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**NMR AND MASS SPECTROSCOPIC TECHNIQUES FOR SOURCE
APPORTIONMENT OF ATMOSPHERIC PARTICULATE MATTER**

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Esame finale anno 2017

To my Family

We are the last generation that can fight climate change
Ban Ki-Moon, UN Secretary – 2015

Non chi comincia ma quel che persevera
Motto Nave Scuola Amerigo Vespucci

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ABSTRACT

Aerosols are ubiquitous in the atmosphere, and play a key role in several environmental processes at local and global scale affecting visibility, air quality, and the climate system. Assessing aerosol impacts on human health, climate change and adopting mitigation and adaptation measurements is a global challenge and third millennium priority. For example, the Po Valley is one of the most critical area in Europe for the air quality, with PM_{2.5} concentrations normally exceeding regulatory thresholds especially in the cold season, whereas the Mediterranean basin, with its vulnerability toward aridification, is considered a *hot spot* for climate change.

Efficient policies aiming to contain the health and climate impacts of atmospheric aerosols rely on the reconstructed budget of PM apportioned into its various natural and anthropogenic fractions, which in turn must be constrained by adequate field observations of aerosol chemical composition. In particular, the investigation of the sources of organic aerosol (OA) has reached a high degree of sophistication to cope with the very high complexity of its molecular composition.

In the present study, proton nuclear magnetic resonance (H-NMR) spectroscopy and aerosol mass spectrometry implemented by an “aerosol chemical speciation monitor” (ACMS) were employed to investigate the chemical composition of submicrometric aerosol collected during a series of intensive field campaigns and to resolve its composition into source-specific fractions including distinct types of primary and secondary organic aerosols (POA and SOA).

During the first study, aerosol samples were collected in the Po Valley, in Bologna (urban background site) and San Pietro Capofiume (rural site, 35 km NE from Bologna), during the summer 2012 (*PEGASOS* project) and fall, winter seasons 2013 (*SUPERSITO* campaigns). The H-NMR data were elaborated to provide concentrations of organic markers and functional group distributions. They were processed afterwards by factor analysis for spectral deconvolution into source-specific spectral profiles and contributions (“factors”). The attribution of H-NMR factors to specific sources was based on available spectral libraries and sometimes integrated with information from ancillary techniques (including organic markers from GC/MS and LC/MS analysis). The results show that biomass burning POA and SOA dominate the composition of oxygenated organic aerosols in the Po Valley in the cold season, whereas humic-like substances (HULIS), related to chemically-aged SOA types (contributed by biogenic sources), are prevalent in the summertime.

In the second part of this thesis work, SOA samples were produced in laboratory using a flow tube reactor designed to simulate prolonged photochemical ageing. The samples were analyzed by H-NMR and high-liquid performance chromatography (HPLC) for the characterization of isoprene, α -pinene and naphthalene SOA products. The composition of aged biogenic and anthropogenic SOA

was compared to the spectral datasets from the Po Valley experiments and highlighted a good match between the H-NMR spectral profile of laboratory aged biogenic (monoterpene) SOA with that of ambient OA in the Po Valley in summertime, confirming that atmospheric HULIS can share a biogenic origin and be produced photochemically.

The third part of this work was dedicated to two field campaigns at coastal and marine sites in the central Mediterranean region: the first one in Civitavecchia – the port of Rome, for the *AIR-SEA Lab* project -, and another one onboard the *Amerigo Vespucci* vessel during the project *Dual Use Vespucci*. On-line aerosol measurements were performed using a mass spectrometer (ACSM) during the spring and summer 2016 with the aim of source apportionment of PM into source contributions from local pollution (in harbors) and background components. Results showed that PM1 total concentration resulted only 22% lower over the open sea with respect to ports, but the fossil fuel component of OA (the hydrocarbon fraction) was much more enriched in harbors than in off-shore areas.

The overall results suggest that H-NMR spectroscopy and ACSM can be profitably used for source apportionment of submicrometric organic aerosols, especially when supported by combination with chromatographic speciation of organic markers, and by techniques of factor analysis for spectral deconvolution.

Papers on the international refereed literature originating from this thesis

Sandrini, S.; Pinxteren, D. van; Giulianelli, L.; Herrmann, H.; Poulain, L.; Facchini, M.C.; Gilardoni, S.; Rinaldi, M.; Paglione, M.; Turpin, B.J.; Pollini, F.; Bucci, S.; Zanca, N.; Decesari, S.: Size-resolved aerosol composition at an urban and a rural site in the Po Valley in summertime: implications for secondary aerosol formation. *Atmospheric Chemistry and Physics*, 16, 10879-10897, 2016.

Zanca, N.; Lambe, A.T.; Massoli, P.; Paglione, M.; Croasdale, D.R.; Parmar, Y.; Tagliavini, E.; Gilardoni, S.; Decesari, S.: Characterizing source fingerprints and ageing processes in laboratory-generated secondary organic aerosols using proton-nuclear magnetic resonance ($^1\text{H-NMR}$) analysis and HPLC HULIS determination. Under revision on *Atmospheric Chemistry and Physics*.

Pietrogrande, M.C.; Barbaro, E.; Bove, M.C.; Clauser, G.; Colombi, C.; Corbella, L.; Cuccia, E.; Dalla Torre, S.; Decesari, S.; Fermo, P.; Gambaro, A.; Gianelle, V.; Lazzeri, P.; Lercher, R.; Massabò, D.; Melchionna, G.; Nardin, T.; Paglione, M.; Perrino, C.; Prati, P.; Visentin, M.; Zanca, N.; Zangrando, R.: Results of an Interlaboratory Comparison of Analytical Methods for quantification of anhydrosugars and biosugars in atmospheric aerosol. Submitted to *Chemosphere*.

Zanca, N.; Decesari, S.; Pietrogrande, M.C.; Visentin, M.; Gilardoni, S.; Paglione, M.: Comparison between NMR PMF factors and GC/MS polar organic tracer datasets for the source apportionment at the Po Valley in the cold season. In preparation.

1. INTRODUCTION

1.1 AN INTRODUCTION TO ATMOSPHERIC AEROSOLS

Atmospheric *aerosol* is generally defined as a suspension of liquid or solid particles in the air, with particle diameters in the range of 10^{-9} – 10^{-4} m, the particle sizes span over several orders of magnitude, ranging from almost macroscopic dimensions down to near molecular sizes (Hinds 1999; Seinfeld and Pandis, 2006; Ruiz-Jimenez J. et al., 2011). The term originated as the gas-phase analogue to *hydrosols* (meaning “water particle” in Greek) and refers to suspension of particles in a liquid (Kulkarni et al., 2011). Particles much greater than 100 μm do not stay airborne long enough to be measured and observed as aerosols. The lower limit is controlled by the size of a cluster of half a dozen or so molecules: this is the smallest entity of the condensed phase that can exist. The definition of aerosol is used to a wide range of clouds of particles found in nature airborne; particles from (re-)suspended soil, welding fumes, atmospheric cloud droplets, airborne particles from volcanic eruptions, smoke from power generation, cigarette smoke, sand storms or clouds formed from pollens, salt particles formed from ocean spray, particles from bacteria or viruses, are all examples of aerosols (Kulkarni et al., 2011; Seinfeld and Pandis 2006; Vicent, 1989).

Many commonly known phenomena such as dust, fume, fog, smog, mist, suspended particulate matter, or smog can be described as aerosols. The most evident examples of aerosols in the atmosphere are clouds, which consist primarily of condensed water with particle diameters on the order of approximately 100 μm . In this PhD thesis, we use aerosol and particulate matter (PM) as synonyms for convenience, since the research is focused on atmospheric solid and liquid (deliquesced) particles (with the exception of cloud and fog droplets) in the atmosphere. The term aerosol technically refers to both the condensed phase particles and the gaseous medium suspended in PM (Kulkarni et al., 2011; Colbeck et Lazaridis, 2010).

Atmospheric aerosol particles originate from a broad assortment of natural and anthropogenic sources. Primary particles are directly emitted from sources such as dust, sea salt, volcanic eruptions, biomass burning, incomplete combustion of fossil fuels, and mechanical processes resulting from the friction of wind over land and sea surfaces that lead to the suspension of mineral dust, and biological materials such as spores, plant fragments and microorganisms. In urban environments, traffic can promote the (re-)suspension of particles as well. Secondary particles instead are formed in the atmosphere by the transformation of reactive gases into particulate matter by chemical reactions, from

the condensation of low volatility gases such as sulfuric acid, ammonia and functionalised organic compounds or upon cooling of the air mass (*gas-to-particle conversion*).

Long-range transboundary air pollution transport is responsible for a significant fraction of the particulate pollution in European cities (European Monitoring and Evaluation Programme - EMEP 2016; Colbeck and Lazaridis, 2010). A major part of this contribution is secondary particulate matter in the form of sulfate, nitrate, ammonium, and organic aerosol particles formed by the oxidation of sulfur dioxide, nitrogen oxides, and organic gaseous species. A recent report on the hemispheric transport of air pollutants concluded that the impact of intercontinental transport of PM on air quality is primarily episodic and associated with major emission events such as fires or dust storms. Such transport can also have large impacts on total atmospheric column loading and, hence, implications for climate change (Keating and Zuber, 2007).

Airborne particles undergo various physicochemical transformations (*atmospheric aging*), comprehending changes of structure, shape, particle size, shape, and composition as illustrated in Figure 1.1. Cloud formation can also lead to fast aerosol ageing, as particles are scavenged (aerosol enter water droplets, Giulianelli et al., 2014) into cloud droplets, chemical reactions and gas absorption occur in the aqueous phase and in the end droplet can re-evaporate originating particles with different chemical composition with respect to the original aerosols (*cloud processing*). Aerosol particles can be scavenged in cloud systems either by impact with cloud droplets or by direct nucleation of water vapor to form new droplets. In the last case, aerosols act as cloud condensation nuclei (CCN) or ice nuclei (IN), depending on atmospheric temperature.

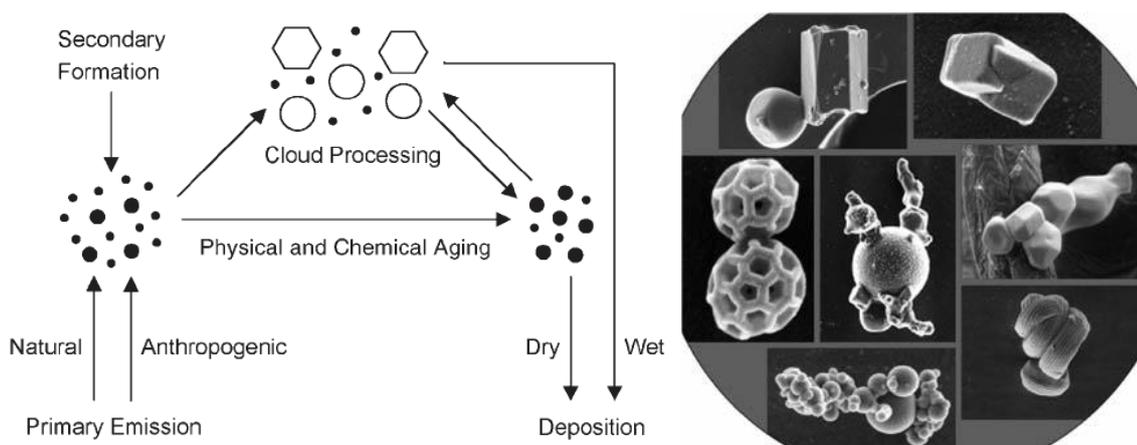


Figure 1.1: Atmospheric cycling of aerosols and examples of common aerosol shapes and compositions as observed by scanning electron microscopy, SEM (from Pöschl, 2005).

In precipitating clouds, the “wet deposition” is a process in which condensation nuclei and other aerosol particles are scavenged and removed from the atmosphere, on the way to the surface. Wet deposition is the main sink of submicrometric atmospheric PM. Dry deposition, conversely, leads PM to be removed by diffusion, convective transport and adhesion to the Earth’s surface without precipitation of hydrometeors. Dry deposition at the global scale is less efficient for fine aerosol fluxes, but cannot be ignored at the urban scale. The typical aerosol particles residence time in the atmosphere range between hours and weeks, depending on aerosol characteristics and meteorological conditions. The aerosol composition, concentration and size distribution are highly variable. In the troposphere (the lower atmosphere), the total particle number varies in the range of about 10^2 – 10^5 cm^{-3} , whereas the mass concentration ranges between 1 to 100 $\mu\text{g m}^{-3}$.

1.2 AEROSOL PHYSICOCHEMICAL CHARACTERISTICS

Particles in the atmosphere have a distribution of sizes, and lognormal distributions are often used for their description (Hinds, 1999). The aerosol size distribution is a crucial parameter that determines the dynamics of aerosols in the atmosphere, their transport, deposition, and residence time. Figure 1.2 presents typical atmospheric aerosol distributions by number, surface area, and volume. The shapes of size distributions, although containing the same modes, look very different according to whether the distribution is plotted for number concentrations or volume concentrations. The reason is that particle populations at the small end of the size distribution can be very abundant in number, but as volume is proportional to the cube of diameter, such particles may contribute only to a small fraction of total aerosol volume. Therefore, particle number size distributions give far more emphasis to small particles compared to particle volume size distributions. In addition, one can derive the mass distribution from the volume distribution data when the particle density is known. The volume distribution is usually bimodal with minimum at ~ 1 μm (divide between coarse and fine particles). Coarse particles are generally formed by mechanical processes such as dust resuspension. They are typically rich in the naturally occurring crustal material (Ca, Fe, and Si) as well as sea salt. The fine particles can be rich in carbon, nitrates, sulfates, and ammonium ions. They are generally formed by combustion or gas-to-particle conversion. The particles in the two modes not only differ in origin but also have different atmospheric fates, as discussed below.

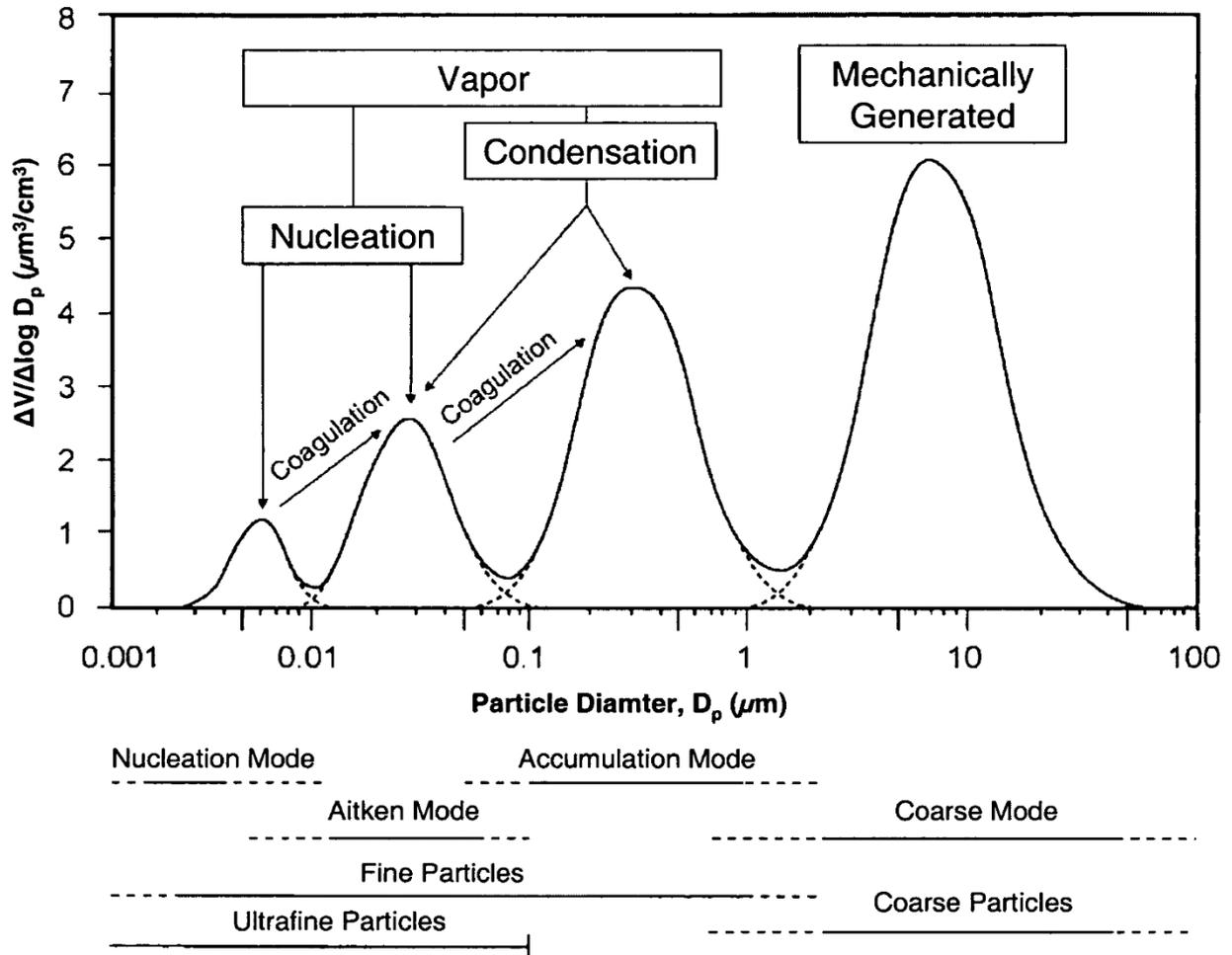


Figure 1.2. Aerosol size distribution with principal modes. Main mechanisms of formation and growth of particles acting in the various size ranges are also shown. (Araujo et al., 2009).

Particles can be categorized according to their size based on (1) their observed modal distribution (Hinds 1999), (2) the 50% cut-off diameter, or (3) from dosimetric variables which are related to human exposure. In the latter case, the most common division is PM_{2.5} and PM₁₀ particles. PM₁₀ is defined as PM which is sampled through a size-selective inlet with a 50% efficiency cut-off for particles of 10 μm aerodynamic diameter. Similarly, the cut-off for PM_{2.5} is 2.5 μm. The 2.5 μm threshold is related to the ability of PM_{2.5} particles to penetrate the lower tracts of the human respiratory system.

Further aerosol populations can be identified according the following terminology:

- *Nucleation mode*: Particles with diameter <10 nm, which are formed through nucleation processes, i.e., by the formation of aerosols directly from gas-phase reactions. The lower limit

of this category is not very well defined but is dictated by instrument capability. An ion aerosol spectrometer can detect particles down to 1.5 nm, close to molecular cluster size, whereas the cut-off for a condensation particles counter is limited to 3 nm.

- *Aitken mode*: Particles with diameter $10 \text{ nm} < d < 100 \text{ nm}$. They originate from combustion emissions or from condensational growth of nucleation-mode particles.
- *Accumulation mode*: Particles with diameter $0.1 \text{ }\mu\text{m} < d < 1 \text{ }\mu\text{m}$. The upper limit coincides with the minimum of the total particle distribution. Particles in this mode are formed by coagulation and condensational growth of Aitken-mode particles. .
- *Ultrafine particles*: Particles of diameter $< 0.1 \text{ }\mu\text{m}$, equivalent to the size range encompassing the Aitken mode and the nucleation mode.
- *Fine particles*: Includes the nucleation, Aitkin, and accumulation modes.
- *Coarse particles*: Particles with diameters between 1 and $10 \mu\text{m}$.

The distinction between fine and coarse particles is fundamental whenever dealing with the physics, chemistry, measurement, and the health effects of atmospheric aerosol, because very different formation, transformation and removal processes characterize the submicron and supermicron regimes (Seinfeld&Pandis, 2006) (Figure 1.3). Coarse particles are formed mainly by mechanical processes like dust suspension or re-suspension or sea spray. Coarse particles have sufficiently large sedimentation velocities to make them settle by dry deposition within a few hours of transport in the lower troposphere, although longer transport ($> 1 \text{ day}$) are possible at high altitudes. Coarse particles never account for more than a few percent of the particles by number concentration, even if they can account for a large fraction in term of particulate mass.

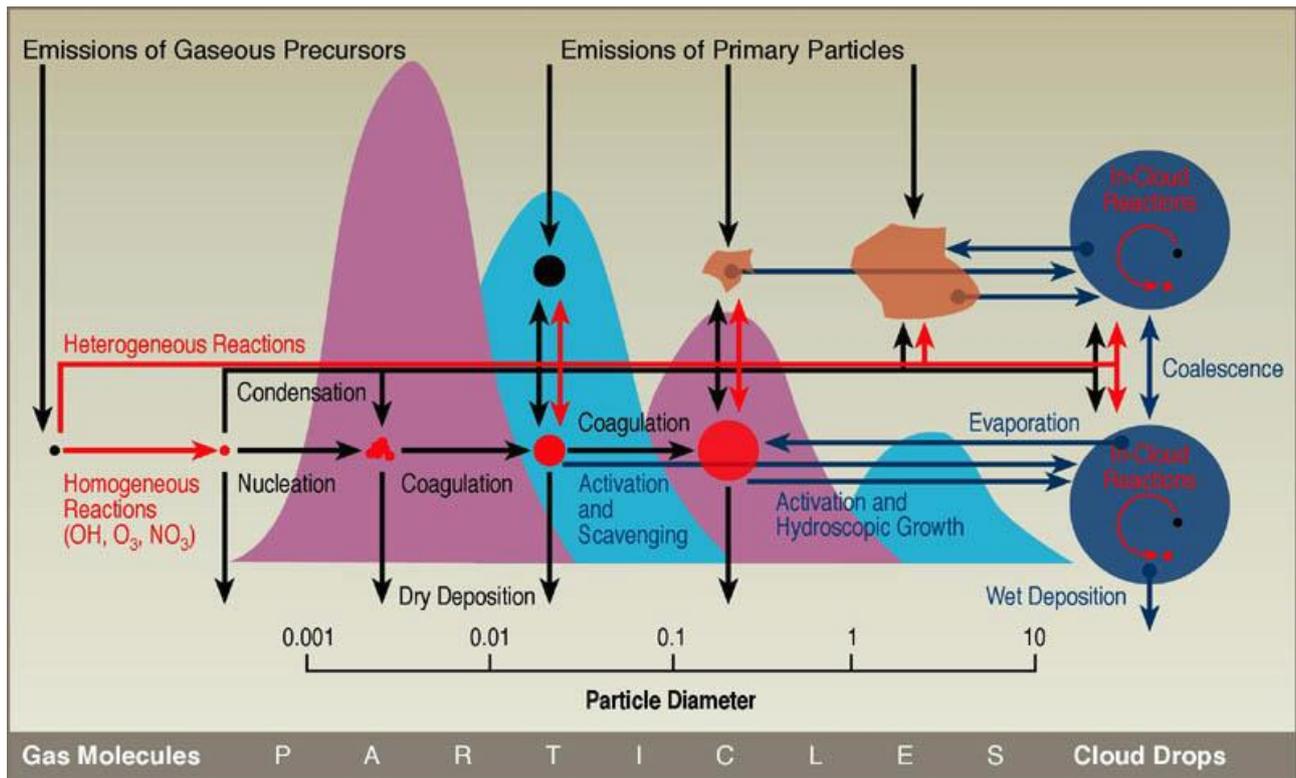


Figure 1.3. Microphysical processes that affect size distribution and chemical composition of atmospheric aerosol. The diagram shows the wide size range of particles and as the aerosol participates in processes through atmospheric chemical reactions in homogeneous and heterogeneous phase or within clouds (Raes et al., *Atm. Env.* 2000).

Fine particles, on the contrary, are mainly generated by secondary processes (e.g. gas-to-particle mechanisms) and by primary sources (e.g. vehicular emissions, biomass burning, etc.). The rapid gas condensation conducts to new particles by nucleation (nucleation mode). This mechanism takes place during the rapid cooling of an exhaust immediately upon dilution in the air, but can occur also by photochemical reactions at ambient temperature. The Aitken mode results from condensation of vapors onto nucleation mode particles and from their coagulation, as well as from primary combustion emissions. Finally, the accumulation mode, usually results from prolonged – several hours to day – condensation of vapours on Aitken particles and, in non-precipitating cloud droplets, from the formation of particles by chemical reactions (Kerminen et al., 2004). Removal processes (deposition, coagulation, diffusion to surfaces) are the slowest in this size range, and, as a consequence, these particles tend to accumulate in the atmosphere (hence the term “accumulation mode”). The most efficient sink for accumulation mode particles is by wet deposition (through precipitations). Accumulation-mode particles usually account for most of the aerosol surface area. They also provide an equivalent or greater contribution to total aerosol mass with respect to coarse particles.

Fine particles, given their small size, penetrate deeply into the human respiratory system, down to the alveola, causing potential systemic health effects. Moreover, because of their long residence time in the atmosphere, accumulation mode particles contribute to transboundary air pollution transport and to the modification of atmospheric transparency over vast geographical areas. For these reasons, my PhD focused on fine (submicron or PM₁) particles.

1.3 AEROSOL CHEMICAL COMPOSITION

Aerosols are ubiquitous in the atmosphere. They comprise a complex mixture of low-volatility and semi-volatile organic and inorganic compounds (Colbeck and Lazaridis M, 2010). Compared to long-lived greenhouse gases, tropospheric aerosol exhibits a chemical composition characterized by a much greater spatial and temporal variability, reflecting the variety of sources, transformations and removal processes. Aerosol chemical constituents can be classified into broad categories: inorganic water-soluble salts such as sulfates, nitrates, ammonium salts and sea salt, soluble and insoluble carbonaceous material, and insoluble inorganic compounds from soil particles and combustion ash. Carbonaceous particles are found in the troposphere as elemental carbon (EC) (or “black carbon”, BC), organic carbon (OC) and carbonate carbon, the latter being negligible in the submicron size range. Produced solely by combustion processes, EC strongly absorbs light and it is responsible for degraded visibility (Bond and Bergstrom, 2006). Organic carbon is produced by both primary sources (e.g., combustion) and gas-to-particle conversion (Castro et al., 1999). Finally, coarse particles are generally associated with sea salt and crustal species emitted by mechanical processes at the Earth surface. Since aerosol surface generally reaches a maximum in the accumulation mode, gas-to-particle formation of organic and inorganic compounds (e.g., ammonium sulfate and nitrate) occur preferentially in fine particles. However, heterogeneous chemical reactions at particle surface may lead some compounds, like nitrate, to form by condensation in both fine and coarse modes. For instance, the condensation of nitric acid on coarse-mode sea salt particles with formation of sodium nitrate and displacement of HCl has been documented (Dasgupta et al., 2007). An overview of the average size-segregated chemical composition of tropospheric aerosols in Europe was first published by Putaud and co-workers (2004), followed by more detailed phenomenologies of the aerosol chemical composition obtained for several European sites (Putaud et al., 2010). In European emission inventories, combustion of fuels within the residential sector is covered by the so-called 'commercial, institutional and household' sector. The fuel combustion in this sector is the major source of primary PM_{2.5} and PM₁₀. In the Figure 1.4 below and example of PM_{2.5} emissions in the EU-28 by sector (EEA, 2016).

