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

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Abstract

The characterization of the molecular composition of organic carbon in both gaseous and aerosol is key to understand the processes involved in the formation and aging of secondary organic aerosol. Therefore a technique using active sampling on cartridges and filters and derivatization followed by analysis using a Thermal Desorption-Gas Chromatography/mass spectrometer (TD-GC/MS) has been used. It aims at studying the molecular composition of organic carbon in both gaseous and aerosol phases (PM2.5) during an intensive field campaign which took place in Corsica (France) during the summer 2013: the ChArMEx (Chemistry and Aerosol Mediterranean Experiment) SOP1b (Special Observation Period 1B) campaign.

These measurements led to the identification of 51 oxygenated (carbonyl and or hydroxyl) compounds in the gaseous phase with concentrations comprised between 21 ng m^{-3} and 3900 ng m^{-3} and of 85 compounds in the particulate phase with concentrations comprised between 0.3 and 277 ng m^{-3}. Comparisons of these measurements with collocated data using other techniques have been conducted showing fair agreement in general for most species except for glyoxal in the gas phase and malonic, tartaric, malic and succinic acids in the particle phase with disagreements that can reach up to a factor of 8 and 20 on average, respectively for the latter two acids.

Comparison between the sum of all compounds identified by TD-GC/MS in the particle phase with the total Organic Matter (OM) mass reveal that on average 18% of the total OM mass can be explained by the compounds measured by TD-GC/MS. This number increase to 24% of the total Water Soluble OM (WSOM) measured by PILS-TOC if we consider only the sum of the soluble compounds measured by TD-GC/MS. This highlights the important fraction of the OM mass identified by these measurements but also the relative important fraction of OM mass remaining unidentified during the campaign and therefore the complexity of characterizing exhaustively the Organic Aerosol (OA) molecular chemical composition.

The fraction of OM measured by TD-GC/MS is largely dominated by di-carboxylic acids which represents 49% of the $PM_{2.5}$ content detected and quantified by this technique. Other contributions to $PM_{2.5}$ composition measured by TD-GC/MS are then represented by tri-carboxylic acids (15%), alcohols (13%), aldehydes (10%), di-hydroxy-carboxylic acids (5%), monocarboxylic acids and ketones (3% each) and hydroxyl-carboxylic acids (2%). These results highlight the importance of poly functionalized carboxylic acids for OM while the chemical processes responsible for their formation in both phases remain uncertain. While not measured by TD-GC/MS technique, HUmic-LIke Substances (HULIS) represent the most abundant identified species in the aerosol, contributing for 59% of the total OM mass on average during the campaign.

14 compounds were detected and quantified in both phases allowing the calculation of experimental partitioning coefficient for these species. The comparison of these experimental partitioning coefficients with theoretical ones, estimated by three different models, reveals large discrepancies varying from 2 to 7 orders of magnitude. These results suggest that the supposed instantaneous equilibrium being established between gaseous and particulate phases assuming a homogeneous non-viscous particle phase is questionable.

1 Introduction

It is now recognized that aerosols have an impact on human health, climate and ecosystems. However, large uncertainties still exist on their effects, especially on climate (Fiore et al., 2015). One of the key solution to reduce these uncertainties is to study the chemical composition of the aerosol organic fraction since organic matter represents a large fraction of fine particles (Jimenez et al., 2009) which impacts are compound-dependent. Molecular characterization of organic aerosol is therefore crucial.

The OA fraction has been widely studied (e.g. De Gouw and Jimenez, 2009; Fuzzi et al., 2006; Glasius and Goldstein, 2016; Jacobson et al., 2000; Jimenez et al., 2009; Kanakidou et al., 2005; Pöschl, 2005; Robinson et al., 2007; Samake et al., 2019; Seinfeld and Pankow, 2003) and many studies allowed to improve our understanding of their molecular composition (e.g. Gallimore et al., 2017; Nguyen et al., 2013; Nozière et al., 2015; Zhang et al., 2011), their sources (e.g. Alves et al., 2012; Jiang et al., 2019; Shrivastava et al., 2007; Woody et al., 2016), and their formation and evolution processes (e.g. Chacon-Madrid and Donahue, 2011; Donahue et al., 2012; Heald et al., 2010; Li et al., 2016; Ng et al., 2011). Organic aerosol can be primary or secondary. Primary Organic Aerosols (POA) are directly emitted in the atmosphere, whereas Secondary Organic Aerosols (SOA) are formed after oxidation of gaseous organic precursors such as Volatile Organic Compounds (VOC). These gaseous compounds, coming from anthropogenic or natural sources, are progressively oxidized by atmospheric oxidants (OH, O_3 and NO_3). During this multi-step oxidation process, the O/C ratio of the product formed rises and their volatility decreases allowing them to condense on existing particles or to form new particles through nucleation processes (Kulmala et al. 2013), leading to SOA formation. Some of the Semi-Volatile Organic Compounds (SVOC) formed during the process can be split between the particulate and gaseous phases. Hamilton et al. (2004) have studied the chemical composition of $PM_{2.5}$ collected in the urban atmosphere of London using a TD-GCxGC-ToF/MS (Thermal desorption comprehensive two dimensional-Gas Chromatography-Time of Flight mass Spectrometer) instrument highlighting the presence of more than 10 000 different organic compounds in their samples. In the same study, 130 Oxygenated Volatile Organic Compounds (OVOC) were also identified while the total number of different VOC in the atmosphere is estimated to be between 10 000 and 100 000 (Goldstein and Galbally, 2007). The large number of species composing the gaseous and particulate phases makes an exhaustive characterization of the atmospheric organic matter challenging.

For this reason, analysis of only the principal components is often used to describe aerosol composition. Positive Matrix Factorization (PMF) applied to Aerosol Mass Spectrometer (AMS) spectra allows retrieving more information on the sources and nature of organic aerosol. Although this classification allows getting insight into the oxidation state of OA, it is not possible to identify chemical processes involved in SOA formation and aging.

It is therefore essential to perform molecular characterization of organic aerosol. This can be achieved using several techniques, for example making use of off-line analyses of filter samplings or online analysis following direct sampling. Coupling Particle Into Liquid-Sampler (PILS) to ion chromatography allow for example the measurement of organic species such as acetate, formate, oxalate and methane sulfonic acid (MSA) (Orsini et al., 2003; Sciare et al., 2011). Parshintsev et al. (2009) also coupled PILS with gas chromatography mass spectrometry (GC-MS), which allowed the measurement of species such as alpha-pinene, pinonaldehyde, cis-pinonic and pinic acids. More recently, PILS was coupled to ultra-high performance liquid chromatography and electrospray ionization – quadrupole – time of flight – mass spectrometry (UPLC/ESI-Q-TOF-MS) allowing the measurement of species as diverse as adenine, adonitol, sorbitol, adipic acid, vanillic acid, azelaic acid cis-pinonic acid and palmitic acid (Zhang et al., 2016). Several studies also use tandem mass spectrometry (MS/MS or MS^n) to get some structural information on compounds present in the organic aerosol thanks to multiple fragmentation (e.g. Fujiwara et al., 2014; Kitanovski et al., 2011; Liu et al., 2015; Nguyen et al., 2011). This technique has led to the identification of species such as carboxylic acids, polycyclic aromatic hydrocarbons (PAH), oxy and nitro-PAH but also oligomers from isoprene photo-oxidation experiments in the presence of low or high NOx concentrations. Development of two-dimensional chromatography (GCxGC or LCxLC) allows reaching lower detection limit separation capacity and allows measuring a larger range of compounds (Hamilton et al., 2004; Parshintsev and Hyötyläinen, 2015). Online chromatographic systems also exist to analyze the composition of the particulate phase. However, difficulties in particle sampling made this type of development challenging. Williams et al. (2006) developed a thermo-desorption Aerosol GC/MS-Flame Ionization Detector (FID) allowing the online measurement of compounds of low polarity and with a small number of chemical functions. GC analysis is usually restricted to compounds of low polarity which excludes many secondary component of OA. A derivatization step is therefore often used before the analysis or even during the sampling to perform OA chemical characterization. For example, O-(2,3,4,5,6-PentaFluoroBenzyl)HydroxylAmine (PFBHA) can be used for measurements of carbonyl compounds, and N,O-bis(trimethylsylil)-trifluoroacetamide (BSTFA) is used to reduce the polarity of hydroxyl compounds (Chiappini et al., 2006; El Haddad et al., 2013; Flores and Doskey, 2015; Pietrogrande et al., 2009; Schoene et al., 1994).

In addition of sample preparation and detection systems, different types of extraction systems exist to avoid multiple steps prior to analysis. For example, Chiappini et al. (2006) have developed a technique using Supercritical Fluid Extraction (SFE)-GC/MS. With this technique, compounds are extracted from the filter by supercritical CO_2 including a derivatization step with BSTFA as reagent inside the extraction cell. Extraction efficiency depends on compound solubilities in the supercritical CO_2 which has a very high solvatation power. Thermo-desorption (TD) is another technique allowing to by-pass preparation steps prior to analysis. This technique relies on the volatilization of collected compounds and is suitable for semi-volatile constituent of SOA. It has the advantage to be commercially available with fully automatized systems, and its high sensibility allows the analysis of very low quantity of aerosol, while low preparation time requirement limits the risk of loss or contamination of analyzed samples (Hays and Lavrich, 2007; Parshintsev and Hyötyläinen, 2015). This technique has been used by Bates et al. (2008) and van Drooge et al. (2009) to quantify particulate PAH, while Ding et al. (2009) used it to measure PAH, alkanes, hopanes and steranes in $PM_{2.5}$.

Although numerous analytical methods exist for SOA chemical characterization, the multiphasic state of lots of compounds is rarely studied. Indeed, gaseous phase chemical characterization is often studied separately using techniques such as Proton Transfer Reaction (PTR)/MS (Hansel et al., 1995; de Gouw and Warneke, 2007; Holzinger et al., 2019) or online/offline GC techniques coupled to various detectors (e.g. FID, MS) (e.g. Barreira et al., 2015; Kajos et al., 2015; Valach et al., 2014). Despite this disconnected treatment between aerosol and gaseous phases, understanding mechanisms controlling the partitioning of SVOC between both phases is key to understand the formation and fate of SOA. A partition coefficient is defined according to the thermodynamic equilibrium to calculate the mass transfer of SVOC into particulate phase (Pankow, 1994). This equilibrium is thought to be dominated by absorption phenomena (Liang et al., 1997) and partition coefficient is therefore calculated accordingly in models. However, the validity of the instantaneous equilibrium between both phases as well as the predominance of absorption processes in the mass transfer process are questionable (Bateman et al., 2015; Fridlind et al., 2000; Healy et al., 2008; Rossignol et al., 2012; Virtanen et al., 2010). It is therefore crucial to test the theoretical partition coefficient against values measured in the field for which in situ measurements of organic compounds in both phases are needed.

The Mediterranean Basin is an excellent location to study organic aerosol formation and aging since it experiences intensive natural and anthropogenic emissions as well as strong photochemistry (Lelieveld et al., 2002). The ChArMEx project (Chemistry and Aerosols Mediterranean Experiments) aimed at assessing the present and future state of the atmosphere in the Mediterranean basin. In this frame, an intensive field campaign was performed at Cape Corsica for 3 weeks during summer 2013 implying numerous instruments to investigate the chemical composition of aerosol and gaseous phases.

As part of this project, this study aims at characterizing the molecular composition of organic carbon in both the gaseous and aerosol phases during the campaign using TD-GC/MS measurements. These measurements were first compared to measurements performed with other techniques (offline cartridges analysis using HPLC and GC/FID-MS as well as PTR-MS for gaseous measurements and filter analysis using Ion chromatography, GC/MS and HPLC). These measurements were used to assess the composition of organic carbon and to estimate the experimental partition coefficient of compounds measured in both phases to be compared with theoretical values.

