



Supplement of

Molecular characterization of gaseous and particulate oxygenated compounds at a remote site in Cape Corsica in the western Mediterranean Basin

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Sect. S1: Sampling devices and TD-GC/MS analysis for the molecular characterization of multiphase organic carbon

S1.1 Gaseous phase

S1.1.1 Gaseous phase sampling

Sampling of gaseous oxygenated compounds was achieved by using commercial sorbent cartridges containing Tenax TA (porous polymers based on 2.6-diphenyl-p-phenylene oxide; Perkin Elmer[™] or Markes[™]) that has been previously impregnated with suitable derivatization agents (see below) following an improved protocol from Rossignol et al. (2012). To maximize the adsorption surface, small particle size of 60/80 mesh has been selected. Ambient air samplings were performed during 6h at a flow rate of 100 mL min⁻¹. A Teflon filter (Zefluor[™] membrane, Pallflex[™], 47 mm) was installed upstream from the cartridges to trap particulate compound that could potentially be adsorbed on Tenax adsorbent. Gaseous phase sampling has been performed using individual pumps (Gilian[™] pump, model LFS-113DC). Prior to sampling, cartridges were heated at 320°C under a small helium flow rate during 4h to eliminate any trace of contamination. Every single cartridge was then analyzed to ensure its cleanliness with quantities below Limit of Detection (LOD) for all measured compounds. During the campaign, 177 gaseous samples were collected following this protocol.

S1.1.2 Sample preparation for gaseous phase

For the analysis of multi-functionalized OVOC by gas chromatography, a derivatization step is needed. It allows the suppression of the reactivity of functions, improving their thermal stability and rising their volatility. The dual derivatization reagents used in this study are PFBHA for carbonyl compounds and MTBSTFA (N-tert-Butyldimethylsilyl-N-methyltrifluoroacetamide) for hydroxyl compounds. The two derivatization processes are performed separately.

S1.1.2.1 Carbonyl compounds

PFBHA has been used as derivatization reagent for the analysis of carbonyls. Cartridges have been impregnated prior to sampling thanks to a glass balloon with 8 arms, containing 0.33mg of solid PFBHA per cartridges mounted on the balloon, and on which the cartridges are installed under a 100 mL min⁻¹ nitrogen flow rate per cartridges at 110°C during 20 minutes. The impregnated cartridges are stored at room temperature until the sampling. After sampling, cartridges are stored at room temperature during 5 days, optimum for the derivatization step using PFBHA (Ho and Yu, 2002), before their analysis.

S1.1.2.2 Hydroxyl compounds and carboxylic acids

MTBSTFA with 1% of TBDMCS (tert-butyldimethylchlorosilane, used as catalyst for the reaction) has been used as derivatization agent for the analysis of hydroxyl compounds. Cartridges are impregnated prior to sampling vaporizing 0.3 μL of MTBSTFA at 275°C using a commercial thermal tube desorber (Dynatherm

Analytical Instruments, model 890) under a flow of Helium of 30 mL min⁻¹ for 11 minutes. The cartridges are then stored at room temperature and sampling is performed within 10 days after impregnation. After sampling, cartridges are stored at 4°C. To ensure complete derivatization of all compounds before the analysis, two deposits of 0.3 μ L of MTBSTFA are achieved on each side of the cartridges which are kept at 60°C during 5h after that. Once the cartridges are back at room temperature, analysis is performed within 5 hours.

S1.2 Particulate phase

S1.2.1 Particulate phase sampling

Sampling of particulate matter was performed over regular (not impregnated) filters and derivatization was performed only after sampling (to avoid chemisorption of gaseous compounds on filters) following a protocol adapted from Rossignol et al. (2012). The sampling device used during the campaign was a modified Speciation Sampler Partisol, model 2300 (Rupprecht & Patashnick Co, Thermo Fisher Scientific). Three ChemComb cartridges, with PM_{2.5} impactors, were mounted to this device to allow the sampling of particulate phase on filters of different nature according to targeted compounds. For carbonyls compounds and non-oxygenated compounds Quartz filters (Pallflex™, 47 mm) were used. For hydroxyl compounds, quartz filters are not suitable because of silanol groups present at their surfaces that can be derivatized instead of the hydroxyl compounds reducing considerably their derivatization yield (Rossignol, 2012). Therefore, for the sampling of this type of compounds, we selected filters of borosilicate glass fibers coated with tetrafluoroethylene (TFE) called hereafter "Teflon quartz filters" (Fiber film, Pallflex™, 47mm). Activated carbon honeycomb denuders were installed upstream from the filters to avoid positive artifacts due to adsorption of gaseous oxygenated compounds on the filters. For cleaning and a best efficiency, denuders were heated at 250°C before being used for each new sample. The sampling flow rate was of 1 m³ h⁻¹ for each sample step. Quartz and Teflon guartz filters were carbonized prior to the sampling respectively at 500°C and 300°C to eliminate any possible contamination. During the campaign, 240 particulate samples were collected following this protocol.

S1.2.2 Sample preparation for particulate phase

S1.2.2.1 Carbonyl compounds

Sampling are performed on quartz filters which are stored at -16°C after sampling waiting for analysis. Then, the filters are cut into two pieces, both inserted into empty and clean stainless steel tubes. These tubes, including grids, are previously sonicated in several bath of ultra-pure water and acetonitrile and then are heated at 400°C under a flow of helium (80mL min⁻¹) during 4h. Deposition of 50 μ L of PFBHA saturated solution (acetonitrile/water (90/10, v/v) with 27 mg mL⁻¹ of PFBHA) are achieved in the tubes to expose adsorbed compounds to the derivatization reagent. Tubes are then stored at room temperature during 5 days to allow derivatization of adsorbed compounds before their analysis.

S1.2.2.2 Hydroxyl compounds and carboxylic acids

Sampling are performed on Teflon quartz filters which are stored at -16°C after sampling waiting for analysis. Derivatization is performed after sampling directly on filters. Filters are put in stainless steel tubes cleaned following the same protocol than for carbonyl compounds. Tubes are then sealed and maintained vertically with 10 μ l of MTBSTFA put in the bottom cap for passive impregnation during 24h at room temperature.

S1.3 Analytical system

The analytical system used in this study is composed by three successive modules: a thermal desorption system, a gas chromatography unit and a mass spectrometer.

The thermal desorption allows the extraction of adsorbed compounds on sample support by increasing the temperature without any preliminary solvent extraction and collecting them on a cold trap before flash injection in GC/MS instrument. The thermal desorption system (Markes[™], model unity 1) is coupled with an automated system (Markes[™], model Ultra 50:50). Thermal desorption parameters are listed in Table S1.1.

The GC/ MS instrument (Agilent Technologies Inc.) used during this study is composed by two modules:

- A GC unit, model 6890 A, associated with a capillary column Integra-Guard Rxi®-5Sil MS (stationary phase: 1.4-bis(dimethylsiloxy)phenylene dimethyl polysiloxane, length: 60m, diameter:
 0.25mm, film thickness: 0.25µm, with 5m pre-column deactivated without any stationary phase; Restek Corporation).
- A Mass spectrometer, model 5973N, equipped with an ionization source in EI (Electronic Impact) or CI (Chemical Ionization; using CH₄ as reagent gas) and associated with a quadrupole.

GC/MS parameters are listed in Table S1.1.

