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# Secondary organic aerosol formation and composition from the photo-oxidation of methyl chavicol (estragole)

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# Abstract

The increasing demand for palm oil for uses in biofuel and food products is leading to rapid expansion of oil palm agriculture. Methyl chavicol (also known as estragole and 1-allyl-4-methoxybenzene) is an oxygenated biogenic volatile organic compound that uses recently identified as the main flexel emission form on all palm plantation in

- that was recently identified as the main floral emission from an oil palm plantation in Malaysian Borneo. The emissions of methyl chavicol observed may impact regional atmospheric chemistry, but little is known of its ability to form secondary organic aerosol (SOA). The photo-oxidation of methyl chavicol was investigated at the European Photoreactor chamber as a part of the atmospheric chemistry of methyl chavicol (AT-MERCH).
- MECH) project. Aerosol samples were collected using a particle into liquid sampler (PILS) and analysed offline using an extensive range of instruments including; high performance liquid chromatography mass spectrometry (HPLC-ITMS), high performance liquid chromatography quadrupole time-of-flight mass spectrometry (HPLC-QTOFMS) and Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS). The
- <sup>15</sup> SOA yield was determined as 18–29% depending on initial precursor (VOC:NO<sub>x</sub>) mixing ratios. In total, 59 SOA compounds were observed and the structures of 10 compounds have been identified using high resolution tandem mass spectrometry. The addition of hydroxyl and/or nitro functional groups to the aromatic ring appears to be an important mechanistic pathway for aerosol formation. This results in the formation of
- <sup>20</sup> compounds with both low volatility and high O: C ratios, where functionalisation rather than fragmentation is mainly observed as a result of the stability of the ring. The SOA species observed can be characterized as semi-volatile to low volatile oxygenated organic aerosol (SVOOA and LVOOA) components and therefore may be important in aerosol formation and growth.





# 1 Introduction

The atmospheric oxidation of volatile organic compounds (VOCs) in the presence of NO<sub>x</sub> results in the formation of tropospheric ozone and secondary organic aerosol (SOA). Whilst SOA formation is known to have adverse effects on climate and human <sup>5</sup> health (Solomon et al., 2007; Bernstein et al., 2004; Davidson et al., 2005; Pöschl, 2005), the VOC oxidation pathways leading to SOA formation are poorly understood (Hallquist et al., 2009). It has been estimated that as many as 10<sup>4</sup>-10<sup>5</sup> VOCs have been detected in the atmosphere, all of which may undergo atmospheric oxidation and contribute to SOA formation (Goldstein and Galbally, 2007). Approximately 90% of all global VOC emissions are from biogenic sources (Guenther et al., 1995). The most abundant biogenic emissions are attributed to isoprene (35-40%), monoterpenes (11-25%) and oxygenated VOCs (reactive other VOCs and other VOCs, 20-30%) (Guenther et al., 1995, 2000). The largest source of biogenic VOC emissions are from vegetation; including trees (which account for ~71% of emissions; Guenther et al., 1995).

- shrubs and crops, with a small emission source from grasslands and soils (Guenther et al., 1995, 2000; Zimmerman, 1979; Wiedinmyer et al., 2004). Oxygenated VOCs (OVOCs) have received more attention recently due to the advances in instrumentation to detect and quantify these compounds in the ambient atmosphere. Despite this, significant uncertainties still remain in our knowledge of the sources, chemical compo-
- <sup>20</sup> sition and atmospheric oxidation mechanisms of OVOCs, in particular higher molecular weight species (> $C_5$ ) (Singh et al., 2000; Steiner et al., 2008; Taipale et al., 2012; Schade and Goldstein, 2001; Bouvier-Brown, 2008).

Methyl chavicol ( $C_{10}H_{12}O$ ), also known as estragole and 1-allyl-4-methoxybenzene, is a  $C_{10}$  aromatic biogenic OVOC emitted from a variety of pine trees (including pon-

<sup>25</sup> derosa pine), shrubs (*Clausena dunniana*, straggley Baeckea) and common herbs (basil, fennel, tarragon) (Werker et al., 1994; Simon et al., 1990; Southwell et al., 2003; Mirov, 1961; Bouvier-Brown et al., 2009; De Vincenzi et al., 2000; Barazani et al., 2002; Adams, 2007; Holzinger et al., 2005, 2010). A recent publication identified significant





methyl chavicol emissions above the canopy of an oil palm plantation in Malaysian Borneo, with a mean midday flux of 0.81 mgm<sup>-2</sup> h<sup>-1</sup> and a mean mixing ratio of 3.0 ppbv (maximum mixing ratio observed ~7.0 ppbv) (Misztal et al., 2010). Methyl chavicol emissions from palm oil plantations were estimated to result in a global emission of

- ~ 0.5 Tg yr<sup>-1</sup> (Misztal et al., 2010). There are currently 43 oil palm producing countries, with the majority of oil palm plantations concentrated in Indonesia and Malaysia (FAO-STAT, 2012). In 2011, there were approximately 7.7 million hectares (Mha) of oil palm plantations in Indonesia (USDA, 2013) and 5.0 Mha in Malaysia (MPOB, 2012). The increasing demand for palm oil for uses in food products and biofuels is resulting in the
- rapid expansion of oil palm agriculture (Fitzherbert et al., 2008). Consequently, methyl chavicol emissions are likely to have a considerable effect on regional chemistry in locations where oil palm plantations are significant. Despite this, there have been few literature reports which have investigated the atmospheric fate of methyl chavicol, including gas-phase degradation, SOA formation, composition and yields.
- <sup>15</sup> The gas phase products formed from the oxidation of methyl chavicol with hydroxyl radicals (<sup>•</sup>OH), and ozone (O<sub>3</sub>) has been investigated by Lee et al. (2006a) and Lee et al. (2006b), and more recently by Bloss et al. (2012), who reported measurements of the gas-phase reactivity of methyl chavicol with <sup>•</sup>OH and O<sub>3</sub>, and by Gai et al. (2013) who in addition investigated the oxidation of methyl chavicol with NO<sub>3</sub>. In the study performed by Lee et al. (2006b) the photo-oxidation of methyl chavicol resulted in
- significant SOA formation (yield 40%) and the formation of two abundant structurally unidentified gas phase compounds, MW 136 ( $C_8H_8O_2$ , yield 42±9%) and MW 150 ( $C_9H_{10}O_2$ , yield 23±5%), detected using proton transfer reaction mass spectrometry (PTR-MS). Bouvier-Brown et al. (2009) identified MW 136 as 4-methoxybenzaldhyde
- in the aerosol phase at Blodgett forest (California, US) and suggested the identification of pinonaldehyde (MW 150) (Holzinger et al., 2005) could be in part attributed to 4-methoxybenzene acetaldehyde (MW 150) identified in Lee et al. (2006b). In addition, Cahill et al. (2006) tentativly identified 4-methoxybenzene acetaldehyde in aerosol samples collected in the Sierra Nevada Mountains. More recently, Gai et al. (2013)





identified a futher two abundant gas phase products, MW 122 4-methoxytoluene, and MW 166 4-methoxybenzeneacteic acid, and identified MW 136 and MW 150 as 4-methoxybenzaldhyde and 4-methoxybenzene acetaldhyde, respectively, in support of the literature. To our knowledge, however, the aerosol phase composition and mecha-<sup>5</sup> nisms of formation from the photo-oxidation of methyl chavicol has largely been unexplored.

The aim of this study is to characterize the SOA oxidation products formed from the photo-oxidation of methyl chavicol and determine their formation mechanisms. Experiments were performed at the European Photoreactor chamber in Valencia, Spain,

as a part of the atmospheric chemistry of methyl chavicol (ATMECH) project. Aerosol samples were collected using a particle into liquid sampler (PILS). SOA composition was investigated using an extensive range of instruments, including; high performance liquid chromatography ion trap mass spectrometry (HPLC-ITMS), high performance liquid chromatography quadrupole time-of-flight mass spectrometry (HPLC-QTOFMS)

and Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS).

### 2 Materials and methods

#### 2.1 Chamber simulation experiments

Experiments were performed at the European Photoreactor (EUPHORE) in Valencia, Spain. The EUPHORE facility comprises of two 200 m<sup>3</sup> hemispheric reaction chambers
<sup>20</sup> made of fluorinated ethyl propylene foil, with housings which may be closed to exclude sunlight. Chamber temperature is near ambient and chamber pressure is maintained at approximately 100 Pa above ambient. Dry scrubbed air is used within the chamber and two large fans ensure homogenous mixing. Further technical information regarding the chamber design and installation can be found in the literature (Becker, 1996; Klotz
<sup>25</sup> et al., 1998; Volkamer et al., 2001; Bloss et al., 2005). A series of experiments were



performed during May 2012 and the initial mixing ratios, chamber temperatures and relative humidities are presented in Table 1.

The chamber was cleaned before each experiment by flushing with scrubbed dry air overnight. Methyl chavicol was introduced into the chamber through a heated air stream. An extensive range of monitors were used to measure chamber temperature (temperature sensor, model PT100), pressure (Barometer, model AIR-DB-VOC), humidity (Hygrometer Watz, model Walz-TS2), solar intensity ( $J_{NO_2}$  Filter Radiometer), ozone (Monitor Labs, model 9810) and  $NO_x$  (Teledyne API, model  $NO_x$ \_API-T200UP; photolytic converter). PTR-MS (Ionikon Analytik) and Fourier transform infra red (FTIR Nicolet Magna, model 550), coupled to a white-type mirror system with an optical path length of 326.8 m, were used to monitor methyl chavicol decay and product formation. The chamber dilution rate was calculated by measuring the decay of an inert tracer gas, sulphur hexafluoride (SF<sub>6</sub>), using FTIR; typical pseudo-first-order rate constants of 2 × 10<sup>-5</sup> s<sup>-1</sup> were obtained, corresponding to a dilution lifetime around 14 h. The formation and evolution of secondary organic aerosol (SOA) was measured using a scanning methility particle sizer (TSL lagerpareted medel 2080) epseiding of a differential

ning mobility particle sizer (TSI Incorporated, model 3080) consisting of a differential mobility analyzer (model 3081) and a condensation particle counter (model 3775).

