu et al.,

2017; Lyu et al., 2017; Li et al., 2018a). Contributions of biomass burning to OC can be determined from the concentrations of levoglucosan and the emission factor of 0.080 as an average emission factor because there isn't reported data about the biomass type and combustion conditions used in the Cypriot region (Eq. (5) (Zhang et al., 2010b and references therein). The equations used are demonstrated below:

Contribution of  $\alpha$ -Pinene oxidation products:

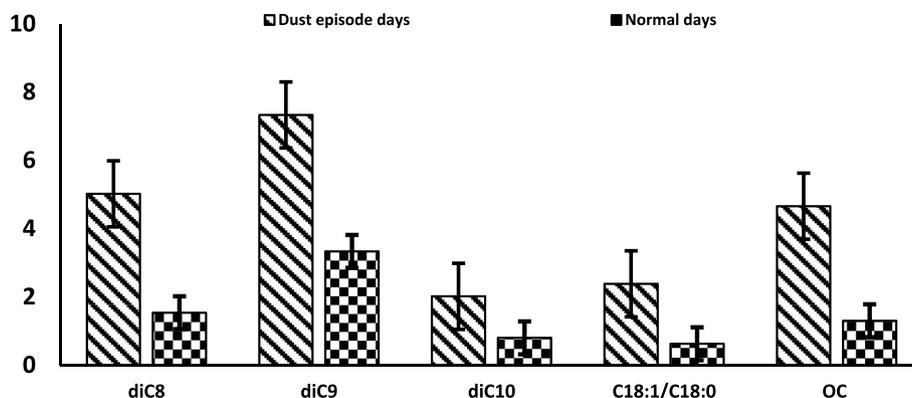
$$\frac{Cpinic acid + Cpinonic acid + C3 - hydroxyglutaric acid}{OC \times 0.231} \times 100\% \quad (3)$$

$$\text{Contribution of biomass burning: } \frac{Clevoglucosan}{OC \times 0.080} \times 100\% \quad (5)$$

It should be noted here that pinene and isoprene oxidation products include only the compounds detected in this work. We know from the literature that more oxidation products of isoprene and pinene exist and moreover, respective equation is used as well for caryophyllene oxidation products (Li et al., 2018a; Kleindienst et al., 2007). Following the equations provided above, the average contributions of biomass burning, pinene oxidation, isoprene oxidation to OC in  $PM_{2.5}$  samples were  $12.8 \pm 14.1\%$ ,  $6.5 \pm 4.1\%$ ,  $6.5 \pm 4.8\%$  respectively with a total contribution of  $25.8 \pm 23.0\%$ . However, the total contribution is expected to be higher assuming that other BVOCs oxidation products may be present in the aerosols. Corresponding different source contributions to aerosol OC in  $PM_{10}$  samples were  $5.8 \pm 4.8\%$  (biomass burning),  $3.2 \pm 2.1\%$  (pinene oxidation products) and  $2.4 \pm 1.4\%$  (isoprene oxidation products) (Table 6). Highest contributor for both PM fractions was biomass burning (nearly 2 times higher in  $PM_{2.5}$ ). Pinene oxidation

**Table 6**  
Average contribution to OC from different sources in  $PM_{2.5}$  and  $PM_{10}$ .

| Species %          | $PM_{2.5}$      | $PM_{10}$      |
|--------------------|-----------------|----------------|
| Pinene oxidation   | $6.5 \pm 4.1$   | $3.2 \pm 2.1$  |
| Isoprene oxidation | $6.5 \pm 4.8$   | $2.4 \pm 1.4$  |
| Biomass burning    | $12.8 \pm 14.1$ | $5.8 \pm 4.8$  |
| Sum                | $25.8 \pm 23.0$ | $11.4 \pm 8.3$ |



**Fig. 10.** Comparison of OC (in  $\mu g m^{-3}$ ), suberic, azelaic and sebacic acids (in  $ng m^{-3}$ ) average concentrations and oleic/stearic acid average ratio during dust episode and normal days for  $PM_{10}$  samples.

contribution was approximately 2 times higher in fine mode while isoprene oxidation contribution was about 2.7 times higher in PM<sub>2.5</sub>. Pinene and isoprene oxidation contribution was fluctuated at similar levels in PM<sub>2.5</sub> fraction, whereas in PM<sub>10</sub> particles pinene contribution was slightly higher. Products of biogenic volatile compounds oxidation accounted for 13.0 ± 4.9% contribution to OC in PM<sub>2.5</sub> samples, versus 5.6 ± 3.5% contribution to OC in PM<sub>10</sub> samples leading to the conclusion that biogenic secondary organic compounds occupy a significant proportion of the organic carbon in the fine particles. Using the previous method Li et al., 2018a found isoprene oxidation the highest contributor to OC (15.7 ± 15.0%), followed by biomass burning and fungi spores contribution (5.2 ± 5.3 and 5.0 ± 6.2, respectively). In contrast with this study, pinene oxidation contributed only for (0.60 ± 1.0%) (Li et al., 2018a).

### 3.5. Source apportionment by principal component analysis

Principal component analysis (PCA) was performed in order to evaluate potential common sources of the species examined in this study. For this purpose, we included in our analyses the compounds that are or may be products of transformation processes. PCA for PM<sub>2.5</sub> and PM<sub>10</sub> aerosol samples are illustrated in (Tables 7 and 8) where loadings > 0.5 are in bold.

Regarding the PM<sub>2.5</sub> samples, four principle components (PCs) explain 71.2% of the total variance. The first component (33.2% of total variance) is heavily loaded with levoglucosan, dicarboxylic acids from 7 to 10 carbon atoms, terephthalic and isophthalic acids, attributing to biomass burning. Recently, biomass burning has been reported to be responsible for increased levels of unsaturated fatty acids, the precursors of high molecular weight dicarboxylic acids (Cao et al., 2017). Therefore, biomass burning may play an important role to the production of pimelic to sebacic acids, even though the correlation of each individual compound with levoglucosan wasn't very strong except for azelaic acid, and the primary emission of the two aromatic acids. Component 2 (15.0% of total variance) includes small linear dicarboxylic acids (succinic, glutaric and adipic) and phthalic acid. Small loadings of trimellitic acid are observed as well; as a result, this component is mainly associated with secondary oxidation of anthropogenic VOCs. The third component (12.8% of total variance) is attributed to pinene oxidation as we observed very tight clusters of pinene oxidation products. Malic acid also presented high loadings in component 3 suggesting that it originates from the same source. Recently, a photodegradation pathway from

**Table 7**  
Principal Component values of PCA for selected compounds in PM<sub>2.5</sub> samples.

| Variance | Component   |             |             |             |
|----------|-------------|-------------|-------------|-------------|
|          | 1           | 2           | 3           | 4           |
|          | 33.2%       | 15.0%       | 12.8%       | 10.2%       |
| diC4     | .054        | <b>.886</b> | .206        | -.073       |
| diC5     | -.009       | <b>.920</b> | -.018       | .016        |
| diC6     | .382        | <b>.809</b> | .094        | -.100       |
| 3-HGA    | .236        | -.054       | <b>.848</b> | -.010       |
| diC7     | <b>.542</b> | .095        | -.020       | -.090       |
| PA       | .332        | .035        | <b>.896</b> | .006        |
| diC8     | <b>.650</b> | .279        | .160        | .463        |
| PHTHA    | .296        | <b>.854</b> | .119        | .069        |
| PNA      | .018        | .176        | <b>.918</b> | -.046       |
| TPHTHA   | <b>.677</b> | .305        | .265        | -.202       |
| IPHTHA   | <b>.571</b> | .254        | .261        | -.062       |
| diC9     | <b>.733</b> | -.005       | .150        | -.206       |
| 2-MGA    | -.056       | -.199       | .083        | <b>.709</b> |
| MTL1     | -.062       | .029        | -.029       | <b>.922</b> |
| MTL2     | -.106       | .142        | -.110       | <b>.918</b> |
| diC10    | <b>.688</b> | .072        | -.020       | .385        |
| TRIM     | .436        | <b>.528</b> | .204        | .278        |
| LEV      | <b>.795</b> | .096        | .244        | -.069       |
| dihC4    | .081        | .278        | <b>.743</b> | .046        |