Thermal	temperature	300°C
desorption	time	15 minutes
parameters for	flow	50 mL min ⁻¹
samples	split flow	No split flow
Thermal	Temperature	From -10°C to 300°C
desorption	Time	12 minutes
parameters for	flow	10 mL min ⁻¹
the trap		
Temperature of tran	sfer lines	200°C
	Carrier gas	Не
	Carrier gas flow	1 mL min ⁻¹
GC Parameters	Temperature gradient	40°C / 10°C min ⁻¹ / 305°C (10 min)
	Split flow	0.2 mL min ⁻¹
	Transfer line temperature to MS	305 °C
	Scan m/z	40 to 800
	Solvent delay	5 min
MS parameters	Quadrupole temperature	150°C
	EI	
	-Source temperature	230°C
	-Ionization Energy	70 eV
	CI	
	-Source temperature	250°C
	-Reagent gas	CH ₄
	-Ionization Energy	50 eV

Table S1.1: Thermal desorption method and GC/MS parameters

S1.4 Internal and external calibration protocol

For a more efficient quantification, internal calibration has been set up for both family of compounds (carbonyl and hydroxyl) and for both phases. This procedure aims at taking into account drift in MS sensitivity and derivatization efficiency. Two types of internal standards are used: substitutes which are deuterated compounds getting at least one derivatized function; and an internal standard which is a compound with no derivatized function. 50 ng of Substitutes are added prior to the derivatization step to take into account every steps of sample preparation as well as analysis steps. The list of substitutes selected is given in Table S1.2. The internal standard selected is pentadecane, because of its low volatility which limit signal variability due to evaporation of the internal standard before the analysis, and 50 ng is added on cartridges grid just before the analysis. In addition of this internal calibration protocol, external calibrations are performed in the same conditions as atmospheric samples, doping the collecting support (i.e. whether filter or adsorbent cartridges) with known amount of external standards (list of external standards can be found in the supplementary material 4). This way, response coefficient used for quantification include the extraction efficiency and the matrix effects. In addition, recovery and matrix effect evaluation for the method can be found in Rossignol et al. (2012).

Table S1.2 : List of substitutes used for internal calibration

Substitutes used for carbonyl compounds	Substitutes used for hydroxyl compounds
3-methylbutanal-d2	Pentanoic acid-d9
Butanal-d8	Heptanoic acid-d13
4-methyl-2-pentanone-d5	Succinic acid-d4
Benzaldehyde-d6	2-methyl-d3-2-propyl-1,3-propanediol
Acetophenone-d8	Glycerol-d8
2-hexanone-d5	Tartaric acid-2,3-d2
2,3-butanedione-d5	
2,5-hexanedione-d10	

Sect. S2: Gaseous ancillary measurements

S2.1 PTR-MS

Measurements of OVOCs (e.g. nopinone, sum of methacrolein and methyl vinyl ketone, propanoic acid and methyl ethyl ketone), among other species (e.g. aromatics and biogenic VOCs) were performed using a Proton Transfer Reaction-Time of Flight Mass Spectrometer (PTR-ToF-MS, KORE Inc[®] 2nd generation). A detailed description of these measurements was given by Michoud et al. (2017, 2018). Briefly, ambient air was sampled through a 5-m long Teflon PFA (PerFluroAlkoxy) line held at 50°C at a flow rate of 1.2 L min⁻¹, leading to a residence time of 3.1s in the sampling line. The PTR-ToF-MS sampling flow rate was set at 150 mL min⁻¹. The instrument was operated at a reactor pressure and a temperature of 1.33 mbar and 40°C, respectively, leading to an E/N ratio of 135 Td.

An automated zero procedure was performed every hour for 10 min. Humid zero air was generated by passing ambient air through a catalytic converter to perform zeros at the same relative humidity than ambient air.

Signals from protonated VOCs were normalized by the signals of H_3O^+ and the first water cluster $H_3O^+(H_2O)$ as proposed by de Gouw and Warneke (2007). Concentrations were calculated using Eq. (1):

$$[R] = \frac{i_{R_net}}{(i_{H_3O^+} + X_r.i_{H_3O^+(H_2O)})} \cdot \frac{150000}{R_{f,R}}$$
(1)

Where [R] represents the mixing ratio of a given VOC, i_{R_net} the net signal of this VOC, i_{H_3O+} and $i_{H_3O+}(H_{2O})$ the signals of H_3O^+ and $H_3O^+(H_2O)$ at m/z 19 and 37 respectively recorded at m/z 21 and 39 to avoid any saturation of the detector and recalculated using the isotopic ratio between ¹⁶O and ¹⁸O. Xr is a factor introduced to account for the effect of humidity on the PTR-MS sensitivity (de Gouw and Warneke, 2007) and is determined experimentally through calibrations performed at various relative humidity for each individual quantified VOCs. It therefore also allows to take into account the reaction pathways of each VOC with the reagent ions (i.e. H_3O^+ and/or with $H_3O^+(H_2O)$. $R_{f,R}$ is the sensitivity determined during calibration experiments (in ncts ppt⁻¹) and normalized to 150 000 counts s⁻¹ of H_3O^+ ions. The latter is the number of counts of reagent ions (not corrected for ion transmission into the ToFMS) observed on this PTR-ToF-MS instrument. Data were recorded at a time resolution of 1 min. During the campaign, calibrations were performed every 3 days using various standards, including a canister containing 15 VOCs (NMHCs, OVOCs and chlorinated VOCs; Restek[®]), a gas cylinder containing 9 NMHCs (Praxair[®]) and a gas cylinder containing 9 OVOCs (Praxair[®]). Information about the composition of these standards can be found in Michoud et al. (2017).

Overall uncertainties are estimated between 6 and 23% depending on the compound considered (Michoud et al., 2017) following the "Aerosols, Clouds, and Trace gases Research InfraStructure network" (ACTRIS) guidelines for uncertainty evaluation (ACTRIS, 2012).

S2.2 GC-FID/MS

OVOCs, including aldehydes, ketones, alcohols, ethers, esters, as well as a few NMHCs, including BVOCs and aromatics, were measured using an online GC/FID-MS instrument. This instrument as well as its setup during the campaign was described by Michoud et al. (2017). Briefly, ambient air was sampled via a KI ozone scrubber and a 5-m long PFA line (1/8") at a flow rate of 15 mL min⁻¹ using an Air server-unity I (Markes International[®]). The sample was pre-diluted (50% dilution) with dry zero air to keep relative humidity below 50%. The sample was then collected in an internal trap, consisting in a 1.9 mm i.d. quartz tube filled with two different sorbents (5 mg of Carbopack B and 75 mg of Carbopack X, Supelco[®]) and cooled at 12.5 °C by a Peltier system. Compounds trapped on the sorbents were then thermally desorbed at 280 °C and injected into the column of a GC (Agilent[®]) equipped with a FID for detection and quantification and with a Mass Spectrometer (MS) for identification. The compounds were separated through a high polar CP-lowox column (30 m×0.53 mm× 10 μ m) (Varian[®]). The time resolution of these measurements is 1h30min. Calibrations were performed during the campaign using a gas cylinder containing 29 VOCs (Praxair). Information about the composition of this standard can be found in Michoud et al. (2017). Overall uncertainties are estimated between 5 and 14% depending on the compound considered (Michoud et al., 2017) following ACTRIS guidelines for uncertainty evaluation (ACTRIS, 2012).

S2.3 Active sampling on DNPH cartridges

Carbonyl compounds were collected continuously for 3 h durations by active sampling on DNPH cartridges (Waters[®]) using an automatic sampler (Tera Environment[®]). Cartridges were then eluted with 3 mL of acetonitrile to extract these compounds; and an aliquot of 20µL was analyzed later by High Performance Liquid Chromatography (HPLC) with UV detection. Ambient air was sampled via a 3-m PFA line (1/4") at 1.5 L min⁻¹ and passed through a KI ozone scrubber and a stainless-steel particle filter (porosity: 2µm). More details about these measurements are given by Michoud et al. (2017; 2018). Calibrations were performed at the laboratory using Supelco[®] standard for DNPH. Overall uncertainties are estimated around 25% (Michoud et al., 2017) following ACTRIS guidelines for uncertainty evaluation (ACTRIS, 2012).