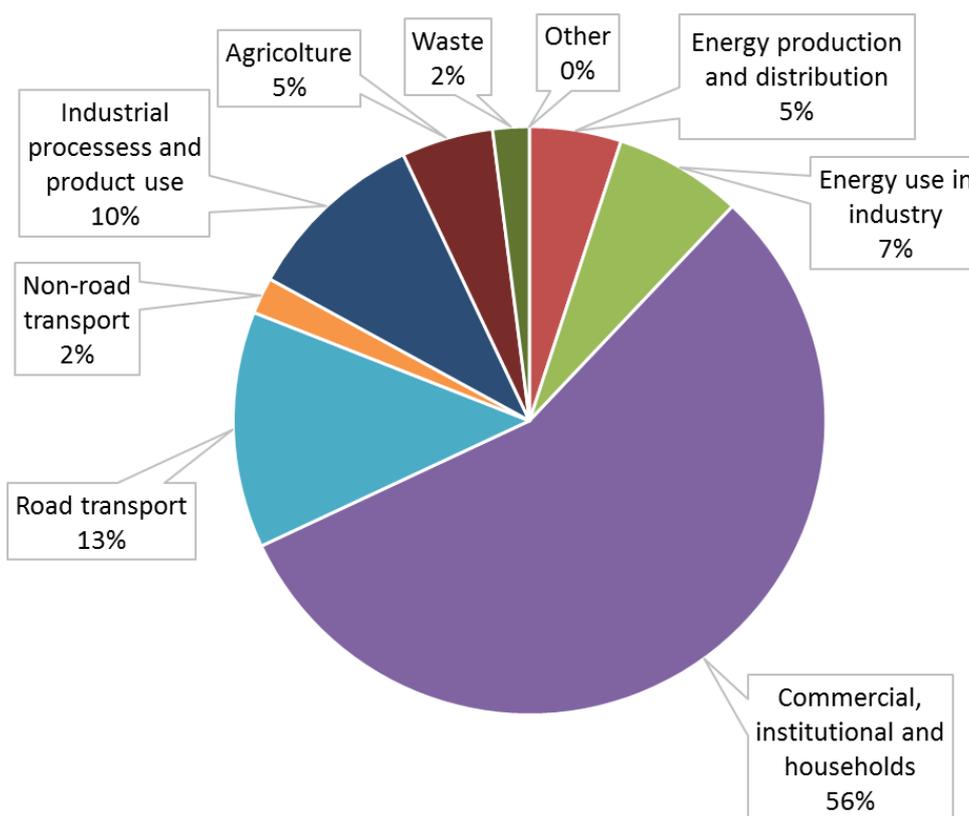


Figure 1.4. PM_{2.5} emissions in the EU-28: share by sector group in 2014.
<http://www.eea.europa.eu/publications/air-quality-in-europe-2016>

1.4 ORGANIC AEROSOL

Organic aerosol (OA) includes a large fraction of the ambient aerosol mass and exert potential important impacts on human health, visibility and on the climate system (e.g. Kanakidou et al., 2005; Jimenez et al., 2009). OA is widespread in all environments and represent a large, sometimes dominant aerosol fraction in the lower troposphere, accounting for 20-90% of atmospheric fine particle mass (Kanakidou et al., 2005; Zhang et al., 2005; Jimenez, 2009; Turpin et al., 2000). OA accounts for complex mixtures of individual organic compounds which are often present at trace levels, with concentrations generally less than a few ng/m³ each (Shimmo et. al., 2004). A wide range of both anthropogenic and natural sources were blamed for OA production, including combustion of fossil fuels, lubricants, industrial emissions, biomass burning, spores and plant debris, and biogenic emission of volatiles (Jacobson et al., 2000). About 2000 Tg/yr of organic compounds are estimated to be emitted into the atmosphere as gases, another 300 Tg/yr as particulate matter (aerosols), and a smaller uncertain fraction is dissolved in fog droplets or cloud. While these quantities represent only

a few percent of the total carbon budget, dominated by CO₂, they represent 10⁴–10⁵ individual compounds (Goldstein et al., 2007) which take part in many atmospheric chemical reactions.

Understanding the processes where organic compounds are involved in the atmosphere depends on how well these compounds are identified (Nozière et al., 2015). Moreover, the chemical fates of trace atmospheric species are often intertwined. The life cycles of the trace organic species are coupled through the complex array of chemical and physical processes in the atmosphere. For instance, the photochemical production of tropospheric ozone does not depend linearly on the concentrations of precursors (volatile organic compounds, VOCs) or catalysts (nitrogen oxides, NO_x), but very much on their ratio (VOC/NO_x), and consequently the production of ozone can be NO_x-limited or alternatively VOC-limited depending on the environment (Seinfeld and Pandis, 2006).

Organic aerosols can be separated into primary (**POA**) and secondary (**SOA**) depending on their process of formation. POA consists of particles that are directly emitted into the atmosphere such as organic compounds formed by combustion processes (that contribute mostly to the fine fraction of OA) or plant particles from biogenic sources (more representative of the coarse fraction). Spray of organic-rich liquid surfaces may inject primary organic particles into the fine fraction. Such mechanism can contribute to the formation of submicron organic particles over high biologically productive oceanic waters (O'Dowd et al., 2004).

SOA in contrast is mainly formed by gas-to-particle conversion processes such as nucleation, condensation and heterogeneous and multiphase chemical reactions (Hallquist et al., 2009). Reactive volatile organic compounds (VOCs) are precursors for SOA. VOCs have been studied as major air pollutants and for their role in tropospheric ozone formation since 1950s (Pitts and Stephens, 1978). However, most low-molecular weight reactive VOCs contributing to ozone formation do not take part substantially in SOA production. Generally, SOA formation yields increase with the molecular weight of parent VOC. For instance, monoterpenes (C₁₀) produce more SOA per unit of VOC mass compared to isoprene (C₅), and less than sesquiterpenes (C₁₅). SOA can be generated in the atmosphere also by chemical transformation (aging) of primary components in the condensed phase.

Global SOA estimations are extremely variable between assessments (Table 1.1). Therefore, constraining the global SOA budget is considered a hot topic in the atmospheric chemistry community (Nozière et al., 2015). The relative contribution of POA and SOA to the overall OA budget and the determination of their main sources remain a highly debated issue due to the persistent discrepancies between measured OA concentrations and the predictions of atmospheric chemistry models that often show an underestimation of the ambient concentrations.

Compounds	Concentrations (Tg yr ⁻¹)	Reference
Biogenic SOAs	270	Andrea, Crutzen et al., (1997)
Biogenic SOAs	13-24	Griffin et al., (1999)
Global biogenic emissions	491-1150	Guenther et al., (1995)
Annual biogenic SOA formation	61-79	Kanakidou et al., (2000)
VOCs isoprene and terpenes	12-70	Kanakidou et al., (2005)
Isoprene	10-120	Matsunaga et al., (2005)
Terpenes	725	Lathi�re et al., (2006)
Terpene oxidation	19	Griffin et al., (1999)
Total organic carbon	69	Liousse et al., (1996)
Total black carbon	12	Liousse et al., (1996)
Total sea salt	5900	Tegen et al. (1997)
Soil dust <1�m	250	Tegen and Fung (1995)
Soil dust <10�m	1000	Tegen and Fung (1995)
Total sulfate (as H ₂ SO ₄)	150	Chin and Jacob (1996)
Biogenic sulfate	32	Koch et al., (1999)
Anthropogenic sulfate	111	Koch et al., (1999)
Nitrate	11,3	Adams et al., (1999)
Ammonium	33,6	Adams et al., (1999)

Table 1.1. A summary of global generated rates of particles into the atmosphere.

Despite the high organic content of aerosol particles, the knowledge about the actual OA sources is still limited: as a matter of fact, the huge complexity of the molecular composition of OA (Shimmo et al., 2004) challenges the resolution of modern analytical techniques and poses limits to the accuracy of OA source apportionment. Moreover, the organic composition of atmospheric particles is highly dynamic in nature, and very much dependent on atmospheric conditions, and this makes the characterization of OA even more challenging because it requires analytical techniques with an adequate time resolution of the measurement (Robinson et al., 2007; Hallquist et al., 2009; Jimenez et al., 2009).

Improving our knowledge on the sources and transformation mechanisms of POA and SOA by means of modern analytical techniques is crucial for developing strategies of reduction and mitigation of OA adverse effects on the environment and on human health.

1.5 ENVIRONMENTAL IMPACTS OF ATMOSPHERIC AEROSOLS

Air pollution is a very important environmental and social issue in both industrialized and developing countries. Air pollutants are emitted from anthropogenic sources, but it should be noted that harmful substances can be emitted or produced also by natural sources (e.g., volcanic SO₂, biogenic precursors of ozone and particulate matter). In turn, biogenic aerosol concentrations are affected by human-driven changes in the photochemistry and in the climate conditions. Air pollutants exert diverse impacts on human health, ecosystems, the built environment and on the climate system. Long-living pollutants are transported or formed over long distances (100 to more than 1000 km) and affect vast geographical areas. Effective measures for improving air quality require a good understanding of the full atmospheric life cycle of air pollutants (EEA, 2016).

1.5.1 AEROSOL AND HEALTH – EUROPEAN AIR QUALITY

The emission reduction adopted in Europe in the last 20 years have significantly improved air quality, and for certain pollutants like SO₂, exceedances of European threshold limits are rare. However, substantial challenges remain for ozone, nitrogen dioxide and especially particulate matter. A large proportion of European populations and ecosystems are still exposed to air pollution that exceeds European standards: approximately 85% of EU population was exposed to concentrations exceeding the stricter World Health Organization (WHO) Air Quality Guidelines (AQGs) value for PM_{2.5} in 2014 (EEA, 2016; <http://www.euro.who.int/en/publications/abstracts/air-quality-guidelines-for-europe>). Estimates of the health impacts attributable to exposure to air pollution indicate that PM_{2.5} concentrations in 2013 were responsible for about 467 000 premature deaths originating from long-term exposure in Europe (over 41 countries), of which around 436 000 were in the EU-28 (see Figure 1.5). The estimated impacts on the population in the same 41 European countries of exposure to NO₂ and O₃ concentrations in 2013 were around 71 000 and 17 000 premature deaths per year, respectively, and in the EU-28 around 68 000 and 16 000 premature deaths per year, respectively. Effective air-quality policies require action and cooperation at global, European, national and local levels, which must reach across most economic sectors and engage the public. Holistic solutions involving technological development, and structural and behavioural changes, must be pursued. In order to support economic prosperity, human well-being and social development, these policies are required and are part of the EU's 2050 vision (EEA, 2016).

Over the last three decades, EU policies have resulted in decreased emissions of air pollutants and noticeable improvements in air quality. This European policy is in line with other international instruments and conventions. Furthermore, national, regional and local authorities play a very

important role not only in implementing EU legislation but also in adopting additional measures to reduce emissions and further protect their populations and the environment from the impacts of air pollution. (EEA, 2016). Significant decreasing trends in the PM₁₀ annual mean were found in 2000–2014 for 75% of a consistent set of European stations. Similarly, PM_{2.5} concentrations, on average, tended to decrease between 2006 and 2014 for all station types. In fact, on 2014, the number of EU Member States with concentrations above the air-quality standards was lower than in 2013, as was the case for the urban population exposed to levels above those standards. However, current trends indicate that there will still be exceedances in 2020.

Numerous epidemiological studies show that fine air particulate matter and traffic-related air pollution are correlated with severe health effects, including enhanced mortality, cardiovascular, respiratory, and allergic diseases (Bernstein et al. 2004; Gauderman et al., 2004; Katsouyanni et al., 2001; Pope et al., 2004; Samet et al., 2005). Moreover, toxicological investigations in vivo and in vitro have demonstrated substantial pulmonary toxicity of model and real environmental aerosol particles, but the biochemical mechanisms and molecular processes that cause the toxicological effects such as oxidative stress and inflammatory response have not yet been resolved. Among the parameters and components potentially relevant for aerosol health effects are the specific surface, transition metals, and organic compounds (Bernstein et al. 2004; Bömmel et al., 2003; Donaldson et al., 2003).

Ultrafine particles ($D_a < 100$ nm) are suspected to be particularly hazardous to human health, because they are sufficiently small to penetrate the membranes of the respiratory tract and enter the blood circulation or be transported along olfactory nerves into the brain (Oberdorster et al. 2004; Nemmar et al., 2002; Oberdorster et al., 2005). Neither for ultrafine nor for larger aerosol particles, however, it is clear which physical and chemical properties actually determine their adverse health effects (particle size, structure, number, mass concentration, solubility, chemical composition, and individual components, etc.).

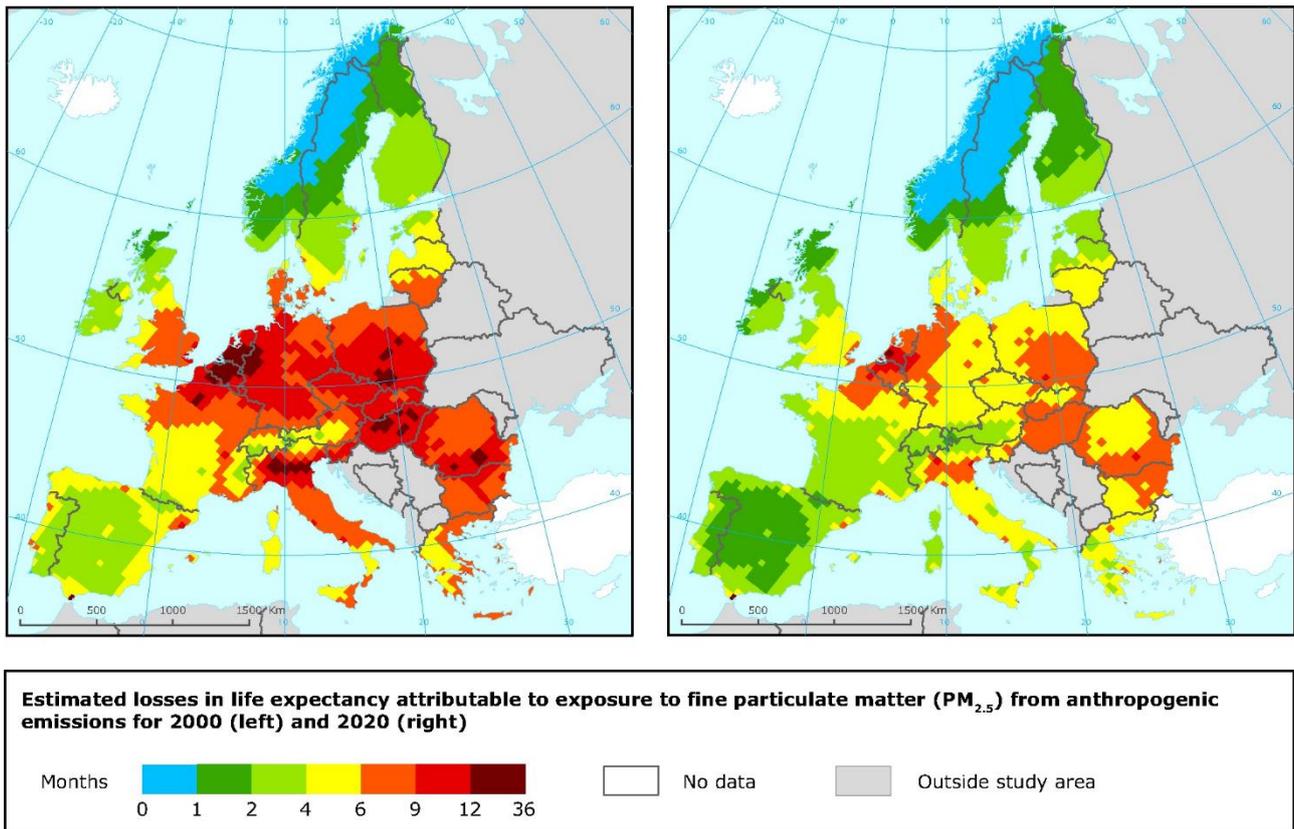


Figure 1.5. Health impact of PM mass concentrations ($\mu\text{g}/\text{m}^3$). Loss in statistical life expectancy (months) that can be attributed to anthropogenic contributions to PM_{2.5} for the year 2000 (left) and for 2020 (right) for the CAFE baseline scenario. <http://www.eea.europa.eu/data-and-maps/figures/health-impact-of-pm-mass-concentrations-g-m3-loss-in-statistical-life-expectancy-months-that-can-be-attributed-to-anthropogenic-contributions-to-pm2-5-for-the-year-2000-left-and-for-2020-right-for-the-cafe-baseline-scenario>

1.5.2 AEROSOL AND CLIMATE: IPCC REPORT

The most comprehensive and recent review about climate change and human impacts on the climate system is the Fifth Assessment Report (AR5) written and published by the **Intergovernmental Panel on Climate Change (IPCC)** in 2013. IPCC is the international panel of experts for assessing the state of the science of climate change. The IPCC was set up in 1988 by the World Meteorological Organization (WMO) and United Nations Environment Programme (UNEP) to provide policymakers with regular assessments of the scientific basis of climate change, its impacts and future risks, and options for adaptation and mitigation. At the end of 2007, the IPCC was awarded the Nobel Peace Prize (IPCC, 2013).

Climate change poses increasingly severe risks for ecosystems, human health and the economy. According to a European Environment Agency report published at the end of January 2017, land and sea temperatures are increasing; precipitation patterns are changing, generally making wet regions in Europe wetter, particularly in winter, and dry regions drier, particularly in summer; sea ice extent, glacier volume and snow cover are decreasing; sea level is rising; and climate-related extremes such as heat waves, heavy precipitation and droughts are increasing in frequency and intensity in many regions. (EEA, 2016).

The Mediterranean Sea region, home to around 480 million people living across 3 continents was identified as one of the main climate change hotspots (i.e. one of the areas most responsive to climate change) due to water scarcity, concentration of economic activities in coastal areas, and reliance on climate-sensitive agriculture (IPCC, 2013). The IPCC temperature projections show a probably increasing of 4-5°C for the end of the century for some Mediterranean areas.

The IPCC reports examine a full set of anthropogenic atmospheric compounds impacting the Earth's radiative budget. Beside CO₂, which is the main anthropogenic green-house gas (GHG) and it is *not* a pollutant, there are also several air pollutants which are also climate forcers, with a potential impact on climate and global warming especially in the short term (i.e. years to decades). Air pollution and climate change are therefore intertwined. Specifically, the climate impact of atmospheric aerosols arises from their ability to reflect solar radiation back to space and from their ability to act as cloud condensation nuclei (CCN). An increased CCN concentrations means higher cloud droplet number, hence higher cloud top reflectivity (higher cloud albedo), but also less probability of precipitation and longer cloud lifetime and increased cloud fraction (Seinfeld and Pandis 2006; IPCC, 2013).

In order to quantify the global warming by the change in Earth's energy balance, the concept of "radiative forcing" (RF) is normally used to quantify the radiative effect of an augmented concentration of atmospheric gases or aerosol due to anthropogenic activities. RF is expressed in Watts per square meter (Wm⁻²).

According to IPCC, there is *very high confidence* that the total anthropogenic RF increase rate since 1960 has been much greater than during earlier industrial-era periods, driven primarily by the continuous increase in concentrations. There is still low agreement among scientists on the time evolution of the total aerosol RF, which is the primary factor for the uncertainty in the total anthropogenic forcing. However, there is a *high confidence* that aerosols have offset a substantial portion of GHG forcing, despite the large uncertainty ranges on aerosol forcing.

Forcing can also be attributed to emissions rather than to the resulting concentration changes (Figure 1.6).

Carbon dioxide is the largest single contributor to historical RF from either the perspective of changes in the atmospheric concentration of CO₂ or the impact of changes in net emissions of CO₂. The relative importance of other forcing agents can vary markedly with the perspective chosen, however. Tropospheric O₃ and black carbon (BC) are examples of air pollutants that are short-lived climate forcers and that contribute directly to global warming. Other PM components, such as organic carbon (OC), ammonium (NH₄⁺), sulfate (SO₄²⁻) and nitrate (NO₃⁻), have a cooling effect. In addition, changes in weather patterns due to climate change may change the transport, dispersion, deposition and formation of air pollutants in the atmosphere. For example, a warmer climate leads to an increase of O₃ production at the ground level, and increased O₃ levels then contribute to more warming. In order to reduce health and ecosystem impacts and cope with the climate change, BC emissions must be cut, along with those of other pollutants that cause tropospheric O₃ formation, such as methane (CH₄) (itself a greenhouse gas).

Air quality and climate change should therefore be tackled together by policies and measures that have been developed through an integrated approach. Examples are the impact on air quality from the large support via taxation of diesel cars (with lower carbon dioxide (CO₂) emissions), or from the increased use of biomass combustion without adequate emission controls (EEA, 2016).

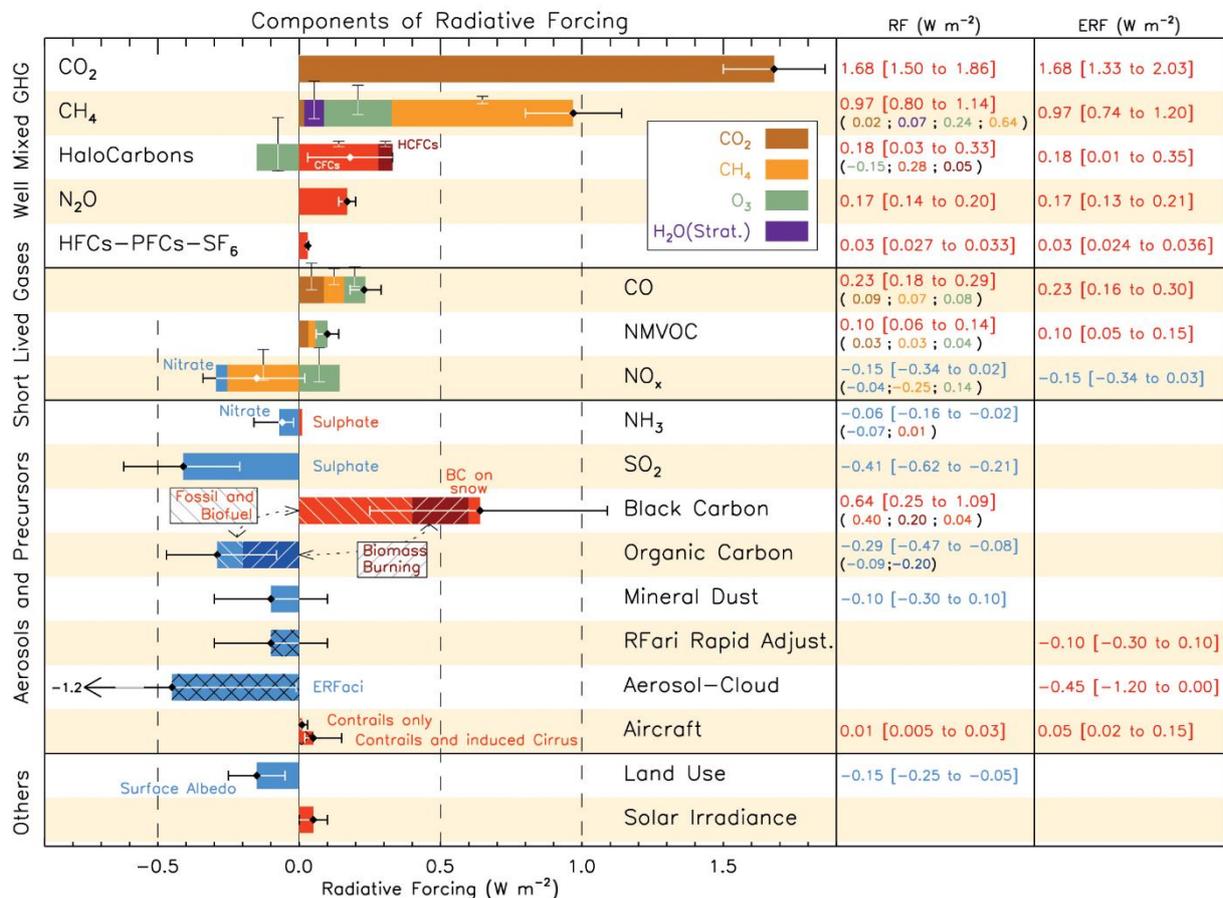


Figure 1.6: Radiative forcing of climate change during the industrial era shown by emitted components from 1750 to 2011. The horizontal bars indicate the overall uncertainty, while the vertical bars are for the individual components (vertical bar lengths proportional to the relative uncertainty, with a total length equal to the bar width for a $\pm 50\%$ uncertainty). Best estimates for the totals and individual components (from left to right) of the response are given in the right column. Values are RF except for the ERF of aerosol-cloud interactions (ERF_{aci}). An additional rapid adjustment to aerosol-radiation interactions of -0.1 [-0.3 to $+0.1$] $W m^{-2}$ is attributable primarily to black carbon. CFCs = Chlorofluorocarbons, HCFCs = Hydrochlorofluorocarbons, HFCs = Hydrofluorocarbons, PFCs = Perfluorocarbons, NMVOC = Non-Methane Volatile Organic Compounds, BC = Black Carbon. (IPCC, 2013).

Atmospheric scientific research is not the only way to approach the issue of air pollution and climate change. The European Union, by EIT (European Institute of Innovation and Technology), founded **Climate-KIC**, the EU's largest public private partnership addressing climate change through innovation to build a zero carbon economy. It addresses climate change across four priority themes: urban areas, land use, production systems, climate metrics and finance. Education is at the heart of these themes to inspire and empower the next generation of climate leaders. It runs programmes for students, start-ups and innovators across Europe via centers in major cities, convening a community of the best people and organizations. The approach starts with improving the way people live in cities. The focus on industry creates the products required for a better living environment, and it look to optimize land use to produce the food people need (<http://www.climate-kic.org/>). During my PhD I followed several Climate-KIC educational activities, as The Journey, the most important summer school about climate change and business, and then I started to be involved in Climate-KIC Alumni activities, organizing meetings and workshop in that topic.

1.6 MEASUREMENT TECHNIQUES FOR ORGANIC AEROSOLS

1.6.1 INTRODUCTION

The determination of organic aerosol (OA) composition encompasses a wide range of analytical techniques, whose characteristics and applications are summarized by some recent review papers (McMurry, 2000; Hoffmann and Warnke, 2007; Rudich et al., 2007; Nozière et al., 2015). Here, some of the most recent advancements in OA and SOA analysis treated by the work of Hallquist et al. (2009) and Nozière et al. (2015) are summarized. A focus on the main techniques employed in this study, i.e. proton-nuclear magnetic resonance spectroscopy (1H -NMR) and aerosol chemical speciation monitor (ACSM) is given.