2 The ChArMEx field campaign

2.1 Description of the Cape Corse ground site

The ChArMEx field campaign took place from July 15th to August 5th 2013 at Ersa in Cape Corsica (France) (42.97°N, 9.38°E) at the top of a hill (533 meters above sea level). The site is located at the northern tip of a thin peninsula, a few kilometers from the sea in all directions (between 2.5 and 6 km) and approximately 30 km north from the nearest urban area (Bastia). Mountains (peaking between 1000 and 1500 m) are limiting transport of urban air masses to the sampling site. The site is surrounded by typical vegetation of Mediterranean areas (maquis shrubland). Apart from this local biogenic influence, the site is mainly influenced by marine, and other natural (e.g. dust) emissions, and by continental and aged air masses due to long range transport. During summer, recirculation of air masses favors secondary aerosol and ozone build up (Millan et al., 1997). More details about the site, atmospheric conditions encountered during the campaign and air mass origin can be found in Michoud et al. (2017).

2.2 Sampling devices and TD-GC/MS analysis for the molecular characterization of multiphase organic carbon

Simultaneous sampling of gas and particulate phases has been conducted using a parallel sampling system with two independent pumps allowing the selection of flow rates specifically adjusted for each phase

Following the sampling, the molecular characterization of gaseous and particulate oxygenated organic compounds, targeting carbonyls and hydroxyl compounds and carboxylic acids, sampled during the campaign has been made using a TD-GC/MS analysis after derivatization steps following the method developed by Rossignol et al. (2012). Detailed description of the gaseous and particulate phase sampling as well as the sample preparation, analytical system and internal and external calibration protocol can be found in supplementary material 1.

Overall uncertainties have been determined taking into account precision, detection limit and systematic errors (including uncertainties on standard concentrations, on calibration, on blank determination and on sampling volume; following Gaussian error propagation). Overall uncertainties have therefore been estimated to be 35% and 54% on averaged in gas phase for carbonyls and hydroxyls and carboxylic acids respectively and to be 41% and 47% on averaged in particulate phase for carbonyls and hydroxyls and carboxylic acids respectively.

2.3 Ancillary measurements

An important set of complementary instruments, dedicated to the measurement of both gaseous and particulate phase, has been deployed at the supersite supporting the interpretation and validation of the TD-GC/MS dataset.

2.3.1 Gaseous ancillary measurements

During the campaign, NO and NO_2 were measured by a commercial ozone chemiluminescence analyzer (Cranox II; Eco Physics®) with a time resolution of 5 min. NO was measured directly, while NO_2 was converted into NO using a photolytic converter. O_3 was measured using a commercial analyzer (TEI 49i; Thermo Environmental Instruments Inc®) using UV absorption with a time resolution of 5 min.

Measurements of VOCs and OVOCs were performed by online techniques (Proton Transfer Reaction-Time of Flight Mass Spectrometer (PTR-ToF-MS) and GC/FID-MS) and off-line method (Active sampling on DNPH cartridges followed by analysis with High Performance Liquid Chromatography (HPLC) with UV detection). Description of the VOC and OVOC measurement techniques can be found in supplementary material 2.

2.3.2 Particulate ancillary measurements

Mass concentrations of PM_{10} and PM_1 were measured during the campaign using two tapered element oscillating microbalance (TEOM) equipped with a filter dynamic measurement system (FDMS) (Thermo Scientific™). In addition, aerosol chemical composition was measured by online technique (aerosol chemical speciation monitor – ACSM, PILS-TOC) and offline-method (Ion chromatography, GC/MS and HPLC) on filters collected daily with 2 HiVol samplers (30 m^3 hr^{-1}) equipped with PM_1 and $PM_{2,5}$ inlets. Description of the aerosol chemical composition measurement techniques can be found in supplementary material 3.

3 Results

3.1 Main conditions during the campaign

3.1.1 Meteorological conditions

Meteorological and environmental conditions are presented in Table 1. Relatively high temperatures were monitored during the campaign (up to 32°C) coinciding with high biogenic emissions from local vegetation and strong photochemistry (Michoud et al., 2017). These conditions led to high ozone concentrations (65 pbbv on average for the overall sampling period and up to 111 ppbv for 5 min measurements), typical of this region during summer (e.g. Lelieveld, 2002; Di Biagio et al., 2015). High relative humidity was encountered at night with values reaching 100% coinciding with foggy conditions observed during several nights at the site. High wind speeds were monitored with maximum reached on the 30th of July 2013 (13.2 m s^{-1}). During the campaign, almost 40% of air masses came from the south-west sector and 20% from the western sector (see Figure 1). Winds coming from south-west sector are predominant during daytime and nighttime and correspond to wind speed maxima. Winds from the west and north-east are also recorded, but during daytime only. Low NO_x concentrations were observed during the campaign (0.57 ppbv on average) with a few spikes above 1 ppbv corresponding to local influence from traffic especially when air masses came from the south (e.g. 27th July).

3.1.2 Particles and organic fraction

Mean, median, maximum and minimum of mass concentrations of PM_{10}, PM_1 and organic fraction in NR-PM_1 are summarized in Table 1 for the whole campaign. The averaged mass concentrations for PM_{10} is 12.0 µg m^{-3}, comparable to observations performed at other remote sites located in the western Mediterranean basin (e.g. 15.5 µg m^{-3} at Montseny, Spain; 11.5 µg m^{-3} between 2010 and 2013 at Montsec, Spain; 14.6 µg m^{-3} at Monte Martano, Italy; 13 µg m^{-3} between 2010 and 2013 at Venaco, France – Moroni et al., 2015; Nicolas, 2013; Querol et al., 2009a, 2009b; Ripoll et al., 2015). The averaged mass concentrations for PM_1 was 8.3 µg m^{-3} during the campaign and represented an important fraction of PM_{10} (69% on average). The amount of PM_1 at Ersa is also comparable to what has been previously measured in other remote sites in the western Mediterranean basin (e.g. 8.2 µg m^{-3} at Montseny, Spain; 7.1 µg m^{-3} between 2010 and 2013 at Montsec, Spain – Minguillón et al., 2015; Ripoll et al., 2015). During the campaign, the organic fraction represented between 40 and 55% of PM_1 mass concentrations (mean of 3.7 µg m^{-3} representing 44% of PM_1 on average).

Time series of mass concentrations of PM_{10}, PM_1 and organic fraction in PM_1 are presented in Figure 2. Highest mass concentrations for PM_{10} and PM_1 are observed between 12 and 21 July (15.7 and 11.0 µg m^{-3} on average respectively for PM_{10} and PM_1). According to back trajectory analysis (Michoud et al., 2017) this period corresponds to low wind speed and hence stationary air masses. A decrease of PM_{10} concentrations is observed from 21 to 25 July (12.0 µg m^{-3} on average) while the ratio PM_1/PM_{10} and organic/PM_1 are the highest (comprised between 0.5 and 1 and 0.3 and 0.7, respectively). During this second period, the PM_{10} and PM_1 fractions are almost the same. This period is also characterized by higher wind speed and air masses coming from the north-eastern sector and therefore includes potential anthropogenic influence from northern Italy. From 26 to 29 July, a rise in PM_{10} mass concentrations is observed coinciding with the warmest temperature of the campaign and air masses coming from the south and characterized by biogenic influence (see Michoud et al., 2017). From 29 July to 3 August, PM_1 concentrations strongly decrease (from 9.3 to 2.6 µg m^{-3} on average) coinciding with higher wind speed and relative humidity while winds came from north-west and north-east directions (see Michoud et al. 2017). During the last period (3-5 August), increase of PM_{10} and PM_1 concentrations is observed and a clear diurnal cycle is monitored for both fractions corresponding to a raise in temperatures. Overall, the organic fraction evolution follows the one of the PM_1 mass fraction.

3.2 Results from the TD-GC/MS analysis

3.2.1 Compound identifications

Detection of functionalized compounds led to the identification of 23 carbonyl compounds and 28 hydroxyl compounds and carboxylic acids in the gaseous phase and of 30 carbonyl compounds and 55 hydroxyl compounds and carboxylic acids in the particulate phase. The entire list of these 97 compounds is presented in supplementary material 4 together with their retention time, their O/C ratio, their calculated saturation vapor pressure, the main fragments of their mass spectra, the method used for their identification, the substitute used to account for the derivatization efficiency, the external standard used for their quantification, the fragment used for quantification, the averaged concentrations measured in both phases, their limits of detection and quantification, and the averaged overall uncertainties. An example of chromatogram is also shown in supplementary material 5. For the carbonyl compounds, the mono-functionalized compounds identified contained from 3 (e.g. propanal) to 10 (e.g. decanal) carbon atoms and from 2 (e.g. glyoxal) to 5 (e.g. 4-oxopentanal) carbon atoms for the bi-functionalized compounds. For the hydroxyl compounds and the carboxylic acids, the mono-functionalized identified compounds contained from 3 (e.g. propanoic acid) to 18 (e.g. octadecanoic acid) carbon atoms. Several poly-functionalized compounds have also been identified: hydroxy-acids and di-acids from 2 (e.g. glycolic acid) to 8 (e.g. mandelic acid) carbon atoms; triols, di-hydroxy-acids, hydroxyl-di-acids, tri-acids from 3 (e.g. glycerol) to 9 (e.g. 2-Hydroxy-4-isopropyl-hexanedioic acid) carbon atoms; and two tetra-functionalized compounds (methyl-tetrols and citric acid).

It is worth noting that several compounds exhibited very close quantities in the air sample and in the blank (designed as “blank” in the supplementary material 4). Therefore, the presence of these compounds in the air sampled cannot be certain. For the compounds that have been quantified successfully and present concentrations significantly above the quantification limit (10σ above averaged blank measurements), higher levels are observed in the gas phase. The averaged concentrations ranged from 21 ng m^{-3} (Mandelic acid) to 1600 ng m^{-3} (glycerol) for hydroxyl compounds in the gas phase and from 0.3 (Pyruvic acid) to 277 (oxalic acid) ng m^{-3} in the particulate phase. For the carbonyl compounds, the averaged concentrations ranged from 85 ng m^{-3} (hexanone) to 3900 ng m^{-3} (4-Oxopentanal) in the gas phase and from 1 ng m^{-3} (e.g. methylpropanal or glyoxal) to 20 ng m^{-3} (4-methylpentanal) in the particulate phase. Figure 3 presents the distribution of all quantified compounds along their saturation vapor pressure and their O/C ratio. The phases in which these compounds were identified are also shown in Figure 3. While compounds only present in the gas or aerosol phase exhibit high and low saturation vapor pressure, respectively, some exceptions are noticeable. Indeed, some gaseous compounds have low vapor pressure (down to $10^{-8.6}$ atm) such as long chain linear mono carboxylic acids (up to 15 carbon atoms) and some compounds only found in the particle phase have high vapor pressure (up to $10^{-0.8}$ atm), normally incompatible with their presence in such phase, such as small mono carbonyls (e.g. methylpropanal, methylbutanone, 2-methylbutanal…). We also found compounds in both phases exhibiting high vapor pressure (up to $10^{-0.4}$ atm), which is normally incompatible with their presence in aerosol phase, such as small carbonyls (e.g. propanal, acrolein, methacrolein, MVK…). This latest point is discussed further in section 4.3.

3.2.2 Data intercomparison

A comparison of data measured by TD-GC/MS with other techniques available on site has been performed, for both phases, to test the reliability of these measurements.