**Table 8**  
Principal Component values of PCA for selected compounds in PM<sub>10</sub> samples.

| Variance | Component   |             |             |             |             |
|----------|-------------|-------------|-------------|-------------|-------------|
|          | 1           | 2           | 3           | 4           | 5           |
|          | 20.6%       | 16.9%       | 15.6%       | 8.9%        | 7.9%        |
| diC4     | <b>.752</b> | .119        | -.078       | -.063       | .084        |
| diC5     | <b>.850</b> | -.111       | -.045       | -.077       | .216        |
| diC6     | <b>.923</b> | .013        | -.068       | .056        | -.038       |
| 3-HGA    | -.032       | .051        | <b>.911</b> | -.082       | .042        |
| diC7     | -.307       | -.205       | .297        | .241        | .087        |
| PA       | -.003       | .212        | <b>.936</b> | -.043       | .048        |
| diC8     | .064        | <b>.883</b> | .153        | .030        | .130        |
| PHTHA    | <b>.735</b> | .088        | .034        | .009        | .033        |
| PNA      | -.026       | .264        | <b>.824</b> | .123        | .234        |
| TPHTHA   | .003        | -.054       | .184        | -.306       | <b>.752</b> |
| IPHTHA   | .061        | .035        | .090        | -.291       | <b>.764</b> |
| diC9     | .130        | <b>.908</b> | .104        | .022        | -.085       |
| 2-MGA    | -.207       | .465        | -.094       | <b>.645</b> | .020        |
| MTL1     | .099        | -.013       | .043        | <b>.917</b> | -.122       |
| MTL2     | -.045       | .016        | .027        | <b>.925</b> | -.221       |
| diC10    | .072        | <b>.824</b> | .177        | .079        | .176        |
| TRIM     | .136        | .111        | -.071       | .205        | <b>.536</b> |
| LEV      | .001        | .074        | .128        | -.052       | <b>.818</b> |
| dihC4    | .390        | .298        | .234        | .047        | -.059       |

3-hydroxyglutaric acid to malic acid was proposed (Hu and Yu, 2013) supporting this hypothesis. The last component (10.2% of total variance) refers to another biogenic source, i.e. isoprene oxidation, through high loads of the two 2-methyltetrols and 2-methylglyceric acid.

In PM<sub>10</sub> samples, five PCs explain 70.0% of the total variance. Contrary with PM<sub>2.5</sub> samples, component 1 (20.6% of total variance) is strongly loaded with C4–C6 diacids and phthalic acid referring to oxidation of anthropogenically emitted compounds. Same component was observed in PM<sub>2.5</sub>, with only difference, the absence of trimellitic acid. The second component is associated with oxidation of unsaturated fatty acids through the heavy loads of C8–C10 diacids. In contrast with PM<sub>2.5</sub> samples, this factor doesn't include levoglucosan, indicating that biomass burning may not affect the formation these diacids in higher aerodynamic diameter particles. The next two are related with biogenic sources as tight clusters of pinene and isoprene oxidation products are observed in components 3 and 4 respectively. The last component is attributed to biomass burning since strong loads of the biomass burning tracer (levoglucosan) were observed. Other than that, high loads of iso- and terephthalic acid in this component indicate that these compounds are primarily emitted through biomass burning. In contrast with PM<sub>2.5</sub> samples, trimellitic acid present loads in this component hint that primary sources prevailed over the secondary. The biggest difference regarding the PCA analysis of PM<sub>10</sub> and PM<sub>2.5</sub> aerosol samples is related to malic acid. Although in PM<sub>2.5</sub> analysis malic acid is clearly loaded in component 3 the PM<sub>10</sub> PCA analysis shows that it is distributed over the first three components. The variety of sources of malic acid is often discussed in the literature as it reported to be secondary product of both biogenic and anthropogenic sources (Claeys et al., 2004; Sato et al., 2007; Hu and Yu, 2013). Moreover, it has been suggested lately that the photochemical oxidation of high molecular weight dicarboxylic acids leads to the formation of their lower homologues (Yang et al., 2008) supporting the statement by (Tedetti et al., 2007) that azelaic acid can be photochemically oxidized and produce lower diacid homologues from C<sub>2</sub>–C<sub>4</sub>. As a result, malic acid is very often correlated with succinic acid and is considered as an intermediate for other atmospheric oxidation processes (Bikkina et al., 2015). From the above and the significant correlation of malic acid with succinic (3.2.3), it seems that succinic may be a source of malic acid, but other sources exist as well.

Principal component analysis is parallel with (Hyder et al., 2012) in which the 3 extracted components included: secondary anthropogenic compounds (component 1), oxidation of unsaturated acids (component 2) and oxidation of naturally emitted compounds (component 3)

explaining 87% of the total variance.

#### 4. Conclusion

Organic carbon, elemental carbon and polar organic compounds including mono and dicarboxylic acids, biogenic secondary organic aerosol tracers, aromatic polycarboxylic acids and tracers of biomass burning were determined from 88 daily aerosol samples ( $n = 44 \text{ PM}_{10}$ ,  $n = 44 \text{ PM}_{2.5}$ ). Secondary organic carbon was calculated and found significantly ( $p < 0.05$ ) higher in  $\text{PM}_{2.5}$  particles. Almost every analyte (except pinonic acid) exhibited significant ( $p < 0.05$ ) higher concentrations in  $\text{PM}_{2.5}$  samples. Among dicarboxylic acids succinic acid was found the most abundant and pimelic acid the least abundant. Pinic acid dominated over the other BSOA tracers and phthalic acid over the aromatic carboxylic acids. Correlations between compounds were mostly parallel between the  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  samples with few exceptions. First, malic acid in  $\text{PM}_{2.5}$  samples was correlated with the sum of monoterpene oxidation products, while in  $\text{PM}_{10}$  samples it was more related with succinic acid indicating different formation pathways. Second, azelaic acid was correlated with levoglucosan in  $\text{PM}_{2.5}$  samples but such correlation wasn't observed in  $\text{PM}_{10}$  samples where it was stronger correlated with C8 and C10 diacids and unsaturated fatty acids. An interesting correlation of isoprene with the 2-methyltetrols of the next day was also observed, while the ratio of 2-methyltetrols to 2-methylglyceric acid showed a decreasing trend with the higher  $\text{NO}_x$  levels. Phthalic acid appears to have different sources relative to its isomers as its association with low molecular weight dicarboxylic acids suggests secondary formation versus primary emissions. Molecular diagnostic ratios of carboxylic acids show that aerosols in Agia Marina Xyliatou are mainly aged and affected from biogenic sources. Dust episodes seem to significantly impact on  $\text{PM}_{10}$  particles and secondary formation may be enhanced during those days. The applied "SOA tracer method" shows biomass burning the highest contributor to OC in both  $\text{PM}_{10}$  ( $5.8 \pm 4.8\%$ ) and  $\text{PM}_{2.5}$  ( $12.8 \pm 14.1\%$ ) samples. Pinene's oxidation contribution to OC was at the same levels with isoprene's in fine particles ( $6.5 \pm 4.1\%$  and  $6.5 \pm 4.8\%$ , respectively), whereas in  $\text{PM}_{10}$  fraction pinene's oxidation was stronger contributor ( $3.2 \pm 2.1\%$  over  $2.4 \pm 1.4\%$ ). Source apportionment via Principal Component Analysis enhanced the outcome that biomass burning and anthropogenic SOA are the major components in  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  samples respectively.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### CRedit authorship contribution statement

**Panagiotis Georgios Kanellopoulos:** Validation, Formal analysis, Investigation, Writing - original draft, Writing - review & editing, Visualization. **Eirini Chrysochou:** Investigation, Writing - review & editing. **Konstantinos Koukoulakis:** Formal analysis, Writing - review & editing. **Emily Vasileiadou:** Validation, Investigation. **Christos Kizas:** Validation. **Chrysanthos Savvides:** Validation. **Evangelos Bakeas:** Conceptualization, Methodology, Formal analysis, Writing - review & editing, Visualization, Resources, Supervision, Project administration.

