

## Supplementary information for:

### Insights into the secondary fraction of the organic aerosol in a Mediterranean urban area: Marseille

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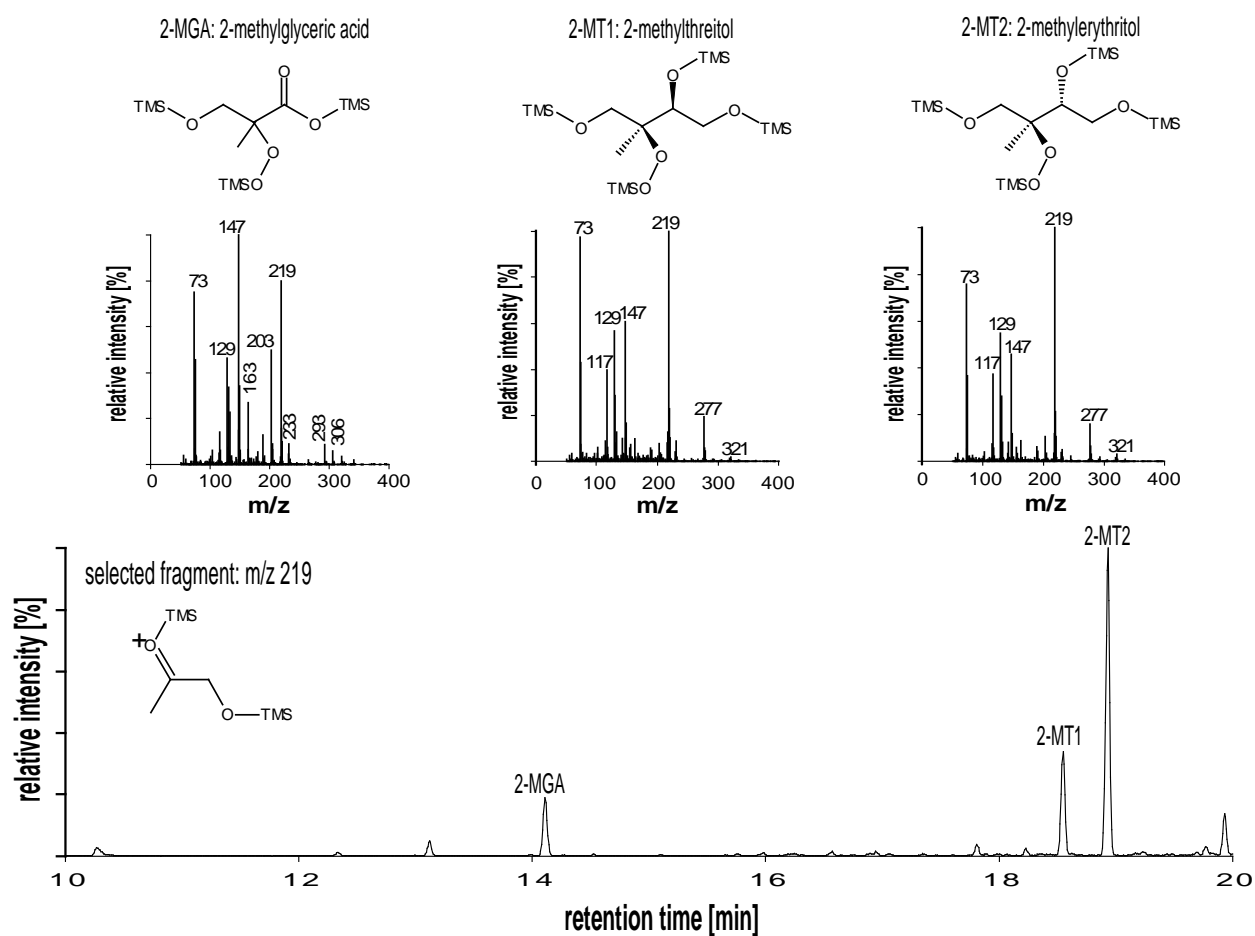
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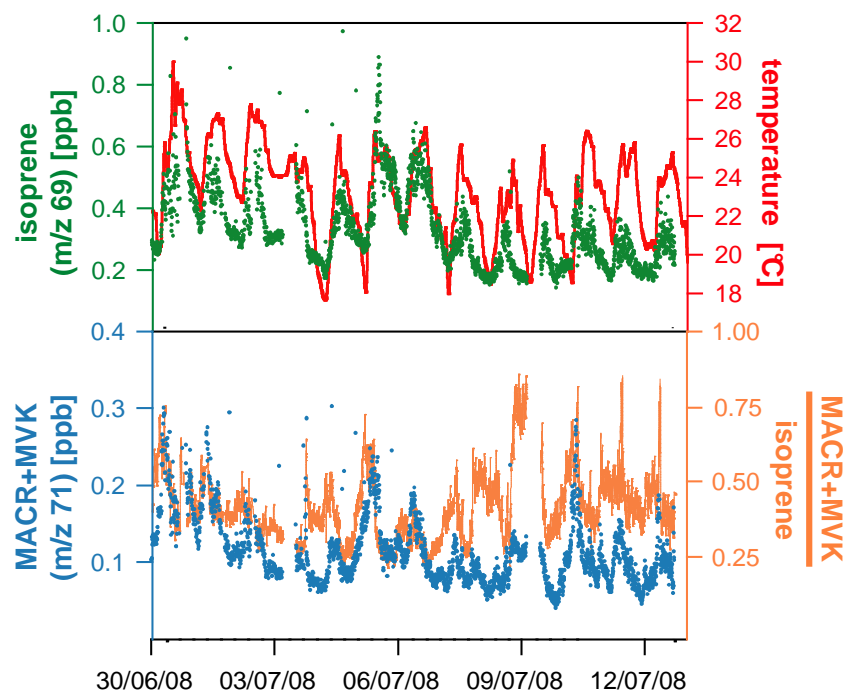
## Notations