3.2.2.1 Gas phase

Comparisons of TD-GC/MS data with PTR-ToF-MS and GC/FID/MS data averaged over the same sampling duration at a similar time step have been performed and are shown in Figure 4 and Figure 5. Fair agreement is found for nopinone (relative differences observed from 1% to 133%), the sum of methacrolein and methyl vinyl ketone (2-155%), propanoic acid (3-107%) and methyl ethyl ketone (0-140%) between TD-GC/MS measurements and measurements performed by PTR-ToF-MS. Good agreement is also found for methyl vinyl ketone (3-168%) and 2-hexanone (3-99%) between TD-GC/MS measurements and measurements performed by GC/FID/MS. Ranges of measured concentrations are similar between these techniques as well as the temporal variation.

Comparisons of TD-GC/MS measurements with DNPH cartridges analysis are presented in Figure 6. For these latter, only the first ten days of the campaign have been validated because of a leak issue in the sampling system of DNPH cartridges after that period (see Michoud et al., 2017; 2018). Ranges of concentrations are in the same order of magnitude between these two techniques for propanal (5-93%), acrolein (18-90%), methacrolein (8-83%), methyl ethyl ketone (17-87%), methylglyoxal (19-99%), hexanal (1-73%) and benzaldehyde (10-115%) even though it is difficult to conclude on their co-variation regarding the small number of data available and the low time resolution for these two techniques. However, glyoxal and methyl vinyl ketone present large differences between the two techniques (factor of 15 and 12 respectively). For glyoxal, Matsunaga (2004) recorded maximum concentrations of 154 ng m^{-3} (≈65 pptv) at a forested site at Moshiri in Hokkaido island, in summer. Washenfelder et al. (2011) recorded maximum glyoxal concentrations of 500 pptv at an urban site in

Los Angeles in summer, while numerous glyoxal precursors exist in urban environment. Therefore, the concentrations measured by TD-GC/MS seem overestimated and measurements from DNPH cartridges analysis seem more consistent with these previous observations. Thermo-degradation of other heavier compounds adsorbed on the Tenax cartridges leading to glyoxal could be an hypothesis for this overestimation. In the case of methyl vinyl ketone, the good agreement observed between TD-GC/MS measurements and GC/FID/MS ones (see Figure 5) tends to indicate that the disagreement observed here is related to an underestimation of the concentrations measured by DNPH cartridge analysis. Furthermore, recent studies on humidity dependence of the DNPH–HPLC–UV method for some ketone compounds, revealed that the collection efficiency is inversely related to relative humidity, with up to 35 %–80 % of the ketones being lost for RH values higher than 50 % at 22 °C (Ho et al., 2014). Furthermore, dimerization issues for MVK during analyses using DNPH method has also been identified, during more recent measurements, that can cause strong underestimation of this technique (>50%).

3.2.2.2 Particulate phase

Comparisons of results from filter analysis by TD-GC/MS and by Ion chromatography, GC/MS and HPLC have been performed and are shown in Figure 7 and Figure 8. The range of concentrations between TD-GC/MS analysis and other techniques are in the same order of magnitude for oxalic acid (relative differences observed from 1% to 111%), pinic acid (13-136%), 2-methylglyceric acid (15-87%), MBTCA (12-95%), glycolic acid (16-104%) and phtalic acid (3-90%). However, a discrepancy is found for malonic acid and tartaric acid which measurements differ both of a factor of 4 on averaged between TD-GC/MS and HPLC analyses. For methyl-tetrols, the analysis performed by TD-GC/MS did not allow to distinguish the two isomers. Temporal evolution of compounds shown in Figure 7 and Figure 8 are also similar from one technique to another, especially for oxalic acid and pinic acid.

Nevertheless, larger disagreements have been observed for some compounds (see Figure 8). An overestimation of TD-GC/MS analysis compared to HPLC analysis of a factor of 8 and 20 on average, respectively for malic acid ad succinic acid, is observed. For malic acid, the external standard used for the estimation of the response factor (glycolic acid) is maybe not appropriate which may explain this discrepancy. As a test, succinic acid and glutaric acid (two other di-acids) have been used as external standard for malic acid quantification with no improvement in the agreement observed. For succinic acid, the authentic standard has been used and such problem cannot explain the discrepancy observed. No interference in the peak region is observed and this cannot neither explain the differences observed.

On the whole, comparisons of TD-GC/MS with other techniques deployed during the campaign are satisfactory for both phases with results at least in the same order of magnitude for the measured absolute concentrations, except for some compounds. Therefore, these observations allow us to use TD-GC/MS data both in gas and aerosol phase to study further the behavior of organic carbon at a molecular level at cape Corsica during ChArMEx campaign, keeping however in mind the potential biases revealed during this data comparison exercise.

4 Discussions

4.1 Description of organic compounds behaviour during the campaign

Time series of every compounds measured by TD-GC/MS in both phases are presented in the supplementary material 6.

Concerning the gaseous phase, several linear mono-aldehydes (C_3 to C_{10}) have been detected and quantified in the same range of concentrations as what has been previously reported by the same technique at another site in Corsica (Rossignol et al., 2016). These compounds are mainly primary compounds emitted by vegetation under stress conditions. For propanal and butanal, some chemical processes and anthropogenic primary sources (especially ship emission) can also be involved (Agrawal et al., 2008). During the campaign, these compounds in the gaseous phase are characterized by daily maxima during daytime and daily minima during nighttime, confirming the predominance of biogenic sources. This diurnal cycle is also found when these compounds are also measured in the particulate phase, which may indicate a thermodynamic equilibrium for these compounds between both phases. Their concentrations are higher at the end of the campaign (30th of July) coinciding with the warmest period suggesting higher local biogenic emission.

At the end of the campaign, an elevation of concentrations is also observed for nopinone, 4-oxopentanal, 2-propenoic acid, methacrylic acid, mandelic acid, glycolic acid and levulinic acid (see supplementary material 6), all known as oxidation products of biogenic compounds (e.g. Fruekilde et al., 1998; Matsunaga et al., 2004; Rossignol et al., 2012). During this period, air masses were coming from the southern sector and travelled during a short period of time (12 to 24h) above Corsica and Sardinia (Michoud et al., 2017; Zannoni et al., 2017). An increase of concentrations is also observed for some monocarboxylic acids such as propanoic acid, pentanoic acid, hexanoic acid, tridecanoic acid, tetradecanoic acid and pentadecanoic acid (see supplementary material 6). Several sources are possible for these compounds that can be either primary or secondary and either biogenic or anthropogenic, especially for small carboxylic acids (C_3 to C_6; Chebbi and Carlier, 1996). Longer chain carboxylic acids are often considered as primary compounds both from biogenic and anthropogenic sources. Nevertheless, the results we obtained here underline the ubiquitous nature of organic acids (including long chains) in the atmosphere. It is remarkable to observe that despite their widespread detection, the knowledge on their sources (including chemical processes) remain scarce. Ozonolysis of alkenes, reactions between aldehydes and HO_2, or hydrolysis of oligomers could be involved.

At the beginning of the campaign (from 13th to 15th July) we observed a rise in concentrations of 4-oxopentanal, 2-hexanone, glycolic acid, 2-propenoic acid and monocarboxylic acids from C_3 to C_7 ((see supplementary material 6). A spike of methacrolein is also observed the 13th of July, highlighting local emission of biogenic precursors as it is during the calm low wind cluster period (Michoud et al, 2017).

Concerning particulate compounds, observations are different than for that gaseous compounds. Indeed, an important peak of concentrations is observed for many compounds from 17th to 19th of July, e.g. 3-isopropylglutaric acid, 3-hydroxy-4,4-dimethylglutaric acid, ketonorlimonic acid, ketolimonic acid, tricarballylic acid and methyltartronic acid (see supplementary material 6). The four first compounds correspond to oxidation products of biogenic precursors such as pinenes and limonene. O/C ratios for these compounds are high, varying from 0.5 (3-isopropylglutaric acid) to 1.3 (methyltartronic acid). This period corresponds to a rise in aerosol mass concentration (see Figure 2), with stagnant air masses and very low wind speed (Michoud et al., 2017). Associated with strong photochemistry, this favored chemical processing and the formation of secondary products with high O/C ratio. Other compounds also show a rise in their concentrations at this time (see supplementary material 6): unsaturated carboxylic acids (crotonic acid, 2-hydroxy-3methyl-2-pentenoic acid), long-chain monocarboxylic acids (hexadecanoic acid and octadecanoic acid), dicarboxylic acids (malonic acid, succinic acid, glutaric acid), unsaturated dicarboxylic acids (maleic acid, fumaric acid, 3-methyl-2-pentendioic acid), erythrose (a triol compound), 2,3-dihydroxypropanoic acid (a dihydroxy acid), hydroxy-diacids (2-hydroglutaric acid, 2-hydroxy-4-isopropylhexandioic acid, 3-hydroxy-2-pentenedioic acid, 3-hydroxy-3-methylglutaric acid, 3-hydroxyhexandioic acid, malic acid) and also 2-MGA, 3-MBTCA and DHOPA.

Higher concentrations for DHOPA, 2-MGA, MBTCA, and HGA are observed from 20 to 24 July (see supplementary material 6). 2-MGA is formed, in presence of NO_x (Ding et al., 2014, Fu et al., 2009; Giorio et al., 2017), through the oxidation of methacrolein and methacrylic acid, both oxidation products of isoprene. This period is characterized by the highest NO_x concentrations of the campaign (averaged concentrations of 1 ppbv against 0.6 ppbv for the rest of the campaign). Some dicarboxylic acids (e.g. malonic acid, succinic acid and glutaric acid) also show a rise in their concentrations during this period. This suggest a strong photochemical activity with an important aging of the air masses collected and an advanced photochemical age for this period, also characterized by high OH missing reactivity observed at the site (Zannoni et al., 2017). On the contrary, from the 27th of July to the end of the campaign, levels of concentrations for these compounds decrease (see supplementary material 6) suggesting less aged air masses. This is also revealed by the higher (cis-pinonic acid + pinic acid)/MBTCA ratio observed during this last period (see supplementary material 6). Indeed, this ratio allows the evaluation of the oxidation state of air masses since cis-pinonic acid and pinic acid are first generation oxidation products of monoterpenes while MBTCA is known to be a higher generation oxidation product (Ding et al., 2014).

Observations of MSA (methanesulfonic acid, CH_3SO_3H) and water soluble HULIS are reported in supplementary material S7. MSA is an oxidation product of dimethyl sulfide (DMS), a gaseous compound emitted by marine phytoplankton activity, and is mostly present in particulate phase. MSA can therefore be used to identify influence of marine chemistry on aerosol composition. Higher MSA concentrations are observed on 23 to 28 July and on 4 August when air masses were coming from the west sectors and spent days above sea (see Michoud et al., 2017) and on the first period of the campaign (15-18 July) when air masses were stagnant with very low wind speed (see Michoud et al., 2017). In summer, HULIS are mostly formed through secondary oligomerization processes in the particulate phase (Baduel et al., 2010). Higher water soluble HULIS concentrations are observed on 20-21 July when air masses are originating from north-east sector bringing continental aged air-masses (Michoud et al., 2017) and on 27 July when air masses were coming from the southern sector with large biogenic influence (Michoud et al. 2017). This is consistent with the formation of HULIS through secondary oligomerization processes in summer from both anthropogenic and biogenic precursors (Srivastava et al., 2018).

4.2 Molecular characterization of particulate matter

A time series of total mass quantified by TD-GC/MS in $PM_{2.5}$ is presented in Figure 9. This sum has been calculated using the QL/2 (quantification limit/2) value when data were below the limit of quantification. The sum of all the compounds measured by TD-GC/MS represents an average of 630 ng m^{-3} for the whole campaign with a minimum of 54 ng m^{-3} and a maximum of 2400 ng m^{-3} measured on the 17th of July.