One of the main limitations to complete characterization of OA, and especially SOA, is the sheer number of individual molecular species present. Most of the OA mass is accounted for by complex mixtures of compounds, including many isomeric forms, and each occurring in very low concentrations. The recovery of particulate compound measurements with respect to total organic carbon varies dramatically between techniques: the methods for individual compounds analysis cannot cope with the full molecular complexity of the samples and generally exhibits low recoveries ($\leq 10\%$), while spectroscopic methods for functional group determination provide a more complete analysis, because for the same chemical composition the number of functionalities is much smaller than the number of individual compounds.

The methods for OA chemical analysis are generally classified into **off-line** and **on-line techniques**. Off-line techniques, e.g., gas chromatography/mass spectrometry (GC/MS), liquid chromatography/MS (LC/MS), nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy, provide detailed information on individual chemical species or functional groups in OA but generally require large amounts of sample, resulting in low time resolution of sampling (several hours to days) and low aerosol size resolution. On-line techniques (e.g., aerosol mass spectrometry, AMS) usually provide less specific information on composition (with respect to chromatographic techniques), i.e., some level of chemical characterization with less details on individual species, but have the advantage of fast acquisition times, providing near real-time data. Figure 1.7 highlights how some of the most important techniques suitable for field applications compare in respect to completeness, chemical resolution, and time/size resolution.

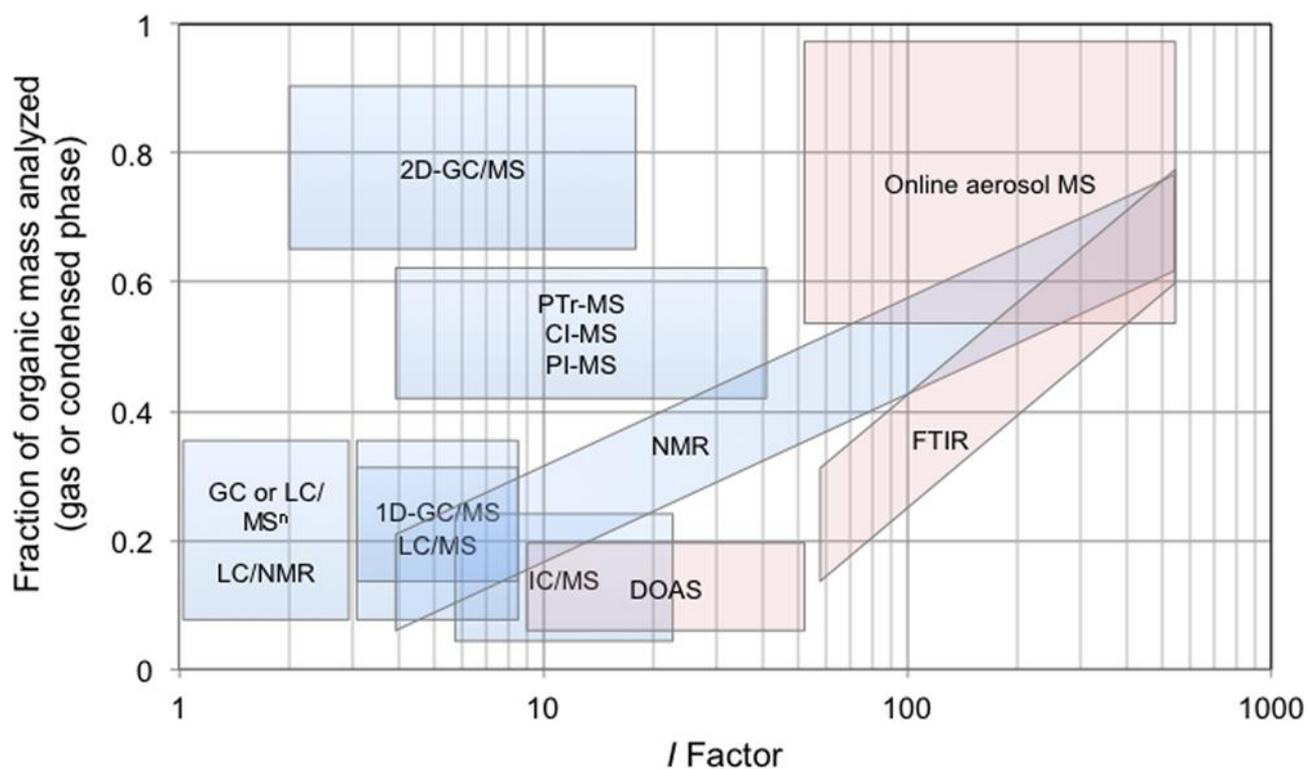


Figure 1.7. Summary of the most abundant analytical techniques used to characterize atmospheric organic compounds as function of their *I* factor, defined as the capability to determine molecular structure of a compound (= number of possible molecules which cannot be resolved by a given analytical techniques from the molecule of interest). A decreasing *I* factor describes the increasing ability of a technique to identify the molecular structure of a compound. The Y axis describes the fraction of the total organic mass of atmospheric samples characterized by a technique. The coupling of two techniques (often involving chromatography) significantly decreases the *I* factor. Techniques frequently coupled to chromatography or suitable to coupling with chromatography are shown in blue, the other in red. (Nozière et al., 2015).

As described above, techniques that provide molecular speciation, represented by GC/MS in the figure, can only do so for a small mass fraction of the OA (of the order of 10%) present in ambient aerosol. Time resolution is typically of many hours although automatic GC/MS systems for semicontinuous measurements, increasing time resolution up to 1 h, are now available (Williams et al., 2006, 2007). Improvements in this type of speciation techniques are highly desirable and are being actively pursued (e.g. Goldstein et al., 2008) but it is very unlikely that in the foreseeable future a single technique will provide full quantitative speciation of OA with a high time resolution.

Spectroscopic techniques, like AMS, FTIR and NMR, can be employed to improve completeness of analysis by exploiting their selectivity to specific chemical classes or functional groups. Mass spectrometric methods, like AMS, benefit of a much higher time and size resolution respect to the other techniques (e.g. DeCarlo et al., 2008) and are suitable for on-line elemental analysis (Aiken et al., 2008). Conversely, FTIR and NMR analysis can be carried out at a reduced time resolution but the resulting spectral data provide a much clearer information on functional group distribution with respect to AMS (e.g. Maria et al., 2003; Decesari et al., 2007).

In conclusion, a perfect field instrument does not exist, and at present a combination of techniques is required for a more complete characterization of OA and in particular of SOA.

1.6.2 OFF-LINE TECHNIQUES

Off-line techniques typically consist in distinct steps: aerosol sampling, laboratory workup and analysis.

1.6.2.1 Aerosol sampling

Sampling is the first step of the characterization of compounds and the choice of sample collection, preparation methods and appropriate analytical techniques can be crucial for their identification (Nozière et al., 2015). Sampling of particulate organic material (organic aerosols) is generally accomplished by collection on filter samplers or, to a lesser extent, with cascade impactors (e.g., MOUDI; DLPI, www.dekati.com) (Barro et al., 2009). The choice of the filter material on which the samples are collected is critical. When the samples have to be analyzed by thermal-optical analysis for total organic, elemental, and total carbon (OC, EC, and TC), quartz-fiber filters are mandatory because they are the only type able to sustain high-temperature treatments. Otherwise, other materials can also be used, for example, polytetrafluoroethylene (Teflon), or aluminum foil in cascade impactors. However, they all give rise to artifacts. In particular, all filter types can result in negative artifacts as the particulate-phase organics collected on the filter may volatilize during sampling. Quartz fiber filters are more prone to positive rather than negative artifacts because of their large adsorption capacity for volatile and semivolatile organic compounds (Turpin et al., 2000; Gelencsér et al., 2004; Mikuska et al., 2009).

Sample preparation

The off-line analysis of OA is performed in laboratory using aerosol samples collected onto filters followed by standard solvent extraction (Cheng and Li, 2004), supercritical fluid extraction (Chiappini et al., 2006) or thermal desorption (Greaves et al., 1985; Veltkamp et al., 1996). A range

of solvents and pre-treatments of the analytes can be used, including chemical derivatization, to increase the range of species analyzed. The specific solvent is often used as an empirical definition for fractions of aerosol organic carbon e.g., the “water-soluble organic carbon” (**WSOC**).

Thermal desorption has gained increasing popularity over the last few years for the measurement of semivolatile, thermally stable organic aerosol components and can be used without any sample preparation when combined with high resolution chromatographic techniques (Hays and Lavrich, 2007).

Solvent extraction or thermal desorption methods allow to extract the majority of particulate organic compounds from the sample, though rarely > 80%, but the real bottleneck in the analysis is the recovery and resolution of the chromatographic techniques. Because of the tremendous molecular complexity, the majority of organic compounds elute as an “unresolved complex mixture” (e.g., Williams et al., 2007).

Semi-preparative ion-exchange chromatography was used to separate WSOC fractions prior to proton NMR analysis (Decesari et al., 2000, 2001). This method allowed the characterization of polycarboxylic acids, including high-molecular weight compounds. The NMR spectra of aerosol polyacids were found to be similar to those characteristic of terrestrial fulvic acids, for example Suwannee River fulvic acid (SRFA, Cappiello et al., 2003). Standards of fulvic acids were often used as surrogates for ambient aerosol in studies of physicochemical properties (Parsons et al., 2004; Topping et al., 2005; Dinar et al., 2006).

1.6.2.3 Off-line molecular speciation methods

There are several atmospheric problems requiring the identification of specific organic compounds. An example is the quantification of the SOA mass resulting from one specific precursor, such as isoprene or α -pinene, at a given site. The approach usually employed consists of monitoring a few compounds that are unique to these processes or sources, called “markers” (Nozière et al., 2015).

The identification of appropriate marker compounds for specific atmospheric processes is a difficult task due to the wide range of complexity and concentrations encountered in smog chamber and atmospheric samples. Important quality criteria for suitable marker compounds are reactivity, stability, and, for condensed-phase compounds, volatility.

The identification and quantification of specific molecular markers for SOA from different precursors are essential for the accurate assessment of their impacts in source apportionment studies. In addition, molecular speciation provides fundamental insights into SOA source processes, that is, the chemical reactions leading to their formation. Furthermore, molecular markers can serve as a “clock” for measuring the OA aging state. A summary of the main classes for molecular markers for POA and

SOA is provided below. I focused on polar compounds, which are the object of this thesis work. Therefore, tracer compounds for POA are presented only for biomass burning, which produces a range of oxidized organic compounds, while POA from fossil fuel combustion, being mainly apolar in nature, are not considered in this short review.

Molecular speciation activities started in the late 1990s for monoterpene SOA, (Glasius et al., 2000; Christoffersen et al., 1998; Yu et al., 1999) and much later for isoprene SOA, that is, after 2004 following the discovery of the 2-methyltetrols in atmospheric aerosol (Claeys et al., 2004). During the past two decades, substantial progress has been made with the structural elucidation of biogenic SOA markers.

Here an update will be given for markers related to isoprene and α -pinene, and information for markers related to other selected biogenic VOCs (“BVOCs”). In recent years, improved mechanistic insights have been obtained about the formation of **isoprene markers** under different experimental (smog chamber) conditions. As explained previously, the 2-methyltetrols, their corresponding sulfate esters, and the C5-alkene triols are generated by the condensed-phase reactions of the C5-epoxydiols produced in the gas-phase from isoprene photooxidation under low-NO_x conditions (Paulot et al., 2009). In polluted areas (high-NO_x conditions), 2-methylglyceric acid and its corresponding sulfate ester are preferentially formed. NO_x-rich atmospheres also lead to the formation of organonitrates, which can subsequently partition to the particle phase and undergo a nucleophilic substitution with water or sulfate (Szmigielski et al., 2010; Darer et al., 2011). Isoprene SOA-related organosulfates identified in ambient fine aerosol include sulfate esters of 3,4-dihydroxybutan-2-one, glycolic acid, 1-hydroxy-3-oxobutane, and hydroxyacetone. As explained in the previous section, their formation, as well as the sulfate ester of 2-methylglyceric acid, was explained by multiphase reactions involving either sulfuric acid or the sulfate radical anion (Schindelka et al., 2013; Galloway et al., 2009; Wang et al., 2013).

Despite the fact that molecular speciation of monoterpene SOA already started in the late 1990s, significant progress has only been made in the past decade with a much more complete molecular speciation of α -pinene SOA and insights into their formation processes. A marker that has received particular attention is 3-methyl-1,2,3-butanetricarboxylic acid, which is now established as a suitable marker for aged α -pinene SOA (Müller et al., 2012). Other novel markers that were structurally characterized include 3-hydroxyglutaric acid, the lactone-containing terpenoic acids, terpenylic acid, terebic acid, 2-hydroxyterpenylic acid, 4-hydroxyterpenylic acid, and diaterpenylic acid acetate (Nozière et al., 2015). Furthermore, high-MW dimers have received attention and have been structurally identified and detected in ambient fine aerosol with the two most prominent ones being diesters with MW 368 and 358 (Yasmeen et al., 2010; Hoffmann et al., 1998; Muller et al., 2008;

Gao et al., 2010; Kristensen et al., 2014) The MW 368 dimer was shown to consist of a pinyl and a hydroxypinonyl monomeric unit, while the MW 358 dimer was found to comprise a pinyl and a diaterpenyl residue (Yasmeen et al., 2010; Gao et al., 2010). Dimers form through ozonolysis in the gas phase the possible involvement of Criegee intermediates (Kristensen et al., 2014). The exact formation mechanism of high-MW dimers warrants further investigation as they are implied in new particle formation.

Organosulfates related to α -pinene detected in ambient fine aerosol include sulfate esters of 2- and 3-hydroxyglutaric acid, hydroxypinonic acid, and isomeric MW 295 nitrooxy organosulfates with a pinane diol skeleton (Surratt et al., 2008). Nitrooxy organosulfates determined in ambient aerosol during intensive field campaigns were shown to form at night-time, in absence of photochemistry (Gomez-Gonzalez et al., 2012) and mediated by NO_3^* radical chemistry. Furthermore, they were also detected in significant concentrations in wintertime in areas impacted by wood burning (Kahnt et al., 2013).

Biomass burning aerosols originate from anthropogenic and natural combustion such as wild fires, agricultural fires, deforestation fires, and residential biomass combustion for cooking and heating. Carbonaceous aerosols from biomass burning are of scientific and public interest because of their occurrence in local, regional, and global environments as well as their impact on human health, air quality, visibility, and climate. Globally, biomass burning is one of the major sources of primary organic aerosols, light absorbing carbon (brown and black carbon), and probably also of SOA (Grieshop et al., 2009). Among biomass burning polar marker compounds, the pyrolysis products of cellulose and hemicelluloses are the most important class of compounds in biomass burning smoke. Cellulose is a macromolecule consisting of several to ten thousand linearly linked D-glucopyranose units, whereas hemicelluloses are smaller macromolecules that contain different monosaccharidic (e.g., mannose and galactose residues) but mainly D-glucopyranose units. Cellulose and hemicelluloses provide a supporting mesh for wood structures and account for 30–40% of woody tissue (Shafizadeh, 1984). The major pyrolysis products of cellulose and hemicelluloses are anhydromonosaccharides, **levoglucosan** (1,6-anhydro- β -D-glucopyranose), galactosan (1,6-anhydro- β -D-galactopyranose), and mannosan (1,6-anhydro- β -D-mannopyranose), and they are widely used as biomass burning marker compounds because they are specific and emitted in considerable amounts (Hornig et al., 1985; Locker et al., 1988; Simoneit et al., 1999).

Another class of polar biomass burning marker compounds is the pyrolysis products of lignin. Lignin is an amorphous biopolymer synthesized by monolignols and accounts for 25–35% of the dry mass of softwood and 18–25% of hardwoods. Its function is to provide strength and rigidity to plant structures (Shafizadeh, 1984; Parham et al., 1984). Its pyrolysis produces mostly substituted phenols

and substituted methoxyphenols with predominantly p-coumaryl alcohol derivatives from grass combustion, pconiferyl alcohol derivatives from softwood combustion, and sinapyl alcohol derivatives from hardwood combustion. This difference may be used as an indicator for the influence of soft or hardwood combustion in ambient aerosols (Hawthorne et al., 1988).

The characterization of individual aerosol markers in highly complex mixtures generally requires chromatographic separation. The two most employed techniques are **GC**, often with derivatization before the separation, and **HPLC**. The selection of a chromatographic column is crucial in the development of a suitable analytical method and must consider the chemical and physical properties of the analytes (volatility, polarity, molecular weight, solubility, etc.). In particular, if the polarities of the stationary phase and of the analyte are similar, their attractive forces are strong and result in a better retention (compound appearing late in the chromatograms). The selectivity and resolution of a column are determined by the intermolecular forces between the stationary phase and the target molecules, including van der Waals, hydrogen bonding, and dipole–dipole interactions (Nozière et al., 2015).

When compounds that are not volatile enough or thermally too labile to pass through the injector and/or the column, derivatization procedures can be applied to the samples before their GC analysis. The procedure consists in reacting the analyte with a derivatization reagent, such as 2,4-dinitrophenylhydrazine, the specific compounds obtained can afterwards be observed by the detector, such as characteristic ions when using mass spectrometric detection (Yu et al., 1998; Edney et al., 2003).

Ion chromatography (IC) offers a simple, reliable, and inexpensive separation and determination for organic ions in complex aerosol mixtures, it is also usually the first choice for the determination of low-MW organic acids in atmospheric aerosols and aqueous (cloud, fog, rain) samples. Ion exchange and ion exclusion are the two possible mechanisms for the IC separation. The former is typically used for polar organic compounds such as low-MW dicarboxylic acids, while the latter is generally applied to less polar organics such as weak acids (Tsai et al., 2008; Fischer et al., 2002; Domingos et al., 2012; Iinuma et al., 2009).

The atmospheric organic compounds identified by IC include water-soluble low-MW organic acids in aerosols, the most common being monocarboxylic (i.e., formic, acetic, pyruvic, and glyoxylic acids), dicarboxylic (i.e., oxalic, succinic, fumaric, malic, tartaric, glutaric, maleic, malonic, α -ketoglutaric, and oxaloacetic acids), and tricarboxylic acids (i.e., citric and cisaconitic acids) (Tsai et al., 2008; Domingos et al., 2012). Some aromatic acids (i.e., phthalic, syringic, 3-hydroxybenzoic, 4-hydroxybenzoic, vanillic, and isovanillic acid) have also been identified in aerosol particles from

smoke samples, and methanesulfonic and methanesulfinic acids both in ambient aerosols and in chamber studies (Facchini et al., 2008; Chen et al., 2012).

UV–vis spectroscopy is not specific and provides mostly bond/functional group identification ($I \geq 100$), its coupling to liquid chromatography greatly improves the level of identification by adding information on retention times and the possibility to compare with reference standards. One of the important applications of HPLC–UV to organic aerosols is the determination of toxic compounds such as polycyclic aromatic hydrocarbons (PAHs) range, but with a poorer sensitivity compared to GC/MS methods (Nozière et al., 2015).

Tandem mass spectrometry (**MS/MS** or MS^n) is widely applied to obtain structural information about organic molecules. The technique is used to produce structural information about a compound by fragmenting its molecular ion inside the mass spectrometer and identifying the resulting product ions. Selected/multiple reaction monitoring is particularly useful to confirm the identity of compounds in atmospheric samples. An example is the detection of carboxylic acids and of nitro-aromatic marker compounds used as biomass burning markers (Kitanovski et al., 2012). This scanning mode is not only highly specific but also highly sensitive. Tandem MS techniques used in combination with LC are very advanced analytical tools for both the detection and the detailed mass spectrometric characterization of organic compounds in complex atmospheric samples (Nozière et al., 2015).

1.6.2.4 Off-line functional group analysis

Functional group analysis using spectroscopic techniques can be used to reduce the complexity of the analysis and improve recovery. The most popular application among the off-line methods is the collection of aerosol on impactors or filters followed by analysis by FTIR spectroscopy to determine the concentration of organic functional groups such as saturated aliphatic (C–C–H), unsaturated aliphatic (C=C–H), aromatic (C=C–H), organosulfur (C–O–S), carbonyl (C=O), organic hydroxyl (COH), etc. (Blando et al., 1998; Havers et al., 1998; Maria et al., 2003; Polidori et al., 2008). The strength of this technique is the ability to measure the total concentrations of certain functional groups, such as amines or organosulfur species, which are difficult to quantify with alternative methods. FTIR spectroscopic analysis was applied during many field campaigns (e.g. Maria et al., 2003; Polidori et al., 2008; Russell et al., 2009). Maria et al. (2003) used aerosol concentrators to obtain sub-1 h time resolution for employ onboard a research aircraft. The OA concentration determined by FTIR spectroscopy showed good agreement with co-located AMS measurements in several studies (Gilardoni et al., 2007; Russell et al., 2009). Sequential solvent rinsing can be used to further separate the organic compounds by polarity (Maria et al., 2003; Polidori et al., 2008). The organic matter to organic carbon (OM/OC) ratio can also be estimated from these measurements

(Gilardoni et al., 2009). NMR techniques were also used in numerous studies (comprising this that I am writing). Both solid and liquid NMR techniques were explored, and the analysis was performed with or without chemical derivatization aimed to increase selectivity to specific functional groups such as carboxylic acids and ketones (Tagliavini et al., 2006, Moretti et al., 2008). Proton NMR spectroscopy was successfully used to characterize biomass burning aerosols in tropical environments (Decesari et al., 2006), and was also proposed as a tool for source attribution of water-soluble organic aerosol including biomass burning, marine and SOA particles (Decesari et al., 2007). A better description of NMR techniques applied to aerosol samples will be carried out in next sections.

1.6.2.5 Nuclear Magnetic Resonance

NMR spectroscopy is a quasi-universal technique for the analysis of organic compounds, and an important technique to support the structural characterization of organic compounds. The general principles of NMR spectroscopy have been described in many text books (Claridge, 2009).

Nuclei with a nuclear spin different from zero, such as ^1H , ^{13}C , and ^{15}N , change orientation when subjected to an external magnetic field and absorbing a radiofrequency. Small deviations, of the order of a few part per millions (ppm), in addition to the “magnetic resonance” at the fundamental nuclei frequency, are induced by the chemical environment of the nucleus, thus providing information on the structure of the molecule. The horizontal scale in ^1H -NMR spectra reports the *chemical shift* (δ), which is the frequency difference of the signals of a defined proton compared to a reference signal:

$$\delta_i = (v_i - v_s) / v_s * 10^6$$

These chemical shifts on typical NMR spectra allow to correlate one nucleus to another and to reconstruct the entire chemical structure. NMR can require procedures to reduce peak overlap, in order to identify molecules in complex mixture containing hundreds of resonances, for example by reducing peak width and narrowing multiplets, the magnetic field can be increased. Alternatively, series of samples from the same experiment can be analyzed by chemometric techniques (e.g., factor analysis, described afterwards) to attempt spectral deconvolution (Wishart, 2008).

Starting from the pioneering studies about OA of Havers et al. (1998) and Suzuki et al., (1998), the technique has gained some interest in the last decade, especially for overcoming specific limitations inherent to the more diffused mass spectroscopy and FTIR methodologies. However, there is still an infrequent use of NMR spectroscopy in atmospheric chemistry where sample loading can be too small to apply ^{13}C and heteronuclear NMR techniques.

NMR has a number of unique advantages. In particular, it is nondestructive, non-biased, and easily quantifiable, requires little or no separation, permits the identification of novel compounds and needs no chemical derivatization. NMR is particularly amenable to compounds that are less tractable to GC-

MS or LC-MS analysis (e.g., sugars, amines, volatile ketones and relatively non-reactive compounds) (Wishart, 2008). The main advantage of NMR spectroscopy over other techniques is that quantitative spectra can be obtained relatively easily, especially with ^1H -NMR spectroscopy, as the line intensity is, in first approximation, directly proportional to the molar concentration of the nucleus of interest. Unfortunately, the most interesting nucleus in organic chemistry, ^{12}C , has a nuclear spin of zero and is therefore NMR-silent. On other hand, the isotope ^{13}C is magnetically active, but because its natural abundance is only 1.1%, the sensitivity of ^{13}C NMR spectroscopy is almost 4 orders of magnitude lower than that of ^1H -NMR. As consequence, the great majority of NMR studies, in the field of atmospheric organic compounds study, was made with proton NMR techniques, and deal with aerosol extracts, cloud, fog, or rainwater, or aqueous solutions of polar VOCs. Suzuki et al. (2001) showed the opportunity to discover new aerosol constituents by proton NMR in strong magnetic fields (≥ 400 MHz), allowing the resolution of hundreds of resonances in atmospheric samples (Suzuki et al., 1998).

Of course, a key disadvantage of NMR spectroscopy is that it is a relatively insensitive technique, with a lower limit of detection of about 1–5 μM and a requirement for relatively large sample sizes (500 μL). However, with the recent introduction of higher field magnets (900 MHz), cryogenically cooled probes (that increase signal by a factor of 3) and small-volume microprobes (60 μL), some of these issues of sensitivity are beginning to become less of a concern (Wishart, 2008).

A common assumption in atmospheric science is that the sensitivity of NMR spectroscopy is too low for a widespread application, requiring a significant amount of aerosol mass, as it is for ^1H -NMR analysis of ambient aerosols. ^1H -NMR spectra of aerosol water-extracts containing even less than 100 μg of carbon (e.g. 30-50 μgC for sample loadings reached even in remote areas) can be easily recorded at 600 MHz. In ^1H -NMR analysis the typical detection limits for individual compound are in the sub ng m^{-3} levels (for time integrated samplings of 12–24 h).

Finally, if a sufficient amount of sample is provided (typically 1 mg of carbon), two-dimensional (2D) NMR techniques can also be applied, such as correlation spectroscopy or heteronuclear single quantum coherence or even heteronuclear multiple bond correlation, which establish the connectivity between chemically distinct H or C atoms in a molecule, and allow the reconstruction of the chemical structure. Thus, 2D NMR has the potential to individual organic compounds even in complex mixtures.

The major limitations of NMR, compared to other off-line techniques, are the complexity of the spectra (in particular for compounds with vast J coupling), the limitation in automaticity for the analysis of huge amount of samples and difficulty to acquire in the second dimension with an adequate sensitivity. In addition, the lack of ^1H -NMR spectra libraries for atmospheric markers identification,

poses a limit to applications of this technique in atmospheric organic compound studies (Nozière et al., 2015).

Taking into account the inherent potential and drawbacks of NMR spectroscopy for environmental sample analysis, increasing efforts have been dedicated in the last decade to formulate applications or atmospheric aerosol analysis, and specifically according different strategies: for the analysis of specific tracers, similarly to GC/MS or for the analysis of functional groups and recognizing spectral fingerprints and their use in factor analysis. Some examples of successful molecular identification in ambient aerosols using NMR methods can be found in the recent literature. Facchini et al. (2008) and Graham et al. (2003) identified several low-molecular-weight amines, such as mono, di, and trimethylamines, diethylamine, methanesulfonate, and hydroxyl-methane-sulfonate, levoglucosan, as well as some major C₆–C₁₀ compounds, formate, pinonic and pinic acid, and levoglucosan. Twelve low molecular weight compounds in WSOC were identified by Suzuki et al. (2001) in a urban environment. MSA and HMSA were detected as major organosulfur compounds. Mannitol was also determined in the coarse particles as a major tracer of biological particles (fungal spores).