# 2.2 Aerosol sampling and sample preparation

A Brechtel Manufacturing Inc (California, US) model 4002 PILS was used for aerosol collection. The PILS inlet was connected to the chamber outlet using approximately 1.5 m of 1/4" stainless steel tubing. Aerosol samples were collected using a PM<sub>1</sub> impactor, with an average flow rate of 13 Lmin<sup>-1</sup>. Acidic, basic and organic gases were removed from the sampled air through the use of denuders, prepared as per manufacture instructions. The wash flow rate was set at 240 µLmin<sup>-1</sup> and consisted of optima LC-MS grade water (Fisher Scientific, UK). The sample flow rate transferred the aerosol water mixture (optima LC-MS grade water) into sealed vials at a flow rate of 200 µLmin<sup>-1</sup> for 30 min per sample. Samples were collected before the addition of





methyl chavicol or NO into the chamber and continued sampling until after the chamber was closed. After sample collection, punctured vial caps were replaced and securely sealed with parafilm. All vials were wrapped in foil to minimise potential degradation from photolysis and were stored at -20 °C until analysis. Collected PILS samples were evaporated to dryness using a V10 vacuum solvent evaporator (Biotage, USA) and redissolved in 300 µL of 50 : 50 methanol : water (optima LC-MS grade, Fisher, UK), with the exception of experiment MC<sub>high</sub>, which was redissolved in 500 µL.

# 2.3 HPLC-ITMS

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SOA composition was investigated using an Agilent 1100 series high performance liquid chromatography (HPLC, Berkshire, UK) coupled to a HTC Plus ion trap mass spectrometer (IT-MS, Bruker Daltonics, Bremen, Germany). A reversed phase Pinnacle C18 150 mm × 4.6 mm, 5 µm particle size column (Thames Resteck, UK) was used. The HPLC mobile phase composition consisted of (A) water (optima LC-MS grade, Fisher, UK) with 0.1 % formic acid (Sigma Aldrich, UK) and (B) methanol (optima LC-MS grade,

- Fisher, UK). Gradient elution was used, starting at 90 % (A) 10 % (B), moving to 0 % (A) 100 % (B) over 60 min, returning to the initial starting conditions at 65 min. A 5 min prerun consisting of the starting mobile phase composition was performed before each sample injection. The flow rate was set at 0.6 mLmin<sup>-1</sup> with a sample injection volume of 60 μL. Electrospray ionisation (ESI) was used, with a dry gas flow rate of 12 Lmin<sup>-1</sup>,
- <sup>20</sup> a dry gas temperature of 365 °C and nebuliser gas pressure of 70 psi (oxygen free nitrogen, OFN, BOC, UK). The MS was operated in alternating polarity mode, scanning from m/z 50 to 600. Tandem MS was achieved through the automated MS<sup>2</sup> function within the Esquire software (Bruker Daltonics, software version 5.2).

#### 2.4 FTICR-MS

<sup>25</sup> A solariX Fourier transform ion cyclotron resonance mass spectrometer with a 9.4 T superconducting magnet (Bruker Daltonics, Coventry, UK) was used and externally







- ics, Breman, Germany). Monoisotopic elemental formulae were calculated using the following restrictions; unlimited C, H and O were allowed and up to 3 N atoms, O: C < 3, H: C > 0.5, DBE < 20, and in positive mode, Na and K adducts were also allowed. The
- <sup>15</sup> accuracy of the molecular formulae (elemental composition) assignment in shown by the error; where the error equals the difference between the exact and measured mass for the assigned molecular formula. The mass error (also referred to as mass accuracy) is displayed in ppm and is calculated by dividing the mass error by the exact mass for the assigned molecular formula and multiplying by 10<sup>6</sup>. The molecular formula score
- <sup>20</sup> refers to the fit of the theoretical and measured isotopic distribution and abundance for the assigned molecular formula, and is displayed in percentage. The molecular formula score is not calculated for a signal to noise (*S/N*) ratio below 5. The combination of a high score and low mass accuracy will result in few potential molecular formula assignments for a compound at a given m/z. A compound with an m/z below 300, with
- a high score (100%) and low mass accuracy (<5ppm) results in only one potential molecular formula (Kind and Fiehn, 2006).





# 2.5 HPLC-QTOFMS

A Dionex ultimate 3000 HPLC (Thermo Scientific Inc, UK) was coupled with an ultra high resolution guadrupole time-of-flight mass spectrometer (HPLC-QTOFMS) (maXis 3G, Bruker Daltonics, Coventry, UK). The HPLC utilised the same reverse phase Pinnacle C18 column and mobile phase composition as described in the HPLC-ITMS 5 analysis. The gradient elution runtime was shortened, starting at 90% (A) 10% (B), moving to 0% (A) 100% (B) over 50 min and returning to the initial starting conditions at 55 min. A 5 min pre-run was performed before each sample injection using the starting mobile phase composition. The flow rate was set to 0.6 mLmin<sup>-1</sup> and the column temperature controlled at 20°C. A user defined autosampler method was created. 10 drawing 58 µL of sample into the sample loop, followed by 2 µL of a 10 ppm external standard mix and 20 µL of 50 : 50 methanol : water (optima LC-MS grade, Fisher, UK). The HPLC-QTOFMS was externally calibrated using ESI-L low concentration tuning mix (Agilent Technologies, UK). ESI was used and the parameters were set to a dry gas flow rate of 10 Lmin<sup>-1</sup>, dry gas temperature of 350 °C and a nebulizer pressure of 15 4 bar (nitrogen, BOC, UK). Tandem mass spectra were acquired for a mass range of m/z 50 to 800 using the auto MS<sup>2</sup> function within the Compass 1.3 micrOTOF-SR3 software, control version 3.0 (Bruker Daltonics, UK). The three most abundant precursor ions per spectrum were automatically selected by the software and subjected to

collision induced dissociation (CID). The collision energy for CID fragmentation was set at 8.0 eV at a collision RF of 800.0 Vpp. The spectral analysis was performed using DataAnalysis 4.0 software (Bruker Daltonics, Breman, Germany). The molecular formula error and score was automatically calculated by the DataAnalysis software using the same methods as described in the FTICR-MS analysis.

#### 25 2.6 Standards and calibrations

A 10 ppm external standard (ES) mix was used to monitor the ITMS detector variation over the course of the sample analysis. The ES mix was also used for the optimisa-





tion of the HPLC-QTOFMS method, internal mass calibration and to determine the retention time shift of the SOA compounds due to the shortening of the gradient elution. The ES mix consisted of 5 compounds, 4-methoxybenzoic acid (Sigma Aldrich, UK, purity 99%), hexanedioic acid (Sigma Aldrich, UK, purity 99%), cis-pinonic acid

Sigma Aldrich, UK, purity 99%), 2-hydroxyhexanoic acid (Acros Organics, Belgium, purity 95%) and 2,6-dimethyl-3-nitrophenol (synthesized by University College Cork). These compounds were selected based on their range of retention times, stability, variety of functional groups and ionisation efficiency in both positive and negative ionisation modes.

#### 10 3 Results and discussion

Three experiments carried out as part of the ATMECH campaign are discussed here: (i)  $MC_{(0)}$ ; a chamber background experiment, where no VOCs or NO<sub>x</sub> were added to the chamber and the chamber housing was opened to expose the chamber to light. None of the methyl chavicol SOA compounds identified were observed in this experiment. (ii) MC<sub>high</sub>; a photo-oxidation experiment with high initial mixing ratios of methyl 15 chavicol (460 ppbv) and NO (92 ppbv) and, (iii) MC<sub>low</sub>; a photo-oxidation experiment with lower mixing ratios of methyl chavicol (212 ppbv) and NO (38 ppbv), with a similar initial VOC: NO<sub>x</sub> ratio (~5:1) to MC<sub>high</sub>. The temporal evolution of NO<sub>x</sub>, O<sub>3</sub>, methyl chavicol and SOA growth are shown in Fig. 1 and show similar profiles to previous aromatic photo-oxidation experiments, with initiation of aerosol formation occurring when 20 the photo-chemical system enters into a relatively "low NO" state (cf. Rickard et al., 2010). The maximum SOA mass observed, corrected for wall loss and chamber dilution, was 420  $\mu g\,m^{-3}$  and 126  $\mu g\,m^{-3}$  in  $MC_{high}$  and  $MC_{low,}$  respectively. The SOA yield (Y) was calculated using the equation given in Odum et al. (1996), where the amount of aerosol mass formed  $[\Delta M_0, \mu gm^{-3}]$  was divided by the amount of methyl chavicol 25 reacted [ $\Delta$ MC,  $\mu$ gm<sup>-3</sup>], assuming spherical aerosol shape with a density of 1.4 gcm<sup>-3</sup>. The SOA yield was determined as 18% and 29% for experiments MC<sub>low</sub> and MC<sub>high</sub>





**Figures** Tables Back Close Full Screen / Esc **Printer-friendly Version** Interactive Discussion

respectively, showing a larger yield at higher initial mixing ratios as seen previously (Song et al., 2005).