This sum is also compared to the organic matter mass concentration in $PM_{2.5}$ (see Figure 9). OM is calculated using the organic carbon (OC) concentration measured by the SUNSET field instrument with a ratio between OC and OM of 1.9 for Cape Corsica as proposed by Michoud et al. (2017). On average 18% of the total OM mass can be explained by the compounds measured by TD-GC/MS for the whole campaign. From 12 to 29 July, oxygenated compounds measured by TD-GC/MS represent more than 20% on average of measured OM while they represented less than 10% between July 29 and August 4. If measured water soluble HULIS are added to these compounds, analysed compounds represent 36% of measured OM on averaged and up to 100% on 16 July.

Some of the compounds identified and quantified by TD-GC/MS, especially carboxylic acids, are soluble in aqueous phase and their presence in aerosol phase could proceed through the transfer from gas phase to deliquescent aerosol. To allow a comparison between TD-GC/MS measurement and WSOC (Water Soluble Organic Carbon) measurements conducted by PILS-TOC, only soluble compounds measured by TD-GC/MS have been selected (see Figure 10). Indeed, we considered only the compounds having a Henry's law constant higher than 10^4 M atm^{-1}. For every compounds measured by TD-GC/MS, the Henry's law constants have been determined by the Structure Activity Relationship (SAR) developed by Raventos-Duran et al. (2010) using the online platform of GECKO-A model (Aumont et al., 2005; http://geckoa.lisa.u-pec.fr/generateur_form.php). At the end, 39 different compounds have been selected for the calculation of this sum and no aldehyde or ketone were kept in this selection.

Comparing the sums of compounds measured by TD-GC/MS considering only soluble ones or considering all of them reveals very similar behaviors and level of concentrations (see Figure 10). On average, soluble compounds represent 72% of the total concentration of PM measured by TD-GC/MS despite the important number of compounds not considered as soluble (26 compounds over 58 not considered). Time series of soluble compounds measured by TD-GC/MS and of WSOM have similar behaviors with higher concentrations during the period comprised between 17 and 23 July and smaller concentrations at the end of the campaign. It is worth noting that WSOM corresponds to PM_1 while TD-GC/MS measurements concern $PM_{2.5}$. On average, the sum of the soluble compounds measured by TD-GC/MS represented 24% of the total WSOM measured by PILS-TOC. If measured water soluble HULIS are added to these soluble compounds, analysed water soluble compounds represent 58% of measured WSOM on averaged and up to 100% on 15 and 17 July.

Time series and average composition of the $PM_{2.5}$ measured by TD-GC/MS are presented respectively in Figure 11 and Figure 12. Almost half of the $PM_{2.5}$ measured by TD-GC/MS are characterized by di-carboxylic acid (49%) with oxalic acid being the most important by far. Other contributors to $PM_{2.5}$ composition measured by TD-GC/MS are tri-carboxylic acids (15%), alcohols (13%), aldehydes (10%), di-hydroxy-carboxylic acids (5%), monocarboxylic acids and ketones (3% each) and hydroxyl-carboxylic acids (2%). High concentrations of di-carboxylic acids are observed from 13 to 28 July (441 ng m^{-3} on average; 51% of the total OM measured by TD-GC/MS). After the 29th of July, the contribution of di-carboxylic acids decreases significantly to reach 30%. The end of the campaign is characterized by intense fresh local biogenic emissions leading to less processed air masses and OM composed mostly by mono-functionalized compounds. On a general basis, organic acids constitute the principal contributors to the fraction of organic aerosol measured by TD-GC/MS during this campaign while only few chemical processes are known to lead to their formation (see section 4.1). The identification of many di-carboxylic acids implies the existence of unknown chemical processes both in gaseous phase and even more probably in particulate phase to explain their formation (Hammes et al., 2019). These missing processes in chemical mechanism included in models might contribute to their inability to reproduce correctly the formation and aging of SOA. If considered, HULIS represent 59% of the total identified OM mass on average, ranging from 21% of contribution at the beginning of the campaign to more than 80% at the end of the campaign (from 31 July to 3 August).

4.3 Partitioning of organic carbon between gaseous and particulate phases

Many of the compounds identified during the campaign are present in both the gas and aerosol phases. The partitioning coefficient is therefore key to understand processes governing the equilibrium between both phases. For the compounds present in both phases, an experimental partitioning coefficient can be determined following eq. 2 relying on the Pankow equilibrium.

$$K_{pe,i} = \frac{F_i/_{TSP}}{A_i} \tag{2}$$

$K_{pe,i}$ corresponds to the experimental partitioning coefficient for the compounds i, F_i corresponds to the concentration in the particulate phase, A_i corresponds to the concentration in gaseous phase and TSP (Total Suspended Particulate matter) corresponds to the total mass concentration of particles measured by TEOM-FDMS for PM_{10} (µg m^{-3}). Uncertainties for experimental partitioning coefficients take into account uncertainties on the measurement of concentrations in both phases (see section 2.2) and on the TEOM measurement (estimated to be 25%).

Further, another expression of the Pankow equilibrium allows for the determination of theoretical partitioning coefficients using eq. 3.

$$K_{pt,i} = \frac{760RTf_{om}}{MW_{om}\zeta_i 10^6 p_{L,i}^0} \tag{3}$$

$K_{pt,i}$ corresponds to the theoretical partitioning coefficient for the compounds I, R to the ideal gas constant, T to the temperature in Kelvin, f_{om} to the OM mass fraction, MW_{om} to the averaged molar mass of compounds constituting organic particulate matter(g mol^{-1}), ζ_i to the activity coefficient, $p_{L,i}^0$ to the saturation vapor pressure (Torr). Saturation vapor pressures have been determined at 295K (averaged temperature of the campaign) using three different models (Moller et al., 2008; Myrdal and Yalkowsky, 1997; Nannoolal et al., 2008). f_{om} has been set to 0.8 using the averaged OC/TC ratio measured by the SUNSET field instrument and ζ_i has been set to 1.27 as suggested by Rossignol, 2012.

Experimental (averaged over the campaign) and theoretical partitioning coefficients obtained for compounds identified in both phases are presented in Table 2 and Figure 13 and are compared to experimental coefficient obtained in a previous field study in Corsica and a chamber study in the

EUPHORE simulation chamber (Rossignol et al., 2016). For most of the compounds, experimental partitioning coefficients obtained for the three campaigns are relatively close to each other, with some differences that can however reach up to an order of magnitude (e.g. dimethylglyoxal or acrolein, even two orders of magnitude for glyoxal). These observed differences are small compared to the differences recorded between experimental and theoretical coefficients, with an observed underestimation of theoretical coefficients varying from 1 to 7 orders of magnitude. It is worth noting that the three models used for theoretical coefficients determination are in good agreement. Higher differences between experimental and theoretical coefficients are observed for hydroxyl compounds and carboxylic acids with a shift of the equilibrium toward the particulate phase for experimental partitioning coefficients. It is worth noting that a denuder is used upstream the filter collection to avoid overestimation of particulate organic matter due to adsorption of semi-volatile compounds onto the filter, therefore excluding potential positive artefact for concentrations of compounds in particulate phase that could have led to overestimation of experimental partitioning coefficients. Furthermore, underestimation of gaseous concentrations for these compounds in such high proportion is unlikely, especially when we look at the comparisons performed for OVOCs with other measurement techniques (see section 3.2.2.1), even for compounds that shows strong disagreement between various analytical methods (e.g. glyoxal).

The differences observed between experimental and theoretical partitioning coefficient may be explained by the high humidity conditions encountered during the campaign (mean RH value of 70%, see Table 1). Indeed, theoretical partitioning coefficient as described by the Pankow equilibrium does not take into account the presence of an aqueous phase or a deliquescent aerosol, while soluble organic compounds can split between gaseous, aqueous and particulate phase. Concerning the partitioning between the gaseous and aqueous phases, the Henry law's constant and the activity coefficients are considered to calculate the thermodynamic equilibrium.

These differences could also be explained by the fact that the equilibrium between both phases is not reached. This could be due to the viscosity of particles. Some studies showed that organic aerosol can be found in various states, from liquid to semi-solid (viscous) (Bateman et al., 2016; Booth et al., 2014, Shiraiwa et al., 2011; Virtanen et al., 2010). The viscosity of the particle can limit the diffusion inside the particle, which can lead to an inhomogeneity in the composition with the formation of a gradient of concentrations between the surface and the center of the particle (Chan et al., 2014; Davies and Wilson, 2015; Zobrist et al., 2011). The equilibrium could therefore only concern an external layer of the particle and the gaseous phase (Davies and Wilson, 2015); or on the contrary a semi-solid external layer, caused by the aging of the particle, could prevent the equilibrium to settle between the particulate bulk and the gaseous phase.

Furthermore, Soonsin et al. (2010) showed that the physical state of the particle can influence the activity coefficient of some compounds and especially of dicarboxylic acids. Partitioning coefficients are calculated considering a liquid phase for aerosols. Considering a solid or semi-solid phase for aerosols would lead to a decrease in the vapor pressure estimation for such compounds and therefore to higher theoretical partitioning coefficients.

In addition, polymerization and oligomerization processes in the particulate phase have been highlighted in previous studies through the identification of compounds with high masses (Hallquist et al., 2009; Kalberer et al., 2004; Lim et al., 2010; Tolocka et al., 2004). The formation of oligomers increases the viscosity of the particle during its aging (Abramson et al., 2013). These reactions could also explain the presence of semi-volatile compounds in the particulate phase in such high proportion, especially for carbonyls that have high vapor pressure and which should not be detected in the aerosol phase based on the theory. Indeed, numerous studies reveal the possibility of formation of oligomers, inside the particle, from carbonyls such as α-di-carbonyls, for example glyoxal or methylglyoxal (Gao et al., 2004a, 2004b; Hastings et al., 2005; Iinuma et al., 2004; Jang et al., 2002, 2003; Jang and Kamens, 2001; Liggio et al., 2005a, 2005b; Lim et al., 2010; Tolocka et al., 2004). These reactions are favored under low water content in the particles even though oligomer production from other reactions can also happen at high relative humidity and in the aqueous phase. On the contrary, under higher humidity conditions, oligomers can form back monomer compounds which in case of viscous particle can be trapped into the particulate phase. It is worth noting that higher experimental partitioning coefficients are found for most compounds on 20 July and 26-27 July while water soluble HULIS concentrations are at their maximum. HULIS are known to be formed through secondary oligomerization processes in summer (Baduel et al., 2010), supporting the hypothesis that these kind of processes might be partly responsible for the disagreement between experimental and theoretical partitioning coefficient.

Even if an analytical artifact cannot be ruled out, for example a fragmentation of oligomers to form back the monomer compounds during the analysis, numerous evidences support the experimental results presented here and suggest that the instantaneous equilibrium being established between gaseous and particulate phases assuming a homogeneous non-viscous particle phase is not fully representative of the real atmosphere.

Conclusion

A multiphasic molecular characterization of oxygenated compounds has been carried out during the ChArMEx SOP 1b field campaign held in Ersa Corsica during July 2013 using an analytical technique based on multi-support sampling (filters and adsorbent containing cartridges), derivatization procedure and TD-GC/MS analysis. The deployment of this analytical technique in the field allows the identification of 97 different compounds in the gas (24 different compounds) and aerosol (50 different compounds) phases, some of them being present in both phases (23 different compounds). These compounds include simple carbonyls, alcohols or carboxylic acids as well as multi-functional compounds up to four functional groups. Among all the quantified compounds, the important contribution of organic acids (67% of the organic aerosol concentration measured by TD-GC/MS) emphasizes the existence of unknown chemical processes in the gaseous phase and even more probably in the particulate and/or aqueous phases to explain their formation. The absence of such processes in chemical mechanisms may contribute to the inability of models to correctly reproduce the formation and aging of SOA.