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#### Appendix A. Supplementary data

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#### References

- Achilleos, S., Wolfson, J.M., Ferguson, S.T., Kang, C.M., Hadjimitsis, D.G., Hadjicharalambous, M., Achilleos, C., Christodoulou, A., Nisantzi, A., Papoutsas, C., Themistocleous, K., Athanasatos, S., Perdikou, S., Koutrakis, P., 2016. Spatial variability of fine and coarse particle composition and sources in Cyprus. *Atmos. Res.* 169 (Part A), 255–270. <https://doi.org/10.1016/j.atmosres.2015.10.005>.
- Al-Naiema, I.M., Stone, E.A., 2017. Evaluation of anthropogenic secondary organic aerosol tracers from aromatic hydrocarbons. *Atmos. Chem. Phys.* 17 (3), 2053–2065. <https://doi.org/10.5194/acp-17-2053-2017>.
- Arashiro, M., Lin, Y.H., Zhang, Z., Sexton, K.G., Gold, A., Jaspers, I., Fry, R.C., Surratt, J. D., 2018. Effect of secondary organic aerosol from isoprene-derived hydroxyhydroperoxides on the expression of oxidative stress response genes in human bronchial epithelial cells. *Environ. Sci. J. Integr. Environ. Res.: Processes Impacts* 20 (2), 332–339. <https://doi.org/10.1039/c7em00439g>.
- Ashworth, K., Boissard, C., Folberth, G., Lathiere, J., Schurgers, G., 2013. *Global Modelling of Volatile Organic Compound Emissions*, vol. 5. Springer, pp. 451–487.
- Atkinson, R., Arey, J., 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. *Atmos. Environ.* 37 (Suppl. 2), 197–219. [https://doi.org/10.1016/S1352-2310\(03\)00391-1](https://doi.org/10.1016/S1352-2310(03)00391-1).
- Balla, D., Voutsas, D., Samara, C., 2018. Study of polar organic compounds in airborne particulate matter of a coastal urban city. *Environ. Sci. Pollut. Control Ser.* 25 (13), 12191–12205. <https://doi.org/10.1007/s11356-017-9993-2>.
- Baltensperger, U., Dommen, J., Alfarra, M.R., Duplissy, J., Gaeggeler, K., Metzger, A., Facchini, M.C., Decesari, S., Finessi, E., Reinnig, C., Schott, M., Warnke, J., Hoffmann, T., Klatzer, B., Puxbaum, H., Geiser, M., Savi, M., Lang, D., Kalberer, M., Geiser, T., 2008. Combined determination of the chemical composition and of health effects of secondary organic aerosols: the POLYSOA project. *J. Aerosol Med. Pulm. Drug Deliv.* 21 (1), 145–154. <https://doi.org/10.1089/jamp.2007.0655>.
- Bardouki, H., Liakakou, H., Economou, C., Sciare, J., Smolik, J., Ždímal, V., Eleftheriadis, K., Lazaridis, M., Dye, C., Mihalopoulos, N., 2003. Chemical composition of size-resolved atmospheric aerosols in the eastern Mediterranean during summer and winter. *Atmos. Environ.* 37 (2), 195–208. [https://doi.org/10.1016/S1352-2310\(02\)00859-2](https://doi.org/10.1016/S1352-2310(02)00859-2).
- Bendle, J., Kawamura, K., Yamazaki, K., Niwai, T., 2007. Latitudinal distribution of terrestrial lipid biomarkers and n-alkane compound-specific stable carbon isotope ratios in the atmosphere over the western Pacific and Southern Ocean. *Geochim. Cosmochim. Acta* 71, 5934–5955. <https://doi.org/10.1016/j.gca.2007.09.029>.
- Bikkina, S., Kawamura, K., Miyazaki, Y., 2015. Latitudinal distributions of atmospheric dicarboxylic acids, oxocarboxylic acids, and  $\alpha$ -dicarbonyls over the western north pacific: sources and formation pathways. *J. Geophys. Res.* 120 (10), 5010–5035. <https://doi.org/10.1002/2014JD022235>.
- Cao, F., Zhang, S.C., Kawamura, K., Liu, X., Yang, C., Xu, Z., Fan, M., Zhang, W., Bao, M., Chang, Y., Song, W., Liu, S., Lee, X., Li, J., Zhang, G., Zhang, Y.L., 2017. Chemical characteristics of dicarboxylic acids and related organic compounds in  $\text{PM}_{2.5}$  during biomass-burning and non-biomass-burning seasons at a rural site of Northeast China. *Environ. Pollut.* 231, 654–662. <https://doi.org/10.1016/j.envpol.2017.08.045>.
- Castro, L.M., Pio, C.A., Harrison, R.M., Smith, D.J.T., 1999. Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. *Atmos. Environ.* 33 (17), 2771–2781. [https://doi.org/10.1016/S1352-2310\(98\)00331-8](https://doi.org/10.1016/S1352-2310(98)00331-8).
- Cavalli, F., Viana, M., Yttri, K.E., Genberg, J., Putaud, J.P., 2010. Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. *Atmos. Meas. Techn.* 3, 79–89. <https://doi.org/10.5194/amt-3-79-2010>.
- Chen, J., Ying, Q., Kleeman, M.J., 2010. Source apportionment of wintertime secondary organic aerosol during the California regional  $\text{PM}_{10}/\text{PM}_{2.5}$  air quality study. *Atmos. Environ.* 44 (10), 1331–1340. <https://doi.org/10.1016/j.atmosenv.2009.07.010>.
- Claeys, M., Graham, B., Vas, G., Wang, W., Vermeylen, R., Pashynska, V., Cafmeyer, J., Guyon, P., Andreae, M.O., Artaxo, P., Maenhaut, W., 2004. formation of secondary organic aerosols through photooxidation of isoprene. *Science* 303 (5661), 1173–1176. <https://doi.org/10.1126/science.1092805>.
- Claeys, M., Szmigielski, R., Kourtev, I., Van Der Veken, P., Vermeylen, R., Maenhaut, W., Jaoui, M., Kleindienst, T.E., Lewandowski, M., Offenberg, J.H., Edney, E.O., 2007. Hydroxydicarboxylic acids: markers for secondary organic aerosol from the photooxidation of  $\alpha$ -pinene. *Environ. Sci. Technol.* 41 (5), 1628–1634. <https://doi.org/10.1021/es0620181>.
- Dayan, U., Ricaud, P., Zbinden, R., Dulac, F., 2017. Atmospheric pollution over the eastern Mediterranean during summer - a review. *Atmos. Chem. Phys.* 17 (21), 13233–13263. <https://doi.org/10.5194/acp-17-13233-2017>.
- Debevec, C., Sauvage, S., Gros, V., Sciare, J., Pikridas, M., Stavroulas, I., Salameh, T., Leonards, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Estève, R., Bainsée, D., Bon-sang, B., Savvides, C., Vrekoussis, M., Logez, N., 2017. Origin and variability in volatile organic compounds observed at an Eastern Mediterranean background site (Cyprus). *Atmos. Chem. Phys.* 17, 11355–11388. <https://doi.org/10.5194/acp-17-11355-2017>.