#### 3.1 SOA composition

- The PILS samples were analysed using a series of complementary analytical techniques. Initially, the HPLC-ITMS was used to screen the PILS samples for SOA species. 5 Any compounds observed in the PILS samples before the introduction of methyl chavicol and NO into the chamber in MC<sub>high</sub> and MC<sub>low</sub> were excluded from further analysis. Compounds which displayed changes in their chromatographic peak areas (and thus concentration) were investigated further. In the MC<sub>high</sub> experiment, 59 SOA compounds were observed in the PILS samples using HPLC-ITMS. Of these compounds, 57 were observed with matching retention times and/or fragmentation patterns in the MC<sub>low</sub> experiment. In MC<sub>high</sub>, fragmentation data was obtained for 56 of the 59 SOA compounds using HPLC-ITMS<sup>2</sup>. In many cases it was not possible to identify the compound structures of the SOA species due to the low mass resolution of the ITMS and lack of commercially available standards. This resulted in the use of the FTICR-MS to aid in the identification of the SOA molecular formulae and compound structures. The
- use of FTICR-MS significantly aided in compound identification, providing the molecular formulae for 49 of the 59 SOA compounds with average error of 0.14 ppm for negative ionisation mode and 5.72 ppm for positive ionisation mode. FTICR-MS<sup>2</sup> could
- not be performed due to the lack of prior chromatographic separation and the low con-20 centration of the SOA compounds. Instead, HPLC-QTOFMS<sup>2</sup> was used to obtain high mass resolution compound fragmentation data for the SOA compounds. The HPLC-QTOFMS identified the molecular formulae of 54 of the 59 SOA compounds with an average error of 4.52 ppm for negative ionisation mode and 27.29 ppm for positive ion-
- isation mode. The use of the HPLC-QTOFMS was complementary to the FTICR-MS, 25 allowing the comparison of two high mass resolution data sets to determine the molecular formulae of the SOA compounds, as shown in Table 2 and Supplement Tables 1



and 2. The use of prior chromatographic separation with the QTOFMS was advantageous and allowed the molecular formulae of the 10 low concentration SOA compounds not identified using FTICR-MS to be determined. Of the 59 SOA compounds, the FTICR-MS and the HPLC-QTOFMS were in agreement of the molecular formulae

- <sup>5</sup> for 37 SOA compounds. Only one high resolution mass spectrometric technique provided the molecular formulae for 14 SOA compounds and for 7 SOA compounds the molecular formulae provided by the HPLC-QTOFMS and FTICR-MS were not in agreement. A complete list of the identified SOA species including the molecular formulae identification and associated errors can be found in the Supplement Tables 1 and 2.
- <sup>10</sup> A Van Krevelen plot of the 59 SOA compounds is shown in Supplement Fig. 1. The average O: C and H: C ratio was determined as 0.44 and 1.29, respectively. Of the 59 SOA compounds, the structures of 10 have been assigned and are shown in Table 2. The structures of (4-methoxyphenyl)acetic acid and 4-methoxybenzoic acid have been confirmed using the retention time and fragmentation patterns of commercially avail-
- <sup>15</sup> able standards. All other compound structures have been determined from the deprotonated or protonated molecular species fragmentations obtained from the HPLC-ITMS<sup>2</sup> and HPLC-QTOFMS<sup>2</sup>. The product ions of two deprotonated molecular species are discussed here as examples to illustrate the methodology used to assign SOA compound structures. Compound 1 with a MW of 243 g mol<sup>-1</sup> was assigned the molecular formula
- $_{20}$  C<sub>10</sub>H<sub>13</sub>NO<sub>6</sub> with 5 double bond equivalents (DBE). Compound 1 contains the same number of carbon atoms and one more degree of saturation than the original VOC precursor, methyl chavicol (C<sub>10</sub>H<sub>12</sub>O). In addition, compound 1 was identified in the first PILS sample containing SOA (shortest reaction time) in the MC<sub>high</sub> experiment. The similarity of the carbon number, degree of saturation, and the identification of this com-
- <sup>25</sup> pound during the initial particle growth, would suggest the structure of compound 1 was similar to that of the precursor, a substituted methoxyphenyl. The product ions of m/z242 [M–H]<sup>-</sup> (compound 1) are summarized in Table 3. Compound 1 was identified as 3-(5-hydroxy-4-methoxy-2-nitrophenyl)propane-1,2-diol using the observed fragments discussed below and shown in Fig. 2. The highest intensity fragment ion at m/z 224





is due to the loss of water ( $H_2O$ ) occurring through hydrogen abstraction, Fig. 2a. The base peak loss of  $H_2O$  would suggest the presence of an aliphatic alcohol, most likely terminal. The loss of  $H_2O$  results in an intermolecular rearrangement of the fragment ion, resulting in the formation of a double bond, indicated by the increase in the DBE by

- <sup>5</sup> 1. The fragment ion at m/z 182 has formed as a result of a subsequent loss of C<sub>2</sub>H<sub>2</sub>O from m/z 224, which is supported by the decrease in the DBE by 1 for the remaining fragment ion. The fragment ion at m/z 182 results from a total loss of C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>, suggesting the presence of a second hydroxyl group on the leaving group, most likely on the adjacent carbon to the first alcohol group, Fig. 2b. The fragment ion at m/z 167 has formed as a result of an odd electron cleavage (OE), resulting in the formation of
- $[C_7H_5NO_4]^{\bullet-}$  and the loss of  $[C_3H_7O_2]^{\bullet}$ , Fig. 2c. OE cleavages are unusual in CID and are often associated with resonance stabilised ring structures and nitrogen containing functional groups (Fu et al., 2006; Holčapek et al., 2007, 2010; Hayen et al., 2002).
- Assuming the remaining deprotonated radical fragment ion at m/z 167 [C<sub>7</sub>H<sub>5</sub>NO<sub>4</sub>]<sup>•</sup> is a substituted methoxyphenyl, the subtraction of the methoxy  $[OCH_3]$  and aromatic 15  $[C_6H_2]^-$  group from the molecular formula would leave N<sub>1</sub>O<sub>3</sub> unaccounted for. This suggests either a nitrate group (R-ONO<sub>2</sub>), or a hydroxyl (R-OH) and a nitro (R-NO<sub>2</sub>) group are attached to the ring. The presence of a nitrate group on the ring is likely to result in the loss of NO<sub>2</sub> or ONO<sub>2</sub> from the fragmentation of the carbon-oxygen or oxygen-nitrogen bond during CID (Zhao and Yinon, 2002; Holčapek et al., 2010). 20 Furthermore, the lability of the nitrate group often results in spontaneous fragmentation in the softest ESI conditions, resulting in the fragment ions ONO<sub>2</sub> and NO<sub>2</sub> at m/z 63 and m/z 47, respectively (Holčapek et al., 2010; Yinon et al., 1997). However, no fragment ion at m/z 63 for ONO<sub>2</sub> was observed. A peak at m/z 137 (intensity 1.33%) was observed and was attributed to [C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>]<sup>•-</sup>, the loss of NO from the fragment ion 25 at m/z 167  $[C_7H_5NO_4]^{\bullet-}$ , Fig. 2c. The loss of NO is a typical for nitro functional groups in negative ionisation mode using CID (Holčapek et al., 2010; Fu et al., 2006; Schmidt et al., 2006; Yinon et al., 1997). The rearrangement of bonds from R-NO<sub>2</sub> to R-ONO results in the loss of NO (Schmidt et al., 2006). Nitro functional groups usually result



in the loss of NO and NO<sub>2</sub>. However, the loss of only NO has been observed for some compounds containing a nitro functional group and has previously been suggested to be the result of an electron donating substituent in the para position to the nitro group, enhancing the loss of NO by resonance stabilisation (Bursey and McLafferty, 1966; Bursey, 1969).

The location of phenyl substitutions has proved to be difficult to determine using CID due to the lack of ring fragmentation as a result of resonance stabilisation. In addition, the N-containing compounds that were observed to undergo ring fragmentation exhibited complex re-arrangements making the identification of these compound structures a difficult task. The most likely locations of phenyl substitutions can be identified however, by considering the formation mechanisms of these compounds in the gas phase (Ziemann and Atkinson, 2012; Calvert et al., 2002). Methyl chavicol has two phenyl substituents, a methoxy group and an hydrocarbon (HC) chain, both of which are ortho, para directing (March, 1992). The stronger activating group of the two phenyl

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- <sup>15</sup> substituents, the methoxy group, will determine the most energetically favoured and resonance stabilised position of an addition to the ring (March, 1992). The para position to the methoxy group is occupied by the HC chain and therefore the initial oxidation of a hydroxyl radical to the ring of methyl chavicol would be most energetically favoured at the ortho position to the methoxy group (Ziemann and Atkinson, 2012). The location
- <sup>20</sup> of the nitro group on the ring is more difficult to assign. Assuming the hydroxyl radical is already attached to the ring, the most strongly activating group would now be the hydroxyl group, which is also ortho, para directing (March, 1992). The ortho position to the hydroxyl group is more sterically hindered by the adjacent HC chain and hydroxyl group, compared to the para position, which is only sterically hindered by the HC chain.
- It is therefore suggested that the nitro group is located in the para position to the hydroxyl group. The suggested location of the nitro and hydroxyl group on the ring is also supported by the mechanism suggested in Bursey (1969) and Bursey and McLafferty (1966), where the loss of only NO is observed for a nitro functional group during CID when an activating group is located in the para position to the nitro group.