Other studies focus mainly on functional group analysis. The rationale for functional group analysis of atmospheric WSOC is based on the approach followed for over two decades for the analysis of terrestrial and aquatic humic substances. Atmospheric WSOC shows ¹H-NMR spectra with five main bands corresponding to broad categories of functional groups, as shown in typical ¹H-NMR spectrum of an atmospheric aerosol water extract reported in Figure 1.8. The most evident feature of the spectrum is the presence of very broad, poorly resolved peaks, deriving from the overlap of a very large number of individual minor contributions. Peaks attributable to individual compounds (amines, MSA, etc.) contribute to a lesser extent to the total integrated area. The broad signals apparently cannot be resolved even by most powerful NMR instruments (Suzuki et al., 1998), leading to the same constraints encountered in GC/MS analysis: only a small number of organic compounds occurring in relatively high concentrations can be identified, the rest appearing as an unresolved mixture of minor constituents.

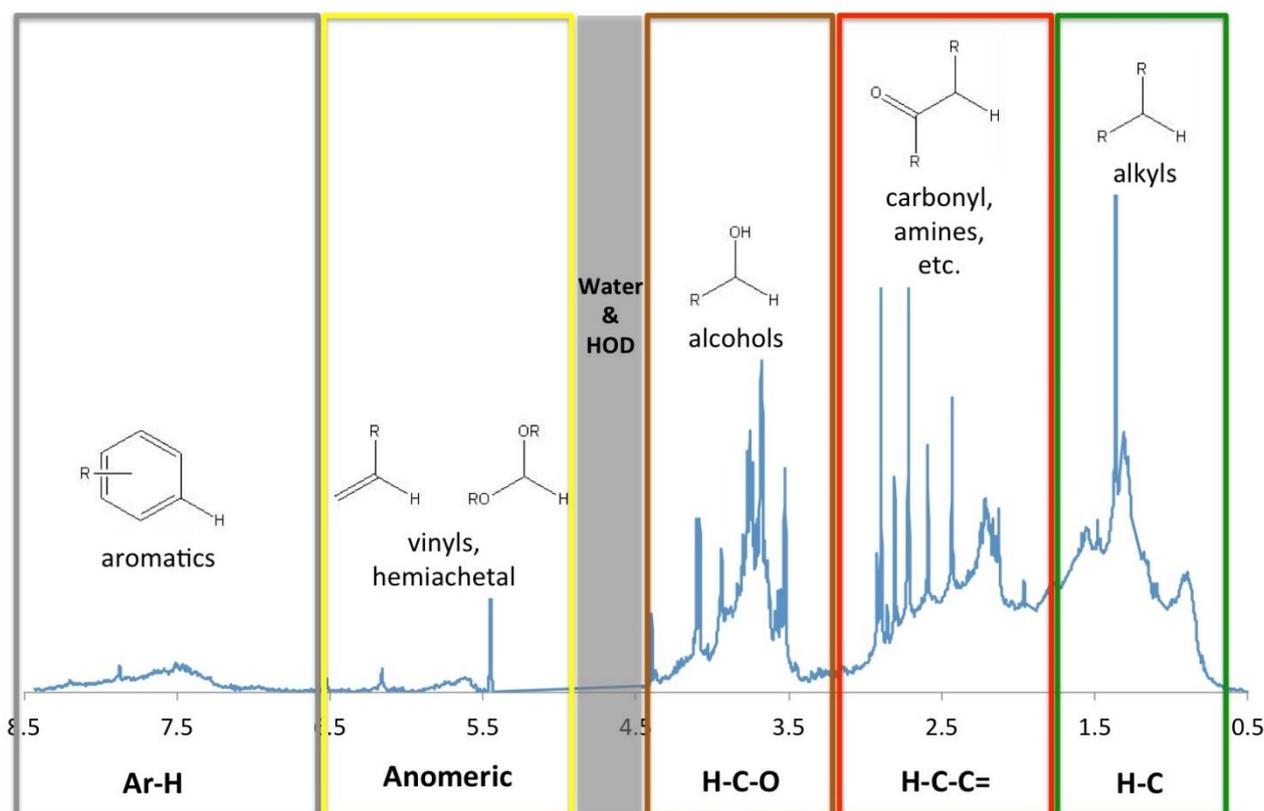


Figure 1.8. $^1\text{H-NMR}$ spectrum (600MHz Varian) of a winter sample with highlighted regions of the spectrum that identify and allow the quantification of distinct functional groups. The X axis shows the chemical shift in ppm.

On the other hand, contrary to the GC/MS, NMR spectroscopy provides an important insight into the average chemical structure of the unresolved portion, since the complex mixture produce spectral bands, which can be attributed to a few categories of functional groups. The most representative categories of functional groups in $^1\text{H-NMR}$ spectra can be listed as follows:

- Ar-H (6.5 – 8.5 ppm): aromatic protons;
- Anomeric and/or vinyl protons (O-CH-O) (5 – 6 ppm): signals singlets, sometimes so low as to be confused with the background noise, due to the vinyl protons, of not completely oxidized isoprene and terpenes derivatives (Claeys et al. 2004), and anomeric protons of sugars derivatives (levoglucosan, glucuronic acid, etc.) in the furaneidic form (O-CH-O). The most studied compound of this family is levoglucosan, a marker of cellulose combustion that can be easily identified, isolated and integrated by NMR, thanks to the peak of its anomeric proton ($\delta = 5.45$ ppm) (Schkolnik and Rudich, 2005).

- H-C-O (3.2 – 4.4 ppm): protons bound to oxygenated aliphatic carbon atoms (hydroxyl and alkoxy groups): aliphatic alcohols, ethers, and esters;
- H-C-C= (1.8 – 3.2 ppm): protons bound to aliphatic carbon atoms adjacent to unsaturated groups like alkenes (allylic protons), carbonyl or imino groups (heteroallylic protons) or aromatic rings (benzylic protons);
- H-C (0.9 – 1.8 ppm): unfunctionalized aliphatic protons.

The abundance of these structural units expressed as organic hydrogen content is measured by the integral of the above bands and calibrated on the integral of the signal of the internal standard. Therefore, this method provides a chemical characterization of the unresolved fraction of WSOC on a quantitative base with no need of specific standards. (Paglione, 2013; Graham et al., 2002; Cavalli et al., 2006; Balasubramanian et al., 2003). Similarly, NMR functional group analysis was applied to the investigation of the composition of SOA produced in laboratory experiments (Finessi et al., 2012).

1.6.3 ON-LINE TECHNIQUES

The analytical techniques described above are suitable for time-integrated samples (using filters, impactors, etc.) analysed off line (i.e., in laboratory). This implies the risk of positive and negative artifacts due to adsorption, evaporation, and chemical reactions during sampling, storing or during analysis in laboratory (e.g., Turpin et al., 2000; Schauer et al., 2003; Subramanian et al., 2004; Dzepina et al., 2007). Off-line techniques are particularly problematic when used on mobile observatories (e.g. ships and research aircrafts). Therefore, on-line techniques, which provide real-time measurements, have revolutionized the chemical analysis of aerosols. The two main types of on-line techniques currently in use are PILS-WSOC and AMS with a growing interest in TD-PTR-MS ones. Particle-into-liquid-samplers (PILS) collect particles into water for subsequent analysis (e.g., IC) (Weber et al., 2001; Sullivan et al., 2004; Sorooshian et al., 2006). A liquid TOC analyzer for continuous measurement of WSOC with a time resolution of a few minutes was coupled to a PILS instrument and deployed in several aircraft campaigns (e.g., Sorooshian et al., 2006, 2007; Peltier et al., 2007; Weber et al., 2007).

1.6.3.1 Aerosol Mass Spectrometer

The Aerodyne **aerosol mass spectrometer (AMS)** was developed for the on-line measurement of organic and inorganic components of aerosols. The principle of the instrument is to draw particles into a vacuum chamber (Liu et al., 1995) and impact them on a tungsten surface (molybdenum in early versions) heated to 600 °C prior to being analyzed by 70 eV EI-MS. Most of the gas material is removed by differential pumping. As explained above, while the 70 eV EI energy implies extensive

molecular fragmentation, it ensures the ionization of nearly all molecules, organic and inorganic, and the compatibility of the data with existing mass spectral databases. The mass spectrum for the aerosol sample is derived by subtracting an internal background obtained from periodically blocking the particle beam. Yet as it contains contributions from both the non-refractory particles (those evaporating on the impaction plate) and the air that was not skimmed off, these contributions are removed by using a “fragmentation table” approach, where marker peaks in the mass spectra are used to quantify these components (Allan et al., 2004). Because of the two-stage desorption and ionization process, the AMS mass spectral data are a quantitative, linear combination of the contributions of the various particle components. AMS gain quantitative information on the overall organic composition and contributions from various sources. One of the simplest forms of analysis is the determination of the fractional contribution of key peaks to the total organic mass concentration. Because m/z 44 mainly corresponds to CO_2^+ from the thermal decomposition of dicarboxylic acids and multifunctional compounds, the fractional contribution of m/z 44 can be taken as a proxy for the oxygen content of the organic fraction (Aiken et al., 2008; Allan et al., 2004). When this is compared to the fractional contribution from m/z 43 (C_3H_7^+ from aliphatic chains and C_2OH_3^+ from alcohols, monocarboxylic acids, and carbonyls), correlations with the general level of atmospheric processing of the organic material can be seen. Similarly, the fractional contribution of m/z 60 (associated with anhydrosugars such as levoglucosan, mannosan, and galactosan) can be used in conjunction with m/z 44 to monitor the evolution of biomass burning aerosols (Cubison et al., 2011; Lack et al., 2013).

1.6.3.2 Aerosol Chemical Speciation Monitor

While the research grade AMS provides valuable information about trends in speciated aerosol mass concentrations for applications that require fast time resolution (1 min or less), it is not well suited for routine air quality monitoring applications because it is expensive to own and requires dedicated scientists to operate and analyze its multidimensional data. **Aerosol Chemical Speciation Monitor (ACSM)**, is an instrument, developed since 2009 by Aerodyne Res., that has many of the capabilities of the AMS but is better suited for monitoring applications. The ACSM is designed and built around the same sampling and detection technology as the state-of-the art research grade AMS systems, but it has lower size, weight, cost, and power requirements than the AMS and is specifically designed to be a stand-alone monitor that is more easily transportable and can operate with minimal user intervention. In the Figure 1.9 below a schematic overview of the instrument is provided.

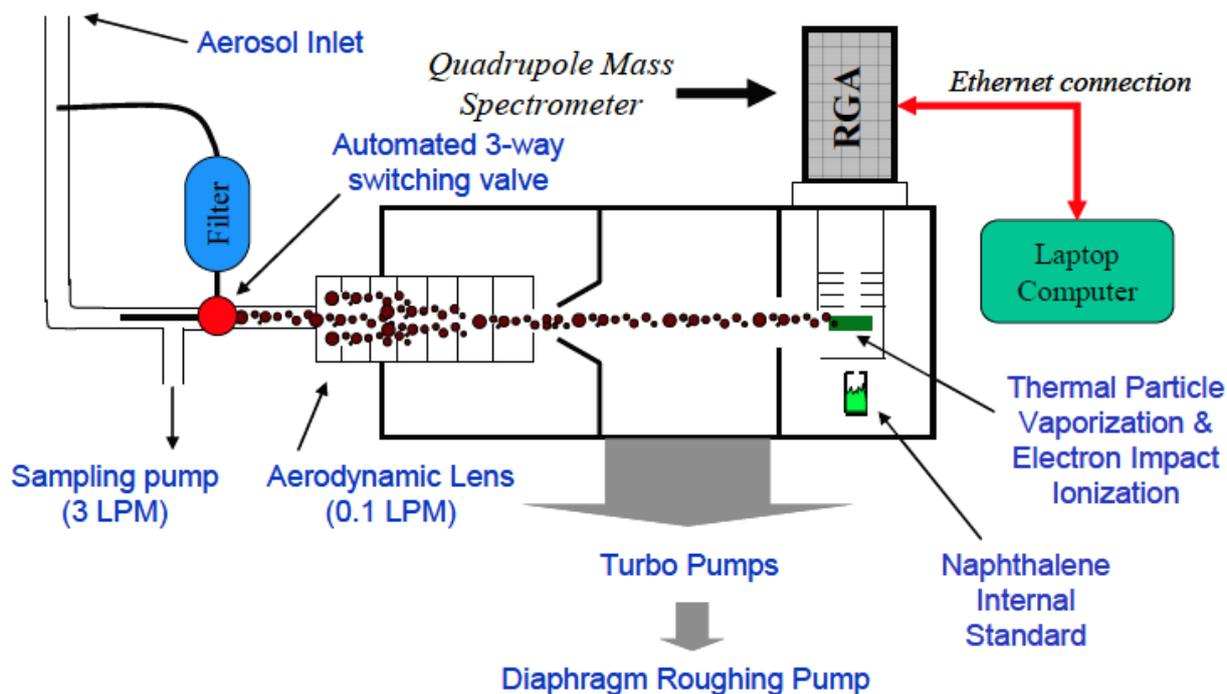


Figure 1.9. Aerosol Chemical Speciation Monitor (ACSM) developed by Aerodyne Res. (http://www.aerodyne.com/sites/default/files/ACSM%20Aerosol%20Chemical%20Speciation%20Monitor%20product%20sheet_0.pdf).

Much of the reduced complexity is due to the fact that the ACSM does not measure size distributions; only aerosol mass spectra are reported. The quadrupole-ACSM measures mass concentrations of non-refractory submicron aerosol components (i.e., organic matter, nitrate, sulfate, ammonium and chloride). It uses lower cost components that reduce its sensitivity and time resolution compared to the AMS, the ACSM has sufficient sensitivity to operate as a monitoring instrument providing chemically speciated mass loadings and aerosol mass spectra at data rates up to 30 min for typical urban aerosol loadings (several $\mu\text{g}/\text{m}^3$) (Ng et al. 2011).

Several papers on aerosol biomass burning, SOAs, seasonality in submicron aerosol and aerosol source apportionment have been published in last years (Bressi et al., 2016; Reyes-Villegas et al., 2016; Budisulistiorini et al., 2015). Shown in Figure 1.10 are the time series of organics, sulfate, nitrate, ammonium, and chloride as well as the average mass fraction of each species measured by the ACSM in the study reported by Ng et al. (2011).

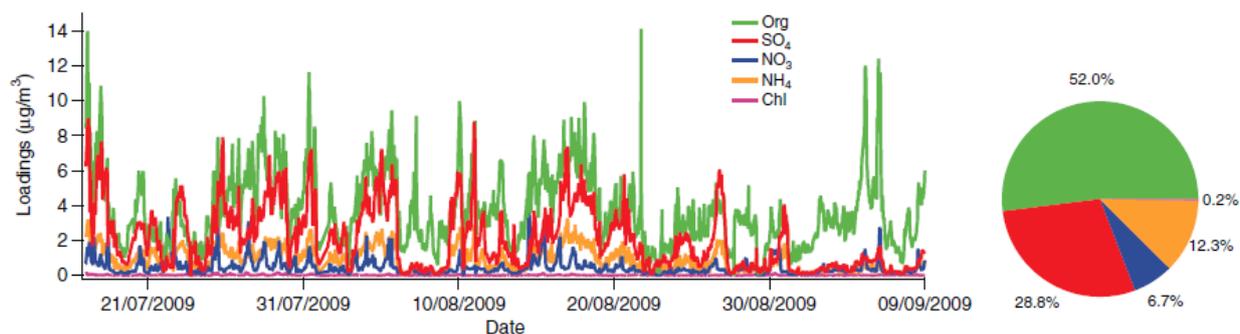


Figure 1.10. Time trends of non-refractory submicron aerosol species measured with the ACSM during the Queens, NY study. The average total loading is $7.2 \mu\text{g}/\text{m}^3$. The time resolution of these measurements is 30 min. The ACSM operated unattended during this study. (Ng et al., 2011).

1.6.4 ORGANIC AEROSOL SOURCE APPORTIONMENT

1.6.4.1 Overview on source apportionment models of atmospheric aerosol

Source apportionment (SA) methods resolve the composition of particulate matter into components related to emission sources, e.g. aerosol based on ambient data registered at monitoring sites (Bruinen et al., 2006; Hopke and Song, 1997; Watson et al., 2002). Viana et al. (2008) provides a review with a clear distinction between three main SA approaches:

(a) *Methods based on the evaluation of monitoring data*
 Basic numerical data treatment is used to identify sources. Examples are: (1) correlation of wind direction with levels of measured components to identify source locations (Henry et al., 2002); (2) the correlation of gaseous pollutants with particulate matter components to identify association with sources; (3) subtraction of levels measured at regional background from those obtained at urban background and/or roadside levels to identify the contributions from the regional background, the city background and the monitored street (Lenschow et al., 2001), or (4) quantification of biogenic aerosol contributions (e.g., isoprene SOA, African dust) by subtracting particulate matter levels at regional background sites from those at urban background locations for specific days (Escudero et al., 2007). These methods are simple, therefore they are mathematical artifact low impacts due to data treatment.

(b) *Methods based on emission inventories and/or dispersion models*
 They simulate pollutant emission, formation, transport and deposition (Eldering and Cass, 1996; Visser et al., 2001). These models require detailed emission inventories that are not so frequent and available, and they are limited by the accuracy of emission inventories, especially when natural emissions are important. These methods have the advantages that they may be used in scenario studies to evaluate the impact of emission abatement strategies on the anthropogenic contribution to ambient

aerosol

concentrations.

(c) *Methods based on the statistical evaluation of chemical data acquired at receptor sites (receptor models)*

Receptor modeling are based on mass and species conservation that can be assumed and a mass balance analysis can be used to identify and apportion sources of generic pollutants and airborne aerosol more specific in the atmosphere (Hopke et al., 2006). Here below in Figure 1.11 an overview of the wide range of statistical models and modeling approaches that are currently available in the literature. One of the main difference between models is the degree of knowledge required about the sources before the application of receptor models.

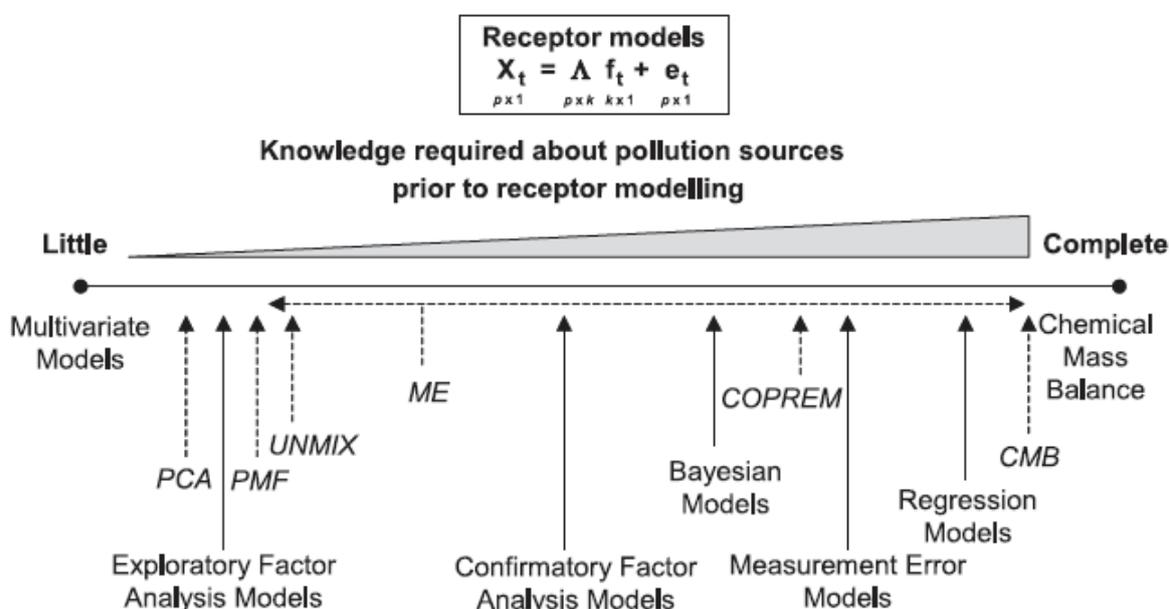


Figure 1.11. Approaches for estimating pollution source contributions using receptor models (modified from Schauer et al., 2006). Specific models are shown in italics and with dotted arrows (Viana et al., 2008).

Receptor models use multivariate analysis (Principal Component/Factor analysis) to estimate sources by a mixture of chemicals measured at the receptor. They require low computational intensity and are independent from emission inventories and meteorological data. These are commonly used tools, because software to perform this type of analysis is widely available and detailed prior knowledge of the sources and source profiles are not required. The choice of the model dimension and the search for non-negative solutions by axis rotations can be based entirely on mathematical criteria. It is a common problem that the resulting components or factors may represent mixtures of emission sources, as opposed to clearly independent source profiles. Source signatures that change with time

are a limitation for this and other types of receptor models. Moreover, since they resolve a mass balance equation are not appropriate for reactive species and perform better in areas relatively close to the sources. For that reason are suitable for urban and regional scales. The type of receptor model to be used depends on the knowledge available about the source profiles (Paglione 2013). When the sources are well known a chemical mass balance approach is preferred whereas pure factor analysis is the choice when no information about the sources is available. Hybrid models can combine both types of approaches (Wählín, 2003; Lanz et al., 2007).

Viana et al. (2008) and Fragkou et al. (2010) indicate in their reviews that the most common receptor models in Europe are Chemical Mass Balance (CMB), PCA (and modifications), and Positive Matrix Factorization (PMF) (Paatero and Tapper, 1994). The receptor model outputs reliability depends on appropriate data collection, in terms of data capture and kind of chemical species, and for PMF, proper expression of uncertainty in the input data. In addition, determining the number of relevant sources and establishing the correspondence between factors and sources still appear as critical steps. Moreover, knowledge is insufficient about the comparability between the output of different models or between different implementations of a model (Paglione 2013).

In order to reduce the influence of expert subjectivity to a minimum, perform intercomparison exercises and compiling quality assurance protocols should be done, achieving improving comparability and reliability of receptor models (Viana et al., 2006; Larsen et al., 2008; Laupisa et al., 2009; Favez et al., 2010). Further improvements in the performance of Receptor Models are expected from the application of advanced tools, which make it possible to combine chemical data with other kind of information (e.g., meteorological data, other chemical methods).

Finally, receptor models have also good prospects in the study of the impact of aerosol on human health. Combining source identification with epidemiological and toxicological data is a promising approach to evaluate air pollution mitigation measures (Belis and Karagulian, 2011).

1.6.4.2 Factor analysis of OA chemical datasets

Principal analysis components (PCA), non-negative methods and a set of multivariate statistical techniques belong all to factor analysis, and they are often used for the characterization of spectroscopic datasets and concentrations matrixes.

Regarding factor analysis, all its different methods are based on the same bilinear model by the equation (1):

$$x_{ij} = \sum_{k=1}^P g_{ik} f_{kj} + e_{ij}$$

(1)

where x_{ij} refers to a particular experimental measurement of concentration species j (one of the analytes or, in this case one point of the mass or NMR spectrum) in one particular sample i . Individual experimental measurements are decomposed into the sum of p contributions or sources, each one of which is described by the product of two elements, one (f_{kj}) defining the relative amount of the considered variable j in the source composition (loading of this variable on the source) and another (g_{ik}) defining the relative contribution of this source in that sample i (score of the source on this sample). The sum is extended to $k=1, \dots, p$ sources, leaving the measurement unexplained residual stored in e_{ij} (Paglione, 2013).

The same model can be described in a compact way by the use of matrix algebra notation in the equation (2):

$$X = G \cdot F + E$$

(2)

X is the data matrix of measurements decomposed into the product of two factor matrices, the loadings matrix (F) defining the chemical composition of the sources, and the score matrix (G) related to the contributions or distribution of these between samples. The noise matrix E contains the experimental error as well as unmodelled variance sources not included in the p components (Paglione, 2013).

In the last years, several publications focused on OA speciation reported data using filter samples (Shrivastava et al., 2007; Jaeckels et al., 2007; Dutton et al., 2010;) collected at low time resolution (typically 24 or 12h). In particular, NMR spectroscopic datasets for atmospheric compositions can be processed for source apportionment of organic aerosols into biogenic, anthropogenic, POA and SOA contributors. Paglione (2013) reported the first attempt of extensive application of factor analysis methods for direct deconvolution of aerosol NMR spectra with a receptor modeling approach and subsequent source apportionment of organic aerosol.

1.6.4.3 NMR, AMS and ACSM PMF

Beyond bulk properties, it is also desirable to quantify the contributions of different sources to the organic aerosol mass. One of the first methods for this application used the fragment ion at m/z 57 ($C_4H_9^+$ from alkanes) and at m/z 44 as the basis for deriving estimates for “hydrocarbon-like” and “oxygenated” organic aerosol, respectively (HOA and OOA) (Zhang et al., 2005). These data were found to correlate well with traffic emissions and secondary sources. A modification of this technique known as multicomponent analysis allows the identification of a second component of OOA through the analysis of residuals. These two types of OOA have been linked to SOA in various stages of atmospheric processing and with different volatilities (Jimenez et al., 2009).

Numerous and consistent results on multivariate models in organic source apportionment have been obtained on OA AMS datasets. Few chemical classes have been obtained by the separation of OA components: hydrocarbon-like OA (HOA) linked to primary emissions (POA), oxygenated OA (OOA) the most processed OA and associated with secondary fraction (SOA), and sometimes other components such as biomass burning OA (BBOA) connected to biomass combustion sources and cooking OA (COA), related to cooking emissions (Zhang et al., 2011; Ulbrich et al., 2009). The same speciation can be used for ACSM factor analysis, that has many of the capabilities of the AMS but is better suited for monitoring applications (Ng et al., 2011).

A more general approach was developed with the use of PMF (Veres et al., 2008) a technique imported from source apportionment methods. Its principle is to identify a number of model contributions, or “factors”, to the overall mass spectrum and to decompose the latter in (weighted) linear combinations of these factors by inverting the corresponding matrix. The model factors derived are comparable to separate characterizations of known sources such as biomass burning and cooking (Nowak et al., 2007). While this approach is a powerful tool in the analysis of the spectra, some cases may be difficult to resolve when a significant number of mass spectral features are in common between factors, such as cooking and exhaust particles or when using a low-resolution mass spectrometer. (Nozière et al., 2015).