Sect. S3: Particulate ancillary measurements

S3.1 ACSM

Measurements of the chemical composition of non-refractory submicron aerosol (NR-PM₁) have been carried out using a quadrupole ACSM (Aerodyne Research Inc., Billerica, MA, USA). These measurements have been described in detail by Michoud et al. (2017). Briefly, the calibration of this instrument with monodispersed (300 nm diameter) ammonium nitrate particles was performed 2 months before the campaign. Because ambient air was dried by a Nafion membrane and because ammonium nitrate was low during the campaign, constant collection efficiency (CE) of 0.5 has been kept. The Q-ACSM was operated continuously during the whole campaign at a time resolution of 30 min.

S3.2 Ionic Chromatography (IC)

Soluble anions and cations were analyzed by ionic chromatography (IC, ThermoFisher ICS3000) following protocol similar to that described elsewhere (e.g. Jaffrezo et al., 1998). Briefly, 38 mm diameter sub-samples from each filter were soaked for 20 min in 10 mL of Milli-Q water with orbital shaking, and then filtered using 0,22 µm-porosity Acrodisc filters before analysis. ASA11-HC and CS16 columns were used for anions and cations analyses, respectively.

S3.3 GC/MS

Organic markers were analyzed by gas chromatography (GC) coupled with mass spectrometry (MS) using the method developed by El Haddad et al. (2011). Filter samples were first spiked with 300µL of a solution containing the internal standard D6-Cholesterol (C₂₄H₄₀D₆₀). Accelerated Solvent Extraction (ASE Dionex 300) was performed with a mixture of acetone/dichloromethane (1/1 v/v) at 100bar and 100°C during 10 min. Sample extracts were concentrated using a Turbo Vap II under N₂ in a water-bath regulated at 40°C to a final volume of 500μL. A fraction of the extracts (50μL) was derivatized at 70°C for 90 min by adding 100µL of N,O-bis(triméthylsilyl)trifluoroacétamide (BSTFA containing 1% of TMCS). Derivatized extracts were then analyzed using a Thermo Trace Ultra GC coupled with a Polaris Q - ion trap operating in the electron impact mode. The GC was equipped with a TR-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness). Aliquots of 1 μL were injected in split mode (split ratio 50) at 280°C. The column temperature program was held at 65°C hold for 2 min, and ramped at 6°C/min up to 300°C, followed by an isothermal hold at 300°C for 20 min. GC-MS response factors were determined using authentic standards. Compounds, for which no authentic standard are available, were quantified using the response factor of compounds with analogous chemical structures. Field blank filters were also treated with the same procedure. Limit of quantification are comprised between 0.02 and 0.20 ng m⁻³ and overall uncertainties are estimated between 5 and 14% depending on the compound considered following LQ and uncertainty evaluation described by El Haddad (2011).

S3.4 HPLC

The analysis of a large array of organic acids (including pinic and phthalic acids, and 3-MBTCA) was conducted using the same water extracts as for IC analyses. In brief, this was performed by HPLC-MS (GP40 Dionex with a LCQ-FLEET Thermos-Fisher ion trap), with negative mode electrospray ionization. The separation column is a Synergi 4 µm Fusion – RP 80A (250×3 mm ID, 4 µm particle size, from Phenomenex). An elution gradient was optimized for the separation of the compounds, with a binary solvent gradient consisting of 0.1% formic acid in acetonitrile (solvent A) and 0.1% aqueous formic acid (solvent B) in various proportions during the 40-minute analytical run (see table S3.1). Column temperature was maintained to 30 °C. Eluent flow rate was 0.5 ml min⁻¹, and injection volume was 250 µl. Calibrations were performed for each analytical batch with solutions of authentic standards. All standards and samples were spiked with internal standards (phthalic-3,4,5,6-d4 acid and succinic-2,2,3,3-d4 acid). The calculation of the final atmospheric concentrations was corrected with the concentrations of internal standards and of the procedural blanks, taking also into account the extraction efficiency varying between 76-116% (depending on the acid).

Time (min)	%A (0.1% aqueous formic acid)	%B (0.1% formic acid in acetonitrile)
Initial step	5	95
0	5	95
20	56	44
22	95	5
27	95	5
29	5	95
35	5	95

Table S3.1: Elution Gradient conditions used for HPLC-ESI-MS

S3.5 OCEC SUNSET field instrument

Concentrations of elemental carbon (EC) and organic carbon (OC) in $PM_{2.5}$ were obtained in the field from an OCEC Sunset field instrument (Sunset Laboratory, Forest Grove, OR, USA; Bae et al., 2004) operated at a flow rate of 8 L min⁻¹ with a denuder set upstream to avoid adsorption of semi-volatile compounds on the filter collecting particles in the instrument. Data were obtained every 2 hours with this instrument.

S3.6 PILS-TOC

 PM_1 water-soluble organic compounds (WSOCs) were measured by a modified PILS (Brechtel Manufacturing Inc., USA; Sorooshian et al., 2006) coupled with an analyzer of total organic carbon (TOC; model Sievers 900; Ionics Ltd, USA). Sciare et al. (2011) and Michoud et al. (2017) described this technique and operating procedures used during the ChArMEx field campaign. Briefly, the PILS-TOC instrument was operated at a flow rate of 15 L min⁻¹ with a dilution factor of 1.30. A 0.45 µm pore size diameter filter in

polyethylene was set in-line in the aerosol liquid flow to analyze the water-soluble OC fraction only and a VOC denuder was set upstream the collection to avoid semi-volatile VOC contamination. Daily blanks were conducted every day for 1h by placing a total filter upstream of the sampling system.

S3.7 HULIS measurements

The water soluble HULIS fraction is analyzed according to a protocol described in detail in Baduel et al. (2009). Briefly, the water-soluble fractions obtained from aerosol samples are passed through a weak anion exchange resin (GE Healthcare^{*}, HiTrapTM DEAE FF, 0.7cm ID x 2.5cm length) without any pretreatment. After this concentration step, the organic matter adsorbed is washed with 12mL of a solution of NaOH 0.04M (J.T.Baker^{*}, pro analysis) to remove neutral components, hydrophobic bases, inorganic anion, mono- and di-acids initially retained in the resin. Finally, HULIS_{WS} are quickly eluted in a single broad peak using 4 mL of a high ionic strength solution of NaCl 1M (Normapur^{*}). All flow rates are set at 1.0 mL min⁻¹. UV-Vis absorption spectra are measured on-line after the extraction system, using a diode array detector (Dionex UV-VIS 340U), and recorded in the range 220-550nm. The HULIS_{WS} fraction is subsequently collected manually and the carbon content is analyzed with a DOC analyser (Shimadzu TOC- $V_{CPH/CPN}$) by catalytic burning at 680°C in oxygen followed by non-dispersive infrared detection of the evolved CO₂.

Sect. S4:

Identification and quantification of compounds during ChArMEx campaign.