Compound 5, with a MW of  $198 \text{ gmol}^{-1}$  was assigned the molecular formula  $C_{10}H_{14}O_4$  with 4 DBE. The product ions of m/z 197  $[M-H]^-$  (compound 5) are summarized in Table 4. Compound 5 was identified as 3-(3-hydroxy-4-methoxyphenyl)propane-1,2-diol from the product ions discussed here and shown in Fig. 3. Both compounds 1 and 5 exhibit similar HC chain fragmentation, with the loss of 18 Da (H<sub>2</sub>O) and 42 Da (C<sub>2</sub>H<sub>2</sub>O<sub>2</sub>), Fig. 3a and b. The product ion  $[C_7H_7O_2]^-$  at m/z 123 resulted from an even electron (EE) loss of  $C_3H_6O_2$ , unlike the OE loss of  $[C_3H_7O_2]^\bullet$  observed for compound 1, Fig. 3c. Compound 5 does not have a nitro group present on the ring and as a result the resonance stabilization of the aromatic ring is lower than in compound 1. The decrease in resonance stabilisation results in an EE cleavage and the abstraction of a hydrogen from the leaving group to the aromatic ring. Hydrogen abstraction from the loss group results in an intermolecular re-arrangement and the loss of  $C_3H_6O_2$ . Therefore, the same HC chain has been suggested for both compounds 1

and 5. Assuming a methoxyphenyl sub-structure, the deprotonated product ion would <sup>15</sup> leave  $[C_6H_3O]^-$  from product ion  $[C_7H_7O_2]^-$  at m/z 123, suggesting a hydroxyl group is attached to the aromatic ring.

# 3.2 Mechanism of formation

A proposed mechanism for the formation of compounds 1, 5, 8, 9 and 10 is shown in Fig. 4. The formation of these compounds can be rationalised as the products of <sup>20</sup> methyl chavicol oxidation by considering typical gas phase oxidation mechanisms (Ziemann and Atkinson, 2012; Calvert et al., 2002). The initial oxidation of methyl chavicol will proceed mainly through the <sup>•</sup>OH radical addition mechanism (Atkinson, 1997b; Calvert et al., 2002; Ziemann and Atkinson, 2012) and can attack the ring and/or the HC chain. <sup>•</sup>OH radical addition can occur on either carbon of the double bond of the HC chain, resulting in the formation of primary and secondary β-hydroxyalkyl radicals.

<sup>25</sup> HC chain, resulting in the formation of primary and secondary  $\beta$ -hydroxyalkyl radicals, with the secondary  $\beta$ -hydroxyalkyl radical pathway being the most favoured (approximately 85% using Peeters et al. (2007) <sup>•</sup>OH addition structure activity relationship)





(Atkinson, 2000, 1997b; Cvetanovic, 1976). The resulting  $\beta$ -hydroxyalkyl radicals react predominantly with O<sub>2</sub> to form  $\beta$ -hydroxyperoxy radicals. The high concentration of NO at the beginning of MC<sub>high</sub> and MC<sub>low</sub> will result in the conversion of NO to NO<sub>2</sub> (leading to O<sub>3</sub> formation) and the formation of  $\beta$ -hydroxyalkoxy radicals as the major pathway.  $\beta$ -hydroxyalkoxy radicals can react with O<sub>2</sub>, decompose or isomerize. Decomposition and isomerisation are expected to be the dominant pathways, with the exception of the HOCH<sub>2</sub>CH<sub>2</sub>O<sup>•</sup> radical (from ethene + <sup>•</sup>OH), for which decomposition and reaction with O<sub>2</sub> can be competitive (Atkinson, 1997b, a; Fuchs et al., 2011).

For both types of  $\beta$ -hydroxyalkoxy radicals formed, decomposition followed by rapid reaction with O<sub>2</sub> leads to the formation of formaldehyde, HO<sub>2</sub> and (4methoxyphenyl)acetaldehyde (Atkinson, 1997b; Orlando et al., 2003). Isomerisation through a 1, 5-H atom shift from the aromatic ring to the HC chain is suggested to be of minor importance due to the resonance stability of the ring. The reaction with O<sub>2</sub> (minor pathway) would result in the loss of HO<sub>2</sub> and the formation of the observed first gener-

- ation compound, 1-hydroxy-3-(4-methoxyphenyl)propan-2-one (compound 9), Fig. 4a. Further oxidation of this compound through the addition of a hydroxyl radical to the ring results in the formation of 1-hydroxy-3-(3-hydroxy-4-methoxyphenyl)propan-2-one (compound 10), Fig. 4b. As discussed in the previous section, the initial hydroxyl addition to the ring will occur at the ortho position to the methoxy group, the position which
- <sup>20</sup> is most energetically favoured and resonance stabilised. Compound 8, 2-hydroxy-3-(3hydroxy-4-methoxyphenyl)propanal, is also suggested to be a second generation compound which has formed through the oxidation of the primary  $\beta$ -hydroxyalkoxy radicals with O<sub>2</sub> (the less favoured pathway) and has been further oxidised by the addition of a hydroxyl radical to the ring, Fig. 4c.

As a relatively "low NO<sub>x</sub> state" is entered in MC<sub>high</sub> and MC<sub>low</sub> the RO<sub>2</sub> + RO<sub>2</sub> reaction will begin to dominate over the competing reaction with NO (Atkinson, 1997b; Stockwell et al., 1990). The cross/self reaction of  $\beta$ -hydroxyperoxy radicals will proceed mainly through two pathways; the radical pathway and non-radical pathway (hydrogen abstraction), with the radical pathway accounting for approximately 30–80 % of



the RO<sub>2</sub> + RO<sub>2</sub> reaction (Atkinson, 1997b; Madronich and Calvert, 1990). The radical pathway (major pathway) will result in the formation of  $\beta$ -hydroxyalkoxy radicals with the loss of  $O_2$ . The  $\beta$ -hydroxyalkoxy radicals can then undergo oxidation through the same mechanisms as discussed above, resulting in a secondary pathway for the for-5 mation of compounds 8, 9 and 10, Fig. 4d-f, respectively. A third minor pathway to the formation of compounds 8, 9 and 10 can also occur through the  $RO_2 + RO_2$  non radical pathway; where one peroxy radical abstracts a hydrogen atom from another peroxy radical, resulting in the formation of an alcohol and carbonyl, respectively, with the loss of O<sub>2</sub> (Madronich and Calvert, 1990; Howard and Ingold, 1968). The hydrogen atom is abstracted from the carbon bonded to the peroxy radical, thus the abstraction 10 of a hydrogen atom from a secondary  $\beta$ -hydroxyperoxy radical will result in the formation of 1-hydroxy-3-(4-methoxyphenyl)propan-2-one (compound 9), Fig. 4g. The further oxidation of this compound though the reaction with <sup>•</sup>OH will result in the formation of 1-hydroxy-3-(3-hydroxy-4-methoxyphenyl)propan-2-one (compound 10), Fig. 4h. Moreover, the abstraction of a hydrogen from a primary  $\beta$ -hydroxyperoxy radical followed by 15 the further oxidation of an 'OH radical to the ring, will result in the formation of 2hydroxy-3-(3-hydroxy-4-methoxyphenyl)propanal (compound 8), Fig. 4i.

The formation of the diol on the HC chain of compound 1 [3-(5-hydroxy-4-methoxy-2-nitrophenyl)propane-1,2-diol], and compound 5 [3-(3-hydroxy-4-

- <sup>20</sup> methoxyphenyl)propane-1,2-diol], could have occurred through two mechanisms; unimolecular isomerisation of the  $\beta$ -hydroxyalkoxy radical through a 1,5 H-atom shift, or the self/cross RO<sub>2</sub> reactions of the  $\beta$ -hydroxyperoxy radicals through the non-radical pathway. The isomerisation pathway would seem unlikely due to the formation of a alkyl radical on the carbon where the H-atom was abstracted, which
- <sup>25</sup> could decompose, isomerise, or react with O<sub>2</sub>, with the latter resulting in the formation of a more oxidised product than observed. Decomposition would result in the formation of a compound with fewer carbon atoms than required, and isomerisation would still result in an alkyl radical. The self/cross reactions of  $\beta$ -hydroxyperoxy radicals would appear to be the more likely pathway, particularly under low NO<sub>x</sub> conditions. After



the formation of a diol on the HC chain, the further oxidation via hydroxyl radical addition to the ring would result in the formation of the third generation SOA compound, 3-(3-hydroxy-4-methoxyphenyl)propane-1,2-diol (compound 5), Fig. 4j. Further addition of NO<sub>2</sub> to the ring of compound 5 through the hydrogen atom abstraction pathway leads to the formation of a fourth generation SOA compound 3-(5-hydroxy-4-methoxy-2-nitrophenyl)propane-1,2-diol (Compound 1), Fig. 4k. A hydroxyl radical can abstract a hydrogen atom from the oxygen-hydrogen bond of the hydroxyl group on the substituted phenol, resulting in the formation of a phenoxy radical and the loss of H<sub>2</sub>O (Forstner et al., 1997; Atkinson, 1994, 2000). The phenoxy radical can then react with NO<sub>2</sub> to form a substituted nitrophenol (Atkinson, 1994, 2000; Forstner et al., 1997).