A sparse literature exists on NMR factor analysis of atmospheric datasets. Paglione et al. (2014) dealt with PMF-AMS and with NMR factor analysis for WSOC samples at a European rural site to quantify the contribution of HULIS to OA. Chalbot et al. (2016) discussed the NMR functional group distribution along with the $^{13}C/^{12}C$ isotopic ratios of water-soluble organic carbon (WSOC) at urban locations. In general, researches are still limited on this topic, due the NMR analysis costs, availability of the technique, and the need of expert researchers for performing PMF on aerosol spectral datasets.

1.7 GENERAL OBJECTIVES

This PhD thesis is dedicated to the chemical characterization of organic aerosol particles using spectroscopic techniques - NMR and mass spectrometric - during field campaigns and laboratory experiments. The experimental activities will be presented in three distinct research themes:

1. The first one concerns the characterization of OA samples by NMR spectroscopy in the Po Valley during a series of intensive field campaigns organized in the frame of the projects PEGASOS and SUPERSITO. The Po Valley, in the North of Italy, is one of the most polluted region in Europe as described in various air quality reports (i.e. http://ec.europa.eu/environment/archives/cafe/pdf/ia_report_en050921_final.pdf), due to the concurrent high density of anthropogenic sources and its orographic and meteorological characteristics particularly disadvantageous for pollutant dispersion. It claims to a loss of life expectancy of 3 years for Po Valley citizens due to the exposure of PM_{2.5}. During the Po Valley experiments, PM₁ aerosol samples were collected at urban and rural stations. Additional samples were collected at a remote site in the high Apennines. I performed the NMR analysis of all WSOC samples (for 4 campaigns), taking care of organic markers and functional groups analysis. Colleagues at CNR-ISAC assisted me in the NMR factor analysis. The elucidation of PM₁ sources was achieved through the analysis of specific markers (e. g. levoglucosan for biomass burning), the functional group distribution (e. g., the aromatics fraction) and the comparison of spectral profiles with existing libraries of NMR spectra characteristic of specific sources.
2. Another research line concerns laboratory experiments of SOA formation performed at the Boston College (<http://www.bc.edu/>). SOA were generated in a Potential Aerosol Mass (PAM) oxidation flow reactor, to simulate prolonged photochemical ageing, using α -pinene, naphthalene and isoprene as precursors. SOA samples were analyzed offline by ¹H-NMR spectroscopy and HPLC determination of humic-like substances (HULIS). The results were compared with previous Aerodyne aerosol mass spectrometer (AMS) measurements. The NMR spectral characteristics were compared with those of environmental samples from the Po Valley. The study was useful to clarify some SOA processes and products, showing that the composition of aged biogenic (monoterpene) SOA particles resembles closely that of ambient aerosols.
3. The last research focused on OA on-line measurements using ACSM during two field campaigns in the central Mediterranean region: AIR-SEA Lab (<http://www.isac.cnr.it/airsealab/?q=node/4>) and Dual Use Vespucci campaigns

(<http://www.isac.cnr.it/en/content/isac-research-amerigo-vespucci-vessel>). The latter involved ACSM and other atmospheric measurements on board of Amerigo Vespucci vessel, the most famous Italian Navy ship. The two campaigns involved extensive aerosol measurements and source apportionment studies at coastal stations as well as during a research cruise. New data on aerosol sources and composition were obtained for a major climate hotspot, the Mediterranean basin. In addition, the measurements performed at the harbors provided original information on the nature and contributions of pollution sources (harbor activities, ship emissions, vehicle traffics and coal power plant emissions). The research was useful to elucidate aerosol source apportionment in the Mediterranean basin, through the regional background processed aerosol, biogenic and anthropogenic sources.

During my PhD, I recorded more than 500 H-NMR spectra. I followed ACMS measurements in 4 different projects. Finally, I took part to an interlaboratory comparison of analytical methods for quantification of anhydrosugars in atmospheric aerosol leaded by the University of Ferrara. Sampling sites description, analytical protocols and research discussions will be reported in the following sections.

2 EXPERIMENTAL, RESULTS AND DISCUSSION

2.1 PART I

CHARACTERIZATION AND SOURCE APPORTIONMENT OF WATER SOLUBLE ORGANIC CARBON IN FINE PARTICULATE MATTER SAMPLES DURING PEGASOS AND SUPERSITO CAMPAIGNS

2.1.1 OVERVIEW

The chemical composition of submicron aerosol particles in the Po Valley, Italy, was investigated during a series of intensive field campaigns held in stations of Region Emilia-Romagna between 2012 and 2014 in the frame of the projects PEGASOS and SUPERSITO. Specifically, PEGASOS (*Pan-European Gas-AeroSol-climate interaction Study*) is an EU FP7 integrated project on atmospheric chemistry – climate interactions (<http://pegasos.iceht.forth.gr/>). PEGASOS conducted a fully integrated analysis of changing emissions and deposition, their link to tropospheric chemical reactions and interactions with climate, and emerging feedbacks between chemistry-climate and surface processes. PEGASOS targeted both local and regional scales, taking into account chemistry and climate feedbacks on the global scale. Three major field campaigns were conducted in Europe, employing both mobile and stationary observatories. The second of such experiments was held in the Po Valley, Italy, in summer 2012 and focused on the production of ozone and secondary aerosols in the “regional pollution”, i.e., the build-up of pollution in rural areas downwind to multiple, diffuse pollution sources. Results of observations from measurements performed using an instrumented van and using a research dirigible can be found in Rosati et al.(2016) and Wolf et al. (2015).

Aerosol samples have been collected on quartz filters by aerosol samplers from the 12th of June 2012 to the 9th of July 2012. One night-time and one daytime sample were collected every day: from 21:00 to 09:00 LT and from 09:00 to 21:00 LT respectively. However, nocturnal sampling actually included several hours of light: from dawn (which in this period of the year occurs at approximately 5:30 am) to 9 am. First results of chemical analysis of PM samples collected during the campaign following the above sampling schedule are presented in the paper by Sandrini et al (2016).

I took part of the PEGASOS project for the analysis of PM1 samples collected during the summer campaign in 2012, and in particular, of the ¹H-NMR and TOC characterization of samples from

Bologna, San Pietro Capofiume and Monte Cimone. Other measurements (ion chromatography, aerosol mass spectrometry, LC/MS) were carried out by researchers of CNR-ISAC and by personnel from other PEGASOS partners belonging to foreign institutions.

In parallel and in synergy with PEGASOS, the project SUPERSITO, funded by Region Emilia-Romagna, was another attempt of deep investigation of the sources and composition of PM in the Po Valley (https://www.arpae.it/dettaglio_generale.asp?id=2121&idlivello=1471). SUPERSITO focused on the chemical, physical and toxicological characteristics of PM and on aerosol health effects. The project implemented two measurement programs: a) a monitoring activity with sampling of PM on a daily basis from 2011 to 2014, and b) a series of intensive observation periods (IOPs) in which a more sophisticated set of aerosol measurements, including high-time resolution aerosol mass spectrometric measurements, were implemented. The routine measurement program was set up at five stations in Emilia-Romagna, while the IOPs were carried out at three stations: a remote site (Mt. Cimone), a rural site in the central part of the Region (S. Pietro Capofiume) and at the main site in Bologna (Figure 2.1). Results emerging from the SUPERSITO project can be found in Rinaldi et al. (2016), Rinaldi et al. (2015), Gilardoni et al. (2015), Pietrogrande et al. (2014).

In the frame of the SUPERSITO project, I took care of the sampling activities in Bologna site and one in San Pietro Capofiume: installation of the aerosol samplers, filter collection and storage. I followed entirely the laboratory workup: from filters water extraction, to TOC and ¹H-NMR analyses, and data elaboration including identification of organic markers and organic functional groups characterization. Finally, I carried out a complete statistical analysis of all results incorporating chemical data from parallel aerosol measurements and analyses (GC/MS data provided by the University of Ferrara on a parallel set of samples from Bologna and S. Pietro Capofiume), as well as ¹H-NMR factor analysis data elaborated by colleagues at CNR-ISAC.

2.1.2 EXPERIMENTAL

2.1.2.1 Sampling sites for organic aerosol analysis

Aerosol sampling was performed during the PEGASOS and SUPERSITO field campaigns in the Po Valley (Italy) at the urban site of **Bologna** (BO - 44° 29' N, 11° 20' E, 54 m a.s.l.) and at the rural site of **San Pietro Capofiume** (SPC - 44°39' N, 11° 37' E, 11 m a.s.l.), 35 km northeast from the city of Bologna. Both sites are located in the eastern part of the Po Valley (Figure 2.1). Bologna is a city of 400.000 inhabitants, the most populous in the southern Po Valley, with a surrounding area

characterized by widespread agricultural and industrial activities and by the presence of several high-traffic roads. Sampling in Bologna was performed in the northern outskirts of the city, on the roof of the Institute of Atmospheric Sciences and Climate of the National Research Council, at about 20 m above the ground. San Pietro Capofiume is a rural site on a flat, agricultural land, and can be considered a good receptor site for regional-scale air pollution in the Po Valley. The comparison between an urban and a rural site provides information on the impact of traffic and other urban sources on the regional background, the differences in secondary aerosol formation resulting from different meteorological conditions, and about the regional and local variability of secondary aerosol formation processes. In addition, the sampling schedule, differentiating between day and night conditions, allowed to investigate the accumulation of aerosol constituents in a stratified atmosphere (more frequent at night) compared to under more turbulent conditions (more frequent in daytime, especially in summer).

A third sampling site hosting measurements during the 2012 PEGASOS campaign was **Mt. Cimone** (44°12' N, 10°42' E, 2165 m asl). Mt. Cimone is the highest peak of the Northern Apennines at the border of two different climatic regions: the continental Europe northwards and the Mediterranean Basin southwards (http://www.isac.cnr.it/cimone/site_location). The station is representative of the free troposphere of the south-central Europe (Rinaldi et al., 2015; Marenco et al., 2006; Landi et al., 2016). The comparison with the observations performed at the low-level sites in Emilia-Romagna provides information on contribution of the transport of aerosols from the western Mediterranean basin into the Po Valley.

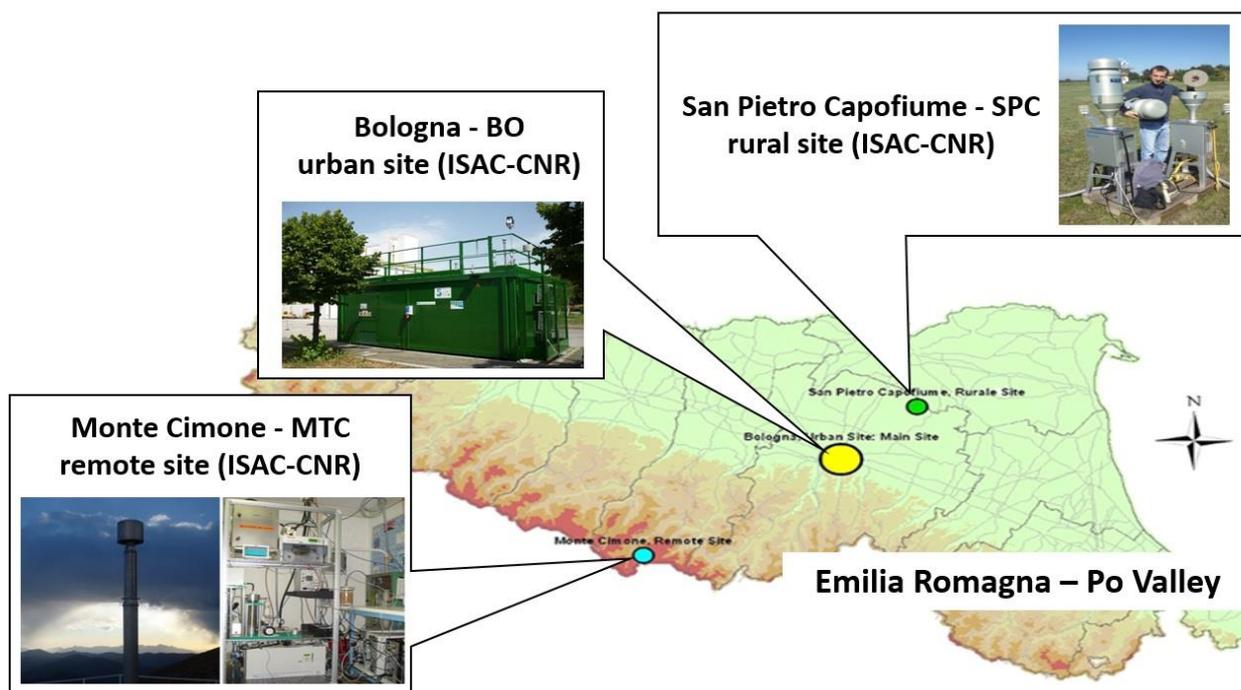


Figure 2.1. Location of the sampling sites. Site symbols: Bologna (BO), the urban site, San Pietro Copofiume (SPC), the rural site, and Monte Cimone (MTC), the remote site.

2.1.2.2 Aerosol sampling

During the PEGASOS and SUPERSITO projects, aerosol samples for off-line chemical analysis were collected on quartz-fiber filters. The filters were washed with Milli-Q water and fired for 1h at 800 °C before sampling in order to reduce their blank values. Aerosol samplers were medium-to-high flow rate types. Specifically, a dichotomous sampler (Universal Air Sampler, model 310, MSP Corporation) operating at a constant nominal flow of 300 l/min was employed in Bologna and at Mt-Cimone to collect fine (PM₁) and coarse (PM₁₋₁₀) particles. The PM₁ samples were collected on 9 cm quartz-fiber filters (Whatman) at both stations for subsequent chemical analysis. A high-volume sampler (Tecora Echo Hivol – equipped with Digital PM₁) operating at a constant nominal flow of 500 l/min was instead employed at the rural site (S. Pietro Capofiume) to collect PM₁ on 15 cm quartz-fiber filters (Whatman).

Typically, two filters per day were collected during the SUPERSITO campaigns: a “daytime” (D) PM₁ sample between 9:00 and 18:00 (local time, UTC+2) followed by an “evening/night-time” (N) sample collected from 18:00 to 09:00. During the PEGASOS campaign, filter samples were collected between 9:00 to 21:00 (D) and between 21:00 to 9:00 (N). All samples were stored frozen until chemical analysis.

A sub-set of samples from each field campaign was selected for extraction and $^1\text{H-NMR}$ analysis. I report below the list of samples that I have analyzed by $^1\text{H-NMR}$ spectroscopy (total 228 samples + 20 blanks) in the frame of the PEGASOS and SUPERSITO projects:

- 55 during the intensive campaign of June/July 2012 in Bologna
- 55 during the intensive campaign of June/July 2012 in San Pietro Capofiume
- 30 during the intensive campaign of June/July 2012 in Monte Cimone
- 18 during the intensive campaign of February 2013 in Bologna
- 20 during the intensive campaign of October 2013 in Bologna
- 20 during the intensive campaign of October 2013 in San Pietro Capofiume
- 30 during the intensive campaign of February 2014 in Bologna

A scheme of the analytical protocol employed to chemically characterize the aerosol samples collected on quartz fiber filters at the various sites is reported below (Figure 2.2).

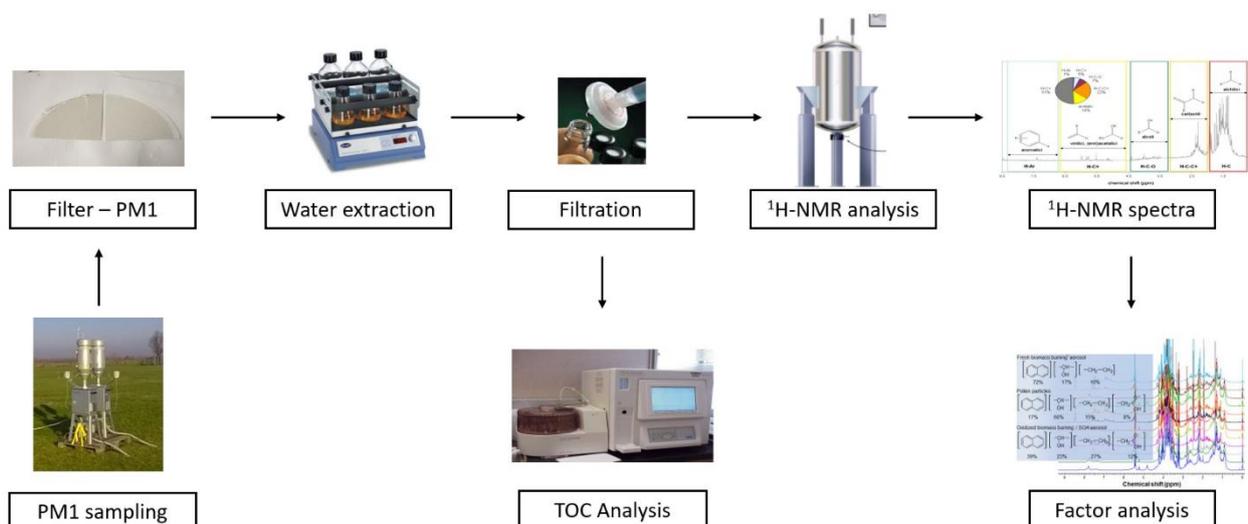


Figure 2.2. Scheme of the analytical protocol deployed to characterize aerosol PM1 samples.

2.1.2.3 Sample extraction and workup

A portion of each filter, between one quarter and three quarters depending on aerosol load, was extracted with deionized ultra-pure water (Milli-Q) in a mechanical shaker for 1 h and the water extract was filtered on PTFE membranes (pore size: 0.45 μm) in order to remove suspended particles. Ultrasonic bath extraction was not employed (Paglione, 2013) to avoid unwanted radical reactions in the aqueous extracts. An aliquot, between 0.4 and 1 mL depending on the load, of the water extracts

was used to determine the water-soluble organic carbon (WSOC) content with a TOC-VCPH analyzer (Shimadzu, Japan). The remaining volume of the extract was devoted to $^1\text{H-NMR}$ analysis.

2.1.2.4 Total Organic Carbon (TOC) analysis

A TOC analyzer (Shimadzu, Japan) was used for the determination of water-soluble organic carbon (WSOC). An aliquot of each sample was analyzed for total carbon (TC) by combustion at $680\text{ }^\circ\text{C}$ in the presence of a catalyst, while another aliquot was acidified in a reaction vessel to determine IC, which was decomposed to CO_2 . In both cases the evolved CO_2 was measured by a nondispersive infrared gas analyzer (NDIR) and the organic fraction (WSOC) was obtained by difference between TC and IC. The instrumental detection limit is $0.2\text{ }\mu\text{g}$ of carbon and the accuracy of the TC measurement resulted better than 5% for $1\text{ }\mu\text{g}$ of carbon (Sandrini et al., 2016).

2.1.2.5 Ion chromatography

Two ion chromatographs (Dionex ICS_2000) were used to determine the water-soluble ionic compounds in the samples. Anions were analyzed using an IonPac AG11 2x50 mm Dionex guard column, an IonPac AS11 2x250 mm Dionex separation column and an ASRS 300 self-regenerating suppressor. A solution of KOH was used as eluent. Its concentration increased from 0.8 mM to 38 mM , in a 35 minutes long run (0.8 mM for 10 min, 5 mM reached at 15 min, 10 mM at 20 min and 38 mM at 35 min). The flow rate was 0.25 mL/min . The chromatographic equipment for cation analysis consisted of an IonPac CG16 3x50 mm Dionex guard column, IonPac CS16 3x250 mm Dionex separation column and CSRS 300 self-regenerating suppressor. The analyses were performed using a solution of MSA as eluent with a flow rate of 0.36 mL/min . The following separation method was used: initial eluent concentration 6 mM , increase to 15 mM in 20 minutes, then 30 mM reached at 30 min and 50 mM from 31 min until 42 min. This program allows to separate both inorganic cations (sodium, ammonium, potassium, magnesium, calcium) and methyl-, dimethyl-, trimethyl-, ethyl- and diethylammonium. The detection limit for the analyzed inorganic ions corresponds to an average air concentration of 4 ng/m^3 , except for sodium, nitrite and calcium for which it is 45 ng/m^3 .

2.1.2.6 GC/MS analysis

GC/MS analysis were performed at the Department of Chemical and Pharmaceutical Sciences, University of Ferrara for comparison with $^1\text{H-NMR}$ datasets during selected field campaigns.

The $\text{PM}_{2.5}$ samples were collected on a quartz fiber filter (4.5 cm diameter) with low volume automatic outdoor samplers (Skypost PM, TCRTECORA Instruments, Corsico, Milan, Italy)

operating at a flow rate of 38.3 l/min for 24 hours from 9:00 to 9:00. After sampling, the procedure outlined in European Standard EN 12341 (CEN, 1998) was applied for equilibration and weighing. The analytical procedure has been described in Pietrogrande et al. (2013) and briefly summarized in the following. PM samples were extracted for 15 min in an ultrasonication bath with 15 mL of methanol:dichloromethane, 9:1 solvent mixture. Then the extracts were filtered using a teflon filter (25 mm, 0.45 μm , Supelco, Bellefonte, PA) to remove insoluble particles and then the filtrates were evaporated to dryness in a centrifugal vacuum concentrator (miVac Duo Concentrator, Genevac Ltd, Ipswich, UK). Prior to GC/MS analysis, the sample extracts were submitted to a silylation reaction for 70 min at 75°C: 40 μL of N,O-bis-(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% of trimethylchlorosilane (TMCS) and 15 μL of pyridine were added to 5 μL of Internal Standard (the deuterated $\text{C}_{12}\text{H}_{26}$, injected quantity: 127.5 ng) and 40 μL of iso-octane.

The GC/MS system was a Scientific Focus-GC (Thermo-Fisher Scientific, Milan, Italy) coupled to PolarisQ Ion Trap Mass Spectrometer (Thermo-Fisher Scientific, Milan, Italy). The column used was a DB-5MS column (L = 30 m, I.D. = 0.25 mm, df = 0.25 mm film thickness; J&W Scientific, Rancho Cordova, CA, USA). The operative conditions for GC/MS analysis are fully described in Pietrogrande et al. (2014). Chromatographic peaks of markers were identified by comparison of the retention time and mass spectrum with standard compounds, literature and library data; quantitative analysis was performed using calibration curves determined using authentic standards. Quality assurance and quality control were assessed by precision, accuracy and sensitivity for polar organic tracers. The procedure provides low detection limits (0.3-1 ng m^{-3}) and good reproducibility ($\text{RSD}\% \leq 7\%$) suitable for applicability in environmental monitoring. Good procedure recoveries ranging from 78 to 104% were evaluated on PM samples spiked with surrogate standards (Pietrogrande et al., 2013).

2.1.2.7 ^1H -NMR spectroscopy: protocol of analysis

The extract was dried under vacuum using a rotary evaporator, and re-dissolved in deuterium oxide (D_2O) for functional group characterization by proton nuclear magnetic resonance (^1H -NMR) spectroscopy (Decesari et al., 2000). All samples were analyzed with a Varian 600 MHz NMR spectrometer (facility of the Industrial Chemistry Department – University of Bologna <http://www.chimica-industriale.unibo.it/it/servizi-e-strutture/strumentazione-scientifica/spettrometri-a-risonanza-magnetica-nmr>), in a 5 mm probe. Sodium 3-trimethylsilyl-(2,2,3,3-d₄) propionate (TSP-d₄) was used as the referred internal standard, adding 50 μL of a TSP-d₄ 0.05% (by weight) solution in a buffered solution of D_2O to stabilize the chemical shifts of the resonances of weak acids and bases (potassium formate/formic acid 10 mmol pH ~3.8). ^1H -NMR analysis parameters were set as following. Temperature: 25°C, number of transitions: 300, pulse

sequence: Presat saturation power: 3dB. The typical total acquisition time for an average WSOC sample load (100 μ g of carbon) was 30 minutes.

$^1\text{H-NMR}$ spectroscopy in protic solvents provides the speciation of hydrogen atoms bound to carbon atoms. On the basis of the range of frequency shifts (the chemical shift, ppm) in which the signals occur, they can be attributed to different H-C containing functional groups. Since aliphatic carbonyls or carboxylic groups do not carry detectable protons, their concentrations can be detected by $^1\text{H-NMR}$ spectroscopy only indirectly, on the basis of the intensity of resonances between 1.9 and 3.0 ppm of chemical shift, which can be attributed to aliphatic groups adjacent to an unsaturated carbon atom, e.g., HC-C=O, HC-COOH or HC-C=C. Since aromatic and vinyl groups are relatively scarce in WSOC atmospheric samples, the unsaturated oxygenated groups provide the greatest contribution. The approach of Decesari et al. (2007) includes a correction for the contribution of benzylic groups (CH-Ar), which is assumed to be proportional to the total aromatic protons and is subtracted from total H-C-C= moieties to derive the aliphatic groups containing oxygenated unsaturated groups (i.e., carbonyls and carboxyls), HC-C=O (Paglione et al. 2014).

In summary, the most representative categories of functional groups in $^1\text{H-NMR}$ spectra can be listed as follows:

- Ar-H (6.5 – 8.5 ppm): aromatic protons.
- Anomeric and/or vinyl protons (O-CH-O) (5 – 6 ppm).
- H-C-O (3.2 – 4.4 ppm): protons bound to oxygenated aliphatic carbon atoms (alkoxy groups): aliphatic alcohols, ethers, and esters;
- H-C-C= (1.8 – 3.2 ppm): protons bound to aliphatic carbon atoms adjacent to unsaturated groups like alkenes (allylic protons), carbonyl or imino groups (heteroallylic protons) or aromatic rings (benzylic protons);
- H-C (0.9 – 1.8 ppm): unfunctionalized aliphatic (alkylic) protons.

As already noticed in the Introduction section, the abundance of these structural units expressed as organic hydrogen content is measured by the integral of the above bands and calibrated on the integral of the signal of the internal standard. Therefore this method provides a chemical characterization of the unresolved fraction of WSOC on a quantitative base with no need of specific standards, analogously to the $^1\text{H-NMR}$ approaches traditionally adopted in biogeochemistry for humic-like substances characterization (Paglione, 2013; Graham et al., 2002; Cavalli et al., 2006; Balasubramanian et al., 2003).

2.1.2.8 ¹H-NMR analysis: accuracy of individual compound analysis

Proton nuclear magnetic resonance spectroscopy (¹H-NMR) was also used for determination of individual organic compounds, such as alkyl-amines and anhydrosugars (levoglucosan). ¹H-NMR spectroscopy is a non-destructive method for the analysis of water-soluble organic tracers in atmospheric PM samples without the need of derivatization (Schkolnik, 2006). During this thesis work, the CNR-ISAC laboratories participated to an intercomparison experiment on anhydrosugars and biosugars determination in PM samples. In order to investigate the possible effect of unknown interferences in the complex PM samples, the study was performed on diverse sample types: a) PM filters retrieved from real atmosphere (16 filters from Milan and 10 filters from Borgo Valsugana (Trento)) to represent different levels of the target sugars as well as different chemical composition of other contaminants; b) 3 synthetic PM filters to represent the single contribution of the investigated analytes on the sampling filter, and finally c) 3 aqueous standard solutions. Ten Italian laboratories participated to the intercomparison exercise. Most of the participating laboratories used high-performance anion-exchange chromatography (AEC) coupled with pulsed amperometric detection (AEC-PAD) (Engling et al., 2006; Caseiro et al., 2007; Iinuma et al., 2009; Piazzalunga et al., 2010) or with mass spectrometric detection (AEC-MS) (Saarnio et al., 2010b). Another procedure is based on High Performance Liquid Chromatography combined with Mass Spectrometry (HPLC-MS) (Dye and Yttri, 2005; Larsen et al., 2006; Piot et al., 2012). Finally, two Gas chromatography-mass spectrometry (GC-MS) methods were investigated, as well established methods for separation and quantification of sugars in environmental samples, using solvent extraction followed by derivatization. Our method based on ¹H-NMR detection was investigated for comparison with the chromatographic methods.