					Identif	ication			Quantification								
		Number					O/C				Gaseous	Phase	Particulate	e phase			
Main Fragments	DMM	of functions	MM	RT (min)	Name	Structure	Log (Saturation Vapor Pressure)	Identification methods	Substitute	External standard	m/z integrated	Concentration (ng/m ³)	m/z integrated	Concentrati on (ng/m ³)	DL/QL (ng/m ³)	Uncertainty (ng/m ³)	
	Carbor	ıyl Comp	ounds														
EI : 117, 161, 181, 236	253	1	58	12.77	Propanal	○ ⊢ H	0.33 10 ^{-0.5}	Standard Rossignol (2012) Müller et al. (2006)	Butanal-d8	Pentanal	181	200 ± 69	181	10 ± 1	Gas 0.07/0.22 Particle 0.08/0.27	Gas 69 Particle 1	
EI : 117, 181, 195, 197, 198, 251	251	1	56	12.87	Acroleine	°↓ ⊢	0.33 10 ^{-0.7}	Standard Rossignol (2012) Jaoui et al. (2014)	3-Methylbutanal-d2	Methacrolein	181	734 ± 125	DMM	6 ± 1	Gas 0.36/1.22 Particle 0.06/0.21	Gas 119 Particle 1	
EI : 43, 181, 239, 250, 267	267	1	72	13.29	Methylpropanal	→ H	$0.25 \\ 10^{-0.8}$	MS/RT Rossignol (2012)	3-Methylbutanal-d2	2-Ethylbutanal	ND	ND	43	1 ± 0,4	Particle 0.07/0.24	Particle 0.4	
EI : 43, 57, 181, 195, 250	267	1	72	13.52	2-Butanone (= Methyl Ethyl Ketone)	° –	0.25 10 ^{-0.8}	Standard Müller et al. (2006)	2-Hexanone-d5	2-Hexanone-d5	DMM – 181	230 ± 18	DMM	blank	Gas 0.54/1.81	Gas 17	
EI : 41, 69, 181, 265	265	1	75	13.77	Methacrolein	→ H	0.25 10 ^{-1.0}	Standard Healy et al. (2008)	3-Methylbutanal-d2	Methacrolein	DMM	230 ± 16	DMM	2 ± 1	Gas 0.15/0.50 Particle 0.06/0.21	Gas 11 Particle 1	
EI : 42, 56, 69, 99, 117, 181, 195, 264, 265	265	1	75	13.85	Methyl Vinyl Ketone (= 3-Buten-2-one)	°,	0.25 10 ^{-1.0}	Standard Healy et al. (2008)	2-Hexanone-d5	3-Buten-2-one	181	539 ± 30	DMM	3 ± 0,5	Gas 0.29/0.95 Particle 0.04/0.14	Gas 74 Particle 0.5	
EI : 41, 56, 131, 181, 195, 235, 264	267	1	72	14.08	Butanal	○ → H	0.25 10 ^{-0.9}	Standard Müller et al. (2006)	Butanal-d8	Pentanal	181	88 ± 75	181	blank	Gas 0.53/1.76	Gas 95	
EI : 58, 100, 181, 221, 253, 281 CI : 282, 310, 322	281	1	86	14.12	3-Methyl-2-butanone		0.2 10 ^{-1.2}	MS/RT/Nist Rossignol (2012)	2-Hexanone-d5	2-Hexanone-d5	ND	ND	DMM	1 ± 1	Particle 0.08/0.27	Particle 1	
EI : 46, 93, 117, 181, 195, 218, 281	281	1	86	14.55	3-Pentanone		0.2 10 ^{-1.3}	MS/RT Rossignol (2012)	2-Hexanone-d5	2-Butanone	181	< QL	ND	ND	Gas 0.06/0.20	/	
EI : 43, 71, 167, 181, 195, 252, 264, 281 CI : 282, 310, 322	281	1	86	14.87	2-Methylbutanal	O H	0.2 10 ^{-1.3}	MS/RT	Butanal-d8	Pentanal	ND	ND	181	1 ± 1	Particle 0.08/0.27	Particle 1	
EI : 41, 55, 69, 161, 181, 222, 239	281	1	86	15.27	Pentanal	∽~~_H	0.2 10 ^{-1.4}	Standard Müller et al. (2006)	Butanal-d8	Pentanal	181	303 ± 129	DMM - 42	2 ± 0,4	Gas 0.07/0.22 Particle 0.01/0.03	Gas 129 Particle 0.4	
EI : 72, 94, 117, 181, 197, 236, 253, 277	295	1	100	15.77	2-Hexanone		0.17 10 ^{-1.7}	Standard Berndt et al. (2003)	2-Hexanone-d5	2-Hexanone	DMM - 42	85 ± 4	72	blank	Gas 0.06/0.19	Gas 4	
EI : 43, 181, 278, 293 CI : 294, 322, 334	293	1	98	16.05	4-Hexen-3-one	\sim	0.17 10 ^{-2.0}	MS/RT/Nist	/	/	ND	ND	181	blank	/	/	

					Identif	ication					Quan	tification				
		Number					O/C				Gaseous	s Phase	Particulate	e phase		
Main Fragments	DMM	of functions	MM	RT (min)	Name	Structure	Log (Saturation Vapor Pressure)	Identification methods	Substitute	External standard	m/z integrated	Concentration (ng/m ³)	m/z integrated	Concentrati on (ng/m ³)	DL/QL (ng/m ³)	Uncertainty (ng/m ³)
EI : 43, 181, 278, 293 CI : 294, 322, 334	293	1	98	16.15	5-Hexen-3-one		0.17 10 ^{-1.7}	MS/RT/Nist	/	/	ND	ND	181	blank	/	/
EI : 43, 98, 117, 131, 161, 181, 264, 279	279	1	84	16.25	3-Methyl-2-butenal		0.2 10 ^{-1.5}	Standard	3-Methylbutanal-d2	3-Methyl-2-butenal	DMM - 15	< QL	181	<ql< td=""><td>/</td><td>/</td></ql<>	/	/
EI : 41, 55, 72, 86, 181, 230, 267, 309	309	1	114	16.39	3-Heptanone		0.14 10 ^{-2.2}	MS/RT/Nist Rossignol (2012)	/	/	ND	ND	DMM	<ql< td=""><td>/</td><td>/</td></ql<>	/	/
EI : 41, 66, 82, 114, 161, 181, 239	295	1	100	16.48	Hexanal	O H	0.17 10 ^{-1.8}	MS/RT/Nist Rossignol (2012)	Butanal-d8	Pentanal	181	311 ± 247	181	3 ± 0,5	Gas 0.07/0.22 Particle 0.08/0.27	Gas 18 Particle 0.5
EI : 41, 99, 161, 181, 222, 239, 252, 295	295	1	100	16.52	4-Methylpentanal		0.17 10 ^{-1.7}	MS/RT/Nist	2-Hexanone-d5	2-Ethylbutanal	ND	ND	43	20 ± 1	Particle 0.07/0.24	Particle 1
EI : 128, 181, 253, 309 CI : 310, 338, 350	309	1	114	16.60	2-Heptanone		0.14 10 ^{-2.2}	MS/RT/Nist Rossignol (2012)	2-Hexanone-d5	4-Heptanone	ND	ND	DMM	< QL	/	/
EI : 62, 110, 181, 248, 291	291	1	96	17.05	2-Furaldehyde	Ľ,→,	0.4 10 ^{-2.1}	MS/RT/Nist	Benzaldehyde-d6	Pentanal	DMM	blank	ND	ND	/	/
EI : 41, 67, 82, 112, 161, 181, 263, 276, 293	293	1	98	17.53	Cyclohexanone		0.17 10 ^{-2.1}	MS/RT/Nist Rossignol (2012) Hamilton et al. (2004)	Acetophenone-d8	2-Butanone	181	744 ± 109	181	blank	Gas 0.09/0.30	Gas 108
EI : 41, 55, 69, 99, 128, 161, 181, 222, 239	309	1	114	17.69	Heptanal	↓ O H	0.14 10 ^{-2.3}	Standard Müller et al. (2006)	Butanal-d8	Pentanal	181	421 ± 122	181	$2\pm0,5$	Gas 0.07/0.22 Particle 0.08/0.27	Gas 122 Particle 0.5
EI : 51, 65, 77, 103, 106, 167, 181, 258, 315	315	1	120	18.77	m-Tolualdehyde	Ç ^î	0.13 10 ^{-3.3}	MS/RT/Nist	Acetophenone-d8	3-Methyl-2-butenal	DMM	407 ± 47	ND	ND	Gas 0.05/0.18	Gas 47
EI : 41, 55, 69, 82, 99, 124, 142, 169, 181, 222, 239	323	1	128	18.85	Octanal	С	0.13 10 ^{-2.7}	MS/RT/Nist Rossignol (2012) Müller et al. (2006)	Butanal-d8	Pentanal	ND	ND	181	blank	/	/
EI : 41, 55, 72, 117, 236, 253, 280, 322 CI : 338, 366, 378	337	1	142	18.90	2,6-Dimethyl-4-heptanone		0.11 10 ^{-2.9}	MS/RT	2-Hexanone-d5	4-Heptanone	ND	ND	181	1 ± 1	Particle 0.15/0.50	Particle 1
EI : 39, 51, 65, 77, 89, 181, 271, 301	301	1	106	19.20	Benzaldehyde	С Ч Н	0.14 10 ^{-2.8}	Standard Müller et al. (2006)	Benzaldehyde-d6	Pentanal	181	586 ± 144	181	blank	Gas 0.07/0.22	Gas 142
EI : 41, 50, 77, 106, 181, 258, 315	315	1	120	19.40	Acetophenone	\sim	0.13 10 ^{-3.1}	Standard Hamilton et al. (2004)	Acetophenone-d8	2-Butanone	ND	ND	181	blank	/	/