Comparisons of these measurements with other measurements performed at the site when available reveal fair agreement on the whole for almost all compounds experiencing redundant measurement in both phase with concentrations at least in the same order of magnitude. Noticeable disagreements (larger than a factor of 8 and up to a factor of 15) have however been found for glyoxal in the gas phase between TD-GC/MS measurements and DNPH cartridges analysis and for malic and succinic acid in the particulate phase between TD-GC/MS measurements and HPLC analysis. Nevertheless, comparisons of TD-GC/MS with other techniques deployed during the campaign are in general agreement, validating their use to conduct further analysis.

While the data obtained are very valuable to provide additional insight into the composition of organic matter for air masses encountered during the campaign, it is worth noting that it represents only a fraction of the total mass of organic matter. Indeed, an attempt to close the mass budget of organic aerosol using the TD-GC/MS measurements reveal that the sum of all particulate oxygenated organic compounds measured by this technique account for 18% of the total OM mass on average for the whole campaign. This portion of OM identified at the molecular scale is not constant and mostly depends on the oxidation state of the sampled air masses. If we only consider the soluble compounds measured by TD-GC/MS, they represent 24% of the total WSOM on average. Therefore, a sizeable fraction of the OM mass was identified by TD-GC/MS analysis, but a very large fraction of OM mass remained unidentified during the campaign, highlighting the complexity of an exhaustive characterization of the OA chemical composition at the molecular scale. An important fraction of this unidentified OM mass is due to HULIS.

Finally, for the compounds quantified in both the gas and the aerosol phases, a comparison between experimental and theoretical partitioning coefficients has been performed revealing in most cases a large underestimation by the theory reaching 1 to 7 orders of magnitude. It indicates that the partitioning theory is most often inappropriate, since it is based on the instantaneous equilibrium being established between gaseous and particulate phases, assuming a homogeneous non-viscous particle phase. Furthermore, the partitioning of semi-volatile compounds is influenced by meteorological conditions (humidity, temperature) and inherent properties of particles (viscosity, water content, organic fraction concentrations, acidity, etc.). In addition, the way these conditions impact the partitioning of semi-volatile compounds strongly depends on the physico-chemical properties of the considered compounds (solubility, saturation vapor pressure, reactivity, etc.).

Data availability.

Access to the data used for this publication is restricted to registered users following the data and publication policy of the ChArMEx program (http://mistrals.sedoo.fr/ChArMEx/ Data-Policy/ChArMEx_DataPolicy.pdf).

Author contributions.

VM and EH participated in the field campaign and prepared the paper with inputs from all co-authors. LC, ELG and JFD were involved in TD-GC/MS measurements and supervised this work. SD, IF, TL, NL and SS participated in the field campaign and were in charge of VOC measurements (GC-FID/MS, PTR-MS, Active sampling on DNPH cartridges). AC and FG were in charge of inorganic trace gases measurements (NOx and O_3). JS participated in the field campaign and was in charge of aerosol measurements by ACSM, OCEC instrument, PILS-TOC and IC. JLJ and NM were in charge of aerosol speciation measurements during the campaign through filter analysis (IC, GC/MS, HPLC, HULIS measurements).

Competing interests.

The authors declare that they have no conflict of interest.

Special issue statement.

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Table 1: meteorological conditions, environmental parameters and mass concentrations of PM_{10}, PM_1 and organic fraction in PM_1 during the ChArMEx campaign at ERSA

Meteorological and Environmental Parameters	**Mean**	**Median**	**Max**	**Min**
Temperature (°C)	23	23	32	19
Relative Humidity (%)	70	73	100	27
Wind Speed (m s^{-1})	3.6	3.1	13.2	-
O_3 (ppbv)	65	65	111	42
NO_x (ppbv)	0.57	0.45	4.93	0.06
Mass concentrations (µg m^{-3})	**Mean (±1σ)**	**Median**	**Max**	**Min**
PM_{10}	12 (±4.8)	12	31	2
PM_1	8.4 (±4.4)	8.4	22	0.2
Organic fraction (PM_1)	3.7 (±1.7)	3.5	8.1	0.2

Table 2: Experimental (averaged over the campaign with ±XX% representing 1σ standard deviation over the campaign) and theoretical partitioning coefficients determined for this study and compared to previous field and chamber campaigns.

	This study	Corsica [a]	EuPhoRe [a]	Kpt,i MOL [b]	Kpt,i NAN [c]	Kpt,i MYR [d]
Propanal	$6.1\mathrm{x}10^{-3}$ ± 75 %	$2.2\mathrm{x}10^{-3}$ ± 50 %		$2.6\mathrm{x}10^{-10}$	$2.6\mathrm{x}10^{-10}$	$4.7\mathrm{x}10^{-10}$
Pentanal	$6.5\mathrm{x}10^{-4}$ ± 106 %**	$1.8\mathrm{x}10^{-4}$ ± 51 %		$3.2\mathrm{x}10^{-9}$	$3.2\mathrm{x}10^{-9}$	$3.8\mathrm{x}10^{-9}$
Hexanal	$1.3\mathrm{x}10^{-3}$ ± 61 %			$1.0\mathrm{x}10^{-8}$	$1.0\mathrm{x}10^{-8}$	$1.1\mathrm{x}10^{-8}$
Heptanal	$5.1\mathrm{x}10^{-4}$ ± 91 %			$3.3\mathrm{x}10^{-8}$	$3.2\mathrm{x}10^{-8}$	$3.4\mathrm{x}10^{-8}$
Acrolein	$7.3\mathrm{x}10^{-4}$ ± 74 %	$6.1\mathrm{x}10^{-3}$ ± 50 %		$3.6\mathrm{x}10^{-10}$	$3.6\mathrm{x}10^{-10}$	$3.7\mathrm{x}10^{-7}$
Methacrolein	$7.3\mathrm{x}10^{-4}$ ± 69 %			$7.2\mathrm{x}10^{-10}$	$7.2\mathrm{x}10^{-10}$	$9.0\mathrm{x}10^{-10}$
Methyl Vinyl ketone	$5.8\mathrm{x}10^{-4}$ ± 57 %			$1.3\mathrm{x}10^{-9}$	$1.3\mathrm{x}10^{-9}$	$5.6\mathrm{x}10^{-10}$
Nopinone	$5.5\mathrm{x}10^{-4}$ ± 53 %			$1.7\mathrm{x}10^{-7}$	$1.7\mathrm{x}10^{-7}$	$1.9\mathrm{x}10^{-7}$
Dimethylglyoxal	$5.0\mathrm{x}10^{-3}$ ± 65 %	$5.6\mathrm{x}10^{-4}$ ± 70 %	$6.2\mathrm{x}10^{-4}$ ± 47 %		$3.4\mathrm{x}10^{-9}$ *	$7.0\mathrm{x}10^{-9}$ *
Methylglyoxal	$3.6\mathrm{x}10^{-3}$ ± 60 %	$2.2\mathrm{x}10^{-2}$ ± 132 %**	$1.3\mathrm{x}10^{-3}$ ± 84 %		$8.6\mathrm{x}10^{-10}$ *	$2.1\mathrm{x}10^{-9}$ *
Levulinic acid	$5.1\mathrm{x}10^{-3}$ ± 77 %			$1.7\mathrm{x}10^{-5}$	$4.4\mathrm{x}10^{-6}$	$2.9\mathrm{x}10^{-6}$
Methacrylic acid	$1.5\mathrm{x}10^{-4}$ ± 198 %**			$8.4\mathrm{x}10^{-8}$	$7.6\mathrm{x}10^{-8}$	$8.9\mathrm{x}10^{-8}$
Glycolic acid	$3.1\mathrm{x}10^{-2}$ ± 268 %**			$8.5\mathrm{x}10^{-5}$	$1.3\mathrm{x}10^{-5}$	$2.0\mathrm{x}10^{-6}$
Glycerol	$1.1\mathrm{x}10^{-2}$ ± 62 %			$7.1\mathrm{x}10^{-4}$	$8.4\mathrm{x}10^{-4}$	$1.3\mathrm{x}10^{-5}$

[a] Rossignol et al., 2016; [b] Moller et al., 2008 (coupled with Nannoolal et al. (2004) method for boiling point determination) ; [c] Nannoolal et al., 2008 (coupled with Nannoolal et al. (2004) method for boiling point determination) ; [d] Myrdal and Yalkowsky, 1997 (coupled with Nannoolal et al. (2004) method for boiling point determination)

* Coefficients extracted from Rossignol, 2012 at temperature of 300 K other parameter (MW_{om} et ζ_i) kept similar.

** Partitioning coefficients are comprised between 0 and 1. Experimental uncertainties greater than 100% mean that the experimental value is comprised between 0 and more than twice its values.

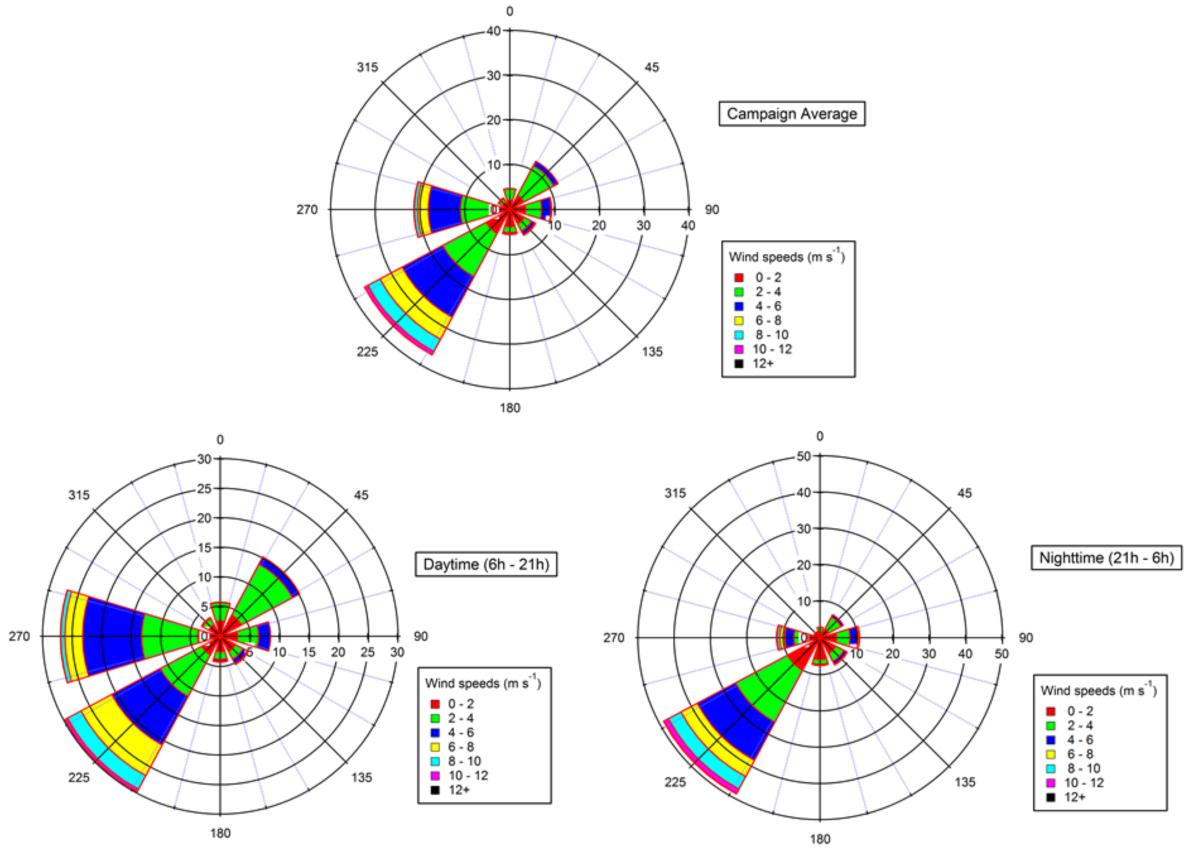


Figure 1 : Wind roses from July 15th to August 5th 2013 (top panel), during daytime only (bottom left panel) and during nighttime only (bottom right panel). Wind direction is expressed in ° and radial axe express the relative occurrence of wind in each 30° sector (%).