- Debevec, C., Sauvage, S., Gros, V., Sellegri, K., Sciare, J., Pikridas, M., Stavroulas, I., Leonaridis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnee, D., Bonsaug, B., Savvides, C., Locoge, N.L., 2018. Driving parameters of biogenic volatile organic compounds and consequences on new particle formation observed at an eastern Mediterranean background site. *Atmos. Chem. Phys.* 18 (19), 14297–14325. <https://doi.org/10.5194/acp-18-14297-2018>.
- Deshmukh, D.K., Haque, M., Kim, Y., Kawamura, K., 2019. Organic tracers of fine aerosol particles in central Alaska: summertime composition and sources. *Atmos. Chem. Phys.* 19, 14009–14029. <https://doi.org/10.5194/acp-19-14009-2019>.
- Ding, X., Wang, X.M., Gao, B., Fu, X.X., He, Q.F., Zhao, X.Y., Yu, J.Z., Zheng, M., 2012. Tracer-based estimation of secondary organic carbon in the Pearl River Delta, south China. *J. Geophys. Res. Atmos.* 117 (5), 1–14. <https://doi.org/10.1029/2011JD016596>.
- Eddingsaas, N.C., Loza, C.L., Yee, L.D., Chan, M., Schilling, K.A., Chhabra, P.S., Seinfeld, J.H., Wennberg, P.O., 2012.  $\alpha$ -Pinene photooxidation under controlled chemical conditions-part 2: SOA yield and composition in low-and high-NOx environments. *Atmos. Chem. Phys.* 12 (16), 7413–7427.
- El Haddad, I., Marchand, N., Temime-Roussel, B., Wortham, H., Piot, C., Besombes, J.L., Baduel, C., Voisin, D., Armengaud, A., Jaffrezo, J.L., 2011. Insights into the secondary fraction of the organic aerosol in a Mediterranean urban area: Marseille. *Atmos. Chem. Phys.* 11 (5), 2059–2079. <https://doi.org/10.5194/acp-11-2059-2011>.
- EN 12341, 2014. Ambient Air - Standard Gravimetric Measurement Method for the Determination of the PM10 or PM2.5 Mass Concentration of Suspended Particulate Matter.
- EN 14662-3, 2015. Ambient Air – Standard Method for the Measurement of Benzene Concentrations – Part 3: Automated Pumped Sampling with in Situ Gas Chromatography.
- EU, 2008. Directive 2008/50/EC of the European parliament and of the council of 21 may 2008 on ambient air quality and cleaner air for Europe. *Orkesterjournalen L 152*, 1–44, 11.6.2008.
- Fall, P.L., 2012. Modern vegetation, pollen and climate relationships on the Mediterranean island of Cyprus. *Rev. Palaeobot. Palynol.* 185 (1), 79–92. <https://doi.org/10.1016/j.revpalbo.2012.08.002>.
- Flores, R.M., Doskey, P.V., 2015. Evaluation of multistep derivatization methods for identification and quantification of oxygenated species in organic aerosol. *J. Chromatogr. A* 1418, 1–11. <https://doi.org/10.1016/j.chroma.2015.09.041>.
- Fu, P.Q., Kawamura, K., Chen, J., Barrie, L.A., 2009. Isoprene, monoterpene, and sesquiterpene oxidation products in the high Arctic aerosols during late winter to early summer. *Environ. Sci. Technol.* 43 (11), 4022–4028. <https://doi.org/10.1021/es803669a>.
- Fu, P.Q., Kawamura, K., Kanaya, Y., Wang, Z.F., 2010. Contributions of biogenic volatile organic compounds to the formation of secondary organic aerosols over Mt. Tai, Central East China. *Atmos. Environ.* 44 (38), 4817–4826. <https://doi.org/10.1016/j.atmosenv.2010.08.040>.
- Fu, P.Q., Kawamura, K., Chen, J., Charrière, B., Sempéré, R., 2013. Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of primary emission and secondary aerosol formation. *Biogeosciences* 10 (2), 653–667. <https://doi.org/10.5194/bg-10-653-2013>.
- Gao, S., Keywood, M., Ng, N.L., Surratt, J., Varutbangkul, V., Bahreini, R., Flagan, R.C., Seinfeld, J.H., 2004. Low-molecular-weight and oligomeric components in secondary organic aerosol from the ozonolysis of cycloalkenes and  $\alpha$ -pinene. *J. Phys. Chem.* 108 (46), 10147–10164.
- Graham, B., Guyon, P., Taylor, P.E., Artaxo, P., Maenhaut, W., Glovsky, M.M., Flagan, R.C., Andreae, M.O., 2003. Organic compounds present in the natural Amazonian aerosol: characterization by gas chromatography-mass spectrometry. *J. Geophys. Res.* Atmos. 108 (D24) <https://doi.org/10.1029/2003JD003990>.
- Guo, H., Zhou, J., Wang, L., Zhou, Y., Yuan, J., Zhao, R., 2015. Seasonal variations and sources of carboxylic acids in PM2.5 in wuhan, China. *Aerosol Air Qual. Res.* 15 (2), 517–528. <https://doi.org/10.4209/aaqr.2014.02.0040>.
- Hallquist, M., Wenger, J.C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N.M., George, C., Goldstein, A.H., Hamilton, A.F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M.E., Jimenez, J.L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, ThF., Monod, A., Prevot, A.S.H., Seinfeld, J.H., Surratt, J.D., Szmigielski, R., Wildt, J., 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* 9 (14), 5155–5236. <https://doi.org/10.5194/acp-9-5155-2009>.
- Haque, M.M., Kawamura, K., Deshmukh, D.K., Fang, C., Song, W., Mengying, B., Zhang, Y.L., 2019. Characterization of organic aerosols from a Chinese megacity during winter: predominance of fossil fuel combustion. *Atmos. Chem. Phys.* 19 (7), 5147–5164. <https://doi.org/10.5194/acp-19-5147-2019>.
- Hatakeyama, S., Ohno, M., Weng, J.H., Takagi, H., Akimoto, H., 1987. Mechanism for the formation of gaseous and particulate products from ozone-cycloalkene reactions in air. *Environ. Sci. Technol.* 21 (1), 52–57. <https://doi.org/10.1021/es00155a005>.
- He, X., Huang, X.H.H., Chow, K.S., Wang, Q., Zhang, T., Wu, D., Yu, J.Z., 2018. Abundance and sources of phthalic acids, benzene-tricarboxylic acids, and phenolic acids in PM 2.5 at urban and suburban sites in southern China. *ACS Earth Space Chem.* 2 (2), 147–158. <https://doi.org/10.1021/acsearthspacechem.7b00131>.
- Ho, K.F., Lee, S.C., Cao, J.J., Kawamura, K., Watanabe, T., Cheng, Y., Chow, J.C., 2006. Dicarboxylic acids, ketocarboxylic acids and dicarbonyls in the urban roadside area of Hong Kong. *Atmos. Environ.* 40 (17), 3030–3040. <https://doi.org/10.1016/j.atmosenv.2005.11.069>.
- Ho, K.F., Cao, J.J., Lee, S.C., Kawamura, K., Zhang, R.J., Chow, J.C., Watson, J.G., 2007. Dicarboxylic acids, ketocarboxylic acids, and dicarbonyls in the urban atmosphere of China. *J. Geophys. Res. Atmos.* 112 (22), 1–12. <https://doi.org/10.1029/2006JD008011>.