The results of the intercomparison are presented by Pietrogrande et al., (under review in *Chemosphere*). Mean percentage error was calculated for levoglucosan concentrations of each of the 29 filters analyzed in all the 10 participating laboratories. The mean values of all samples are reported in Table 2.1. The mean $\epsilon\%$ (percentage error related to mean values) for the various samples ranged from -11 to +33%, that is consistent with the overall accuracy of each analytical method. The accuracy found in this study is better than that (from -63 to 20 %) reported by Yttri in a similar intercomparison study involving 13 laboratories using AEC-PAD, AEC-MS, LC-MS and GC-MS methods (Yttri et al., 2015).

	AEC-PAD1	AEC-PAD2	AEC-PAD3	AEC-PAD4	AEC-PAD5	AEC-MS	GC-MS1	GC-MS2	LC-MS	¹ H-NMR
Levoglucosan										
Mean (µg cm ⁻²)	3.69	3.17	4.06	3.49	1.64	3.52	4.00	2.81	4.27	6.72
S.D.	4.31	3.75	4.74	3.41	2.23	4.91	3.86	3.36	4.95	4.20
I.C.	1.64	1.43	1.80	1.30	0.85	1.87	1.47	1.28	1.88	1.60

Table 2.1. Concentration data (µg cm⁻²) reported as aggregated results by each of the laboratories reporting levels of anidrosugars in the current intercomparison: nine laboratories for levoglucosan and seven for mannosan and galactodsan. The mean values (mean), standard deviation (SD) and confidence limit (IC at p<0.05) were calculated from the concentrations of 29 samples measured each laboratory.

As a general conclusion, the results obtained are encouraging with respect to precision and accuracy and suggest that levels of levoglucosan in PM samples obtained by most common analytical methods provide comparable results. The procedures involving liquid (AEC and LC) and gas chromatography and ¹H-NMR analysis provide similar results, despite the GC-based procedures are by far the most commonly used one within the research community and they also have the longest record of use.

Second, the different extraction conditions, i.e., water versus solvent, involving derivatization, do not significantly influence the obtained results at the concentration levels investigated in this study. Finally, no significant differences can be attributed to the choice of the detection system, such as PAD or by mass spectrometry, ¹H-NMR shows standard deviation and confidence limit consistent with the other techniques. The concentrations found using the ¹H-NMR method are the highest compared to the other techniques, but ¹H-NMR is the only technique without separation or derivatization hence less prone to sample losses.

However, because of a certain degree of variability between methods, results from this study clearly demonstrate that attention must be paid to quality assurance of each laboratory procedure in terms of intralaboratory precision and accuracy, that are particularly challenging for highly complex samples such as PM collected in urban sites (Pietrogrande et al., under review).

2.1.2.9 ¹H-NMR analysis: spectral deconvolution

Factor analysis (FA) includes several multivariate statistical techniques that have been used in the recent years for aerosol source apportionment on the basis of internal correlation of observations at a receptor site (Paglione et al., 2014, Viana et al., 2008). In this respect, the application of factor analysis techniques to NMR spectral data sets is relatively new in the atmospheric sciences, but

employed in other fields as metabolomics in biochemistry (Wishart 2008; Markley et al., 2017). The criteria for selecting the optimum solutions are complex and have been summarized in Zhang et al. (2011) and Paglione et al. (2014). The factor analysis method used in this study is multivariate curve resolution with an alternating least squares approach (MCR-ALS). MCR-ALS (multivariate curve resolution-alternating least squares) is most used for NMR spectra deconvolution, is user-friendly, and is the most stable method within used by the atmospheric community (Tauler et al., 1995; <http://www.mcrals.info/>). Other methods, like PMF, have been used for a comparison.

The ^1H -NMR spectra undergo several steps of processing before being subjected to factorial analysis in order to remove spurious sources of variability: a) a polynomial fit was applied for baseline subtraction; b) an accurate alignment of the spectra using the singlet of the internal standard (located at 0 ppm) as a reference position was set; c) the peaks of the filter blanks were meticulously subtracted. Finally (d) the spectra were binned over 0.03 to 0.04 ppm of chemical shift (depending on the data set) with the purpose of average out residual variability in sample peak position. The resulting NMR spectra of reduced resolution (about 300 data points) were subjected to factor analysis. The results of factor analysis, i.e., factor contributions and factor profiles, were interpreted by means of the comparison with the time trends of tracer compounds and by the comparison with reference spectra, respectively. A full description of factor analysis methods applied to atmospheric ^1H -NMR datasets is reported by Paglione (2013).

2.1.3 RESULTS: DETERMINATION OF THE CHEMICAL COMPOSITION OF THE ORGANIC FRACTION OF PM BY PROTON NUCLEAR MAGNETIC RESONANCE ($^1\text{H-NMR}$) SPECTROSCOPY

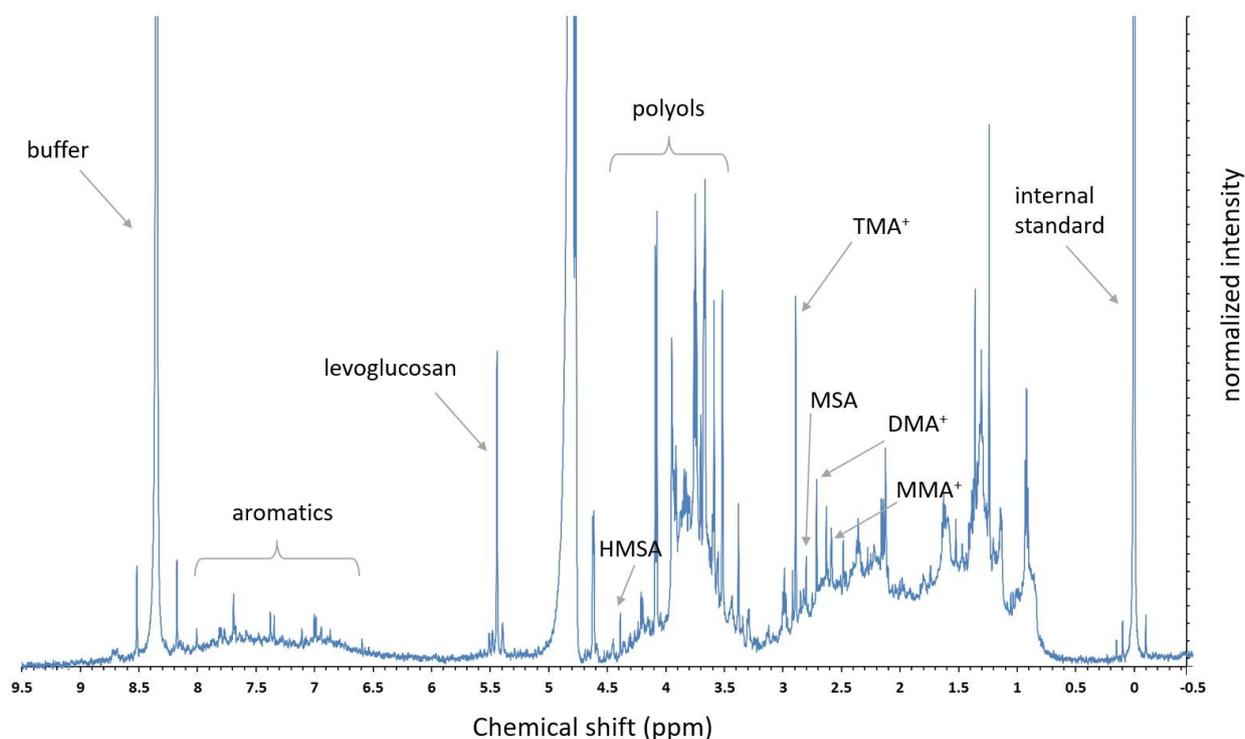


Figure 2.3. $^1\text{H-NMR}$ spectrum of the sample collected at Bologna sampling site on 08022013 (N). The resonances of wood pyrolysis products (levoglucosan) and of some low molecular weight amines are marked in the spectrum. The methanesulfonic acid (MSA) is a secondary aerosol tracer that is formed in the atmosphere from the reduced sulfur emissions (DMS). The X axis shows the proton chemical shift in ppm.

2.1.3.1 Analysis of molecular markers

The H-NMR analysis techniques are particularly useful for the determination of the composition of the organic polar fraction of the aerosol, and specifically for the analysis of organic compounds present in ionic form (amines in the form of ammonium salt and strong acids) that they have poor elution properties of gas chromatographic columns. The applicability of the analytical method overlaps techniques as LC/MS while it is complementary to GC/MS methods, although some compounds can be determined both by H-NMR methods that GC/MS, as the levoglucosan. Three classes of compounds are considered in this study:

1) Low molecular weight amines: mono-methyl, di-methyl and tri-methyl-amine (respectively **MMA**, **DMA** and **TMA**). Amine compounds present in the particulate in the form of ammonium salt (their pKa is greater than 9 while the atmospheric aerosol pH is acidic) explains the absorption of these volatile organic compounds in aerosol particles. The sources of these compounds in the atmosphere include biomass combustion and emission from agricultural and livestock activities. Some amines, such as DMA, are also emitted from biogenic sources (anaerobic processes in soil and water).

2) **Sulfur compounds**: methanesulfonic acid (**MSA**), and hydroxy-methanesulfonic acid (**HMSA**). Both acids are present in dissociated form in the particulate, often as salts and ammonium or alkali metal. They are compounds of secondary origin (SOA) produced by chemical reactions in the atmosphere from reduced sulfur compounds. In the case of MSA, of the precursor is dimethyl sulphide (DMS) which originates for decomposition of organic matter (sources from livestock activities) or from the metabolism of phytoplankton in the oceans (Andreae et al., 1985). The oxidation of DMS in the atmosphere is mediated by radical processes, mostly photochemical, even if some oxidants can also be present in the absence of light in polluted atmospheres (NO_3^* radical). The HMSA instead is an addition product of formaldehyde (HCHO) and sulfur dioxide (SO_2) and the reaction takes place in the liquid phase (droplets of mist, cloud, aerosols hygroscopic at relative humidities above the deliquescence point) and it does not require the presence of light or radical. SO_2 is emitted by anthropogenic emissions (combustion) while formaldehyde is an oxidized products of anthropogenic and biogenic VOCs.

3) **Levogluconan** is the main cellulose pyrolysis product, is produced by the incomplete combustion of biomass containing plant material. It is a stable organic marker with respect to hydrolysis reactions. However, it can be degraded photochemically.

The concentrations of the aforementioned classes of compounds during the various periods of intensive observation of SUPERSITO and PEGASOS are discussed below. The concentration of low-molecular-weight amines, monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA) at the urban site (Bologna) was an average $14.25 \pm 6.89 \text{ ng/m}^3$. The summer samples of the campaign from June to July 2012 (PAGOSOS) show the highest concentrations, with an average in Bologna of $18.51 \pm 6.56 \text{ ng/m}^3$ and peaks up to 80 ng/m^3 . DMA and TMA were more abundant than MMA. During the winter campaigns, the average of the sum of the three low-molecular-weight amines in Bologna was $42.76 \pm 6.89 \text{ ng/m}^3$. In February 2013, TMA was the most abundant amine (Figure 2.4), while DMA and MMA were predominant in October 2013. Amine concentrations did not show any significant difference between daytime and nighttime conditions. The total concentration of the low molecular weight amines at the rural site of San Pietro

Capofiume was on average $70.06 \pm 11.06 \text{ ng/m}^3$. Similarly to the urban site, the summer samples (June - July 2012) showed the highest concentrations, with an average of $29.23 \pm 12.51 \text{ ng/m}^3$ and peaks of 180 ng/m^3 . The most abundant species was MMA followed by DMA and TMA. During the winter campaigns, the average sum of amine concentrations was $52.44 \pm 9.62 \text{ ng/m}^3$ with similar values to the urban site. In winter, MMA was always the most concentrated amine species in S. Pietro Capofiume. While during the summer campaign of 2012 a clear diurnal trend in concentrations cannot be found, the daytime concentrations were greater than nocturnal ones during the winter campaigns. In Mt. Cimone, finally, the total average concentration of low molecular weight amines in Mt. Cimone was $60.66 \pm 9.26 \text{ ng/m}^3$ during the 2012 summer campaign, with TMA and DMA being the dominant species.

Comparing the three sites of sampling, Bologna, San Pietro Capofiume and Monte Cimone, the amines are more abundant at San Pietro Capofiume compared to Bologna and to Monte Cimone in the summer, while the concentrations of Bologna and San Pietro Capofiume are similar in winter. The higher low molecular weight amines concentrations in San Pietro Capofiume in the summer are consistent with the higher emissions of amines from agricultural activities in the rural sectors of the Po Valley. By contrast, in the cold season the volatile emissions are at a minimum and the atmospheric stratification (thermal inversions) tends to homogenize the concentrations between urban and rural sites in the Po Valley.

When looking at the sulfur-species, we can notice that in winter HMSA was much more enriched in the aerosol than MSA: the average HMSA concentration was $26.06 \pm 24.61 \text{ ng/m}^3$ and with peaks of 200 ng/m^3 , while the mean MSA concentrations was $34.26 \pm 18.41 \text{ ng/m}^3$. In summer the trend is reversed, with a higher concentration of MSA compared to HMSA, with the former reaching levels of 90 ng/m^3 . Such seasonal pattern of HMSA can be explained by two effects: 1) HMSA is a compound which is easily degraded photochemically, 2) deliquesced aerosol particles and fog droplets, in which HMSA forms, are more abundant in winter than in summer in the Po Valley. In the rural site San Pietro Capofiume, high concentrations of MSA are found in the summer period, with an average of $124.61 \pm 41.15 \text{ ng/m}^3$ and peaks of 200 ng/m^3 , while HMSA is less concentrated with a mean value of $19.73 \pm 7.00 \text{ ng/m}^3$. In Mt. Cimone in summertime, the MSA concentrations are about twice those of HMSA, with an average of $36.06 \pm 14.68 \text{ ng/m}^3$. In Monte Cimone we can assume MSA of marine biological origin and imported from Western Mediterranean basin. The difference in concentration of MSA between Monte Cimone and San Pietro Capofiume suggests that roughly 70% of MSA at the rural site originates from agricultural activities in the Po Valley. The concentrations of levoglucosan, marker of biomass burning, were investigated in summer and winter samples at the urban and rural sites. Levoglucosan was detected prevalently in autumn-winter

samples with a campaigns average between both sites of $150.20 \pm 89.59 \text{ ng/m}^3$ and with peaks of 300-400 ng/m^3 . Such high levoglucosan concentrations are typical of rural sites in Europe during the wintertime (Puxbaum et al., 2007). Levoglucosan exhibited higher concentrations at night with respect to daytime, indicating that wood burning products accumulate efficiently near the ground when the atmosphere is stably stratified. Levoglucosan was found in San Pietro Capofiume with concentrations similar to Bologna, with mean values $164.26 \pm 85.99 \text{ ng/m}^3$ in winter.

A summary of all markers values in ng/m^3 collected in SUPERSITO and PEGASOS campaigns and analyzed by $^1\text{H-NMR}$ is reported in the Table 2.2 below.

ng/m^3	levoglucosan	HMSA	MSA	TMA	DMA	MMA	sum amines	average amines
BO summer 2012	32.66	13.72	65.97	8.59	22.68	24.25	55.52	18.51
standard deviation	(± 29.71)	(± 3.99)	(± 21.17)	(± 2.99)	(± 7.88)	(± 8.81)	(± 6.56)	(± 6.56)
SPC summer 2012	43.84	25.74	124.61	17.98	28.93	40.79	87.69	29.23
standard deviation	(± 21.75)	(± 10.00)	(± 41.15)	(± 7.13)	(± 12.46)	(± 17.94)	(± 12.51)	(± 12.51)
MTC summer 2012	21.36	11.37	36.06	24.99	21.82	13.85	60.66	20.22
standard deviation	(± 8.09)	(± 4.93)	(± 14.68)	(± 9.75)	(± 10.97)	(± 7.05)	(± 9.26)	(± 9.26)
summer average	32.62	16.94	75.54	17.18	24.48	26.29	67.95	22.65
standard deviation	(± 19.85)	(± 6.31)	(± 25.67)	(± 6.63)	(± 10.44)	(± 11.27)	(± 9.45)	(± 9.45)
BO February 2013	176.14	23.12	23.33	12.97	10.89	13.2	37.06	12.35
standard deviation	(± 124.88)	(± 26.61)	(± 15.01)	(± 6.89)	(± 5.79)	(± 6.04)	(± 6.24)	(± 6.24)
BO October 2013	110.2	23.75	32.17	8.37	19.85	20.25	48.47	16.16
standard deviation	(± 57.89)	(± 16.97)	(± 14.02)	(± 3.53)	(± 10.14)	(± 8.97)	(± 7.55)	(± 7.55)
SPC October 2013	164.26	31.32	47.29	10.88	16.32	25.24	52.44	17.48
standard deviation	(± 85.99)	(± 30.25)	(± 26.19)	(± 5.32)	(± 9.27)	(± 14.26)	(± 9.62)	(± 9.62)
winter average	150.2	26.06	34.26	10.74	15.69	19.56	45.99	15.33
standard deviation	(± 89.59)	(± 24.61)	(± 18.41)	(± 5.25)	(± 8.40)	(± 9.76)	(± 7.80)	(± 7.80)

Table 2.2. A summary of all markers values in ng/m^3 collected in SUPERSITO and PEGASOS campaigns and analyzed by $^1\text{H-NMR}$.

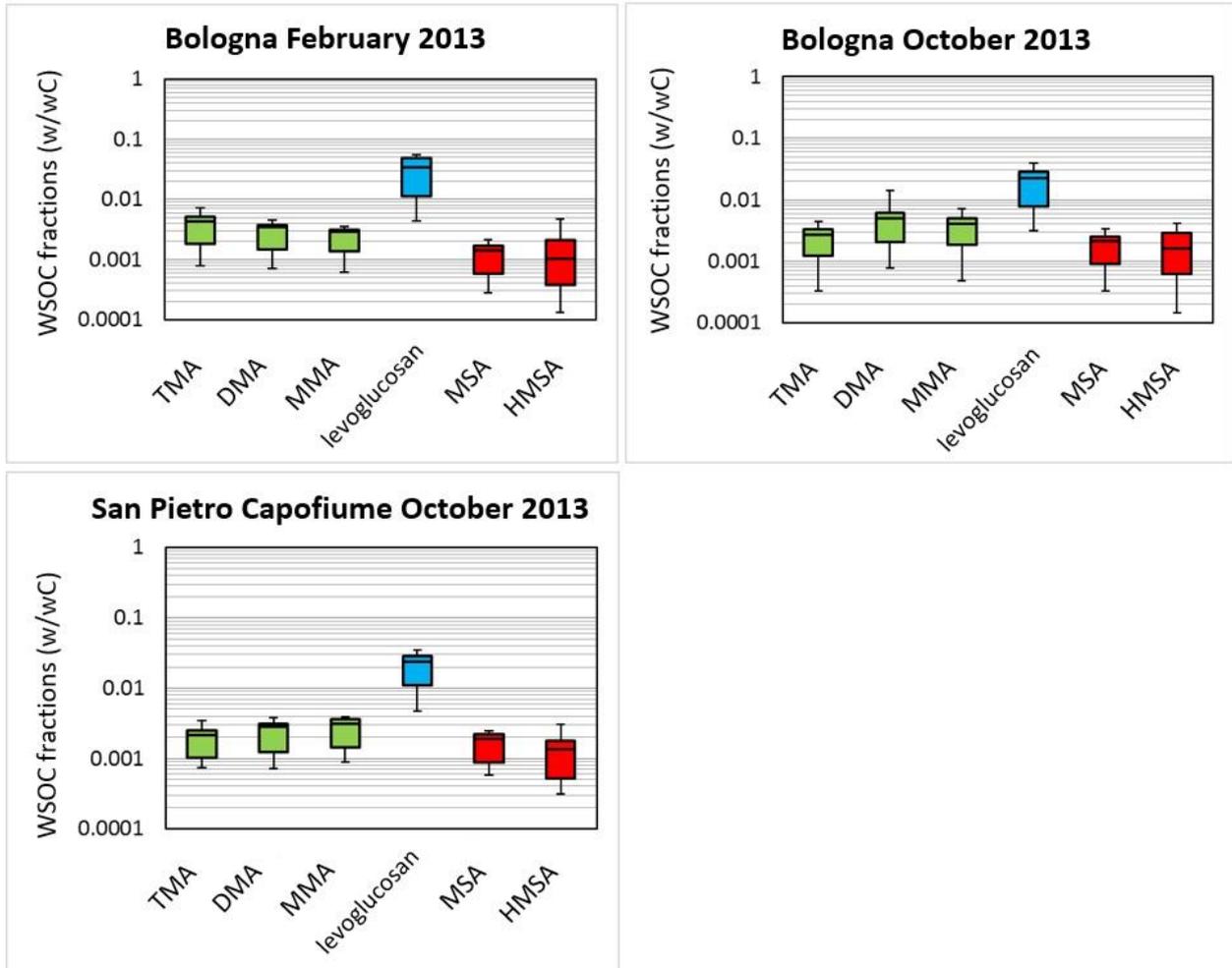
The contribution of organic carbon accounted for by the analyzed tracer compounds to total WSOC (measured in the extract with a TOC analyzer) is shown in Figure 2.4. Apart from levoglucosan, that in the cold season can account for 3 - 8% of WSOC, the contribution of the other markers ranges in the % of WSOC. The contribution of levoglucosan decreases considerably during the summer period,

down to around 1% at both the urban and rural site, indicating that the contribution of primary aerosols from combustion of biomass is dramatically lower in the summer and evenly distributed homogeneously at the regional scale. The contribution of amines is higher in summer than in the cold season, reaching a level of about 1% of WSOC for DMA and MMA at the urban site and at San Pietro Capofiume. The thermodynamic equilibrium of semi-volatile amine salts (such as aminium chlorides) should depress the concentrations of particulate amines in the hot season, therefore an increase in their concentration in particulate matter can only be explained by a marked increase in emissions. It is possible that atmospheric amines in the rural Po Valley are contributed by the evaporation (amplified by the high summer temperatures) from biomass in storage facilities of sewage for agriculture or livestock facilities. In respect to the sulfur compounds, in general a greater variability is observed for HMSA content compared to MSA, which can be explained by the fact that the formation of HMSA, being governed by the presence of liquid water (fog, clouds, etc.), is strongly influenced by the meteorological variability. The contributions of the two sulfur compounds to WSOC are of the same order of magnitude in the fall and winter, whereas the fraction represented by MSA exceeds HMSA in the summer at all stations. In fact, the contribution of MSA in the cold season is around 1-2 ‰ and reaches 6-10 ‰ in summer. These observations indicate a change in the nature of SOA formation processes: photochemical product increase in the summer period (as the MSA) while the formation of organic aerosols for heterogeneous chemical reactions (as for HMSA) is limited by the reduced availability of liquid water. A special case is represented by the measures undertaken at the rural site San Pietro Capofiume in a previous SUPERSITO campaign in November 2011, showing a very low HMSA contribution, although in those days there was a lot of fog in the Po Valley. The explanation of this behavior is the following: when the sampling occurs during fog events, part of the aerosol is not sampled because is captured by the droplets ("scavenging") (Gilardoni et al., 2014). This scavenging process is selective and favorable to the removal of larger and more hygroscopic particles. It is possible that HMSA is enriched in the fraction of particles that preferentially leads to the formation of fog droplets, which conversely explains the low content of this compound in aerosol samples (enriched "interstitial" aerosols).