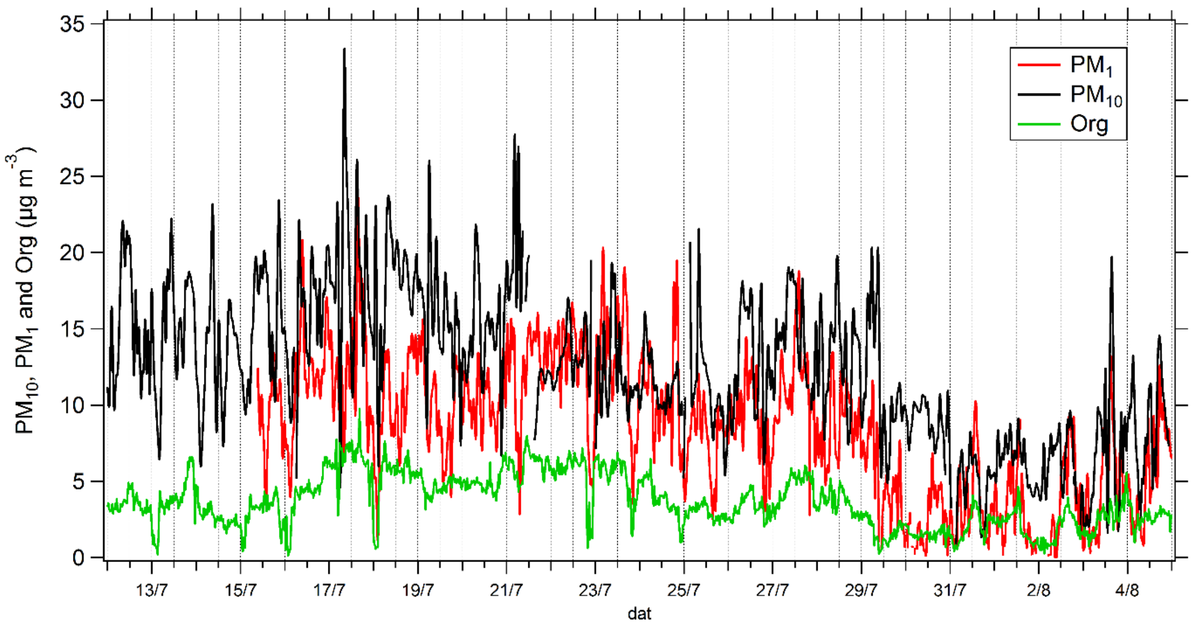


Figure 2 : Time series of mass concentrations of PM$_{10}$ (black line), PM$_1$ (red line) and organic fraction in NR-PM$_1$ (green line).

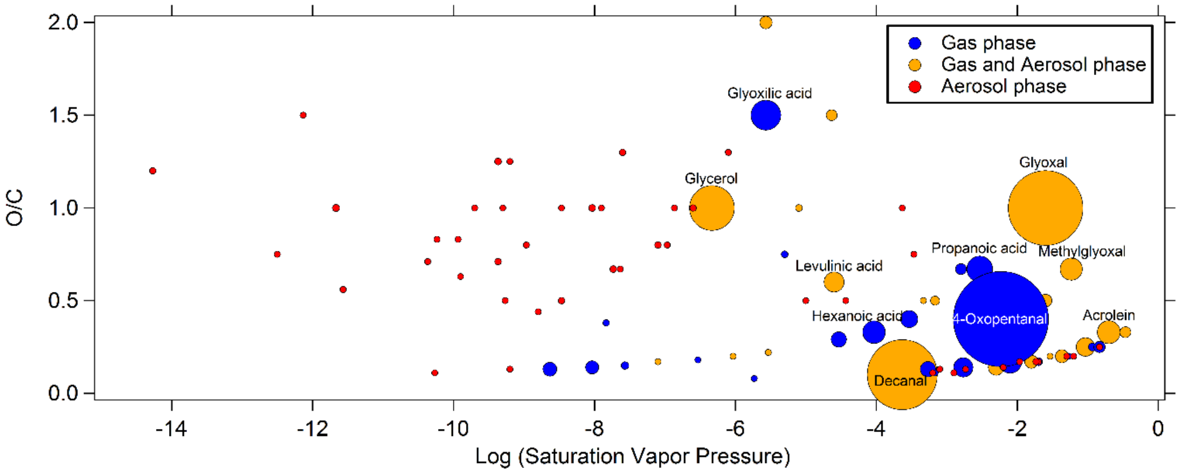


Figure 3: Distribution of compounds identified by TD-GC/MS during the ChArMEx campaign according to the logarithm of their saturation vapor pressure (horizontal axis) and of their O/C ratio (vertical axis). The phase in which they are detected is color-coded: blue for compounds only detected in the gas phase, red for aerosol phase only and orange for compounds detected in both phases. Each dot represents a single compound and the dot area is proportional to the sum of concentrations if detected in both phases from 0.3 ng m^{-3} for the smallest dot to 3.9 µg m^{-3} for the biggest one. Name of some noticeable compounds are also given.

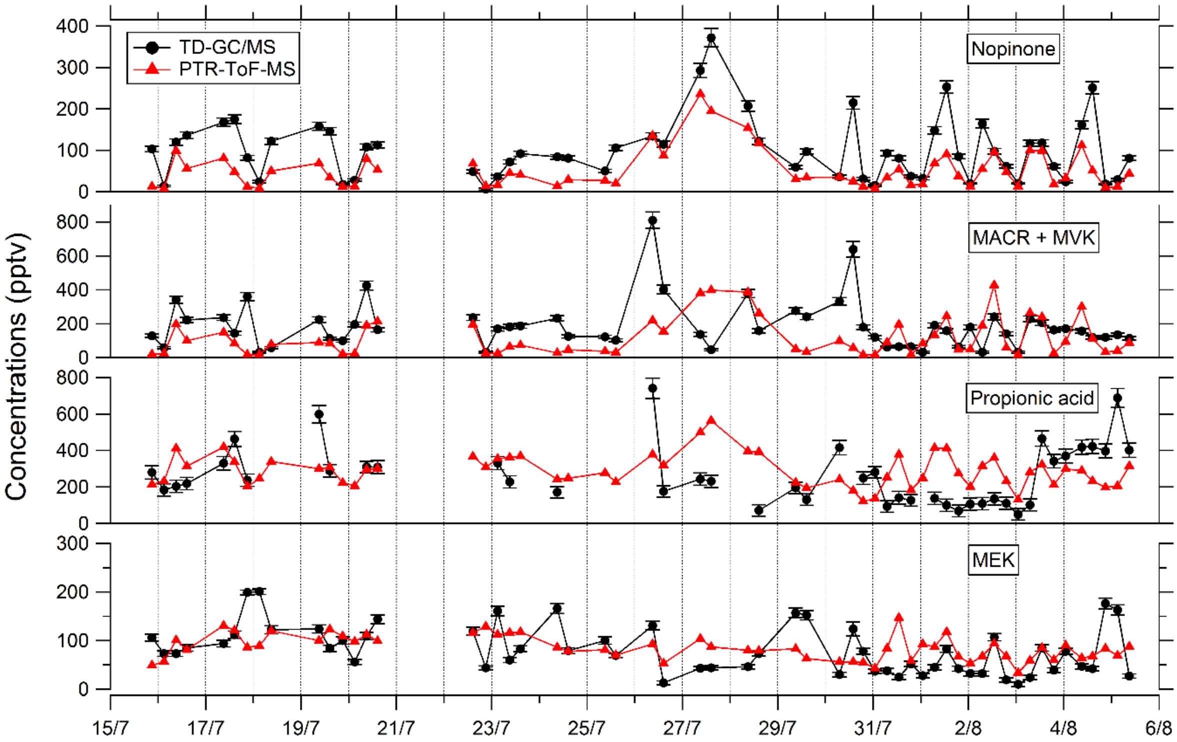


Figure 4 : Comparison of ATD-GC-MS data with PTR-ToF-MS data averaged over the same time step for nopinone, the sum of methacrolein and methyl vinyl ketone, propionic acid and methyl ethyl ketone. Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements. Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements.

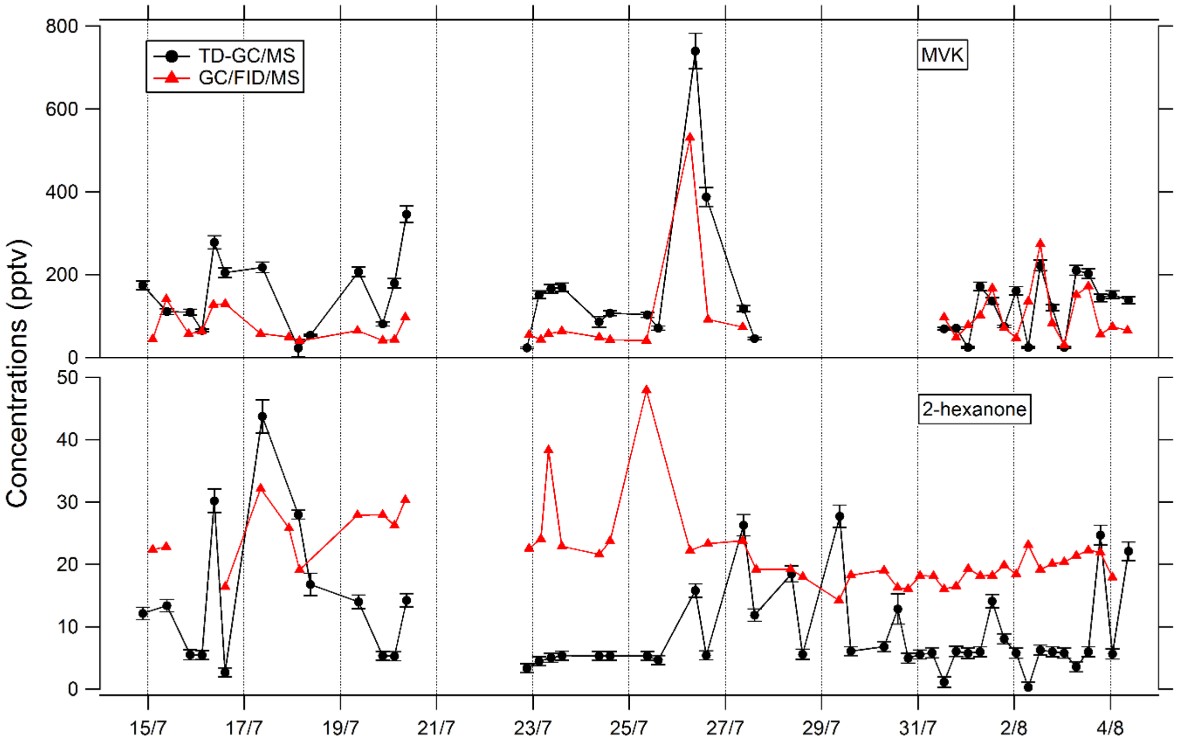


Figure 5 : Comparison of ATD-GC-MS data with GC/FID/MS data averaged over the same time step for methyl vinyl ketone and 2-hexanone. Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements. Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements.