- Ho, K.F., Lee, S.C., Ho, S.S.H., Kawamura, K., Tachibana, E., Cheng, Y., Zhu, T., 2010. Dicarboxylic acids, ketocarboxylic acids,  $\alpha$ -dicarbonyls, fatty acids, and benzoic acid in urban aerosols collected during the 2006 Campaign of Air Quality Research in Beijing (CAREBeijing-2006). *J. Geophys. Res. Atmos.* 115 (19), 1–14. <https://doi.org/10.1029/2009JD013304>.
- Hoffmann, T., Odum, J.R., Bowman, F., Collins, D., Klockow, D., Flagan, R.C., Seinfeld, J.H., 1997. formation of organic aerosols from the oxidation of biogenic hydrocarbons. *J. Atmos. Chem.* 26 (2), 189–222.
- Hong, Z., Zhang, H., Zhang, Y., Xu, L., Liu, T., Xiao, H., Hong, Y., Chen, J., Li, M., Deng, J., Wu, X., Hu, B., Chen, X., 2019. Secondary organic aerosol of PM 2.5 in a mountainous forest area in southeastern China: molecular compositions and tracers implication. *Sci. Total Environ.* 653, 496–503. <https://doi.org/10.1016/j.scitotenv.2018.10.370>.
- Hu, D., Yu, J.Z., 2013. Secondary organic aerosol tracers and malic acid in Hong Kong: seasonal trends and origins. *Environ. Chem.* 10 (5), 381–394. <https://doi.org/10.1071/EN13104>.
- Huang, M., Zhang, W., Gu, X., Hu, C., Zhao, W., Wang, Z., Fang, L., 2012. Size distribution and chemical composition of secondary organic aerosol formed from Cl-initiated oxidation of toluene. *Journal of Environ. Sci.* 24 (5), 860–864. [https://doi.org/10.1016/S1001-0742\(11\)60840-1](https://doi.org/10.1016/S1001-0742(11)60840-1).
- Hyder, M., Genberg, J., Sandahl, M., Swietlicki, E., Jönsson, J. Åke, 2012. Yearly trend of dicarboxylic acids in organic aerosols from south of Sweden and source attribution. *Atmos. Environ.* 57, 197–204. <https://doi.org/10.1016/j.atmosenv.2012.04.027>.
- Iakovides, M., Stephanou, E.G., Apostolaki, M., Hadjicharalambous, M., Evans, J.S., Koutrakis, P., Achilleos, S., 2019. Study of the occurrence of airborne Polycyclic Aromatic Hydrocarbons associated with respirable particles in two coastal cities at Eastern Mediterranean: levels, source apportionment, and potential risk for human health. *Atmos. Environ.* 213, 170–184. <https://doi.org/10.1016/j.atmosenv.2019.05.059>.
- Jaoui, M., Lewandowski, M., Docherty, K., Offenberg, J.H., Kleindienst, T.E., 2014. Atmospheric oxidation of 1,3-butadiene: characterization of gas and aerosol reaction products and implications for PM2.5. *Atmos. Chem. Phys.* 14 (24), 13681–13704. <https://doi.org/10.5194/acp-14-13681-2014>.
- Jaoui, M., Lewandowski, M., Offenberg, J.H., Docherty, K.S., Kleindienst, T.E., 2017. Ozonolysis of A/B-farnesene mixture: analysis of gas-phase and particulate reaction products. *Atmos. Environ.* 169, 175–192. <https://doi.org/10.1016/j.atmosenv.2017.08.065>.
- Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C.J., Swietlicki, E., Putaud, J.P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G.K., Winterhalter, R., Myhre, C.E.L., Tsigaridis, K., Vignati, E., Stephanou, E.G., Wilson, J., 2005. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* 5 (4), 1053–1123. <https://doi.org/10.5194/acp-5-1053-2005>.
- Kanakidou, M., Mihalopoulos, N., Kindap, T., Im, U., Vrekoussis, M., Gerasopoulos, E., Dermitzi, E., Unal, A., Kocak, M., Markakis, K., Melas, D., Kouvarakis, G., Yousef, A.F., Richter, A., Hatzianastassiou, N., Hilboll, A., Ebojic, F., Wittrock, F., von Savigny, C., Burrows, J.P., Ladstaetter-Weissenmayer, A., Moubasher, H., 2011. Megacities as hot spots of air pollution in the East Mediterranean. *Atmos. Environ.* 45 (6), 1223–1235. <https://doi.org/10.1016/j.atmosenv.2010.11.048>.
- Kang, M., Fu, P., Aggarwal, S.G., Kumar, S., Zhao, Y., Sun, Y., Wang, Z., 2016. Size distributions of n-alkanes, fatty acids and fatty alcohols in springtime aerosols from New Delhi, India. *Environ. Pollut.* 219, 957–966. <https://doi.org/10.1016/j.envpol.2016.09.077>.
- Kautzman, K.E., Surratt, J.D., Chan, M.N., Chan, A.W.H., Hersey, S.P., Chhabra, P.S., Dalleska, N.F., Wennberg, P.O., Flagan, R.C., Seinfeld, J.H., 2010. Chemical composition of gas- and aerosol-phase products from the photooxidation of naphthalene. *J. Phys. Chem.* 114 (2), 913–934. <https://doi.org/10.1021/jp908530s>.
- Kavouras, I.G., Stephanou, E.G., 2002. Particle size distribution of organic primary and secondary aerosol constituents in urban, background marine, and forest atmosphere, 2002. *J. Geophys. Res.* 107 (D8) <https://doi.org/10.1029/2000JD000278>. AAC 7-1-AAC 7-12.
- Kawamura, K., Gagosian, R.B., 1987. Implications of [omega]-oxocarboxylic acids in the remote marine atmosphere for photo-oxidation of unsaturated fatty acids. *Nature* 325, 330–332.
- Kawamura, K., Kaplan, I.R., 1987. Motor exhaust emission as a primary source of dicarboxylic acids in Los Angeles ambient air. *Environ. Sci. Technol.* 21 (1), 105–110. <https://doi.org/10.1021/es00155a014>.
- Kawamura, K., Ikushima, K., 1993. Seasonal changes in the distribution of dicarboxylic acids in the urban atmosphere. *Environ. Sci. Technol.* 27 (10), 2227–2235. <https://doi.org/10.1021/es00047a033>.
- Kawamura, K., Ishimura, Y., Yamazaki, K., 2003. Four years' observations of terrestrial lipid class compounds in marine aerosols from the western North Pacific. *Global Biogeochem. Cycles* 17 (1). <https://doi.org/10.1029/2001gb001810>, 3-1-3-19.
- Kawamura, K., Tachibana, E., Okuzawa, K., Aggarwal, S.G., Kanaya, Y., Wang, Z.F., 2013. High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and alpha-dicarbonyls in the mountaintop aerosols over the North China Plain during wheat burning season. *Atmos. Chem. Phys.* 13, 8285–8302. <https://doi.org/10.5194/acp-13-8285-2013>.
- Kawamura, K., Bikkina, S., 2016. A review of dicarboxylic acids and related compounds in atmospheric aerosols: molecular distributions, sources and transformation. *Atmos. Res.* 170, 140–160. <https://doi.org/10.1016/j.atmosres.2015.11.018>.
- Kelly, F.J., Fussell, J.C., 2012. Size, source and chemical composition as determinants of toxicity attributable to ambient particulate matter. *Atmos. Environ.* 60, 504–526. <https://doi.org/10.1016/j.atmosenv.2012.06.039>.