In conclusions, the analysis of organic marker compounds in aerosol aqueous extracts from the PEGASOS and SUPERSITO intensive field campaigns showed the dominant influence of biomass burning in particulate organic composition of the Po Valley background in the autumn and winter months. In addition, the presence of low molecular weight amines (mono-, di- and tri-methyl amines) witnesses a PM source from agriculture and animal husbandry both in winter and in the summer. Finally, the increase of HMSA in winter months indicate that secondary organic aerosol formation

can occur also in conditions of reduced photochemistry, via chemical reactions in deliquesced particles and fog droplets.

a)



b)

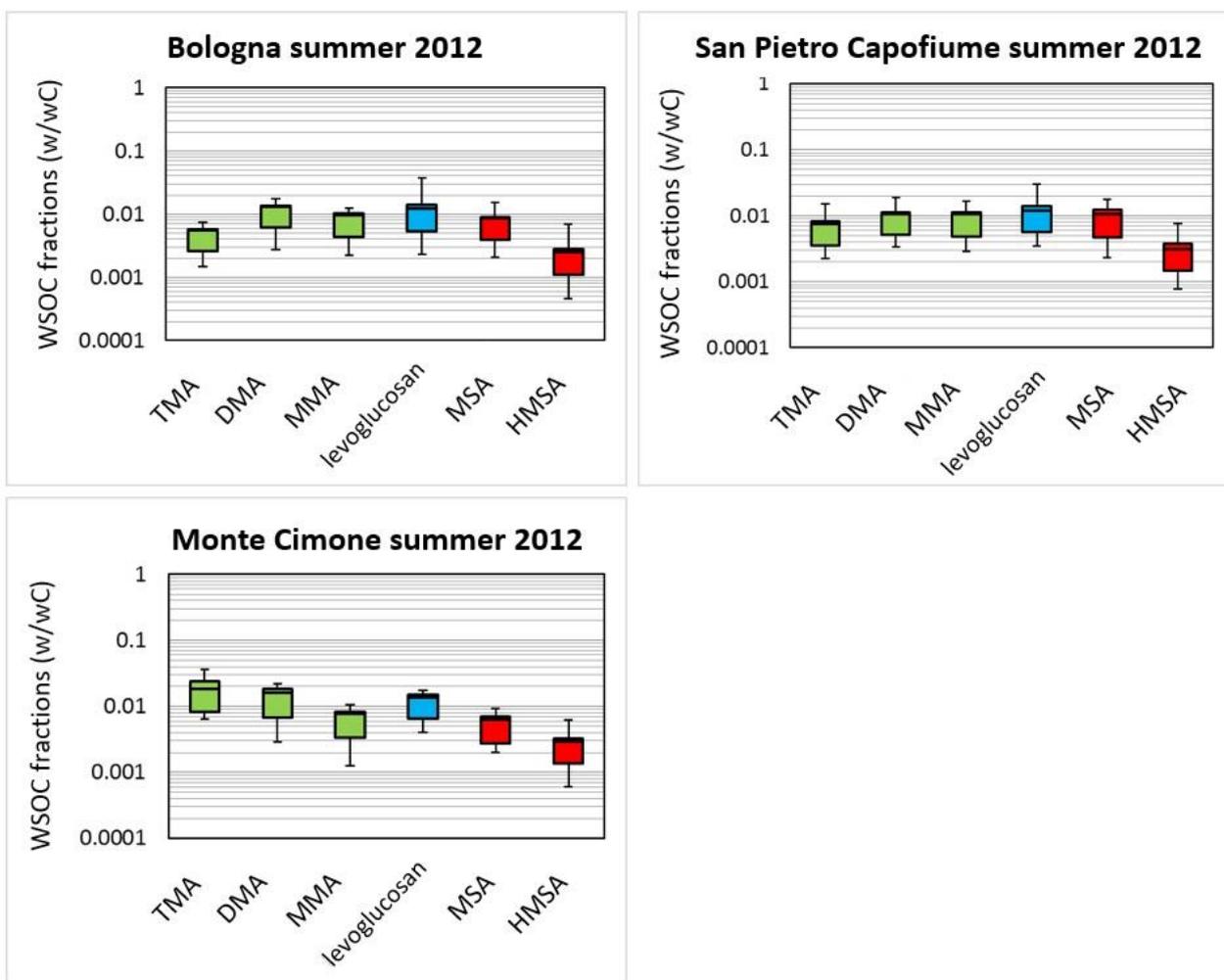


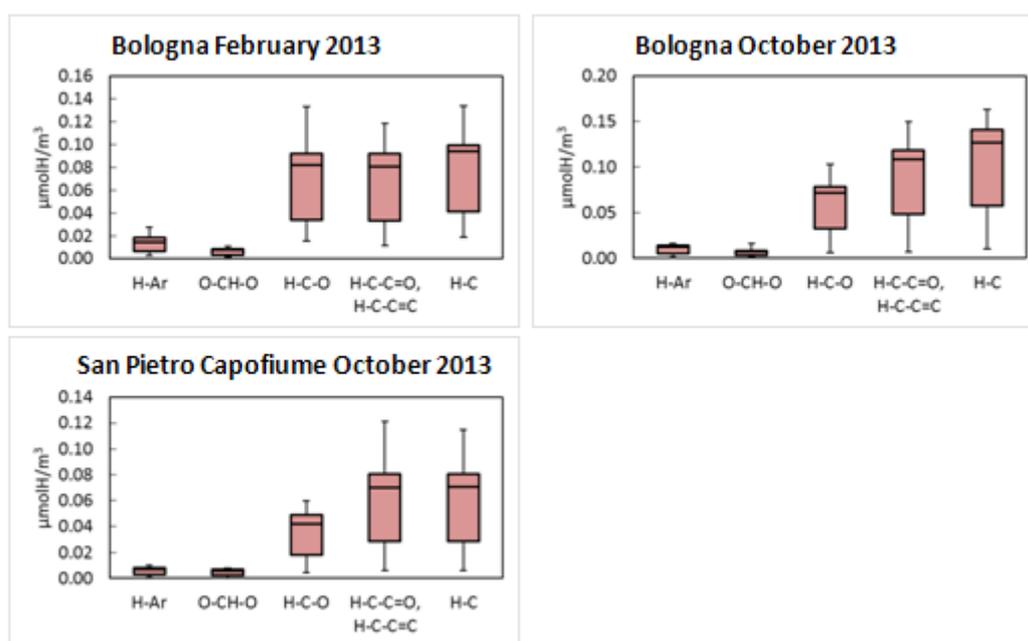
Figure 2.4: Statistics of concentrations of low molecular weight amines, levoglucosan, MSA and HMSA, expressed as fractions of the water-soluble organic carbon (WSOC) (=carbon content of organic tracers measured by $^1\text{H-NMR}$ analysis with respect to the total WSOC determined by TOC analysis the aqueous extract). The graphs at the top (a) show the results for the MS, those at the bottom (b) for rural stations. The "box & whisker" diagram shows the medians, the first and third quartiles, and the minimum and the maximum of the frequency distribution of the WSOC fraction for each compound.

2.1.3.2 Functional groups analysis

Figure 2.5 shows statistics for the concentrations of $^1\text{H-NMR}$ functional groups determined on the eight sets of samples collected during the SUPERSITO and PEGASOS campaigns. The concentrations are expressed in μmol of organic non-exchangeable hydrogen on cubic meter of air. The non-exchangeable hydrogen atoms are the ones not participating to acid/base reactions in aqueous solution, therefore they are mostly H-C systems. Since the stoichiometric ratio of these hydrogen atoms and the carbon atoms on the same functional group varies between 1 and 3 for the aliphatic groups but can be significantly less than 1 for the aromatic groups, the low concentrations of aromatic groups shown in Figure 2.5 equivalent in reality at concentrations in moles of aromatic carbon that can be 3 to 4 times more. Consequently, the composition observed in the winter of 2013 at the urban site is characterized by a significant content of aromatic structures. The two winter campaigns shows another distinctive feature, i.e., the high contribution from alkoxy groups (H-C-O). The concentration of alkoxy groups is quite comparable with the those of the other two major aliphatic groups (H-C-C= and HC) in winter, while it is half of each of them during the autumn campaigns, and becomes one third in the summer for all sites. Such seasonal change in functional group distribution can be explained by considering a yearly cycle of WSOC sources. In winter, biomass combustion sources supply water-soluble organic compounds rich of aromatics (from lignin pyrolysis) and alkoxy groups (from pyrolysis of cellulose and lignin), while the formation of SOA from photochemical sources in the summer is responsible for the production of compounds containing aliphatic acids and ketones (H-C-C=) and with alkyl residues systems (H-C) but with few alcohol or ether groups (H-C-O). The attribution of WSOC main sources, according to the $^1\text{H-NMR}$ functional groups distribution, is based on the comparison with $^1\text{H-NMR}$ compositions determined for environmental samples obtained in near-source conditions (e.g., a coastal site for marine aerosols). This approach allowed to describe variation ranges for the $^1\text{H-NMR}$ specific compositions for some macro-sources, and in particular for biomass combustion aerosols, for SOA, and for marine aerosols (Decesari et al., ES & T 2007). The ratio of the acyl (H-C-C=O) to alkoxy (C-H-O) groups is the main parameter that allows to discriminate $^1\text{H-NMR}$ compositions for these three types of WSOC. Figure 2.6 encloses a synthetic $^1\text{H-NMR}$ functional groups distribution for the PEGASOS and SUPERSITO campaigns. First of all, most of the samples show an anticorrelation between the contribution of alkoxy and acyl groups to the total of aliphatic groups. The contribution of other aliphatic groups (containing amines and sulfonates) is negligible and can be ignored in the SUPERSITO and PEGASOS samples. It follows that no one sample is classified as predominantly of marine origin, whereas almost all samples belong into areas characteristic of biomass burning or SOA

products, with a certain percentage of unassigned cases. The winter samples from Bologna show the highest contributions of alkoxy groups (H-C-O), also beyond the area indicated for biomass combustion aerosols in Decesari et al. (2007). They are an the extreme case of primary biomass burning aerosols, consistent with the very high levoglucosan content in the same samples. In the summer, the vast majority of samples presents typical SOA characteristics (85% of cases for Bologna site, 93% for San Pietro Capofiume site). The data from winter campaigns show the most diverse behavior. In the case of San Pietro Capofiume, October 2013, 30% of the samples were classified as SOA whereas 65% were classified biomass burning aerosol. Overall, these results indicate that functional group distribution of WSOC in the Po Valley is primarily dictated by seasonal variations in the sources, with a prevalence of SOA in the summer and biomass burning in fall-winter. These findings are in agreement with literature data from previous studies in the Po Valley and at other continental locations in Western Europe (Puxbaum et al., 2007; Gilardoni et al., 2016; Sandrini et al., 2016; Decesari et al., 2014; Paglione et al., 2014).

a)



b)

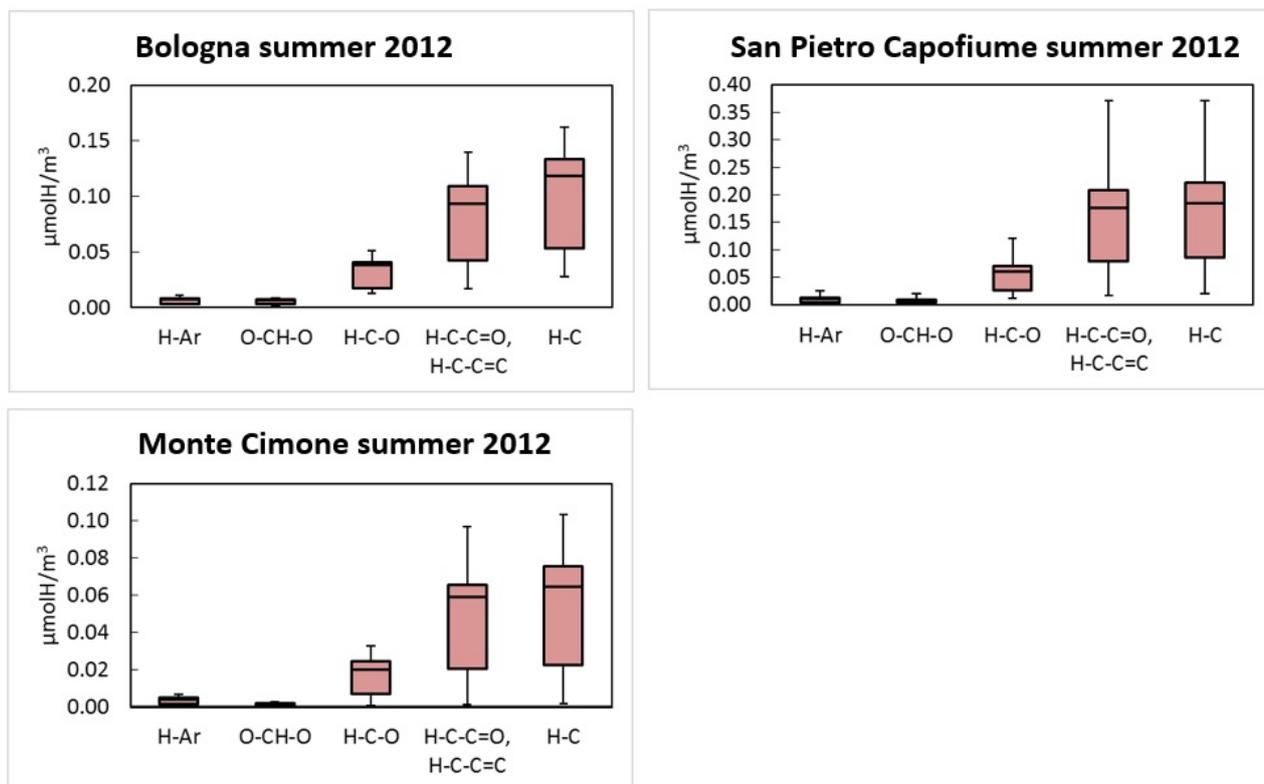


Figure 2.5. Concentration of $^1\text{H-NMR}$ functional groups for a) in the cold season b) in the summer campaign - PEGASOS. The "box and whisker" plot shows the median, the first and third quartiles and minimum and maximum concentrations.

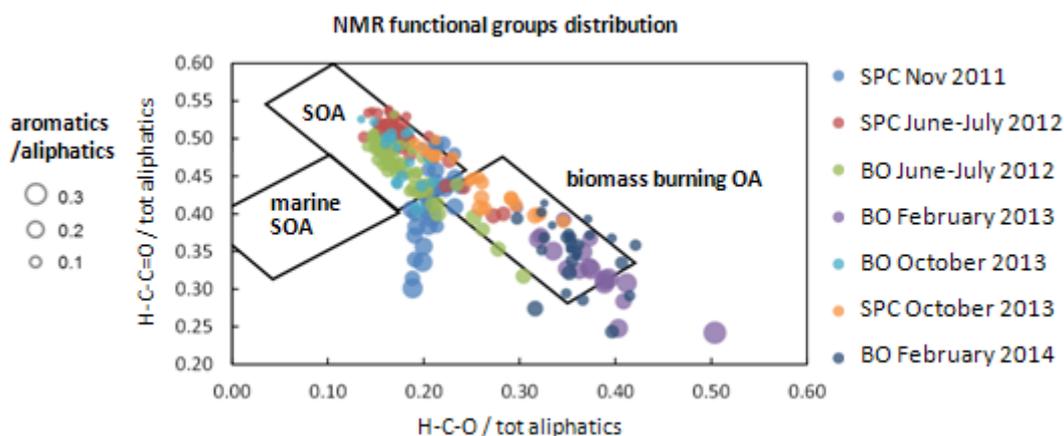


Figure 2.6. Distribution of $^1\text{H-NMR}$ functional groups and attribution of the main sources of WSOC according to the method of Decesari et al. (2007). Concentrations are expressed in moles of carbon fractions, calculated from the concentrations in moles of H organic measured from the analysis $^1\text{H-NMR}$ and applying average stoichiometric ratios, as described in Decesari et al. (2007). Data from

other two SUPERSITO campaigns were included: November 2011 in San Pietro Capofiume and February 2014 in Bologna.

2.1.3.3 Source apportionment of WSOC by ¹H-NMR factor analysis

Below we present a summary of the results of characterization of polar organic aerosol sources (WSOC) based on factor analysis applied to ¹H-NMR datasets for specific field campaigns. The interpretation of factor spectral profiles was based on the presence of tracer compounds, by molecular resonances, and on the comparison with a library of reference spectra recorded in the laboratory or in the field during near-source studies. The physical nature of the factors was also interpreted on the basis of correlation analysis employing atmospheric tracers (Paglione et al., 2014).

I first focus on the February 2013 and October 2013 intensive observation periods which provided good opportunities to investigate the contributions of biomass burning sources. It should be noted that in the cold season, atmospheric PM is also enriched of products of fossil fuel combustion (from traffic and household heating in urban areas), but fossil fuel burning mainly produces water-insoluble organic compounds which are not recovered by my analytical protocols designed for WSOC.

2.1.3.4 CASE 1. Winter campaign: February 2013 at the urban site

The field experiment was carried out during the winter season, when the contribution of domestic heating is maximum and the photochemistry is strongly reduced by the low solar angle and the frequent overcast sky conditions. The Figure 2.7a and 2.7b show ¹H-NMR spectral profiles and source assignment for the WSOC factors identified for the autumn and winter SUPERSITO campaigns. The results show a significant contribution of primary aerosols from biomass burning during both experiments. The presence of biomass burning is clear in February 2013 represented by factor named “BB-POA” (biomass burning – primary organic aerosol). Alkoxy groups dominate BB-POA factor (45%), followed by acyls and benzyls (21%), alkyls (16%) and aromatics (14%). Anomeric groups (4%) are mainly contributed by anhydrosugars. Two SOA factors were extracted by factor analysis. The first one, “BB-SOA” (biomass burning – secondary organic aerosol), was attributed to atmospheric “ageing” of biomass burning aerosols witnessed by the presence of aromatic, alkoxy groups and residuals of levoglucosan. The main functional groups acyls and benzyls (44%), alkyls (33%) and alkoxy groups (16%). The second SOA factor, named “nonBB SOA” (non biomass burning SOA), points to a SOA class of unknown origin. Its functional group distribution is dominated by alkyl groups (47%), followed by acyls (29%) and by alkoxy (16%).

When looking at the contributions of the three factors to total WSOC, the sum of BB-POA and BB-SOA_Aq account for $\frac{3}{4}$ of the total analyzed WSOC, indicating that biomass burning was by far the largest contribution to oxygenated organic aerosols in winter in the Po Valley urban atmosphere.

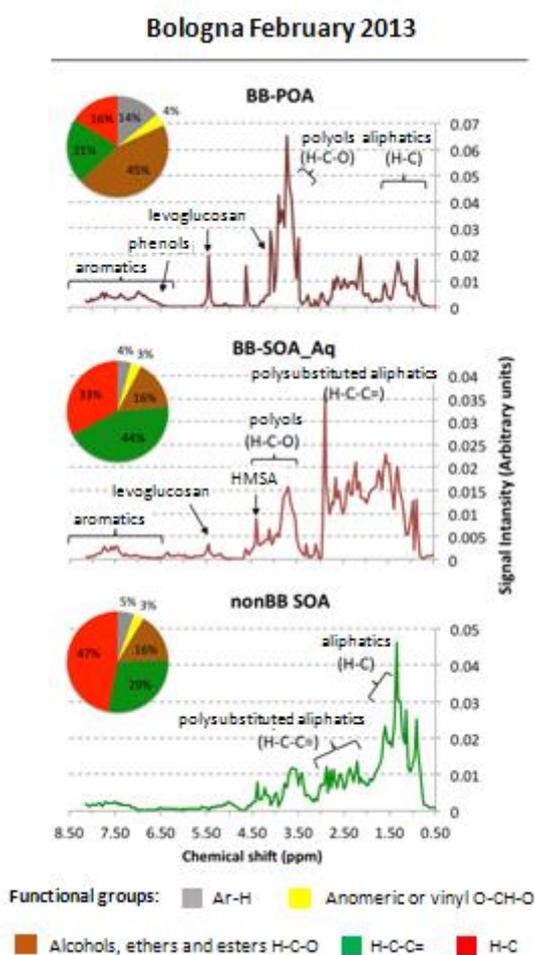


Figure 2.7a. $^1\text{H-NMR}$ profiles of factors polar organic aerosols (water-soluble). MCR-ALS method of factor analysis was applied to the series of 18 $^1\text{H-NMR}$ spectra at 400-point resolution. Legend: "BB-POA" (primary aerosols from biomass burning, "BB" = "biomass burning"), "BB-SOA" (secondary aerosols resulting from chemical transformations of biomass burning products), "BB-SOA_Aq" (secondary aerosols resulting from the chemical transformations of the products of combustion of biomass which take place in the aqueous phase, indicated by the presence of "HMSA" = hydroxy-methanesulfonic acid), "nonBB SOA" (SOA other sources). "TMA", "DMA", "MMA" are abbreviations of certain amines of low molecular weight (Tri-, Di- Mono-methylamines, respectively). The diagrams at the top left cakes of each profile represents the relative distribution of the functional groups of each source (legend with color codes below the graph).

2.1.3.5 CASE 2: Autumn campaigns: field measurements at the urban and the rural station in October 2013

Autumn is a transition season in northern Italy, with variable weather conditions and precipitations. Compared to winter campaign, during the October 2013 field experiment a smaller percentage of primary biomass burning compounds (<30%) was found. The proportion of SOA components unrelated to biomass burning ("not BB SOA") increased, especially in Bologna where they could result from urban emissions. The majority of organic compounds, however, is attributable to a secondary aerosol component which is still associated to biomass burning markers, although sometimes in traces, and its important contribution (50-60%) of "BB SOA" must be considered as an upper limit. A higher ratio of secondary versus primary biomass burning compounds in October compared to the February case is plausible because photochemical reactions are more efficient in fall than in winter.

Contrary to the February 2013 campaign, in October parallel sets of samples were collected at the urban and at the rural site. The factor analysis of the two records of ¹H-NMR spectra led to similar outcomes (Figure 2.7b). The first factor refers to primary biomass burning aerosol (BB-POA), followed by three SOA factors: two related to biomass burning ("BB-SOA_Aq." and "BB-SOA_not-aq.") and the last one of unassigned source ("nonBB-SOA"). The functional groups distribution of BB-POA is characterized by a high contribution of alkoxy (SPC 35%, BO 29%), alkyls and benzyls (SPC 28%, BO 33%) and only to a lesser extent alkyls (SPC 26%, BO 31%), similarly to the Bologna winter campaign. The BB-POA factors are also characterized by the presence of levoglucosan and by phenols (~6.5-7.0ppm) in the aromatic region (Figure 2.7b). The ¹H-NMR spectral profiles of the first two SOA factors show significant concentrations of aromatic compounds and traces of levoglucosan suggesting that these classes of secondary organic compounds originated from atmospheric oxidation of biomass burning particles. The first of such "BB-SOA" types, named "BB-SOA_Aq", exhibits a functional group distribution with a lesser contribution of alkoxy (SPC 10%, BO 15%) with respect to BB-POA and much greater proportions of acyls/benzyls (SPC 44%, BO 41%) and alkyls (SPC 37% and BO 31%). "BB-SOA_Aq" is characterized by the presence of HSMA, tracer of SOA from heterogeneous reactions involving the uptake of gaseous species in deliquesced aerosol particles. The other SOA related to biomass burning, "BB-SOA_not-aq", shows functional group distributions similar to BB-SOA_Aq but no HSMA. The last SOA factor, "nonBB_SOA", of uncertain source assignment, exhibits a functional group distribution dominated by alkyls (SPC 37%, BO 41%). In summary, primary biomass burning compounds were the dominant fraction of water-soluble OA in February 2013 (BB-POA 44%), whereas in October 2013 secondary organic aerosol from atmospheric transformation of biomass burning products provided the major contribute (BO 56%,

SPC 61%). In conclusion, factor analysis of $^1\text{H-NMR}$ datasets during the fall and winter campaigns showed the importance of secondary aerosols associated with chemical changes that occur in the atmosphere upon emissions of biomass burning primary compounds (gas and particles).

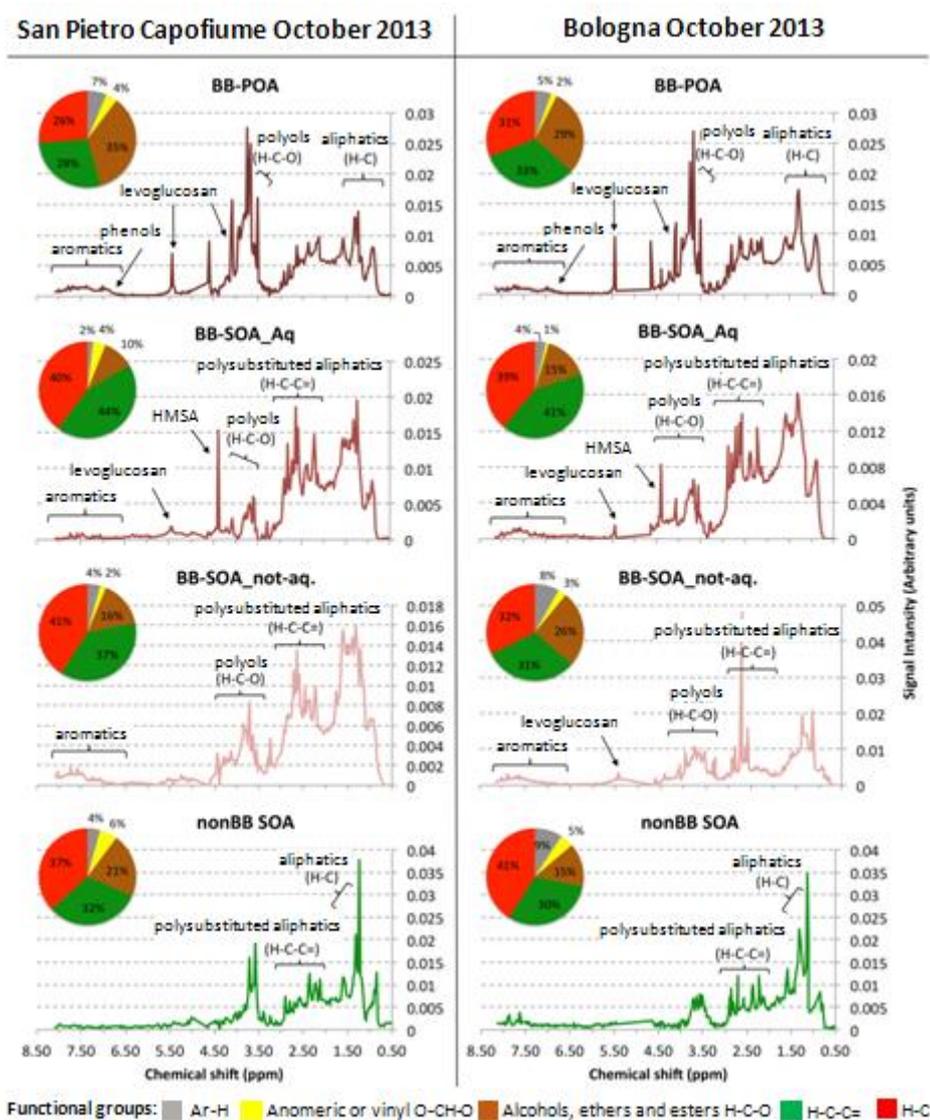


Figure 2.7b. $^1\text{H-NMR}$ profiles of factors polar organic aerosols (water-soluble). MCR-ALS method of factor analysis was applied to the series of 40 $^1\text{H-NMR}$ spectra (20 SPC and 20 BO) at 400-point resolution. Legend: "BB-POA" (primary aerosols from biomass burning, "BB" = "biomass burning"), "BB-SOA_Aq" (secondary aerosols resulting from the chemical transformations of the products of combustion of biomass which take place in the aqueous phase, indicated by the presence of "HMSA" = hydroxy-methanesulfonic acid), "BB-SOA_not-aq" (secondary aerosols resulting from chemical

transformations of biomass combustion products, other than BB-SOA_Aq), "nonBB-SOA" (SOA other sources). The diagrams at the top left cakes of each profile represents the relative distribution of the functional groups of each source (legend with color codes below the graph).

The average contribution of $^1\text{H-NMR}$ factors to the observed mass of organic aerosols is summarized below in the Figure 2.8:

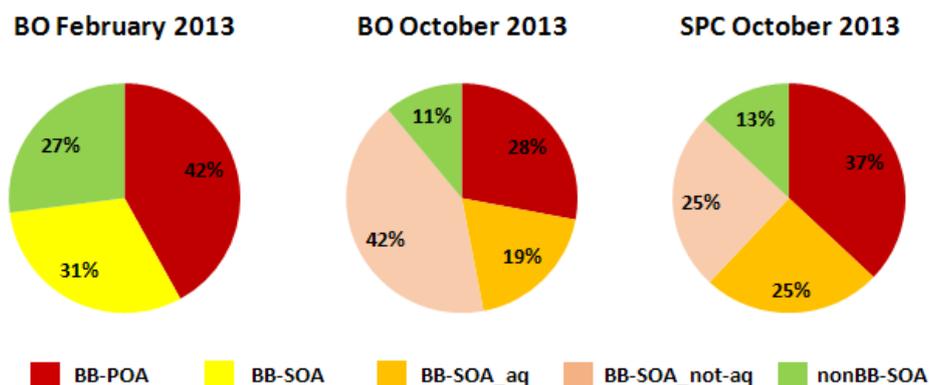


Figure 2.8. Contribution of $^1\text{H-NMR}$ factors to the observed mass of organic aerosols (water-soluble).