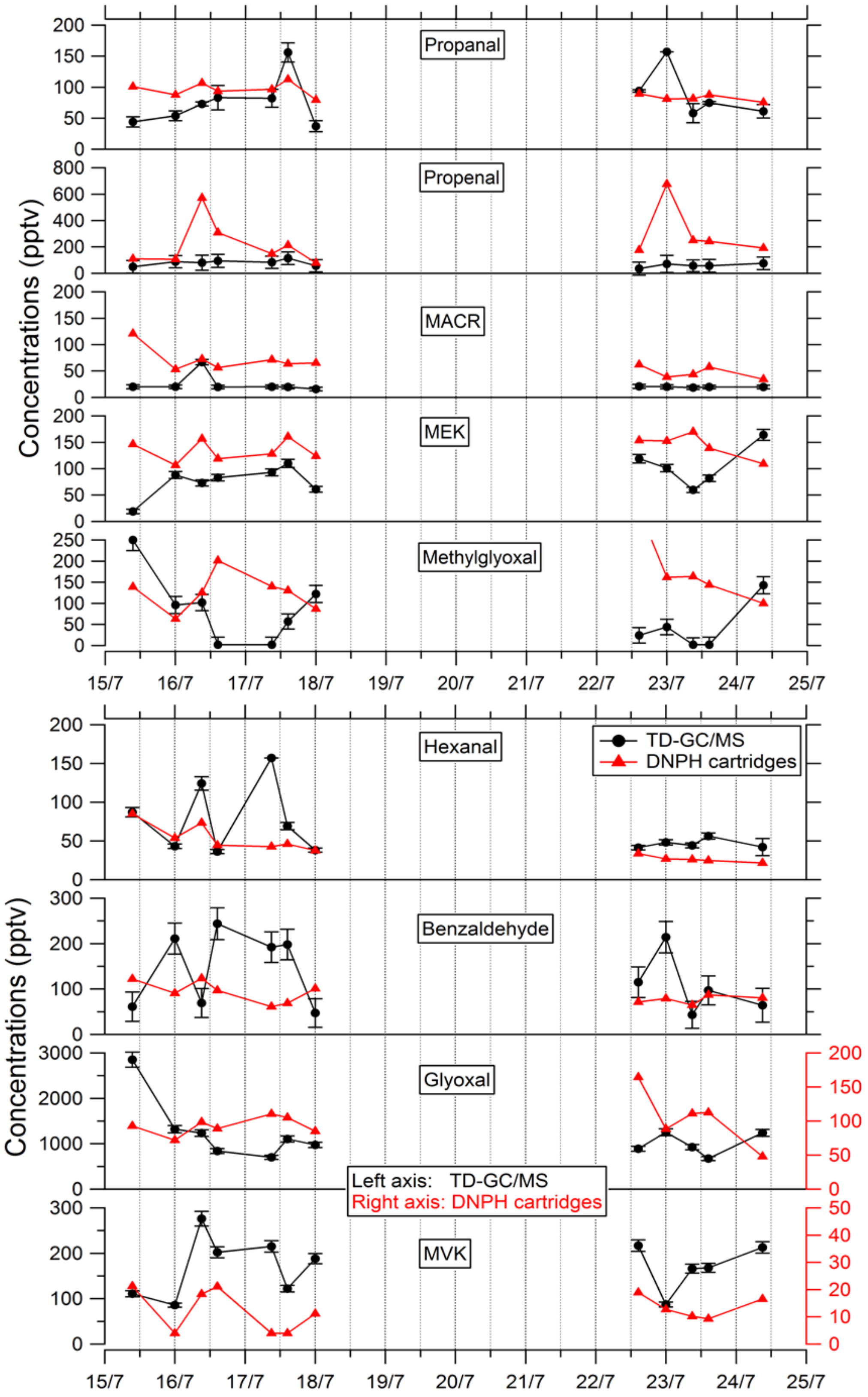


Figure 6 : Comparison of ATD-GC-MS data with DNPH cartridges analysis for 9 OVOCs. Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements. Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements.

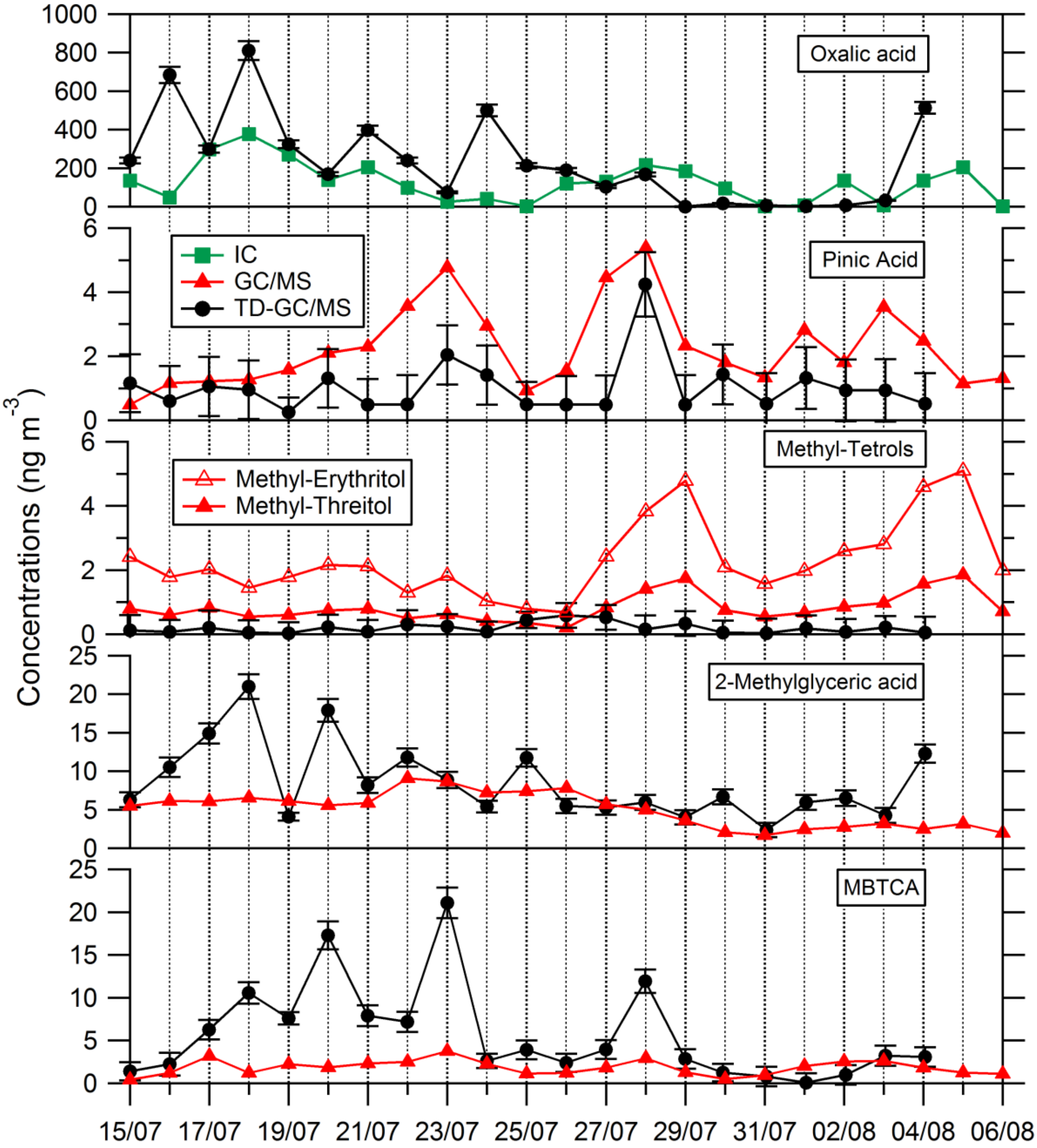


Figure 7 : Comparison of ATD-GC-MS data with ion chromatography and GC/MS analysis for particulate oxalic acid, pinic acid, methyl tetrols, 2-methylglyceric acid and MBTCA (3-Methyl-1,2,3-tricarboxylic acid). Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements. Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements.

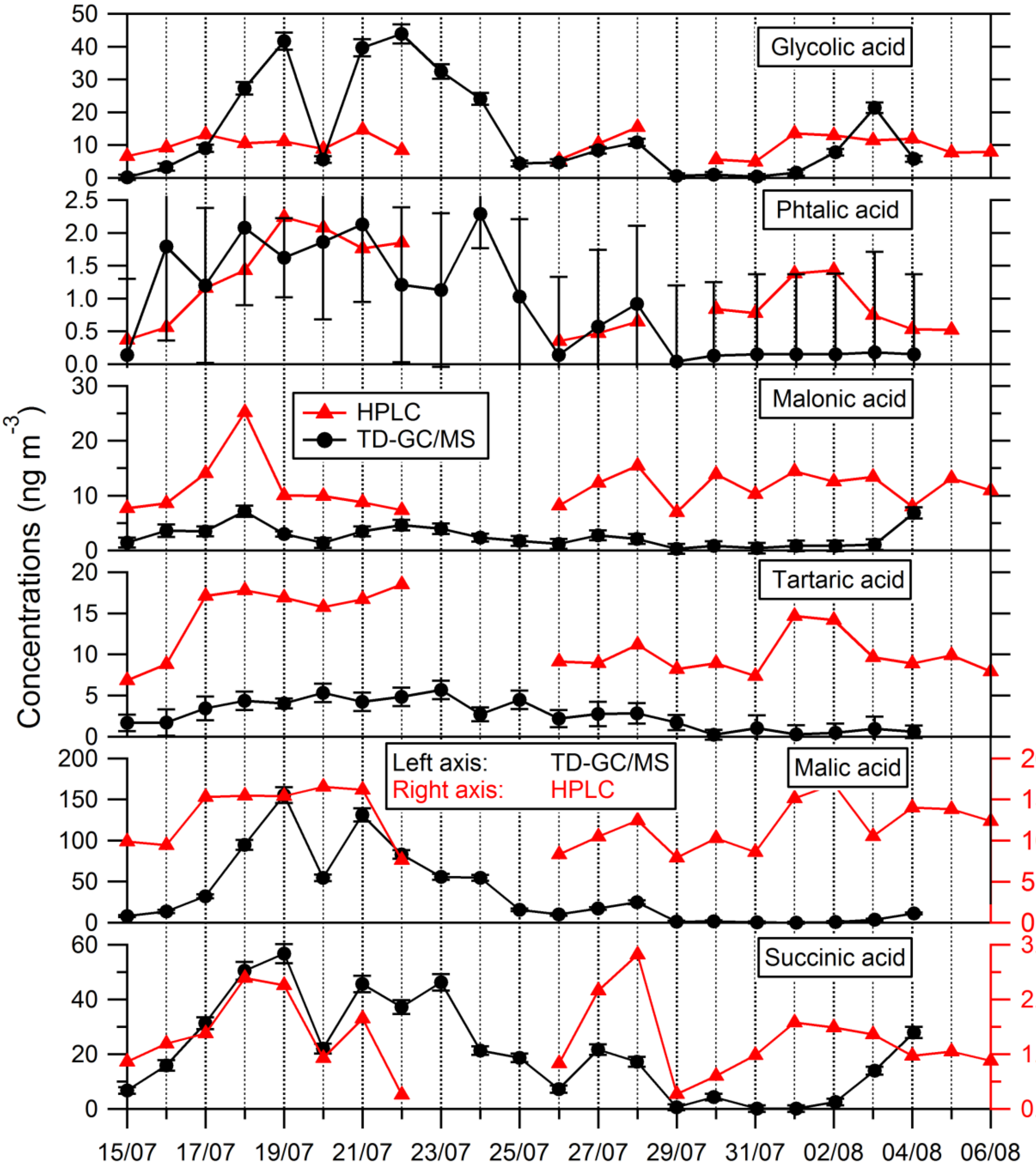


Figure 8: Comparison of ATD-GC-MS data with HPLC analysis for particulate glycolic acid, phtalic acid, malonic acid, tartaric acid, malic acid and succinic acid. Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements. Error bars correspond to the 1σ uncertainties of TD-GC/MS measurements.