2-MGA	: 2-methylglyceric acid
2-MT1	: 2-methylthreitol
2-MT2	: 2-methylerythritol
2-MT	: 2-methyltetrols (sum of 2-MT1 and 2-MT2)
A1	: 3-hydroxyglutaric acid
A2	: 3-(2-hydroxyethyl)-2,2-dimethylcyclobutane carboxylic acid
A3	: 3-hydroxy-4,4-dimethylglutaric acid
A4	: 3-acetylglutaric acid
A5	: 3-acetyladipic acid
A6	: 3-isopropylglutaric acid
A7	: 3-methyl-1,2,3-butanetricarboxylic
BSOA	: Biogenic Secondary Organic Aerosol
BSOC	: Biogenic Secondary Organic Carbon
BSTFA	: N,O-bis(trimethylsilyl)-trifluoroacetamide
C	: $\beta$ -caryophyllenic acid
CI	: Chemical Ionization
CMB	: Chemical Mass balance
CMB-SOC	: CMB unapportioned OC (mostly from secondary origin)
EC	: Elemental Carbon
EI	: Electron Ionization
$f_c$	: Contemporary Fraction
$f_f$	: Fossil Fraction
$f_m$	: Modern Fraction
$f_{SOC}$	: marker based approach established by Kleindienst et al., 2007 for the apportionment of SOC derived from specific hydrocarbons
HULIS	: HUmic Like Substances
HULIS <sub>WS</sub>	: Water Soluble HUmic Like Substances
HULIS <sub>T</sub>	: Total HUmic Like Substances
iEPOX	: isoprene dihydroxyperoxide
iRO <sub>2</sub>	: isoprene hydroxyperoxy radicals
iROOH	: isoprene hydroxyhydroperoxides
L	: 3-carboxyheptanoic acid
MACR	: methacrolein
MD	: Molecular Weight of TMS Derivatives
MVK	: methylvinylketone
MW	: Molecular Weight
OA	: Organic Aerosol
OC	: Organic Carbon
OM	: Organic Matter