					Identi	fication					Quan	ification				
		Number					O/C				Gaseous	Phase	Particulate	e phase		
Main Fragments	DMM	of functions	ММ	RT (min)	Name	Structure	Log (Saturation Vapor Pressure)	Identification method	Substitute	External standard	m/z integrated	Concentration (ng/m ³)	m/z integrated	Concentrati on (ng/m ³)	DL/QL (ng/m ³)	Uncertainty (ng/m ³)
EI : 41, 55, 69, 81, 99, 117, 156, 161, 181, 222, 239	337	1	142	19.65	Nonanal	↓ O H	0.11 10 ^{-3.2}	MS/RT/Nist Rossignol (2012) Matsunaga et al. (2003)	Butanal-d8	Pentanal	ND	ND	181	blank	/	/
EI : 181, 221, 253, 276, 290	333	1	138	19.80	Nopinone	H ₃ C _C CH ₃	0.11 10 ^{-3.3}	Standard Cahill et al, (2006)	2-Hexanone-d5	Nopinone	DMM - 43	673 ± 44	DMM - 43	3 ± 0,3	Gas 0.15/0.50 Particle 0.17/0.58	Gas 41 Particle 0.3
EI : 41, 79, 95, 110, 152, 181, 290 CI : 334, 362, 374	333	1	138	20.30	Ketolimonene	-	0.11 10 ^{-3.2}	MS/RT Rossignol (2012)	Acetophenone-d8	2-Butanone	181	<ql< td=""><td>ND</td><td>ND</td><td>/</td><td>/</td></ql<>	ND	ND	/	/
EI : 41, 55, 69, 83, 99, 117, 161, 181, 222, 239	351	1	156	20.97	Decanal	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0.10 10 ^{-3.6}	MS/RT/Nist Rossignol (2012) Matsunaga et al. (2003)	Butanal-d8	Pentanal	181	2809 ± 192	181	$1\pm0,5$	Gas 0.07/0.22 Particle 0.08/0.27	Gas 192 Particle 0.5
EI : 99, 117, 161, 181, 195, 239, 448	448	2	58	21.77	Glyoxal	н	1.0 10 ^{-1.6}	Standard Matsunaga et al. (2004)	2,3-Butanedione-d6	Glyoxal	DMM	3017 ± 184	DMM - 197	1 ± 0,2	Gas 0.01/0.04 Particle 0.04/0.13	Gas 184 Particle 0.2
EI : 41, 55, 161, 181, 195, 222, 239, 265, 462	462	2	72	21.82	Methylglyoxal	о Ч н	0.67 10 ^{-1.2}	Standard Matsunaga et al. (2004)	2,3-Butanedione-d6	Methylglyoxal	DMM - 197	700 ± 69	DMM - 197	13 ± 1	Gas 0.02/0.06 Particle 0.04/0.13	Gas 59 Particle 1
EI : 42, 99, 161, 181, 195, 279, 446, 476	476	2	86	22.41	Dimethylglyoxal		0.5 10 ^{-1.6}	Standard Rossignol (2012) Jaoui et al, (2012)	2,3-Butanedione-d6	Dimethylglyoxal	DMM - 197	286 ± 63	181	9 ± 1	Gas 0.12/0.41 Particle 0.04/0.13	Gas 59 Particle 1
EI : 42, 82, 161, 181, 195, 208, 252, 279, 293, 309, 490	490	2	100	23.50	4-Oxopentanal	С С Н	0.4 10 ^{-2.2}	Standard Matsunaga et al. (2004)	2,3-Butanedione-d6	4-Oxopentanal	DMM - 181	3903 ± 182	ND	ND	Gas 0.19/0.65	Gas 166
	Hydro	xyl compo	unds an	d carboxy	lic acids											
EI : 45, 55, 73, 75, 85, 99, 129, 171	186	1	72	10.36	2-Propenoic acid	∞⊥он	0.67 10 ^{-2.8}	MS/RT/Nist	Pentanoic-d9 acid	Methacrylic acid	DMM - 57	211 ± 106	ND	ND	Gas 0.003/0.01	Gas 106
EI : 75, 115, 131, 149, 173	188	1	74	10.58	Glyoxilic acid	о н он	1.5 10 ^{-5.6}	Standard Cahill et al, (2006)	Pentanoic-d9 acid	Methacrylic acid	DMM - 57	1042 ± 225	ND	ND	Gas 0.003/0.01	Gas 221
EI : 45, 75, 115, 131, 149, 173	188	1	74	10.44	Propanoic acid	∽щон	0.67 10 ^{-2.5}	MS/RT/Nist Cahill et al, (2006)	Heptanoic acid -d13	Heptanoic acid	DMM - 57	862 ± 106	ND	ND	Gas 0.002/0.01	Gas 102
EI : 41, 69, 99, 143, 185	200	1	86	11.48	Methacrylic acid	ОН	0.5 10 ^{-3.2}	Standard	Pentanoic-d9 acid	Methacrylic acid	DMM - 57	128 ± 111	DMM - 57	0,4 ± 1	Gas 0.003/0.01 Particle 0.02/0.06	Gas 109 Particle 0.01