- Kleanthous, S., Vrekoussis, M., Mihalopoulos, N., Kalabokas, P., Lelieveld, J., 2014. On the temporal and spatial variation of ozone in Cyprus. *Sci. Total Environ.* 476–477, 677–687. <https://doi.org/10.1016/j.scitotenv.2013.12.101>.
- Kleindienst, T.E., Jaoui, M., Lewandowski, M., Offenber, J.H., Lewis, C.W., Bhav, P.V., Edney, E.O., 2007. Estimates of the contributions of biogenic and anthropogenic hydrocarbons to secondary organic aerosol at a southeastern US location. *Atmos. Environ.* 41 (37), 8288–8300. <https://doi.org/10.1016/j.atmosenv.2007.06.045>.
- Kleindienst, T.E., Jaoui, M., Lewandowski, M., Offenber, J.H., Docherty, K.S., 2012. The formation of SOA and chemical tracer compounds from the photooxidation of naphthalene and its methyl analogs in the presence and absence of nitrogen oxides. *Atmos. Chem. Phys.* 12 (18), 8711–8726. <https://doi.org/10.5194/acp-12-8711-2012>.
- Klejnowski, K., Janoszka, K., Czaplicka, M., 2017. Characterization and seasonal variations of organic and elemental carbon and levoglucosan in PM10 in Krynica Zdroj, Poland. *Atmosphere* 8 (10), 190. <https://doi.org/10.3390/atmos8100190>.
- Kroll, J.H., Seinfeld, J.H., 2008. Chemistry of secondary organic aerosol: Formation and evolution of low volatility organics in the atmosphere. *Atmos. Environ.* 42 (16), 3593–3624. <https://doi.org/10.1016/j.atmosenv.2008.01.003>.
- Kundu, S., Kawamura, K., Andreae, T.W., Hoffer, A., Andreae, M.O., 2010a. Molecular distributions of dicarboxylic acids, ketocarboxylic acids and  $\alpha$ -dicarbonyls in biomass burning aerosols: implications for photochemical production and degradation in smoke layers. *Atmos. Chem. Phys.* 10 (5), 2209–2225. <https://doi.org/10.5194/acp-10-2209-2010>.
- Kunwar, B., Kawamura, K., 2014. One-year observations of carbonaceous and nitrogenous components and major ions in the aerosols from subtropical Okinawa Island, an outflow region of Asian dusts. *Atmos. Chem. Phys.* 14 (4), 1819–1836. <https://doi.org/10.5194/acp-14-1819-2014>.
- Li, J.J., Wang, G.H., Cao, J.J., Wang, X.M., Zhang, R.J., 2013. Observation of biogenic secondary organic aerosols in the atmosphere of a mountain site in central China: temperature and relative humidity effects. *Atmos. Chem. Phys.* 13 (22), 11535–11549. <https://doi.org/10.5194/acp-13-11535-2013>.
- Li, L., Lai, W., Pu, J., Mo, H., Dai, D., Wu, G., Deng, S., 2018a. Polar organic tracers in PM2.5 aerosols from an inland background area in Southwest China: correlations between secondary organic aerosol tracers and source apportionment. *J. Environ. Sci. (China)* 69, 281–293. <https://doi.org/10.1016/j.jes.2017.06.002>.
- Li, J., Wang, G., Wu, C., Cao, C., Ren, Y., Wang, J., Li, J., Cao, J., Zeng, L., Zhu, T., 2018b. Characterization of isoprene-derived secondary organic aerosols at a rural site in North China Plain with implications for anthropogenic pollution effects. *Sci. Rep.* 8 (1), 1–10. <https://doi.org/10.1038/s41598-017-18983-7>.
- Liakakou, E., Vrekoussis, M., Bonsang, B., Donousis, C., Kanakidou, M., Mihalopoulos, N., 2007. Isoprene above the Eastern Mediterranean: seasonal variation and contribution to the oxidation capacity of the atmosphere. *Atmos. Environ.* 41 (5), 1002–1010. <https://doi.org/10.1016/j.atmosenv.2006.09.034>.
- Liakakou, E., Bonsang, B., Williams, J., Kalivitis, N., Kanakidou, M., Mihalopoulos, N., 2009. C2–C8 NMHCs over the Eastern Mediterranean: seasonal variation and impact on regional oxidation chemistry. *Atmos. Environ.* 43 (35), 5611–5621. <https://doi.org/10.1016/j.atmosenv.2009.07.067>.
- Liao, H., Henze, D.K., Seinfeld, J.H., Wu, S., Mickley, L.J., 2007. Biogenic secondary organic aerosol over the United States: comparison of climatological simulations with observations. *J. Geophys. Res. Atmos.* 112 (D6) <https://doi.org/10.1029/2006JD007813>.
- Lin, Y.H., Arashiro, M., Martin, E., Chen, Y., Zhang, Z., Sexton, K.G., Gold, A., Jaspers, I., Fry, R.C., Surratt, J.D., 2016. Isoprene-derived secondary organic aerosol induces the expression of oxidative stress response genes in human lung cells. *Environ. Sci. Technol. Lett.* 3 (6), 250–254. <https://doi.org/10.1021/acs.estlett.6b00151>.
- Lyu, X.P., Guo, H., Cheng, H.R., Wang, X.M., Ding, X., Lu, H.X., Yao, D.W., Xu, C., 2017. Observation of SOA tracers at a mountainous site in Hong Kong: chemical characteristics, origins and implication on particle growth. *Sci. Total Environ.* 605–606, 180–189. <https://doi.org/10.1016/j.scitotenv.2017.06.161>.
- Ma, Y., Willcox, T.R., Russell, A.T., Marston, G., 2007. Pinic and pinonic acid formation in the reaction of ozone with  $\alpha$ -pinene. *Chem. Commun.* (13), 1328–1330. <https://doi.org/10.1039/b617130c>.
- Mochida, M., Kitamori, Y., Kawamura, K., Nojiri, Y., Suzuki, K., 2002. Fatty acids in the marine atmosphere: factors governing their concentrations and evaluation of organic films on sea-salt particles. *J. Geophys. Res. Atmos.* 107 (D17), 4325. <https://doi.org/10.1029/2001JD001278>.
- Mochida, M., Kawabata, A., Kawamura, K., Hatsushika, H., Yamazaki, K., 2003. Seasonal variation and origins of dicarboxylic acids in the marine atmosphere over the western North Pacific. *J. Geophys. Res. Atmos.* 108 (D6), 4193. <https://doi.org/10.1029/2002JD002355>.
- Mologousi, A.I., Bakeas, E.B., 2016. Multivariate optimization of a simple and sensitive method for the determination of secondary biogenic organic compounds in airborne particles. *Anal. Methods* 8 (20), 4047–4055. <https://doi.org/10.1039/c5ay02758f>.
- Navazo, M., Durana, N., Alonso, L., Gómez, M.C., García, J.A., Ildardia, J.L., Gangoiti, G., Iza, J., 2008. High temporal resolution measurements of ozone precursors in a rural background station. A two-year study. *Environ. Monit. Assess.* 136 (1–3), 53–68. <https://doi.org/10.1007/s10661-007-9720-4>.
- Oliveira, C., Pio, C., Alves, C., Evtuygina, M., Santos, P., Gonçalves, V., Nunes, T., Silvestre, A.J.D., Palmgren, F., Wahlin, P., Harrad, S., 2007. Seasonal distribution of polar organic compounds in the urban atmosphere of two large cities from the North and South of Europe. *Atmos. Environ.* 41 (27), 5555–5570. <https://doi.org/10.1016/j.atmosenv.2007.03.001>.
- Pietrogrande, M.C., Bacco, D., Visentin, M., Ferrari, S., Poluzzi, V., 2014. Polar organic marker compounds in atmospheric aerosol in the Po Valley during the Supersito campaigns - Part 1: low molecular weight carboxylic acids in cold seasons. *Atmos. Environ.* 86, 164–175. <https://doi.org/10.1016/j.atmosenv.2013.12.022>.