Compounds 2, 3, 4, 6 and 7, contain acid functional groups and less carbon atoms than the original VOC precursor, methyl chavicol. These compounds appear to be later generation SOA species and could have formed through a number of potential mecha-

- <sup>15</sup> nisms, such as reactions with ozone (O'Neal and Blumstein, 1973; Orzechowska and Paulson, 2005; Neeb et al., 1996; Calvert et al., 2000), and/or with hydroxyl radicals (Forstner et al., 1997), although the detailed reaction mechanisms for the formation of organic acids from hydroxyl radicals has not been properly established (Carlton et al., 2009). Compounds 4 and 7 appear to be the further oxidation products of compounds
- 20 2 and 6, through the addition of a hydroxyl radical to ring. In addition, compound 3 appears to be the further oxidation product of compound 7, through a second addition of a hydroxyl radical to the ring. Here we suggest the second addition of the hydroxyl radical to the ring of compound 7 is in the para position to the hydroxyl group, the most resonance stabilised and least sterically hindered position.

# 25 3.3 Atmospheric relevance

The SOA yield obtained in this study for the photo-oxidation of methyl chavicol, in  $MC_{low}(18\%)$  and  $MC_{high}$  (29%) are comparatively lower than the 40% SOA yield reported previously (Lee et al., 2006b), although there are a number of key differences





between the two studies. Lee et al. (2006b) used ammonium sulfate seed (compared to the nucleation only experiments presented here), which has been shown to substantially increase SOA yields (Czoschke et al., 2003; Gao et al., 2004; Jang et al., 2002; Zhou et al., 2011). In addition, the percentage relative humidity (% RH) was approximately 5 times greater in the study performed by Lee et al. (2006b). Recent 5 publications have shown that the SOA mass formed from a substituted aromatic compound (p-xylene), increases with increasing % RH, approximately by a factor of 2 over a % RH range of 5 to 75 % (Zhou et al., 2011; Healy et al., 2009). Moreover, the hydrocarbon to NO<sub>v</sub> ratio (HC: NO<sub>v</sub>) in the study performed by Lee et al. (2006b) was greater (HC/NO<sub>x</sub> =  $\sim$  8) than that in this study (HC/NO<sub>x</sub> =  $\sim$  5), which may account for 10 the lower SOA yield obtained in this study (Kroll and Seinfeld, 2008). Nevertheless, it is clear the photo-oxidation of methyl chavicol results in significant SOA formation. Recent literature has shown oxygenated biogenic VOCs containing 10 carbon atoms (including eucalyptol, verbenone, linalool) resulted in an SOA yield between 16 to 20%, with the use of acidic seed (linuma et al., 2008; Varutbangkul et al., 2006; Lee et al., 2006b). 15

- It is difficult to directly compare SOA yields from the oxidation of a similar VOC precursor in the literature due to the limitations of using chamber derived data (Camredon et al., 2007). However, reported SOA yields of methyl chavicol were the highest of all oxygenated VOCs investigated (SOA yield 26–40%) (Lee et al., 2006b; Varutbangkul
- et al., 2006). Although these experiments are at concentrations higher than the real atmosphere, they suggest that methyl chavicol can act as an important SOA precursor in regions where methyl chavicol emissions are significant, such as downwind from pine forests and oil palm plantations.

Four compounds with a MW of 122, 136, 150 and 166 were observed in the gas phase using PTR-MS and may be attributed to 4-methoxytoluene, 4methoxybenzaldhyde, 4-methoxybenzene acetaldehyde and (4-methoxyphenyl)acetic acid, respectively, in agreement with Lee et al. (2006b), Spada et al. (2008) and Gai et al. (2013). However, in contrast to Cahill et al. (2006) and Bouvier-Brown et al. (2009) 4-methoxybenzaldhyde (MW 136) and 4-methoxybenzene acetaldehyde





(MW 150) were not identified in the aerosol phase in this study. Compound vapour pressures were calculated using the UManSysProp website (http://ratty.cas.manchester.ac. uk/informatics/) at 298.15 K, using the Nannoolal vapour pressure and boiling point extrapolation method (Nannoolal et al., 2004, 2008) and the saturation concentration ( $C^*$ ,  $\mu gm^{-3}$ ) determined (Donahue et al., 2006a). The calculated volatility of these compounds suggests they are intermediate VOCs (4-methoxybenzaldehyde,  $C^* = 4.96 \times 10^5 \,\mu gm^{-3}$  and 4-methoxybenzene acetaldehyde,  $C^* = 3.02 \times 10^5 \,\mu gm^{-3}$ ). The use of gas phase scrubbers for organics in the PILS sampler used in this study may indicate that previous ambient observations are due to positive artifacts from gas phase absorption to filters.

The saturation concentration ( $C^*$ ,  $\mu gm^{-3}$ ) (Donahue et al., 2006a) and O:C ratio were determined for all the identified compounds and plotted in a O:C/log<sub>10</sub> ( $C^*$ ,  $\mu gm^{-3}$ ) volatility basis set space (Donahue et al., 2013; Jimenez et al., 2009), as shown in Fig. 5. All of the identified SOA compounds retained the aromatic ring, with O:C ratios between 0.20 to 0.62 and bit C ratios between 1.11 and 1.40. The evidetion

- O: C ratios between 0.30 to 0.63 and H: C ratios between 1.11 and 1.40. The oxidation of methyl chavicol and its early generation products resulted in the formation of low vapour pressure and a high O: C ratio species, due to the lack of ring fragmentation. This resulted in the movement of the SOA compounds to lower volatilities and higher O: C ratios, thus functionalisation rather than fragmentation was mainly observed. The
- <sup>20</sup> majority of the SOA species underwent oxidation on the aromatic ring, through the addition of <sup>•</sup>OH and/or NO<sub>2</sub>. The formation of compound 1 (3-(5-hydroxy-4-methoxy-2-nitrophenyl)propane-1,2-diol) through the addition of a NO<sub>2</sub> group on the aromatic ring resulted in the movement of this species to the low volatility oxygenated organic aerosol region (LVOOA), and just outside the extremely low volatility oxygenated or-
- 25 ganic aerosol (ELVOOA) nucleator region proposed by Donahue et al. (2013). Ring addition appears to be an important pathway, resulting in the formation of low volatility species with high O:C ratios, which may also be important for other aromatic compounds. The structures of only 10 of the 59 SOA compounds have so far been iden-





tified. Further work is required to characterize the SOA formed from methyl chavicol oxidation at different mixing ratios and with different oxidants ( $O_3$ ,  $NO_3$ ).

Supplementary material related to this article is available online at http://www.atmos-chem-phys-discuss.net/13/33105/2013/ acpd-13-33105-2013-supplement.pdf.

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# References

15

Adams, R. P.: Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry, 4th edn., Allured Publishing Corporation, Carol Stream, 2007.

Atkinson, R.: Gas-phase trosposheric chemistry of organic compounds, J. Phys. Chem. Ref. Data, Monograph, 2, 1–216, 1994.

Atkinson, R.: Atmospheric reactions of alkoxy and  $\beta$ -hydroxyalkoxy radicals, Int. J. Chem. Kinet., 29, 99–111, doi:10.1002/(sici)1097-4601(1997)29:2<99::aid-kin3>3.0.co;2-f, 1997a.

<sup>20</sup> Atkinson, R.: Gas-phase tropospheric chemistry of volatile organic compounds: 1. Alkanes and alkenes, J. Phys. Chem. Ref. Data, 26, 215–290, 1997b.

Atkinson, R.: Atmospheric chemistry of VOCs and NO<sub>x</sub>, Atmos. Environ., 34, 2063–2101, doi:10.1016/s1352-2310(99)00460-4, 2000.

Barazani, O., Cohen, Y., Fait, A., Diminshtein, S., Dudai, N., Ravid, U., Putievsky, E., and Fried-

<sup>25</sup> man, J.: Chemotypic differentiation in indigenous populations of *Foeniculum vulgare* var. *vulgare* in Israel, Biochem. Syst. Ecol., 30, 721–731, 2002.





- Becker, K.: EUPHORE: Final Report to the European Commission, Contract# EV5V-CT92-0059, Bergische Universität Wuppertal, Wuppertal, Germany, 1996.
- Bernstein, J. A., Alexis, N., Barnes, C., Bernstein, I. L., Nel, A., Peden, D., Diaz-Sanchez, D., Tarlo, S. M., and Williams, P. B.: Health effects of air pollution, J. Allergy Clin. Immun., 114, 1116–1123, 2004.
- Bloss, C., Wagner, V., Bonzanini, A., Jenkin, M. E., Wirtz, K., Martin-Reviejo, M., and Pilling, M. J.: Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against environmental chamber data, Atmos. Chem. Phys., 5, 623–639, doi:10.5194/acp-5-623-2005, 2005.
- <sup>10</sup> Bloss, W. J., Alam, M. S., Rickard, A. R., Hamilton, J. F., Pereira, K. L., Camredon, M., Muñoz, A., Vázquez, M., Alacreu, P., Ródenas, M., and Vera, T.: Atmospheric chemistry of methyl chavicol (estragole), AGU Fall Meeting, San Francisco, Fall meeting 3 to 7 December 2012, A33L-0313, 2012.

Bouvier-Brown, N. C.: Quantifying Reactive Biogenic Volatile Organic Compounds: Implica-

- tions for Gas- and Particle-Phase Atmospheric Chemistry, ProQuest, University of California, Berkeley, CA, 2008.
  - Bouvier-Brown, N. C., Goldstein, A. H., Worton, D. R., Matross, D. M., Gilman, J. B., Kuster, W. C., Welsh-Bon, D., Warneke, C., de Gouw, J. A., Cahill, T. M., and Holzinger, R.: Methyl chavicol: characterization of its biogenic emission rate, abundance, and oxidation
- <sup>20</sup> products in the atmosphere, Atmos. Chem. Phys., 9, 2061–2074, doi:10.5194/acp-9-2061-2009, 2009.
  - Bursey, M. M.: Influence of steric inhibition of resonance on ion intensities in mass spectra, J. Am. Chem. Soc., 91, 1861–1862, doi:10.1021/ja01035a053, 1969.