					Identif	ication					Quan	tification				
		Number					0/C				Gaseous	Phase	Particulate	e phase		
Main Fragments	DMM	of functions	MM	RT (min)	Name	Structure	Log (Saturation Vapor Pressure)	Identification method	Substitute	External standard	m/z integrated	Concentration (ng/m ³)	m/z integrated	Concentrati on (ng/m ³)	DL/QL (ng/m ³)	Uncertainty (ng/m ³)
EI : 43, 73, 75, 103, 115, 145	202	1	88	11.96	Pyruvic acid	ОН	1 10 ^{-3.6}	Standard Kawamura et Yasui (2005)	Pentanoic-d9 acid	Pyruvic acid	DMM - 57	interferences	DMM - 57	0,3 ± 1	Particle 0.02/0.06	Particle 0.01
EI : 41, 75, 99, 143, 185	200	1	86	12.44	Crotonic acid	∽он	0.5 10 ^{-3.3}	Standard	Pentanoic-d9 acid	Crotonic acid	DMM - 57	<ql< td=""><td>DMM - 57</td><td>2 ± 0,5</td><td>Particle 0.01/0.03</td><td>Particle 0.5</td></ql<>	DMM - 57	2 ± 0,5	Particle 0.01/0.03	Particle 0.5
EI : 41, 58, 75, 115, 129, 159, 201	216	1	102	13.12	Pentanoic acid	○ → OH	0.4 10 ^{-3.5}	Étalon	Heptanoic acid -d13	Heptanoic acid	DMM - 57	483 ± 70	DMM - 57	blank	Gas 0.002/0.01	Gas 69
EI : 47, 58, 75, 115, 129, 173	230	1	116	13.50	3-Ethylbutyrique acid	ОН	0.33 10 ^{-3.9}	MS/RT	Pentanoic-d9 acid	2-Ethylbutyric acid	DMM - 57	118 ± 55	ND	ND	Gas 0.003/0.01	Gas 64
EI : 41, 75, 131, 173, 215	230	1	116	14.51	Hexanoic acid	ОН	0.33 10 ^{-4.0}	MS/RT/Nist Rossignol (2012)	Heptanoic acid -d13	Heptanoic acid	DMM - 57	722 ± 73	DMM - 57	blank	Gas 0.002/0.01	Gas 70
EI : 43, 75, 99, 129, 145, 155, 173, 181, 215	230	1	116	15.30	Levulinic acid	U OH	0.6 10 ^{-4.6}	standard Jaoui et al. (2006)	Heptanoic acid -d13	Levulinic acid	DMM - 85	606 ± 91	DMM - 57	10 ± 1	Gas 0.01/0.04 Particle 0.03/0.11	Gas 83 Particle 1
EI : 41, 75, ,95, 116, 131, 187, 229	244	1	130	15.64	Heptanoic acid	↓ OH	0.29 10 ^{-4.5}	Standard Rossignol (2012)	Heptanoic acid -d13	Heptanoic acid	131	399 ± 48	DMM - 57	blank	Gas 0.002/0.01	Gas 48
EI : 41, 57, 73, 85, 103, 133, 147, 189, 219, 247	304	2	76	17.27	Glycolic acid	ноон	1.5 10 ^{-4.6}	Standard Cahill et al, (2006)	Heptanoic acid -d13	Glycolic acid	147	201 ± 67	115	19 ± 2	Gas 0.01/0.03 Particle 0.01/0.05	Gas 61 Particle 1
EI : 41, 57, 73, 115, 133, 147, 189, 217, 247, 275, 317	332	2	104	17.40	3,3-dihydroxy-2-butanone	но он	0.75 10 ^{-3.5}	MS/RT	Heptanoic acid -d13	Glycolic acid	ND	ND	DMM - 57	<ql< td=""><td>/</td><td>/</td></ql<>	/	/
EI : 41, 57, 73, 117, 131, 147, 189, 201, 231, , 301	316	2	88	17.53	2-Buten-1,4-diol	но	0.5 10 ^{-4.4}	Standard	Heptanoic acid -d13	Succinic acid	ND	ND	147	<ql< td=""><td>/</td><td>/</td></ql<>	/	/
EI : 41, 57, 73, 115, 147, 189, 261, 303	318	2	90	17.67	Oxalic acid	но сн	2 10 ^{-5.6}	Standard Cahill et al, (2006)	Heptanoic acid -d13	Succinic acid	DMM - 57	<ql< td=""><td>115</td><td>277 ± 17</td><td>Particle 0.10/0.33</td><td>Particle 14</td></ql<>	115	277 ± 17	Particle 0.10/0.33	Particle 14
EI : 43, 57, 73, 99, 117, 133, 147, 173, 189, 247, 275, 317	332	2	104	17.87	2-Hydroxy-2- methylpropanoic acid	но он	0.75 10 ^{-5.3}	Nist/MS/RT Rossignol (2012)	Heptanoic acid -d13	Glycolic acid	147	41 ± 100	DMM - 57	blank	Gas 0.01/0.03	Gas 2
EI : 41, 57, 73, 75, 115, 133, 147, 189, 218, 303, 318	318	2	90	18.18	3-Hydroxypropanoic acid	но	1 10 ^{-5.1}	Nist/SM/TR Rossignol (2012)	Heptanoic acid -d13	Glycolic acid	DMM - 57	39 ± 62	DMM - 57	<ql< td=""><td>Gas 0.01/0.03</td><td>Gas 93</td></ql<>	Gas 0.01/0.03	Gas 93
EI : 41, 75, 117, 129, 131, 171, 215, 257	272	1	158	18.45	Nonanoic acid	ОН	0.22 10 ^{-5.5}	MS/RT/Nist Rossignol (2012)	Heptanoic acid -d13	Heptanoic acid	131	blank	DMM - 57	blank	/	/

					Identif	ication					Quan	tification				
	1	Number					O/C				Gaseou	is Phase	Particul	ate phase		
Main Fragments	DMM	of functions	MM	RT (min)	Name	Structure	Log (Saturation Vapor Pressure)	Identification method	Substitute	External standard	m/z integrated	Concentration (ng/m ³)	m/z integrated	Concentrati on (ng/m ³)	DL/QL (ng/m ³)	Uncertainty (ng/m ³)
EI : 41, 57, 73, 115, 133, 147, 189, 275, 317	332	2	104	18.81	Malonic acid	но он	1.3 10 ^{-6.1}	Nist/MS/RT Cahill et al, (2006)	Heptanoic acid -d13	Succinic acid	ND	ND	73	3 ± 1	Particle 0.02/0.06	Particle 1
EI : 45, 57, 73, 133, 147, 157, 185, 259, 301	316	2	88	19.11	2-Hydroxy-2-propenoic acid	он он	1 10 ^{-3.6}	MS/RT	Heptanoic acid -d13	Glycolic acid	ND	ND	DMM - 57	<ql< td=""><td>/</td><td>/</td></ql<>	/	/
EI : 41, 57, 73, 133, 147, 199, 273, 315	330	2	102	19.36	3-Hydroxy-2-butenoic acid	он о	0.75 10 ^{-4.1}	Nist/MS/RT	Heptanoic acid -d13	Glycolic acid	ND	ND	DMM - 57	<ql< td=""><td>/</td><td>/</td></ql<>	/	/
EI : 41, 75, 129, 131, 229, 271	286	1	172	19.65	Decanoic acid	С	0.2 10 ^{-6.0}	Nist/MS/RT Cahill et al, (2006)	Heptanoic acid -d13	Heptanoic acid	DMM - 57	blank	DMM - 57	blank	/	/
EI : 41, 57, 73, 117, 133, 147, 189, 287, 329	344	2	116	19.97	Maleic acid	но — ООООООО	1 10 ^{-6.9}	Nist/MS/RT Cahill et al, (2006)	Heptanoic acid -d13	Succinic acid	ND	ND	DMM - 15	2 ± 1	Particle 0.03/0.09	Particle 1
EI : 41, 57, 73, 115, 129, 147, 189, 243, 289, 331	346	2	118	20.14	Succinic acid	но сон	1 10 ^{-6.6}	Standard Cahill et al, (2006)	Heptanoic acid -d13	Succinic acid	MMD - 57	blank	DMM - 131	27 ± 2	Particle 0.09/0.31	Particle 2
EI : 41, 73, 115, 147, 189, 229, 303, 345	360	2	132	20.23	A2-Methylsuccinic acid	но с он	0.8 10 ^{-7.0}	MS/RT Kawamura et Yasui (2005)	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM- 57	blank	/	/
EI : 41, 57, 73, 75, 115, 133, 147, 289, 301, 343	358	2	130	20.32	2-Hydroxy-3-Methyl-2- pentenoic acid	ОН ОН	0.5 10 ^{-5.0}	MS/RT/Nist	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM - 57	4 ± 1	Particle 0.03/0.08	Particle 1
EI : 41, 57, 73, 75, 84, 113, 133, 156, 230, 245, 287, 329	344	2	116	20.47	Fumaric acid	но с он	1 10 ^{-6.9}	MS/RT/Nist Rossignol (2012) Cahill et al, (2006)	Heptanoic acid -d13	Succinic acid	ND	ND	DMM - 15	3 ± 1	Particle 0.03/0.09	Particle 1
EI : 41, 57, 75, 95, 129, 131, 243, 285, 300	300	1	186	20.51	Undecanoic acid	он основности	0.18 10 ^{-6.5}	Nist/MS/RT Cahill et al, (2006)	Heptanoic acid -d13	Heptanoic acid	DMM - 57	blank	ND	ND	/	/
EI : 41, 57, 75, 83, 97, 115, 129, 143, 185, 227, 243, 285	300	1	186	20.83	1-Dodecanol	~~~~он	0.08 10 ^{-5.7}	MS/RT/Nist	Heptanoic acid -d13	Heptanoic acid	DMM - 57	blank	ND	ND	/	/
EI : 41, 57, 73, 75, 129, 147, 189, 303, 345	360	2	132	21.17	Glutaric acid	но он	0.8 10 ^{-7.1}	Standard Cahill et al, (2006)	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM - 57	16 ± 1	Particle 0.03/0.08	Particle 1
EI : 41, 57, 73, 89, 115, 133, 147, 171, 189, 245, 377, 419	434	3	92	21.33	Glycerol	но он	1 10 ^{-6.3}	Standard Jaoui et al. (2014)	Glycerol-d8	Glycerol	DMM - 57	1646 ± 131	DMM - 57	56 ± 4	Gas 0.01/0.05 Particle 0.08/0.28	Gas 150 Particle 3
EI : 73, 75, 147, 189, 221, 257, 295, 323, 365	380	2	152	21.65	Mandelic acid		0.38 10 ^{-7.8}	MS/RT	Heptanoic acid -d13	Glycolic acid	DMM - 57	21 ± 1	ND	ND	Gas 0.01/0.03	Gas 1