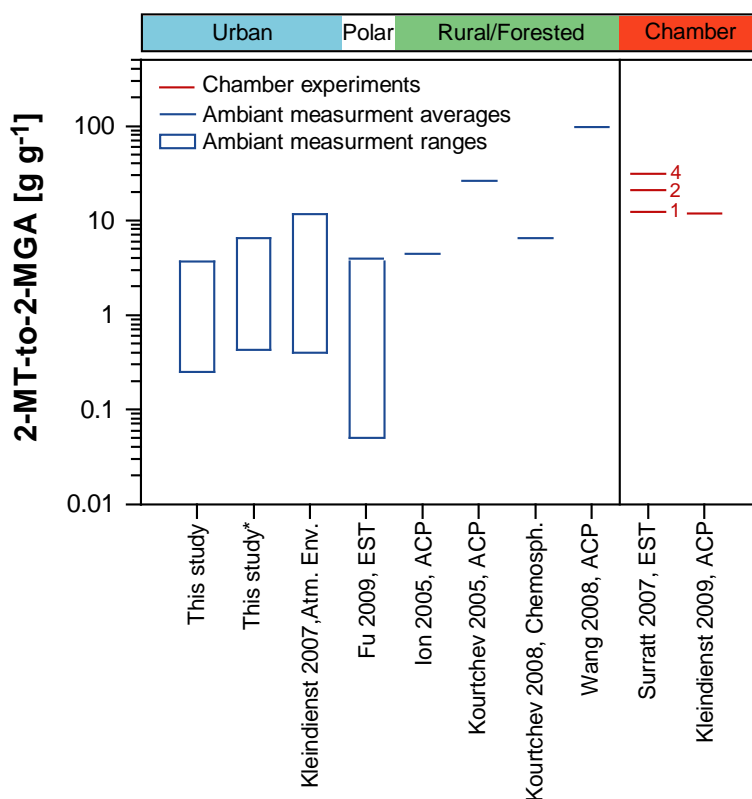
OOA	: Oxygenated Organic Aerosol derived from AMS/PMF analysis
OPOA	: Oxidized Primary Organic Aerosol
Other SOC	: OC fraction that is not attributed to traditional BSOC or to POC
PA	: pinic acid
PC <sub>C</sub>	: Primary Contemporary Carbon
PC <sub>F</sub>	: Primary Fossil Carbon
PM	: Particulate Matter
POA	: Primary Organic Aerosol
POC	: Primary Organic Carbon
POC <sub>C</sub>	: Primary Contemporary Organic Carbon
POC <sub>F</sub>	: Primary Fossil Organic Carbon
PNA	: pinonic acid
RT	: Retention time
SOA	: Secondary Organic Aerosol
SOC	: Secondary Organic Carbon
SOC <sub>C</sub>	: Secondary Contemporary Organic Carbon
SOC <sub>F</sub>	: Secondary Fossil Organic Carbon
TC <sub>C</sub>	: Total Contemporary Carbon
TC <sub>F</sub>	: Total Fossil Carbon
TEOM-FDMS	: Tapered Element Oscillating Microbalance – Filter Dynamic Measurement System
TMS	: trimethylsilyl
TOC	: Total Organic Carbon
Traditional BSOC	: sum of BSOC derived from isoprene, $\alpha$ -pinene and $\beta$ -caryophyllene estimated using $f_{\text{SOC}}$ approach
VOC	: Volatile Organic Compounds



**Figure S1:** GC-MS chromatogram (selected ion: m/z 219) of BSTFA derivatives of isoprene SOC markers in ambient PM<sub>2.5</sub>.



**Figure S2:** Temporal trends of isoprene (m/z 69) [ppb] and the sum of methacrolein and methylvinylketone (MACR+MVK, m/z 71) [ppb] measured by HS-PTRMS. Also shown are temporal trends of temperature [°C] and (MACR+MVK)-to-isoprene ratio.



**Figure S3:** comparison of 2-MT-to-2-MGA ratios found in ambient aerosol and chamber experiments (Ion et al., 2005;Kourtchev et al., 2005;Kleindienst et al., 2007;Surratt et al., 2007;Kourtchev et al., 2008;Wang et al., 2008;Fu et al., 2009;Kleindienst et al., 2009). For Surratt et al. (2007), the numbers 1, 2, and 4 denote neutral, mid acidic and high acidic seed aerosol.