- Pikridas, M., Vrekoussis, M., Sciare, J., Kleanthous, S., Vasiliadou, E., Kizas, C., Savvides, C., Mihalopoulos, N., 2018. Spatial and temporal (short and long-term) variability of submicron, fine and sub-10  $\mu$ m particulate matter (PM1, PM2.5, PM10) in Cyprus. *Atmos. Environ.* 191, 79–93. <https://doi.org/10.1016/j.atmosenv.2018.07.048>.
- RAR, 2002. Summary Risk Assessment Report for 1,3-butadiene, CAS: 106-99-0 (European Commission), pp. 2–6. Special Publication I.02.110.
- Ren, L., Fu, P., He, Y., Hou, J., Chen, J., Pavuluri, C.M., Sun, Y., Wang, Z., 2016. Molecular distributions and compound-specific stable carbon isotopic compositions of lipids in wintertime aerosols from Beijing. *Sci. Rep.* 6 (May), 1–12. <https://doi.org/10.1038/srep27481>.
- Rattanavaraha, W., Chu, K., Budisulistiorini, S.H., Riva, M., Lin, Y.H., Edgerton, E.S., Baumann, K., Shaw, S.L., Guo, H., King, L., Weber, R.J., Neff, M.E., Stone, E.A., Offenber, J.H., Zhang, Z., Gold, A., Surratt, J., 2016. Assessing the impact of anthropogenic pollution on isoprene-derived secondary organic aerosol formation in PM<sub>2.5</sub> collected from the Birmingham, Alabama, ground site during the 2013 Southern Oxidant and Aerosol Study. *Atmos. Chem. Phys.* 16, 4897–4914. <https://doi.org/10.5194/acp-16-4897-2016>.
- Ren, Y., Wang, G., Tao, J., Zhang, Z., Wu, C., Wang, J., Li, J., Wei, J., Li, H., Meng, F., 2019. Seasonal characteristics of biogenic secondary organic aerosols at Mt. Wuyi in Southeastern China: influence of anthropogenic pollutants. *Environ. Pollut.* 252, 493–500. <https://doi.org/10.1016/j.envpol.2019.05.077>.
- Sandrini, S., Fuzzi, S., Piazzalunga, A., Prati, P., Bonasoni, P., Cavalli, F., Bove, M.C., Calvello, M., Cappelletti, D., Colombi, C., Contini, D., de Gennaro, G., Di Gilio, A., Fermo, P., Ferrero, L., Gianelle, V., Giuliano, M., Ielpo, P., Gilardoni, S., 2014. Spatial and seasonal variability of carbonaceous aerosol across Italy. *Atmos. Environ.* 99, 587–598. <https://doi.org/10.1016/j.atmosenv.2014.10.032>.
- Sato, K., Hatakeyama, S., Imamura, T., 2007. Secondary organic aerosol formation during the photooxidation of toluene: NOx dependence of chemical composition. *J. Phys. Chem.* 111 (39), 9796–9808. <https://doi.org/10.1021/JP071419F>.
- Schauer, J.J., Kleeman, M.J., Cass, G.R., Simoneit, B.R.T., 1999. Measurement of emissions from air pollution sources. 1. C1 through C29 organic compounds from meat charbroiling. *Environ. Sci. Technol.* 33 (10), 1566–1577. <https://doi.org/10.1021/es980076j>.
- Shannigrahi, A.S., Pettersson, J.B.C., Langer, S., Arrhenius, K., Hagström, M., Janhäll, S., Hallquist, M., Pathak, R.K., 2014. N-Alkanolic monocarboxylic acid concentrations in urban and rural aerosols: seasonal dependence and major sources. *Atmos. Res.* 143, 228–237. <https://doi.org/10.1016/j.atmosres.2014.01.020>.
- Sheesley, R.J., Schauer, J.J., Bean, E., Kenski, D., 2004. Trends in secondary organic aerosol at a remote site in Michigan's upper peninsula. *Environ. Sci. Technol.* 38 (24), 6491–6500. <https://doi.org/10.1021/es049104q>.
- Shrivastava, M., Cappa, C.D., Fan, J., Goldstein, A.H., Guenther, A.B., Jimenez, J.L., Kuang, C., Laskin, A., Martin, S.T., Ng, N.L., Petaja, T., Pierce, J.R., Rasch, P.J., Roldin, P., Seinfeld, J.H., Shilling, J., Smith, J.N., Thornton, J.A., Volkamer, R., Wang, J., Worsnop, D.R., Zaveri, R.A., Zelenyuk, A., Zhang, Q., 2017. Recent advances in understanding secondary organic aerosol: implications for global climate forcing. *Rev. Geophys.* 55 (2), 509–559. <https://doi.org/10.1002/2016RG000540>.
- Siciliano, T., Siciliano, M., Malitesta, C., Proto, A., Cucciniello, R., Giove, A., Iacobellis, S., Genga, A., 2018. Carbonaceous PM10 and PM2.5 and secondary organic aerosol in a coastal rural site near Brindisi (Southern Italy). *Environ. Sci. Pollut. Control Ser.* 25 (24), 23929–23945. <https://doi.org/10.1007/s11356-018-2237-2>.
- Simoneit, B.R.T., Mazurek, M.A., 1982. Organic-matter of the troposphere. 2. Natural background of biogenic lipid matter in aerosols over the rural western United-States. *Atmos. Environ.* 16 (9), 2139–2159. [https://doi.org/10.1016/0004-6981\(82\)90284-0](https://doi.org/10.1016/0004-6981(82)90284-0).
- Simoneit, B.R.T., 1985. Application of molecular marker analysis to vehicular exhaust for source reconciliations. *Int. J. Environ. Anal. Chem.* 22 (3–4), 203–232. <https://doi.org/10.1080/03067318508076422>.
- Simoneit, B.R.T., 2002. Biomass burning - a review of organic tracers for smoke from incomplete combustion. *Appl. Geochem.* 17 (3), 129–162. [https://doi.org/10.1016/S0883-2927\(01\)00061-0](https://doi.org/10.1016/S0883-2927(01)00061-0).
- Simoneit, B.R.T., Medeiros, P.M., Didyk, B.M., 2005. Combustion products of plastics as indicators for refuse burning in the atmosphere. *Environ. Sci. Technol.* 39 (18), 6961–6970. <https://doi.org/10.1021/es050767x>.
- Stephanou, E.G., Stratigakis, N., 1993. Oxocarboxylic and  $\alpha,\omega$ -dicarboxylic acids: photooxidation products of biogenic unsaturated fatty acids present in urban aerosols. *Environ. Sci. Technol.* 27 (7), 1403–1407. <https://doi.org/10.1021/es00044a016>.
- Stone, E.A., Zhou, J.B., Snyder, D.C., Rutter, A.P., Mieritz, M., Schauer, J.J., 2009. A comparison of summertime secondary organic aerosol source contributions at contrasting urban locations. *Environ. Sci. Technol.* 43 (10), 3448–3454. <https://doi.org/10.1021/es8025209>.
- Stone, E.A., Yoon, S.C., Schauer, J.J., 2011. Chemical characterization of fine and coarse particles in Gosan, Korea during springtime dust events. *Aerosol Air Qual. Res.* 11 (1), 31–43. <https://doi.org/10.4209/aaqr.2010.08.0069>.
- Surratt, J.D., Murphy, S.M., Kroll, J.H., Ng, N.L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Claeys, M., Flagan, R.C., Seinfeld, J.H., 2006. Chemical composition of secondary organic aerosol formed from the photooxidation of isoprene. *J. Phys. Chem.* 110 (31), 9665–9690. <https://doi.org/10.1021/jp061734m>.
- Szmigielski, R., Surratt, J.D., Vermeylen, R., Szmigielska, K., Kroll, J.E., Ng, N.L., Murphy, S.M., Sorooshian, A., Seinfeld, J.H., Claeys, M., 2007. Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol formed from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion

- trap mass spectrometry. *J. Mass Spectrom.* 42 (1), 101–116. <https://doi.org/10.1002/jms.1146>.
- Tedetti, M., Kawamura, K., Narukawa, M., Joux, F., Charrière, B., Sempéré, R., 2007. Hydroxyl radical-induced photochemical formation of dicarboxylic acids from unsaturated fatty acid (oleic acid) in aqueous solution. *J. Photochem. Photobiol. Chem.* 188 (1), 135–139. <https://doi.org/10.1016/j.jphotochem.2006.11.029>.
- Theodosi, C., Panagiotopoulos, C., Nourara, A., Zarmas, P., Nicolaou, P., Violaki, K., Kanakidou, M., Sempéré, R., Mihalopoulos, N., 2018. Sugars in atmospheric aerosols over the eastern mediterranean. *Prog. Oceanogr.* 163, 70–81. <https://doi.org/10.1016/j.pocean.2017.09.001>.
- Van Pinxteren, D., Neustüß, C., Herrmann, H., 2014. On the abundance and source contributions of dicarboxylic acids in size-resolved aerosol particles at continental sites in central Europe. *Atmos. Chem. Phys.* 14 (8), 3913–3928. <https://doi.org/10.5194/acp-14-3913-2014>.
- Volkamer, R., Jimenez, J.L., San Martini, F., Dzepina, K., Zhang, Q., Salcedo, D., Molina, L.T., Worsnop, D.R., Molina, M.J., 2006. Secondary organic aerosol formation from anthropogenic air pollution: rapid and higher than expected. *Geophys. Res. Lett.* 33, L17811. <https://doi.org/10.1029/2006GL026899>.
- Wang, G., Xie, M., Hu, S., Gao, S., Tachibana, E., Kawamura, K., 2010. Dicarboxylic acids, metals and isotopic compositions of C and N in atmospheric aerosols from inland China: implications for dust and coal burning emission and secondary aerosol formation. *Atmos. Chem. Phys.* 10 (13), 6087–6096. <https://doi.org/10.5194/acp-10-6087-2010>.
- WHO, 2006. WHO Air Quality Guidelines for Particulate Matter, Ozone, Nitrogen Dioxide and Sulfur Dioxide – Global Update 2005 – Summary of Risk Assessment.
- Williams, J.E., van Velthoven, P.F.J., Brenninkmeijer, C.A.M., 2013. Quantifying the uncertainty in simulating global tropospheric composition due to the variability in global emission estimates of Biogenic Volatile Organic Compounds. *Atmos. Chem. Phys.* 13, 2857–2891. <https://doi.org/10.5194/acp-13-2857-2013>.
- Xu, G., Jiao, L., Zhang, B., Zhao, S., Yuan, M., Gu, Y., Liu, J., Tang, X., 2017. Spatial and temporal variability of the PM<sub>2.5</sub>/PM<sub>10</sub> ratio in Wuhan, Central China. *Aerosol Air Qual. Res.* 17 (3), 741–751. <https://doi.org/10.4209/aaqr.2016.09.0406>.
- Yang, L.M., Yu, L.E., Ray, M.B., 2008. Potential photooxidation pathways of dicarboxylic acids in atmospheric droplets. *Am. J. Environ. Sci.* 4 (5), 462–466. <https://doi.org/10.3844/ajessp.2008.462.466>.
- Yin, H.L., Qiu, C.Y., Ye, Z.X., Li, S.P., Liang, J.F., 2014. Seasonal variation and source apportionment of organic tracers in PM<sub>10</sub> in Chengdu, China. *Environ. Geochem. Health* 37 (1), 195–205. <https://doi.org/10.1007/s10653-014-9636-1>.
- Yokouchi, Y., Ambe, Y., 1986. Characterization of polar organics in airborne particulate matter. *Atmos. Environ.* 20 (9), 1727–1734. [https://doi.org/10.1016/0004-6981\(86\)90121-6](https://doi.org/10.1016/0004-6981(86)90121-6).
- Zangrando, R., Barbaro, E., Kirchgorg, T., Vecchiato, M., Scalabrin, E., Radaelli, M., Dordević, D., Barbante, C., Gambaro, A., 2016. Five primary sources of organic aerosols in the urban atmosphere of Belgrade (Serbia). *Sci. Total Environ.* 571, 1441–1453. <https://doi.org/10.1016/j.scitotenv.2016.06.188>.
- Zhang, Y.Y., Müller, L., Winterhalter, R., Moortgat, G.K., Hoffmann, T., Pöschl, U., 2010a. Seasonal cycle and temperature dependence of pinene oxidation products, dicarboxylic acids and nitrophenols in fine and coarse air particulate matter. *Atmos. Chem. Phys.* 10 (16), 7859–7873. <https://doi.org/10.5194/acp-10-7859-2010>.
- Zhang, Z., Engling, G., Lin, C.Y., Chou, C.C.K., Lung, S.C.C., Chang, S.Y., Fan, S., Chan, C.Y., Zhang, Y.H., 2010b. Chemical speciation, transport and contribution of biomass burning smoke to ambient aerosol in Guangzhou, a mega city of China. *Atmos. Environ.* 44 (26), 3187–3195. <https://doi.org/10.1016/j.atmosenv.2010.05.024>.
- Zhao, X., Wang, X., Ding, X., He, Q., Zhang, Z., Liu, T., Fu, X., Gao, B., Wang, Y., Zhang, Y., Deng, X., Wu, D., 2014. Compositions and sources of organic acids in fine particles (PM<sub>2.5</sub>) over the Pearl River Delta region, south China. *Journal of Environ. Sci.* 26 (1), 110–121. [https://doi.org/10.1016/S1001-0742\(13\)60386-1](https://doi.org/10.1016/S1001-0742(13)60386-1).
- Zhu, C., Kawamura, K., Kunwar, B., 2015. Effect of biomass burning over the western North Pacific Rim: wintertime maxima of anhydrosugars in ambient aerosols from Okinawa. *Atmos. Chem. Phys.* 15, 1959–1973. <https://doi.org/10.5194/acp-15-1959-2015>.
- Zhu, Y., Yang, L., Kawamura, K., Chen, J., Ono, K., Wang, X., Xue, L., Wang, W., 2017. Contributions and source identification of biogenic and anthropogenic hydrocarbons to secondary organic aerosols at Mt. Tai in 2014. *Environ. Pollut.* 220 (Pt B), 863–872. <https://doi.org/10.1016/j.envpol.2016.10.070>.

## Web References

News. Last accessed at 12/12/2019). <https://www.airquality.dli.mlsi.gov.cy/news/archive/2017?page=0>.