					Identif	ication					Quant	ification				
Main Fragments	DMM	Number of	ММ	RT (min)	Name	Structure	O/C Log (Saturation Vapor Pressure)	Identification method	Substitute	External standard	Gaseou	is Phase	Particul	ate phase		
		functions									m/z integrated	Concentration (ng/m ³)	m/z integrated	Concentrati on (ng/m ³)	DL/QL (ng/m ³)	Uncertainty (ng/m ³)
EI : 39, 75, 89, 129, 131, 257, 299	314	1	200	21.70	Dodecanoic acid	CH CH	0.17 10 ^{-7.1}	MS/RT Rossignol (2012) Cahill et al, (2006)	Heptanoic acid -d13	Heptanoic acid	DMM - 57	blank	DMM - 57	blank	/	/
EI : 41, 57, 73, 133, 147, 159, 175, 177, 189, 221, 231, 391, 433	448	3	106	22.06	2,3-Dihydroxypropanoic acid	но он	1.3 10 ^{-7.6}	Nist/MS/RT Rossignol (2012) (Kourtchev et al., 2008b)	Pentanoic-d9 acid Glycerol- d8	Glycerol	ND	ND	DMM - 57	20 ± 2	Particle 0.08/0.28	Particle 2
EI : 41, 57, 73, 111, 147, 227, 309, 317, 343, 359	374	2	146	22.27	Hexanedioic acid	но	0.67 10 ^{-7.6}	MS/RT/Nist Rossignol (2012) Cahill et al, (2006)	Heptanoic acid -d13	Succinic acid	ND	ND	DMM - 15	1 ± 1	Particle 0.03/0.09	Particle 0.2
EI : 41, 57, 73, 115, 133, 147, 189, 231, 245, 273, 303, 318, 377, 405, 447	462	3	120	22.43	2-Methylglyceric acid (= 2-MGA)	но сн	1 10 ^{-7.9}	Standard Claeys et al. (2004)	Pentanoic-d9 acid Glycerol- d8	Glycerol	ND	ND	DMM - 57	9 ± 1	Particle 0.07/0.24	Particle 1
EI : 41, 73, 133, 147, 185, 197, 271, 315, 343	372	2	144	22.48	3-Methyl-2-pentenedioic acid	но	0.67 10 ^{-7.7}	MS/RT/Nist	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM - 57	30 ± 2	Particle 0.03/0.08	Particle 2
EI : 41, 57, 73, 115, 133, 147, 189, 207, 221, 263, 271, 377, 405, 447	462	3	120	22.55	Erythrose or Erythrulose		1.0 10 ^{-8.0}	MS/RT Jaoui et al. (2014)	Pentanoic-d9 acid	2-MGA	ND	ND	DMM - 57	45 ± 3	Particle 0.07/0.24	Particle 3
EI : 41, 75, 129, 178, 206, 271	328	1	214	22.59	Tridecanoic acid	, , , , , , , , , , , , , , , , , , ,	0.15 10 ^{-7.6}	MS/RR Rossignol (2012) Cahill et al, (2006)	Heptanoic acid -d13	Heptanoic acid	DMM - 57	65 ± 68	ND	ND	Gas 0.002/0.01	Gas 68
EI: 41, 57, 73, 115, 133, 147, 175, 185, 189, 213, 287, 317, 345, 391, 419, 461	476	3	134	22.82	Methyltartronic acid	ноон	1.25 10 ^{-9.2}	MS/RT	Heptanoic acid -d13	Succinic acid	ND	ND	DMM - 131	6 ± 1	Particle 0.09/0.31	Particle 1
EI : 41, 57, 73, 75, 111, 147, 185, 317, 345, 387	402	2	174	23.15	Ketonorlimonic acid	но со	0.71 10 ^{-9.4}	MS/RT Rossignol (2012) Kleindienst et al. (2007)	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM - 57	15 ± 1	Particle 0.03/0.08	Particle 1
EI : 41, 69, 96, 75, 129, 207, 285	342	1	228	23.54	Tetradecanoic acid		0.14 10 ^{-8.0}	Nist/MS/RT Cahill et al, (2006)	Heptanoic acid -d13	Heptanoic acid	DMM - 57	314 ± 100	DMM - 57	blank	Gas 0.002/0.01	Gas 95
EI : 41, 73, 115, 133, 147, 189, 217, 247, 287, 419, 461	476	3	134	23.57	Malic acid	но с он	1.25 10 ^{-9.4}	Standard Rossignol (2012) Cahill et al, (2006)	Heptanoic acid -d13	Glycolic acid	ND	ND	DMM - 15	33 ± 3	Particle 0.03/0.09	Particle 3
EI : 41, 73, 115, 147, 189, 217, 273, 301, 331, 405, 433, 475	490	3	148	23.72	DHOPA (=4-Oxo-2,3- dihydroxypentanoic acid)	о он он он он он	1.0 10 ^{-9.3}	Standard Kleindienst et al. (2004)	Tartric acid-d2	Glutaric acid	ND	ND	DMM - 57	2 ± 0,1	Particle 0.96/3.19	Particle 0.1
EI : 41, 57, 73, 105, 119, 133, 147, 163, 189,221, 263, 337, 359, 379	394	2	166	23.87	1,2-Benzenedicarboxylic acid	HO	0.5 10 ^{-9.3}	Nist/MS/RT Kleindienst et al. (2012)	Heptanoic acid -d13	Succinic acid	ND	ND	DMM - 131	4 ± 1	Particle 0.09/0.31	Particle 1