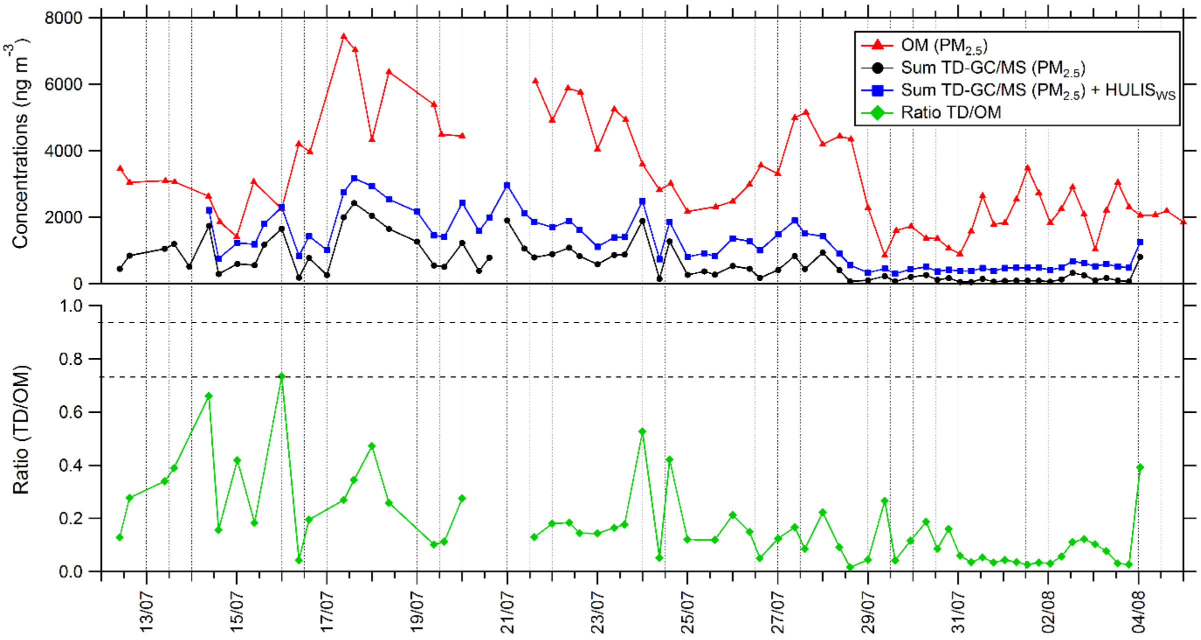


Figure 9: Time series of organic matter in PM$_{2.5}$ (red line), total sum of PM$_{2.5}$ from TD-GC/MS analysis (black line), total sum of PM$_{2.5}$ from TD-GC/MS analysis and water soluble HULIS analysis (blue line), and ratio of these two measurements (green line).

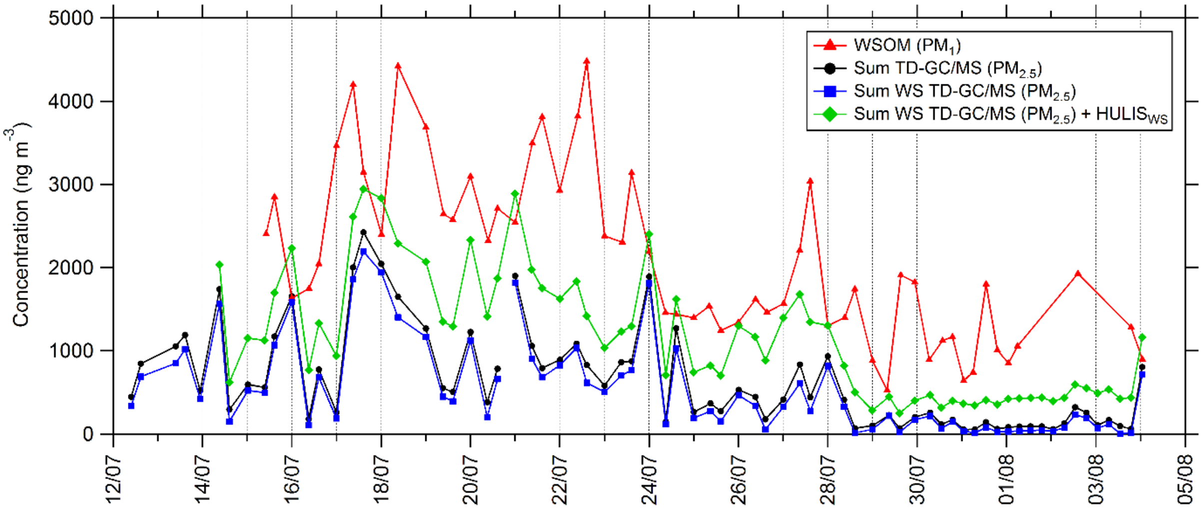


Figure 10: Time series of PM$_1$ water soluble organic matter (WSOM; red line), total sum of PM$_{2.5}$ measured by TD-GC/MS (black line), total sum of compounds measured by TD-GC/MS and having henry's law constant higher than 10^4 M atm^{-1} measured by TD-GC/MS (WS TD-GC/MS, blue line), and total sum of water soluble compounds measured by TD-GC/MS and water soluble HULIS (green line).

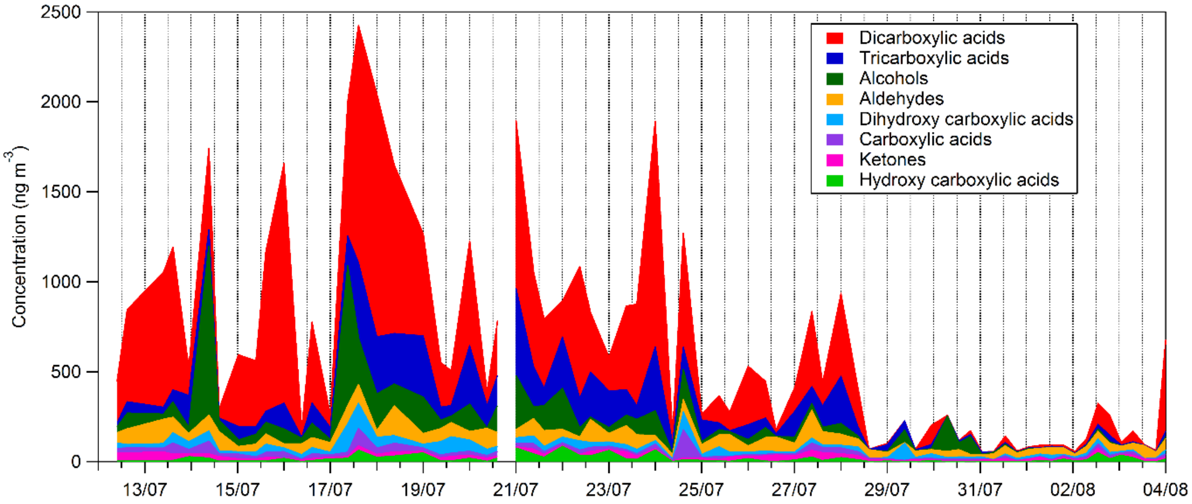


Figure 11: Time series of the composition of the sum of all compounds concentrations measured by TD-GC/MS.

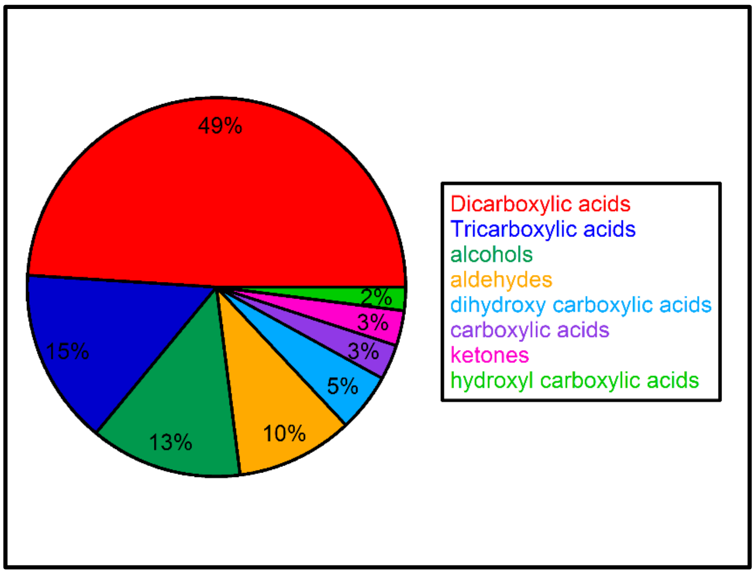
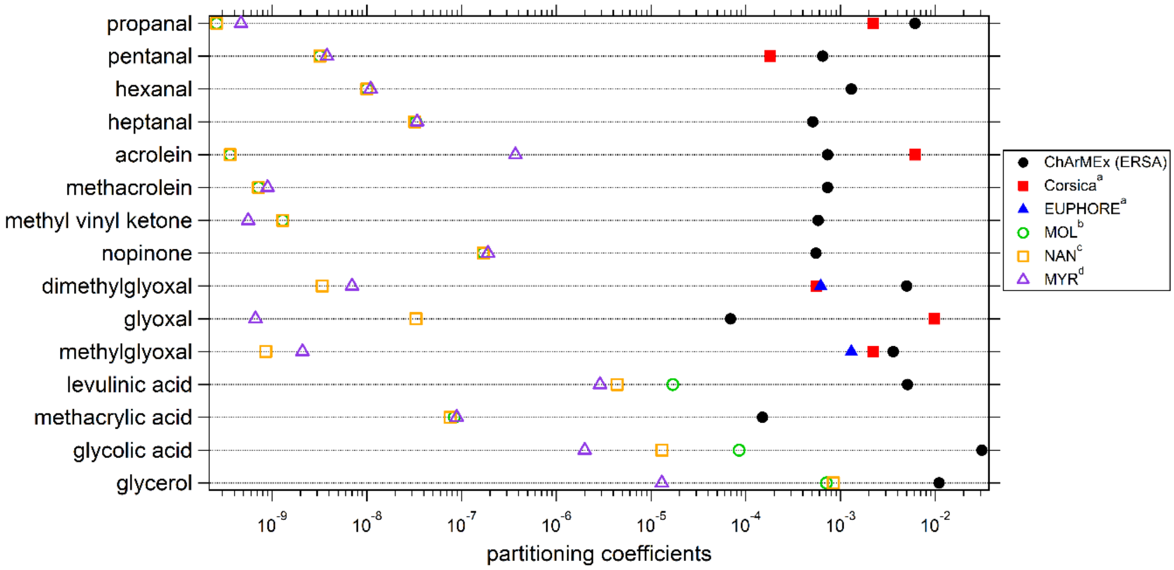


Figure 12: Campaign averaged relative composition of the sum of all compounds measured by TD-GC/MS in the organic aerosol phase (hydroxyl-carboxylic acid-light green area, ketone-pink area, carboxylic acid-purple area, dihydroxy carboxylic acid-light blue area, aldehyde-orange area, alcohol-dark green area, tricarboxylic acid-dark blue area, dicarboxylic acid-red area).



[a] Rossignol et al., 2016; [b] Moller et al., 2008 (coupled with Nannoolal et al. (2004) method for boiling point determination) ; [c] Nannoolal et al., 2008 (coupled with Nannoolal et al. (2004) method for boiling point determination) ; [d] Myrdal and Yalkowsky, 1997 (coupled with Nannoolal et al. (2004) method for boiling point determination)

Figure 13: Experimental and theoretical partitioning coefficients determined for this study and compared to previous field and chamber campaigns.