Bursey, M. M. and McLafferty, F. W.: Rearrangements and "flat-topped metastable ions"

- <sup>25</sup> in the mass spectra of substituted nitrobenzenes, J. Am. Chem. Soc., 88, 5023–5025, doi:10.1021/ja00973a047, 1966.
  - Cahill, T. M., Seaman, V. Y., Charles, M. J., Holzinger, R., and Goldstein, A. H.: Secondary organic aerosols formed from oxidation of biogenic volatile organic compounds in the Sierra Nevada Mountains of California, J. Geophys. Res., 111, D16312, doi:10.1029/2006JD007178. 2006.

30

Calvert, J. G., Atkinson, R., Kerr, J., Madronich, S., Moortgat, G., Wallington, T. J., and Yarwood, G.: The Mechanisms of Atmospheric Oxidation of the Alkenes, Oxford University Press, New York, 2000.





Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G.: The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons, Oxford University Press, New York, 2002.

Camredon, M., Aumont, B., Lee-Taylor, J., and Madronich, S.: The SOA/VOC/NO<sub>x</sub> system: an

explicit model of secondary organic aerosol formation, Atmos. Chem. Phys., 7, 5599–5610, doi:10.5194/acp-7-5599-2007, 2007.

Carlton, A. G., Wiedinmyer, C., and Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene, Atmos. Chem. Phys., 9, 4987–5005, doi:10.5194/acp-9-4987-2009, 2009.

- <sup>10</sup> Cvetanovic, R.: Chemical kinetic studies of atmospheric interest, 12th International Symposium on Free Radicals, 4–9 January, Laguna Beach, CA, 1976.
  - Czoschke, N. M., Jang, M., and Kamens, R. M.: Effect of acidic seed on biogenic secondary organic aerosol growth, Atmos. Environ., 37, 4287–4299, 2003.

Davidson, C. I., Phalen, R. F., and Solomon, P. A.: Airborne particulate matter and human health: a review, Aerosol Sci. Tech., 39, 737–749, 2005.

15

30

De Vincenzi, M., Silano, M., Maialetti, F., and Scazzocchio, B.: Constituents of aromatic plants: II. Estragole, Fitoterapia, 71, 725–729, 2000.

Donahue, N., Robinson, A., Stanier, C., and Pandis, S.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, Environ. Sci. Technol., 40, 2635–2643, 2006a.

- <sup>20</sup> Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, Environ. Sci. Technol., 40, 2635–2643, doi:10.1021/es052297c, 2006b.
  - Donahue, N., Chuang, W., Ortega, I. K., Riipinen, I., Riccobono, F., Schobesberger, S., Dommen, J., Kulmala, M., Worsnop, D., and Vehkamaki, H.: How do organic vapors contribute to
- new-particle formation?, Faraday Discuss., 165, 1–13, doi:10.1039/c3fd00046j, 2013. Fitzherbert, E. B., Struebig, M. J., Morel, A., Danielsen, F., Brühl, C. A., Donald, P. F., and Phalan, B.: How will oil palm expansion affect biodiversity?, Trends Ecol. Evol., 23, 538–545, doi:10.1016/j.tree.2008.06.012, 2008.

Food and Agriculture Organization of the United Nations: available at: http://faostat3.fao.org/ faostat-gateway/go/to/home/E (last access: 11 August 2013), 2012.

Forstner, H. J., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol from the photooxidation of aromatic hydrocarbons: molecular composition, Environ. Sci. Technol., 31, 1345– 1358, 1997.





Fu, X., Zhang, Y., Shi, S., Gao, F., Wen, D., Li, W., Liao, Y., and Liu, H.: Fragmentation study of hexanitrostilbene by ion trap multiple mass spectrometry and analysis by liquid chromatography/mass spectrometry, Rapid Commun. Mass Sp., 20, 2906–2914, 2006.

Fuchs, H., Bohn, B., Hofzumahaus, A., Holland, F., Lu, K. D., Nehr, S., Rohrer, F., and Wahner, A.: Detection of HO<sub>2</sub> by laser-induced fluorescence: calibration and interferences from

- <sup>5</sup> ner, A.: Detection of  $HO_2$  by laser-induced fluorescence: calibration and interferences from  $RO_2$  radicals, Atmos. Meas. Tech., 4, 1209–1225, doi:10.5194/amt-4-1209-2011, 2011.
  - Gai, Y., Wang, W., Ge, M., Kjaergaard, H. G., Jørgensen, S., and Du, L.: Methyl chavicol reactions with ozone, OH and NO<sub>3</sub> radicals: rate constants and gas-phase products, Atmos. Environ., 77, 696–702, doi:10.1016/j.atmosenv.2013.05.041, 2013.
- Gao, S., Ng, N. L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J., Yoo, K. Y., Beauchamp, J. L., Hodyss, R. P., Flagan, R. C., and Seinfeld, J. H.: Particle phase acidity and oligomer formation in secondary organic aerosol, Environ. Sci. Technol., 38, 6582–6589, doi:10.1021/es049125k, 2004.

Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the earth's atmosphere. Environ. Sci. Technol., 41, 1514–1521, 2007.

15

30

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., and McKay, W.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, 1995.

Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., and Fall, R.: Natural emissions of non-

- <sup>20</sup> methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America, Atmos. Environ., 34, 2205–2230, 2000.
  - Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maen-
- haut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.

Hayen, H., Jachmann, N., Vogel, M., and Karst, U.: LC-electron capture APCI-MS for the determination of nitroaromatic compounds, Analyst, 127, 1027–1030, 2002.

Heald, C., Kroll, J., Jimenez, J., Docherty, K., DeCarlo, P., Aiken, A., Chen, Q., Martin, S., Farmer, D., and Artaxo, P.: A simplified description of the evolution of organic aerosol com-





position in the atmosphere, Geophys. Res. Lett., 37, L08803, doi:10.1029/2010gl042737, 2010.

- Healy, R. M., Temime, B., Kuprovskyte, K., and Wenger, J. C.: Effect of relative humidity on gas/particle partitioning and aerosol mass yield in the photooxidation of *p*-xylene, Environ.
- <sup>5</sup> Sci. Technol., 43, 1884–1889, 2009.

25

- Holčapek, M., Lísa, M., Volná, K., Almonasy, N., and Přikryl, J.: Occurrence of radical molecular ions in atmospheric pressure chemical ionization mass spectra of heterocyclic compounds, J. Mass Spectrom., 42, 1645–1648, doi:10.1002/jms.1318, 2007.
- Holčapek, M., Jirásko, R., and Lísa, M.: Basic rules for the interpretation of atmospheric pres-
- sure ionization mass spectra of small molecules, J. Chromatogr. A, 1217, 3908–3921, 2010.
   Holzinger, R., Lee, A., Paw, K. T., and Goldstein, U. A. H.: Observations of oxidation products above a forest imply biogenic emissions of very reactive compounds, Atmos. Chem. Phys., 5, 67–75, doi:10.5194/acp-5-67-2005, 2005.

Holzinger, R., Kasper-Giebl, A., Staudinger, M., Schauer, G., and Röckmann, T.: Analysis

of the chemical composition of organic aerosol at the Mt. Sonnblick observatory using a novel high mass resolution thermal-desorption proton-transfer-reaction mass-spectrometer (hr-TD-PTR-MS), Atmos. Chem. Phys., 10, 10111–10128, doi:10.5194/acp-10-10111-2010, 2010.

Howard, J. A. and Ingold, K. U.: Self-reaction of sec-butylperoxy radicals. Confirmation of the

- Russell mechanism, J. Am. Chem. Soc., 90, 1056–1058, doi:10.1021/ja01006a037, 1968. linuma, Y., Böge, O., Keywood, M., Gnauk, T., and Herrmann, H.: Diaterebic acid acetate and diaterpenylic acid acetate: atmospheric tracers for secondary organic aerosol formation from 1,8-cineole oxidation, Environ. Sci. Technol., 43, 280–285, doi:10.1021/es802141v, 2008. Jang, M., Czoschke, N. M., Lee, S., and Kamens, R. M.: Heterogeneous atmospheric aerosol
  - production by acid-catalyzed particle-phase reactions, Science, 298, 814–817, 2002.
  - Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaatto-
- vaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E., Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimono, A., Sun, J. Y.,





Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of organic aerosols in the atmosphere, Science, 326, 1525–1529, doi:10.1126/science.1180353, 2009.

Kind, T. and Fiehn, O.: Metabolomic database annotations via query of elemental compositions: mass accuracy is insufficient even at less than 1 ppm, BMC Bioinformatics, 7, 234, doi:10.1186/1471-2105-7-234, 2006.

Klotz, B., Sørensen, S., Barnes, I., Becker, K. H., Etzkorn, T., Volkamer, R., Platt, U., Wirtz, K., and Martín-Reviejo, M.: Atmospheric oxidation of toluene in a large-volume outdoor photore-

- actor: in situ determination of ring-retaining product yields, J. Phys. Chem. A, 102, 10289– 10299, 1998.
  - Kroll, J. H. and Seinfeld, J. H.: Chemistry of secondary organic aerosol: formation and evolution of low-volatility organics in the atmosphere, Atmos. Environ., 42, 3593–3624, doi:10.1016/j.atmosenv.2008.01.003, 2008.
- <sup>15</sup> Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes, J. Geophys. Res., 111, D07302, doi:10.1029/2005JD006437, 2006a.

Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Sein-

- feld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, J. Geophys. Res., 111, D17305, doi:10.1029/2006JD007050, 2006b.
   Madronich, S. and Calvert, J. G.: Permutation reactions of organic peroxy radicals in the troposphere, J. Geophys. Res.-Atmos., 95, 5697–5715, doi:10.1029/JD095iD05p05697, 1990.
   March, J.: Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, John Wiley &
- <sup>25</sup> Sons, New York, 1992.

Mirov, N. T.: Composition of Gum Turpentines of Pines, USDA forest service, Technical Bulletin No. 1239, 158 pp., 1961.

- Misztal, P. K., Owen, S. M., Guenther, A. B., Rasmussen, R., Geron, C., Harley, P., Phillips, G. J., Ryan, A., Edwards, D. P., Hewitt, C. N., Nemitz, E., Siong, J., Heal, M. R., and Cape, J. N.:
- Large estragole fluxes from oil palms in Borneo, Atmos. Chem. Phys., 10, 4343–4358, doi:10.5194/acp-10-4343-2010, 2010.
  - Nannoolal, Y., Rarey, J., Ramjugernath, D., and Cordes, W.: Estimation of pure component properties: Part 1. Estimation of the normal boiling point of non-electrolyte organic com-





pounds via group contributions and group interactions, Fluid Phase Equilibr., 226, 45–63, doi:10.1016/j.fluid.2004.09.001, 2004.

- Nannoolal, Y., Rarey, J., and Ramjugernath, D.: Estimation of pure component properties: Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions, Fluid Phase Equilibria, 269, 117–133, 2008.
- Neeb, P., Horie, O., and Moortgat, G. K.: Gas-phase ozonolysis of ethene in the presence of hydroxylic compounds, Int. J. Chem. Kinet., 28, 721–730, doi:10.1002/(sici)1097-4601(1996)28:10<721::aid-kin2>3.0.co;2-p, 1996.

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Offical Portal of Malaysian Palm Oil Board: available at: http://bepi.mpob.gov.my/ (last access: 11 April 2013), 2012.

Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.: Gas/particle partitioning and secondary organic aerosol yields, Environ. Sci. Technol., 30, 2580–2585, doi:10.1021/es950943+, 1996.

Orlando, J. J., Tyndall, G. S., and Wallington, T. J.: The atmospheric chemistry of alkoxy radicals, Chem. Rev., 103, 4657–4690, 2003.

Orzechowska, G. E. and Paulson, S. E.: Photochemical sources of organic acids. 1. Reaction of ozone with isoprene, propene, and 2-butenes under dry and humid conditions using SPME, J. Phys. Chem. A, 109, 5358–5365, doi:10.1021/jp050166s, 2005.

O'Neal, H. E. and Blumstein, C.: A new mechanism for gas phase ozone–olefin reactions, Int. J. Chem. Kinet., 5, 397–413, 1973.

- Peeters, J., Boullart, W., Pultau, V., Vandenberk, S., and Vereecken, L.: Structure-activity relationship for the addition of OH to (poly)alkenes: site-specific and total rate constants, J. Phys. Chem. A, 111, 1618–1631, doi:10.1021/jp0669730, 2007.
- Pellegrin, V.: Molecular formulas of organic compounds: the nitrogen rule and degree of unsaturation, J. Chem. Educ., 60, p. 626, doi:10.1021/ed060p626, 1983.
- Pöschl, U.: Atmospheric aerosols: composition, transformation, climate and health effects, Angew. Chem. Int. Edit., 44, 7520–7540, doi:10.1002/anie.200501122, 2005.
- Rickard, A. R., Wyche, K. P., Metzger, A., Monks, P. S., Ellis, A. M., Dommen, J., Baltensperger, U., Jenkin, M. E., and Pilling, M. J.: Gas phase precursors to anthropogenic secondary organic aerosol: using the master chemical mechanism to probe detailed ob-
- secondary organic aerosol: using the master chemical mechanism to probe detailed observations of 1,3,5-trimethylbenzene photo-oxidation, Atmos. Environ., 44, 5423–5433, doi:10.1016/j.atmosenv.2009.09.043, 2010.





33132

- Schade, G. W. and Goldstein, A. H.: Fluxes of oxygenated volatile organic compounds from a ponderosa pine plantation, J. Geophys. Res., 106, 3111–3123, 2001.
- Schmidt, A.-C., Herzschuh, R., Matysik, F.-M., and Engewald, W.: Investigation of the ionisation and fragmentation behaviour of different nitroaromatic compounds occurring as polar
- <sup>5</sup> metabolites of explosives using electrospray ionisation tandem mass spectrometry, Rapid Commun. Mass Sp., 20, 2293–2302, doi:10.1002/rcm.2591, 2006.
  - Singh, H., Chen, Y., Tabazadeh, A., Fukui, Y., Bey, I., Yantosca, R., Jacob, D., Arnold, F., Wohlfrom, K., Atlas, E., Flocke, F., Blake, D., Blake, N., Heikes, B., Snow, J., Talbot, R., Gregory, G., Sachse, G., Vay, S., and Kondo, Y.: Distribution and fate of selected oxygenated
- organic species in the troposphere and lower stratosphere over the Atlantic, J. Geophys. Res.-Atmos., 105, 3795–3805, doi:10.1029/1999jd900779, 2000.
  - Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K., Tignor, M., and Miller, H.: Climate change 2007: the physical science basis: working Group I contribution to the fourth assessment report of the IPCC, Cambridge University Press, Cambridge, 2007.
- <sup>15</sup> Song, C., Na, K., and Cocker, D. R.: Impact of the hydrocarbon to NO<sub>x</sub> ratio on secondary organic aerosol formation, Environ. Sci. Technol., 39, 3143–3149, doi:10.1021/es0493244, 2005.
  - Southwell, I. A., Russell, M. F., Smith, R. L., and Vinnicombe, A.: Ochrosperma lineare, a new source of methyl chavicol, J. Essent. Oil Res., 15, 329–330, 2003.
- <sup>20</sup> Spada, N., Fujii, E., and Cahill, T. M.: Diurnal cycles of acrolein and other small aldehydes in regions impacted by vehicle emissions, Environ. Sci. Technol., 42, 7084–7090, doi:10.1021/es801656e, 2008.
  - Steiner, A. L., Cohen, R. C., Harley, R. A., Tonse, S., Millet, D. B., Schade, G. W., and Goldstein, A. H.: VOC reactivity in central California: comparing an air quality model to
- <sup>25</sup> ground-based measurements, Atmos. Chem. Phys., 8, 351–368, doi:10.5194/acp-8-351-2008, 2008.
  - Stockwell, W. R., Middleton, P., Chang, J. S., and Tang, X.: The second generation regional acid deposition model chemical mechanism for regional air quality modeling, J. Geophys. Res., 95, 16343–16367, 1990.
- Taipale, R., Rantala, P., Kajos, M., Patokoski, J., Ruuskanen, T., Aalto, J., Kolari, P., Bäck, J., Hari, P., Kulmala, M., and Rinne, J.: Oxygenated VOC and monoterpene emissions from a boreal coniferous forest, EGU General Assembly Conference Abstracts, 9735, 2012.





- United States Department of Agriculture, Global Crop Production Analysis: available at: http://www.pecad.fas.usda.gov (last access: 11 April 2013), 2013.
- Varutbangkul, V., Brechtel, F. J., Bahreini, R., Ng, N. L., Keywood, M. D., Kroll, J. H., Flagan, R. C., Seinfeld, J. H., Lee, A., and Goldstein, A. H.: Hygroscopicity of secondary organic
- <sup>5</sup> aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related compounds, Atmos. Chem. Phys., 6, 2367–2388, doi:10.5194/acp-6-2367-2006, 2006.
  - Werker, E., Putievsky, E., Ravid, U., Dudai, N., and Katzir, I.: Glandular Hairs, Secretory Cavities, and the Essential Oil in the Leaves of Tarragon (*Artemisia dracunculus* L.), Journal of Herbs, Spices Med. Plants, 2, 19–32, 1994.
- Wiedinmyer, C., Guenther, A., Harley, P., Hewitt, N., Geron, C., Artaxo, P., Steinbrecher, R., and Rasmussen, R.: Global Organic Emissions from Vegetation, in: Emissions of Atmospheric Trace Compounds, edited by: Granier, C., Artaxo, P., and Reeves, C., Advances in Global Change Research, Springer Netherlands, 115–170, 2004.

Yinon, J., McClellan, J. E., and Yost, R. A.: Electrospray ionization tandem mass spectrometry

collision-induced dissociation study of explosives in an ion trap mass spectrometer, Rapid Commun. Mass Sp., 11, 1961–1970, doi:10.1002/(sici)1097-0231(199712)11:18<1961::aidrcm99>3.0.co;2-k, 1997.

- J. Chromatogr. A, 977, 59–68, doi:10.1016/S0021-9673(02)01349-3, 2002.
   Zhou, Y., Zhang, H., Parikh, H. M., Chen, E. H., Rattanavaraha, W., Rosen, E. P., Wang, W., and Kamens, R. M.: Secondary organic aerosol formation from xylenes and mixtures of toluene and xylenes in an atmospheric urban hydrocarbon mixture: water and particle seed effects (II), Atmos. Environ., 45, 3882–3890, doi:10.1016/j.atmosenv.2010.12.048, 2011.
- <sup>25</sup> Ziemann, P. J. and Atkinson, R.: Kinetics, products, and mechanisms of secondary organic aerosol formation, Chem. Soc. Rev., 41, 6582–6605, doi:10.1039/c2cs35122f, 2012.
  - Zimmerman, P. R.: Testing of hydrocarbon emissions from vegetation, leaf litter and aquatic surfaces, and development of a methodology for compiling biogenic emission inventories, Final Report, Washington State University Pullman, Washington, 1979.