					Identifi	cation					Quant	tification				
		Number					O/C				Gaseou	is Phase	Particul	ate phase		
Main Fragments	DMM	of functions	MM	RT (min)	Name	Structure	Log (Saturation Vapor Pressure)	Identification method	Substitute	External standard	m/z integrated	Concentration (ng/m ³)	m/z integrated	Concentrati on (ng/m ³)	DL/QL (ng/m ³)	Uncertainty (ng/m ³)
EI : 55, 75, 129, 157, 171, 214, 357, 399	414	2	186	24.04	Pinic acid	о он	0.44 10 ^{-8.8}	Standard (Yu et al., 1999a)	Heptanoic acid -d13	Pinic acid	ND	ND	DMM - 57	4 ± 1	Particle 1.11/3.70	Particle 1
EI : 41, 55, 75, 97, 105, 111, 125, 185, 199, 227, 331, 359, 401	416	2	188	24.26	Ketolimonic acid	нощо он	0.63 10 ^{-9.9}	MS/RT Rossignol (2012) Kleindienst et al. (2007)	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM - 57	6 ± 1	Particle 0.03/0.08	Particle 1
EI : 73, 75, 111, 129, 157, 185, 213, 271, 299, 317, 345, 387	402	2	174	24.42	3-Isopropyl-pentanedioic acid	но	0.5 10 ^{-8.5}	MS/RT Jaoui et al. (2005)	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM - 57	17 ± 2	Particle 0.03/0.08	Particle 2
EI : 75, 83, 89, 97, 129, 207, 299, 341	356	1	242	24.46	Pentadecanoic acid	Jan Carlor	0.13 10 ^{-8.6}	Nist/MS/RT Cahill et al, (2006)	Heptanoic acid -d13	Heptanoic acid	DMM - 57	335 ± 110	ND	ND	Gas 0.002/0.01	Gas 109
EI : 44, 73, 115, 133, 147, 175, 227, 259, 301, 355, 433, 447, 459, 475	490	3	148	24.47	HGA (=3-Hydroxyglutaric acid)	но он о	1.0 10 ^{-9.7}	Standard Rossignol (2012) Claeys et al. (2007)	Tartric acid-d2	Glutaric acid	ND	ND	DMM – 57	5 ± 0,3	Particle 0.59/1.95	Particle 0.3
EI : 41, 57, 73, 115, 133, 147, 149, 171, 189, 245, 261, 273, 303, 331, 359, 405, 433, 475	490	3	148	24.51	2-Hydroxyglutaric acid	но он	1.0 10 ^{-9.7}	MS/RT Rossignol (2012) (Kourtchev et al., 2008b)	Tartric acid-d2	Glutaric acid	ND	ND	DMM – 57	3 ± 1	Particle 0.03/0.08	Particle 1
EI : 39, 73, 99, 115, 133, 147, 185, 315, 345, 419, 431, 447, 461, 476, 489	504	3	162	24.76	3-Hydroxy-3-methylglutaric acid	но он о	0.83 10 ^{-9.9}	MS/RT/Nist	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM - 57	4 ± 0,2	Particle 0.03/0.08	Particle 0.2
EI : 73, 133, 147, 189, 259, 299, 375, 431, 447, 473	488	3	146	24.77	3-Hydroxy-2-pentenedioic acid	но он о	1.0 10 ^{-8.5}	Nist/MS/RT	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM - 57	4 ± 1	Particle 0.03/0.08	Particle 3
EI : 41, 73, 115, 147, 203, 287, 315, 373, 447, 489	504	3	162	25.02	2-Hydroxy-2-methylglutaric acid	но но он	0.83 10 ^{-9.9}	MM/RT	Tartric acid-d2	Glutaric acid	ND	ND	DMM - 57	1 ± 0,2	Particle 0.03/0.08	Particle 1
EI : 41, 73, 105, 147, 189, 217, 259, 301, 329, 461, 503	518	3	176	25.11	3-Hydroxy-4,4- dimethylglutaric acid	но сононнонно	0.71 10 ^{-10.4}	MS/RT Kleindienst et al. (2007)	Heptanoic acid -d13	Succinic acid	ND	ND	DMM - 57	7 ± 0,4	Particle 0.002/0.01	Particle 3
EI : 43, 75, 117, 129, 313, 355	370	1	256	25.24	Hexadecanoïc acid	~~~~~~ ² _{0H}	0.13 10 ^{-9.2}	MS/RT Rossignol (2012) Cahill et al, (2006)	Heptanoic acid -d13	Heptanoic acid	131	blank	DMM - 57	7 ± 1	Particle 0.03/0.09	Particle 1

					Identi	fication			Quantification								
		Number					0/2				Gaseou	is Phase	Particul	ate phase			
Main Fragments	DMM	of functions	MM	RT (min)	Name	Structure	O/C Log (Saturation Vapor Pressure)	Identification method	Substitute	External standard	m/z integrated	Concentration (ng/m ³)	m/z integrated	Concentrati on (ng/m ³)	DL/QL (ng/m ³)	Uncertaint (ng/m ³)	
EI : 45, 59, 73, 115, 133, 147, 231, 273, 447, 489	504	3	162	25.54	3-Hydroxyhexanedioic acid	HO HO OH OH	0.83 10 ^{-10.2}	MS/RT Rossignol (2012)	Heptanoic acid -d13	Glutaric acid	ND	ND	DMM - 57	7 ± 0,4	Particle 0.03/0.08	Particle 0.4	
EI : 41, 57, 73, 115, 147, 289, 461, 475, 503	518	3	176	25.84	Tricarballylic acid	но странов	1.0 10 ^{-11.7}	Standard Fu et Kawamura (2011)	Heptanoic acid -d13	Tricarballylic acid	ND	ND	73	49 ± 3	Particle 2.68/8.94	Particle 2	
EI : 73, 99, 115, 147, 189, 255, 287, 317, 329, 489, 531	546	3	204	26.17	MBTCA (= 3-Methyl-1,2,3- tricarboxylic acid)	но но он	0.75 10 ^{-12.5}	Standard (Szmigielski et al., 2007a)	Tartric acid-d2	Glutaric acid	ND	ND	DMM - 57	7 ± 1	Particle 0.94/3.13	Particle 1	
EI : 45, 55, 73, 115, 133, 147, 189, 199, 221, 281, 373, 549, 591	606	4	150	26.26	Tartaric acid	но Н он он	1.5 10 ^{-12.1}	Standard Cahill et al, (2006)	Tartric acid-d2	Tartric acid	ND	ND	DMM - 57	4 ± 1	Particle 0.59/1.98	Particle 1	
EI : 41, 73, 89, 115, 147, 231, 303, 403, 535,	592	4	136	26.07	Methyl-Tetrols (2 spikes) 2-methylerythritol and 2-methylthreitol	но он он	0.8 10 ^{-9.0}	MS/RT Claeys et al. (2004)	Tartric acid-d2	Glutaric acid	ND	ND	DMM - 57	0,3 ± 0,02	Particle 0.03/0.08	Particle 0.4	
EI : 41, 57, 73, 115, 147, 191, 241, 317, 357, 431, 489, 531	546	3	204	26.74	2-Hydroxy-4-isopropyl- hexanedioic acid	но	0.56 10 ^{-11.6}	MS/RT Kleindienst et al. (2007)	Tartric acid-d2	Glutaric acid	ND	ND	DMM - 57	1 ± 0,01	Particle 0.03/0.08	Particle 0.03	
EI : 41, 43, 73, 75, 129, 341, 383	398	1	284	26.90	Octadecanoic acid	о он	0.11 10 ^{-10.3}	MS/RT Rossignol (2012) Cahill et al, (2006)	Heptanoic acid -d13	Heptanoic acid	DMM - 57	blank	DMM - 57	4 ± 1	Particle 0.01/0.02	Particle 1	
EI : 73, 115, 147, 189, 357, 403, 431, 459, 591, 633	648	4	192	27.78	Citric acid	но странов	1.2 10 ^{-14.3}	Standard Kawamura et Yasui (2005)	Tartric acid-d2	Citric acid	ND	ND	73	15 ± 1	Particle 0.35/1.18	Particle 0.5	



Sect. S5: Example of chromatogram for hydroxyl compounds and carboxylic acids in the gaseous phase



Sect. S6: Time series of compounds measured during ChArMEx campaign (in the gas phase in red and in the particulate phase in blue).















13/07 15/07 17/07 19/07 21/07 23/07 25/07 27/07 29/07 31/07 02/08 04/08

0.0































Gaseous phase
 Particulate phas











13/07 15/07 17/07 19/07 21/07 23/07 25/07 27/07 29/07 31/07 02/08 04/08 06/08







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