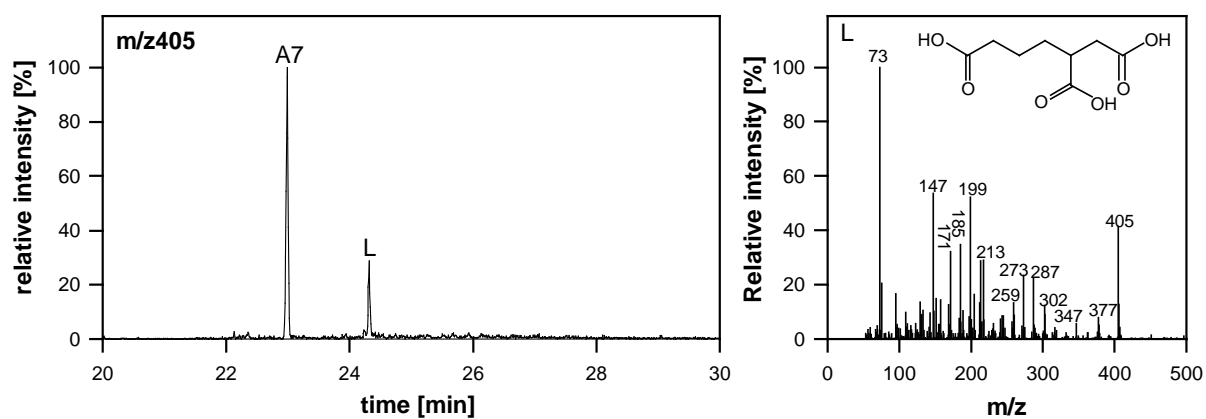
The 2-MT-to-2-MGA ratio represents a key parameter in the estimation of isoprene SOA, as discussed in section 4.1.3. In this study this ratio ranges from 0.3 to 3.7 g g<sup>-1</sup> and a strong dependence upon the NO<sub>x</sub> concentrations has been highlighted (higher ratios at lower NO<sub>x</sub> concentrations). This result suggests that the fate of isoprene RO<sub>2</sub> plays a major role in the formation of 2-methyltetrols (2-MT) and 2-methylglyceric acid (2-MGA).

Figure S3 compares 2-MT-to-2-MGA ratios obtained in this study with those reported in different environments and chamber experiments (Ion et al., 2005;Kourtchev et al., 2005;Kleindienst et al., 2007;Surratt et al., 2007;Kourtchev et al., 2008;Wang et al., 2008;Fu et al., 2009;Kleindienst et al., 2009). The first noteworthy feature in this figure is that 2-MT-to-2-MGA ratios found in ambient measurements span more than three orders of magnitude [0.05-100 g g<sup>-1</sup>], suggesting that this ratio and hence the fate of isoprene RO<sub>2</sub> seems to be highly dependant on the ambient oxidation conditions. It can be noticed furthermore that this wide range of ratios encompasses the one found in our study.

In order to compare our 2-MT-to-2-MGA ratios with those reported in Kleindienst et al. (2007) at the urban site of the Research Triangle Park, North Carolina, one has to consider the biases induced by the use of different quantification surrogates. In our case, we have used the glyceric acid and the threitol as surrogate standards to quantify the atmospheric concentrations of 2-MGA and 2-MT, respectively. For contrast, a single compound (cis-ketopinic acid) was used in Kleindienst et al. (2007) for the

quantification of both compounds in ambient aerosol and chamber experiments. Using a single compound instead of the two surrogates used here would increase our 2-MT-to-2-MGA ratios by a systematic factor of 1.7 (indicated in Figure 1 by the term “**This study\***”) and allows the direct comparison with Kleindienst et al. (2007) data. In such conditions, the range of ratios found in this study matches the range measured by Kleindienst et al. (2007).

With respect to the same ratio reported in chamber experiments, the measured values are significantly higher than those found in urban environments (This study, Kleindienst et al. (2007)), which is one of the most influencing sources of uncertainty in the estimation of isoprene SOA (section 4.1.3). In particular, under no  $\text{NO}_x$  where the 2-MT are predominant compounds and the 2-MT-to-2-MGA are the highest (Surratt et al., 2006;Paulot et al., 2009), the value reported in Kleindienst et al. (2009) for isoprene OH-oxidation is  $12 \text{ g g}^{-1}$  (Kleindienst et al., 2009). Consequently, in urban sites, one would expect that inputs of  $\text{NO}_x$  would lead to lower values (Surratt et al., 2006;Paulot et al., 2009), which is totally in agreement with our findings.



**Figure S4:** GC-MS chromatogram (selected ion:  $m/z$  405) of BSTFA derivatives of C8-tricarboxylic acids in ambient  $PM_{2.5}$ . A7 denotes 3-methyl-1,2,3-butanetricarboxylic acid a marker of  $\alpha$ -pinene, which originate from further reaction of pinic acid (Szmigielski et al., 2007;Kourtchev et al., 2009). L is tentatively identified as 3-carboxyheptanedioic acid, a specific marker of  $\delta$ -limonene SOA by comparison of its mass spectral patterns to that reported in Kourtchev et al. (2009).



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