Zhao, X. and Yinon, J.: Identification of nitrate ester explosives by liquid chromatographyelectrospray ionization and atmospheric pressure chemical ionization mass spectrometry,

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13, 33105–	13, 33105–33144, 2013							
SOA form composition photo-ox methyl	SOA formation and composition from the photo-oxidation of methyl chavicol							
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Table 1. The initial experimental mixing ratios, temperature and relative humidity range for the experiments discussed.

Exp.	Date	Exp. description	Initial mi	ixing ratio <sup>6</sup>	a	Experimental range <sup>b</sup>		
			MC <sup>c</sup>	$MC^{c}$ NO NO <sub>2</sub> O <sub>3</sub>		O <sub>3</sub>	Temp	RH
			[ppbv]	[ppbv]	[ppbv]	[ppbv]	[K]	[%]
MC(0)	8 May 2012	Chamber background	0	0.3	0.7	0	294–312	0.7–4.7
MClow	11 May 2012	Photosmog low concentration	212	38	8	2	298-308	0.9–14.7
MC <sub>high</sub>	15 May 2012	Photosmog high concentration	460	9	3	5	297–306	2.1–10.7

<sup>a</sup> On the opening of the chamber covers.

<sup>b</sup> From the opening to the closing of the chamber covers. <sup>c</sup> FTIR measurement.

**Table 2.** The 10 structurally identified SOA compounds including; retention time ( $t_R$ ), molecular formula (MF) identification and associated errors using HPLC-ITMS, FTICR-MS and HPLC-QTOFMS.

Compound	IUPAC name	Compound				MC <sub>high</sub>		
		structure	MW [gmol <sup>-1</sup> ]	t <sub>R</sub>	FTICR-MS MF	FTICR-MS MF error [ppm]	HPLC- QTOFMS MF	HPLC- QTOFMS MF error [ppm]
1	3-(5-hydroxy-4-methoxy-2- nitrophenyl)propane-1,2-diol	OF OH OF OH H <sub>3</sub> C-O	243	22.2	C <sub>10</sub> H <sub>13</sub> NO <sub>6</sub>	0.6	C <sub>10</sub> H <sub>13</sub> NO <sub>6</sub>	-0.7
2	(4-methoxyphenyl)acetic acid	OH H <sub>3</sub> C <sup>-O</sup>	166	28.1	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	0.8	C <sub>9</sub> H <sub>10</sub> O <sub>3</sub>	1.2
3	2,5-dihydroxy-4- methoxybenzoic acid	HO O HO OH H <sub>3</sub> C <sup>O</sup>	184	10.2	a		C <sub>8</sub> H <sub>8</sub> O <sub>5</sub>	48
4	(3-hydroxy-4- methoxyphenyl)acetic acid	он он н <sub>3</sub> с~Он	182	16.1	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	0.8	C <sub>9</sub> H <sub>10</sub> O <sub>4</sub>	-0.3





#### Table 2. Continued.

Compound	IUPAC name	Compound	MC <sub>high</sub>						
		structure	MW [gmol <sup>-1</sup> ]	t <sub>R</sub>	FTICR-MS MF	FTICR-MS MF error [ppm]	HPLC- QTOFMS MF	HPLC- QTOFMS MF error [ppm]	
5	3-(3-hydroxy-4- methoxyphenyl)propane-1,2- diol	ОН ОН Насто	198	20.2	C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>	0.9	C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>	2.4	
6	4-methoxybenzoic acid	HO O H <sub>3</sub> C <sup>O</sup>	152	30.1	C <sub>8</sub> H <sub>8</sub> O <sub>3</sub>	0.3	$C_8H_8O_3$	-1.4	
7	3-hydroxy-4-methoxybenzoic acid	HO O HO OH H <sub>3</sub> C	168	33.0	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	1.2	C <sub>8</sub> H <sub>8</sub> O <sub>4</sub>	0.2	
8	2-hydroxy-3-(3-hydroxy-4- methoxyphenyl)propanal	о он	196	25.2	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	1	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub>	2.5	





#### Table 2. Continued.

Compound	IUPAC name	Compound	MC <sub>high</sub>						
		structure	MW [gmol <sup>-1</sup> ]	t <sub>R</sub>	FTICR-MS MF	FTICR-MS MF error [ppm]	HPLC- QTOFMS MF	HPLC- QTOFMS MF error [ppm]	
9	1-hydroxy-3-(4- methoxyphenyl)propan-2-one	OH H <sub>3</sub> CC	180	27.6	a		C <sub>10</sub> H <sub>12</sub> O <sub>3</sub>	-7.8	
10	1-hydroxy-3-(3-hydroxy-4- methoxyphenyl)propan-2-one	HO O H <sub>3</sub> CO	196	19.8	$C_{10}H_{12}O_4^{\ b}$	5	C <sub>10</sub> H <sub>12</sub> O <sub>4</sub> <sup>b</sup>	9.4	

<sup>a</sup> Deprotonated or protonated molecular species not observed in FTICR-MS spectra due to low concentration.

<sup>b</sup> Identified as [M + Na]<sup>+</sup>, the Na adduct has been removed from molecular formula and molecular weight corrected.

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**Table 3.** Deprotonated molecular species fragmentation for compound 1, obtained from the use of the HPLC-ITMS<sup>2</sup> and the HPLC-QTOFMS<sup>2</sup>.

MF	[M–H] <sup>–</sup>	DBE	Fragment ion [ <i>m/z</i> ]	Fragment ion MF	DBE	Loss [Da]	Electron fragmentation	Fragment ion MF error [ppm]	MF Score [%]	Fragmentation shown
C <sub>10</sub> H <sub>13</sub> NO <sub>6</sub>	242	5	224	C <sub>10</sub> H <sub>10</sub> NO <sub>5</sub>	6	18	EE	-2.1	100	Fig. 2a
			182	C <sub>8</sub> H <sub>8</sub> NO <sub>4</sub>	5	(18 + 42) = 60	EE	-1	100	Fig. 2b
			167	C <sub>7</sub> H <sub>5</sub> NO <sub>4</sub>	5 <sup>a</sup>	(18 + 57) = 75	OE	8.8	100	Fig. 2c
			137	$C_7H_5O_3$	4 <sup>b</sup>	105	OE	-19.2	100	Fig. 2c

The highest intensity fragment ion is shown in bold. DBE = double bond equivalent. Electron fragmentation, EE = even electron, OE = odd electron. MF = molecular formula.

<sup>a</sup> DBE was manually calculated, as automated DBE calculation is incorrect for radical fragment ions (DBE = 5.5–0.5 (for one "hydrogen atom deficiency") = 5, see Pellegrin (1983) for the calculation of DBE and DBE correction for radical ions).

<sup>b</sup> DBE manually calculated, (DBE = 5–1 (for two "hydrogen atom deficiencies") = 4).

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**Table 4.** Deprotonated molecular species fragmentation for compound 5, obtained from the use of the HPLC-ITMS<sup>2</sup> and the HPLC-QTOFMS<sup>2</sup>.

MF	[M-H] <sup>-</sup>	DBE	Fragment ion $[m/z]$	Fragment ion MF	DBE	Loss [Da]	Electron fragmentation	Fragment ion MF error [ppm]	MF Score [%]	Fragmentation shown
C <sub>10</sub> H <sub>14</sub> O <sub>4</sub>	197	4	<b>179</b> 137 123	$\begin{array}{c} \textbf{C_{10}H_{11}O_3} \\ \textbf{C_8H_9O_2} \\ \textbf{C_7H_7O_2} \end{array}$	5 4 4	<b>18</b> (18 + 42) = 60 74	EE EE EE	<b>-19.3</b> -0.5 -3.4	<b>100</b> 100 100	<b>Fig. 3a</b> Fig. 3b Fig. 3c

The highest intensity fragment ion is shown in bold. DBE = double bond equivalent. Electron fragmentation, EE = even electron. MF = molecular formula.









**Fig. 2.** Proposed deprotonated molecular species fragmentation for compound 1 in negative ionisation mode. Dashed lines indicate the location of fragmentation.







**Fig. 3.** Proposed deprotonated molecular species fragmentation for compound 5 in negative ionisation mode. Dashed lines indicate the location of fragmentation.





**Fig. 4.** Mechanism of formation for the identified SOA compounds, compounds 1, 5, 8, 9 and 10, shown in brackets, refer to Table 2 for compound identification. See text for the explanation of the mechanism, letters refer to the text explanation. Boxes highlight identified SOA compounds.







**Fig. 5.** Oxygen to carbon ratio (O : C) and saturation concentration  $\log_{10} (C^*, \mu g m^{-3})$  (Donahue et al., 2006b) space to show the movement of the identified SOA compounds to lower volatilities upon oxidation in MC<sub>high</sub>. Related generations of compounds are shown in the same colour. The change of shape but use of the same colour indicates a change in the SOA compound structure through the reaction with \*OH radicals or NO<sub>2</sub>. See legend for SOA compound identification and refer to Table 2. O: C/log<sub>10</sub> (C<sup>\*</sup>,  $\mu g m^{-3}$ ) space with associated volatilities have been redrawn from Donahue et al. (2013) and Jimenez et al. (2009).