To further investigate the nature and sources of the $^1\text{H-NMR}$ factors of WSOC, we examined the correlations between the time trends of the above factors with those of molecular tracers determined in PM samples collected in parallel during the same experiment, in Bologna and at S. Pietro Capofiume. In particular, organic markers were analysed in PM_{2.5} aerosol samples by GC/MS providing a full set of biogenic and anthropogenic carbonaceous species: sugars, carboxylic acids and phenols typical of Po Valley region and monitored for SUPERSITO campaigns. The concentrations and molecular distributions of such organic markers are extensively discussed by Pietrogrande et al. (2014, 2015, 2016). Additional tracer compounds (organic and inorganic) were provided by ion chromatographic (IC) analysis of impactor samples collected in the same experiment. Six scatter plots between specific $^1\text{H-NMR}$ factors and concentrations of organic markers characterized by GC/MS are shown in Figure 2.9.

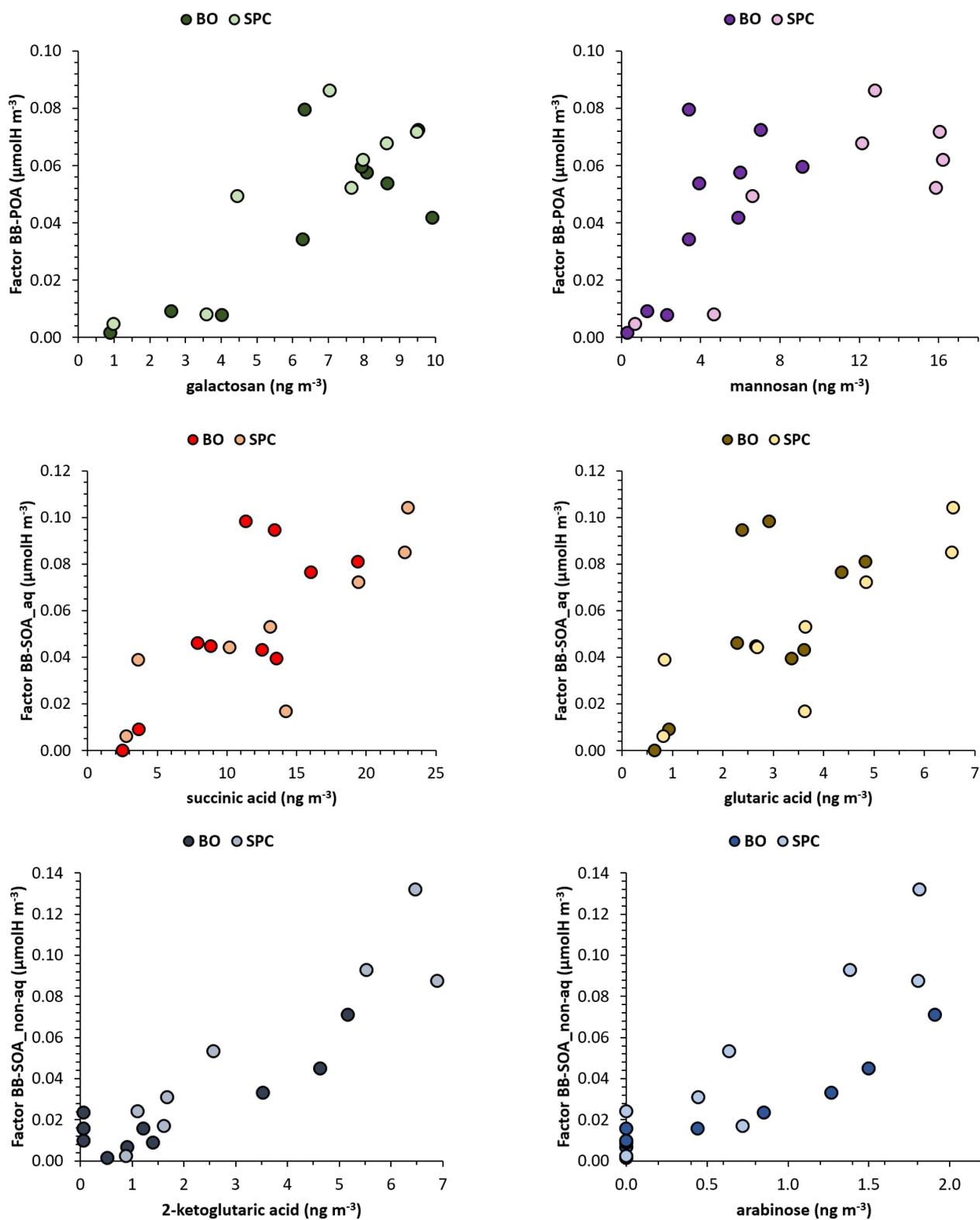


Figure 2.9. Scatter plots between concentrations of selected $^1\text{H-NMR}$ factors and of organic markers characterized by GC/MS. All data referred to the SUPERSITO campaign of October 2013 hold in Bologna (urban site) and San Pietro Capofiume (rural site).

The characteristics of the time trends of the ¹H-NMR factors are described below, together with the correlations found with the concentration trends of GC/MS and IC marker compounds (Tables 2.3 and 2.4):

- **Factor 1 (F1) BB-POA**

Biomass burning primary organic aerosol concentrations showed a marked diurnal variability with maxima at the night-time, indicating production from the ground sources and atmospheric accumulation/dispersion governed by the diurnal cycle of the planetary boundary layer during days of high pressure conditions (Paglione et al. 2014). Good correlations (Pearson correlation coefficient r) were found with the concentration trends of major biomass burning tracers: levoglucosan ($r = 0.92$ in Bologna and 0.50 in SPC) and potassium ($r = 0.81$ in SPC). Good correlations are also found with levoglucosan isomers, galactosan and mannosan ($r = 0.91/0.89$ in Bologna and $r = 0.86/0.82$ in SPC for galactosan/mannosan). All anhydrosugars and potassium are among best known atmospheric tracers of biomass burning. Also the time trend of benzoic acids (3-hydroxybenzoic acid and 4-hydroxybenzoic acid) showed good correlation with the trend of BB-POA (respectively $0.87/0.70$ for Bologna and $0.57/0.70$ for SPC). Hydroxy-benzoic acids originate from photo-oxidation reactions (Kawamura and Yasui, 2005; Yang et al., 2008), but can also be produced by burning of grasses and other non-woody vegetation (Simoneit, 2002). Erythritol is the only polyol showing good correlation with BB-POA ($r = 0.79$ for Bologna and 0.60 for SPC). Erythritol is considered a tracer for primary biological aerosol particles (Graham et al., 2003) and for dust from soils and unpaved roads (Simoneit et al., 2004). Finally, phenolic acids and carbonyls (syringaldehyde, vanillic acid and acetovanillone) all show good correlation with BB-POA in Bologna ($r = 0.93/0.68/0.70$, respectively) and partly (only vanillic acid, $r = 0.73$) in S. Pietro Capofiume. Phenolic acids are tracers of lignin pyrolysis. Vanillic acid, for example, is produced by both softwood and hardwood (Simoneit, 2002).

- **Factor 2 (F2) BB-SOA_Aq**

The concentration trend of BB-SOA-Aq shows a marked diurnal variability with maxima at day-time, pointing to a photochemical origin. The inspection of the BB-SOA_Aq ¹H-NMR spectral profile highlighted the presence of HMSA, a tracer for aqueous-phase SOA formation, and at the same time a functional group composition dominated by a dominant contribution from alkyl and acyl groups, pointing to the occurrence of aliphatic carbonyls and carboxylic acids. The comparison with the GC/MS and IC data confirmed that the time trend of BB-SOA_Aq is correlated with those of most common dicarboxylic aliphatic acids: oxalic, malonic and succinic acids are the most abundant carboxylic acids in urban areas, where they

originate prevalently from photochemical production rather than direct emissions in traffic exhausts (Kundu et al. 2010; Ho et al. 2007). Good correlation between oxalate (analyzed by IC) and the two BB-SOA factors (F2 and F3) were found for both sites (respectively $r = 0.60/0.66$ for Bologna and $0.74/0.85$ for SPC). Succinic acid, often the most abundant dicarboxylic acid after oxalic acid in biomass burning aerosols (Kundu et al. 2010), shows good correlation with BB-SOA_Aq at both sites ($r = 0.85$ for Bologna and 0.83 for SPC). Other aliphatic dicarboxylic acids with time trends correlated with that of BB-SOA_Aq include malonic, glutaric, malic and adipic acid. Malic acid and succinic acid were sometimes identified as tracers of secondary organic aerosol originated from traffic exhausts (Hsieh et al., 2008; Van Drooge et al., 2012). Phthalic acid, another tracer for anthropogenic SOA (Olivera et al., 2007; Ho et al., 2011), also shows good correlations with factor BB-SOA_Aq in Bologna 1 ($r = 0.75$). Possible precursors of phthalic acid are naphthalene and polycyclic aromatic hydrocarbons in combustion emissions. Azelaic acid, another SOA tracer originating from oleic acid oxidation in biomass burning plumes or in cooking emissions, shows good correlations with BB-SOA_Aq only in SPC ($r = 0.81$). In summary, BB-SOA_Aq was correlated several SOA molecular tracers including benzoic acids and other products of chemical transformation of combustion aerosols.

- **Factor 3 (F3) BB-SOA_not-aq**

The concentration time trend of BB-SOA_not-aq show little night-to-day variations and it is mainly driven by changes in the regional background aerosol concentrations. The comparison with the GC/MS tracers shows a pattern similar to that of BB-SOA_Aq, with several positive correlations for aliphatic carboxylic acids. Nevertheless, good correlations were also found between BB-SOA_not-Aq and keto- and hydroxyl- carboxylic acids, like .2-ketoglutaric acid and glycolic and malic acid. The former was sometimes used as a SOA tracer for aged traffic exhausts (Hsieh et al., 2008; Van Drooge et al., 2012). Malic acid can form from photo-oxidation of aliphatic carboxylic acids, but can also be emitted by biomass burning (Kundu et al., 2010). Another tracer found to be correlated with BB-SOA_not-aq is pimelic acid, which, similarly to azelaic acid, can be produced by photo-oxidation of unsaturated carboxylic acids, such as oleic and linoleic acids (Ho et al., 2011; Hyder et al., 2012). Interestingly, BB-SOA_not-aq correlated with a polyol, arabinose, ($r = 0.95$ for Bologna and 0.91 for SPC), which is commonly considered as a tracer for primary organic aerosols. Arabinose is emitted by various biogenic sources in the spring/summer season. It is a constituent of pectin, a polysaccharide contained in non-woody tissues, such as

leaves and needles. Arabinose can be emitted as uncombusted material during biomass burning (Medeiros et al. 2006). On the other hand, it was sometimes found uncorrelated with other biomass burning tracers (Sullivan et al., 2004). Past laboratory studies indicate that arabinose can form from oxidation of levoglucosan and glucose (Holmes, 2008; Marcq et al., 2009; Stapley and Bemiller, 2007; Zhou et al., 2016; Renard et al., 2013, 2015). We can therefore hypothesize that arabinose is actually a tracer of *secondary* biomass burning aerosols in the Po Valley and similar environments.

- **Factor 4 (F4) nonBB-SOA**

The ¹H-NMR spectral profile of nonBB-SOA could not be reconciled with any reference spectra in available libraries and certainly does not recover any features of the spectra typical of biomass burning. The contribution of this factor to total WSOC is small at both site (11% of the sum of the factors in Bologna and 13% in SPC). Correlation factors with most GC/MS tracers are small. A modest correlation was found with pinonic acid ($r = 0.58$ in Bologna and 0.43 in SPC), a photo-oxidation reaction products of α -pinene (Kavouras et al. 1998). A relatively good correlation was found in Bologna also for a few biogenic sugars, mannitol, glucose and mycose (respectively $0.72/0.59/0.73$). Mannitol is a specific tracer for airborne fungal spores (Fu et al. 2013). Sucrose and glucose originate from plant materials such as pollen, fruits, and their fragments (Speranza et al., 1997; Pacini, 2000). These tracers come from synthesis of primary sugars, generally detected in the spring (Pietrogrande et al. 2014). Overall, the correlation with some biogenic sugars and with pinonic acid suggest a biogenic origin for nonBB-SOA.

Correlations NMR factors vs polar GC/MS markers	Bologna October 2013				San Pietro Capofiume October 2013			
	BB-POA	BB-SOA_aq	BB-SOA_non-aq.	nonBB-SOA	BB-POA	BB-SOA_aq	BB-SOA_non-aq.	nonBB-SOA
glycolic acid	0.28	0.32	0.76	-0.69	0.40	0.58	0.76	-0.28
malonic acid	0.56	0.74	0.32	-0.56	0.41	0.82	0.41	-0.60
maleic acid	0.12	0.50	0.31	-0.53	0.06	0.39	0.47	-0.17
succinic acid	0.41	0.85	0.71	-0.88	0.63	0.84	0.47	-0.66
glutaric acid	0.48	0.73	0.69	-0.81	0.61	0.85	0.40	-0.70
malic acid	0.38	0.69	0.72	-0.84	0.45	0.58	0.78	-0.30
glyoxylic acid	0.22	0.46	0.67	-0.77	0.22	0.48	0.36	-0.36
adipic acid	0.21	0.62	0.53	-0.64	0.48	0.80	0.49	-0.60
3-OH benzoic acid	0.87	0.39	-0.07	-0.27	0.57	0.58	0.05	-0.64
4-OH benzoic acid	0.70	0.14	-0.17	0.11	0.70	0.70	0.55	-0.59
2-ketoglutaric acid	-0.20	0.27	0.87	-0.72	0.25	0.20	0.94	0.09
azelaic acid	0.14	0.03	-0.15	0.44	0.71	0.81	0.35	-0.79
pinonic acid	-0.59	-0.79	-0.47	0.58	-0.77	-0.40	-0.25	0.43
phtalic acid	-0.04	0.75	0.39	-0.44	0.19	0.36	0.82	-0.03
pimelic acid	0.24	0.57	0.80	-0.74	0.42	0.55	0.77	-0.27
erythritol	0.79	0.78	0.11	-0.44	0.60	0.67	0.52	-0.59
arabinose	-0.11	0.32	0.95	-0.73	0.40	0.32	0.91	-0.07
galactosan	0.91	0.75	0.01	-0.33	0.86	0.67	0.17	-0.84
mannosan	0.89	0.56	-0.10	-0.23	0.82	0.65	0.31	-0.75
levoglucosan	0.92	0.67	0.06	-0.28	0.50	0.67	0.19	-0.72
xylitol	-0.41	-0.57	-0.38	0.37	0.03	0.13	0.24	-0.04
ribitol	-0.23	-0.51	-0.52	0.29	-0.39	0.28	0.14	0.08
mannose	-0.35	-0.58	-0.33	0.38	-0.13	0.38	0.32	-0.04
mannitol	-0.31	-0.66	-0.71	0.72	-0.63	-0.23	-0.49	0.31
glucose	-0.26	-0.58	-0.65	0.59	-0.24	0.23	-0.13	-0.11
sucrose	-0.59	-0.55	-0.37	0.42	-0.56	-0.05	-0.80	0.07
mycose	-0.33	-0.64	-0.79	0.73	-0.73	-0.31	-0.65	0.38
vanillin	0.08	-0.22	-0.23	0.11	0.14	-0.16	0.00	-0.18
syringaldehyde	0.28	-0.07	-0.26	0.12	0.16	0.24	0.34	-0.09
syringic acid	0.93	0.47	-0.21	-0.20	0.23	0.40	-0.01	-0.52
vanillic acid	0.68	0.23	-0.33	0.11	0.73	0.39	0.04	-0.72
acetovanillone	0.70	0.15	-0.49	0.42	0.32	0.02	-0.03	-0.32

Table 2.3. Pearson correlation coefficients (r) between $^1\text{H-NMR}$ WSOC factors and simple chemical tracers. Carboxylic acids are reported in blue, anhydrosugars and biosugars in green, phenols in violet.

Correlations NMR factors vs IC markers	Bologna October 2013				San Pietro Capofiume October 2013			
	BB-POA	BB-SOA_aq	BB-SOA_non-aq.	nonBB-SOA	BB-POA	BB-SOA_aq	BB-SOA_non-aq.	nonBB-SOA
Acetate	0.47	0.63	0.78	-0.38	0.83	0.62	0.73	-0.88
Formate	0.54	0.55	0.64	-0.34	0.75	0.72	0.83	-0.94
MSA	0.49	0.51	0.52	-0.23	0.74	0.66	0.78	-0.94
Chloride	0.24	-0.05	-0.14	0.05	0.89	0.09	0.13	-0.55
Nitrite	-0.16	0.36	-0.21	-0.21	0.56	-0.34	-0.30	-0.35
Nitrate	0.61	0.50	0.59	-0.16	0.82	0.61	0.61	-0.91
Sulfate	0.17	0.68	0.87	-0.39	0.22	0.68	0.88	-0.56
Oxalate	0.47	0.60	0.66	-0.27	0.67	0.74	0.85	-0.88
Sodium	-0.56	-0.53	-0.37	0.06	0.14	-0.07	0.11	-0.01
Ammonium	0.45	0.60	0.69	-0.20	0.69	0.75	0.84	-0.90
MA	0.42	0.62	0.71	-0.24	0.77	0.55	0.73	-0.88
EA	0.17	0.24	0.57	-0.71				
Potassium	0.57	0.61	0.60	-0.32	0.81	0.42	0.60	-0.91
DMA	0.66	0.49	0.66	-0.47	0.87	0.35	0.49	-0.87
DEA	0.25	0.30	0.36	0.24	0.41	0.39	0.56	-0.48
Magnesium	-0.31	-0.43	-0.13	-0.26	0.60	-0.15	0.04	-0.34
Calcium	0.73	0.02	0.25	-0.56	0.47	0.14	0.11	-0.22

Table 2.4. Pearson correlation coefficients (r) between $^1\text{H-NMR}$ WSOC factors and simple chemical tracers analysed by ion chromatography.

Overall, the results indicate that the anhydrosugars (levoglucosan and its isomers, galactosan and mannosan) showed good correlations with BB-POA factor at both sites, whereas aliphatic dicarboxylic acids, ketoacids and hydroxyacids, and benzoic acids showed instead high correlations with the two BB-SOA factors. Finally, a minor factor of non biomass burning origin can be tentatively associated to biogenic sources. In conclusion, the comparison of datasets from distinct analytical methodology proved to be particularly useful to constrain the source apportionment of the polar fraction of organic particulate matter.

2.1.3.6 CASE 3: June-July 2012 (PEGASOS)

In summertime, in absence of emissions from domestic heating in the Po Valley, submicron aerosol WSOC is expected to be contributed mainly by secondary organic aerosols. The $^1\text{H-NMR}$ results of the June-July 2012 PEGASOS campaign show a series of organic components attributable to different chemical families of SOA, which the biogenic or anthropogenic nature remains mostly undefined. Various attempts were made to attribute these factors to specific SOA sources. The spectral profiles obtained by factor analysis of the full $^1\text{H-NMR}$ record were compared with libraries of reference $^1\text{H-NMR}$ spectra for SOA, and in particular with the spectra of:

- biogenic SOA from oxidation of alpha-pinene in the presence of varying concentrations of NO_x (Paul Scherrer Institute, the 2006-2008 POLYSOA reaction chamber experiments);

- biogenic SOA from oxidation of mixtures of monoterpenes and sesquiterpenes to low concentrations of NO_x (Research Centre of Juelich, Germany, EUCAARI 2008 reaction chamber experiments);
- anthropogenic SOA from oxidation of aromatic hydrocarbons in the presence of high concentrations of NO_x (Paul Scherrer Institute, the 2006-2008 POLYSOA reaction chamber experiments).

The comparison of the PEGASOS spectral profiles with the reference spectra of SOA produced in laboratory experiments was inconclusive, which means that a) the library is incomplete and lacking of some of the products that are important precursors for the Po Valley environment, or b) the photochemical conditions in the summer period lead to the formation of SOA also on time scales of several days, for which the current experimental laboratory conditions are not fully representative (in other words, the environmental SOA tend to be too "processed" or "aged" than those of the laboratory, or in any case chemically different). Most of the PEGASOS samples exhibit functional group distributions and spectral profiles typical of "humic-like substances" (HULIS) (Paglione et al., 2014), with a high amount of acyls (from carboxylic acids) and which reaction chamber experiments struggle to reproduce (see Part II of this thesis work).

The characterization of ¹H-NMR factors during the summer is therefore limited to the inspection of time trends, from which information about source footprint can be derived: factors with a high frequency variability must be related to local sources, whereas factors with a "smoothed" time trend are linked to slowly changing regional-scale sourced. In particular, for the valley sampling sites (Bologna and San Pietro Capofiume), we observe the following contributions (Figure 2.10a and 2.10b):

- SOA containing HULIS and methanesulfonic acid (MSA). They are present in more or less constant concentrations during the entire period of the campaign and the presence of tracers of marine sources (MSA) suggests that are supra-regional background aerosol: the basin of origin would extend to the western Mediterranean, which was upstream of the Po Valley during most of the experiment.
- SOA containing humic-like substances (HULIS). They are the major aerosol component of the regional background aerosol in this season and are enriched in periods of intense photochemical activity and weather conditions characterized by stagnation, hence promoting accumulation. The analysis of the correlations with oxidized molecular markers of isoprene indicates that the precursors of HULIS in this summer environment can be linked to the plant emissions (see below).
- "fresh" or "local" SOA enriched in nocturnal samples. They trace the (probably anthropogenic) polar organic compounds which accumulate overnight in the lowest atmospheric layer capped by

thermal inversions. They constitute a small fraction of the analyzed mass of organic particulate matter (5-15%). Their composition is completely different from that of HULIS. It is dominated by aliphatic compounds with abundant contribution of amines and alkoxy groups (or alcohol) and depleted of carbonyl and carboxyl groups, indicating that these secondary organic compounds have not undergone an aging in the atmosphere and must be produced in situ.

- SOA that contain HULIS similar to those of the second type but with a higher concentration of carbonyls compared to the carboxylic acids. They were found only at the rural station (S. Pietro Capofiume) and could be a less aged component of HULIS, formed in the central areas of the valley, where the highest relative humidity triggers aerosol chemical processes in deliquesced aerosol particles.

At the remote site of Monte Cimone station, only two factors were observed:

- SOA containing HULIS very similar to those found in BO and SPC, which shows that these SOA belong aerosol regional background and can be transported in residual layers (i.e., lifted layers of boundary layer air) throughout the lower troposphere.

- SOA of a different type, which have chemical composition characterized by a lower abundance of carboxyl groups than HULIS, and a more local source, because its concentrations at Mt. Cimone have a clear diurnal pattern, with a higher contribution during daylight hours, when the transport of air from the lower altitudes of the station is maximum. However, it is not found in lowland stations (BO and SPC), suggesting that the rural areas of the Apennines, with their biogenic emissions, can be responsible for the formation of these SOA.

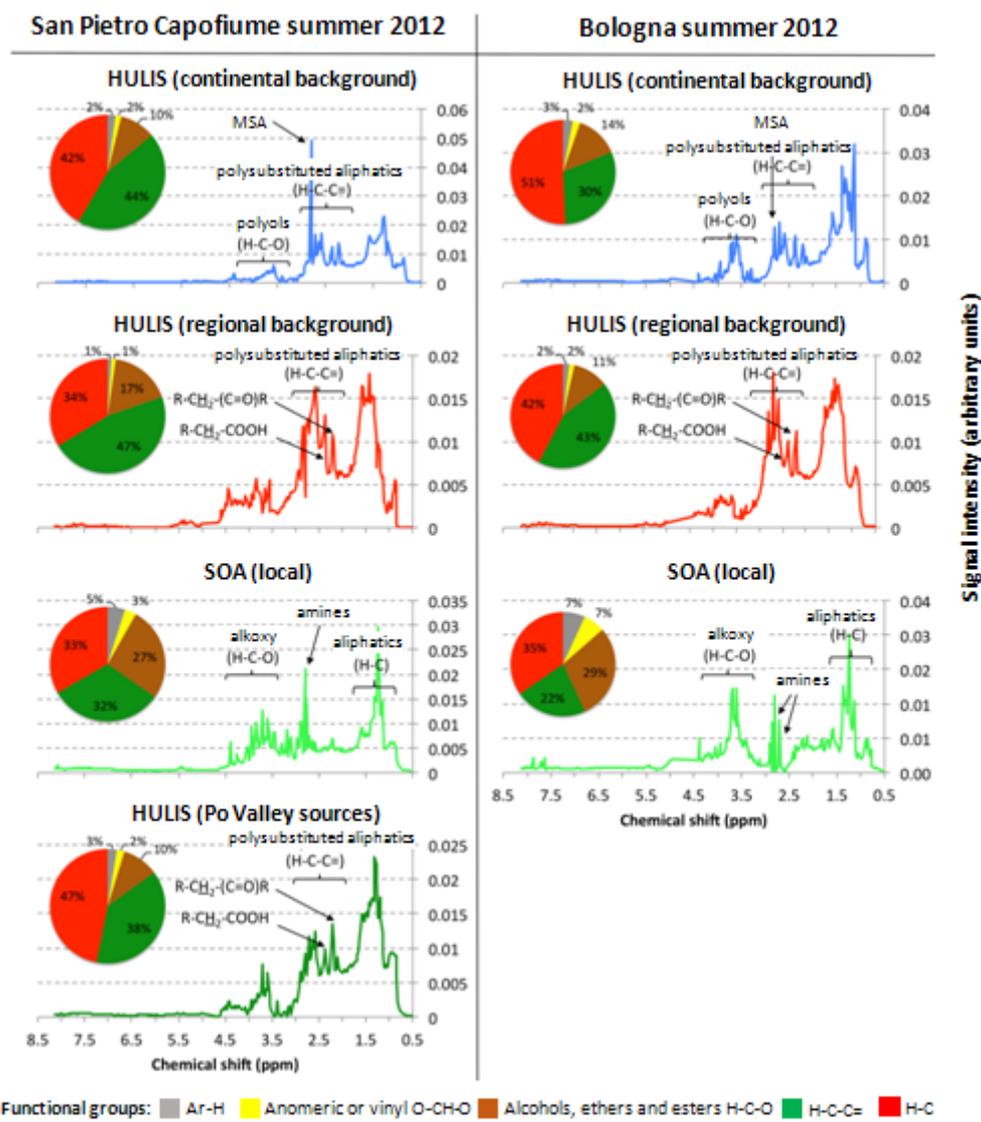


Figure 2.10a. $^1\text{H-NMR}$ profiles of Bologna and San Pietro Capofiume factors polar organic aerosols (WSOC). The definition of "HULIS" and significant differences between the various fractions is discussed in the text. The top left pie chart of each profile represent the relative distribution of the functional groups of each source (legend with color codes below the graph).

Monte Cimone summer 2012

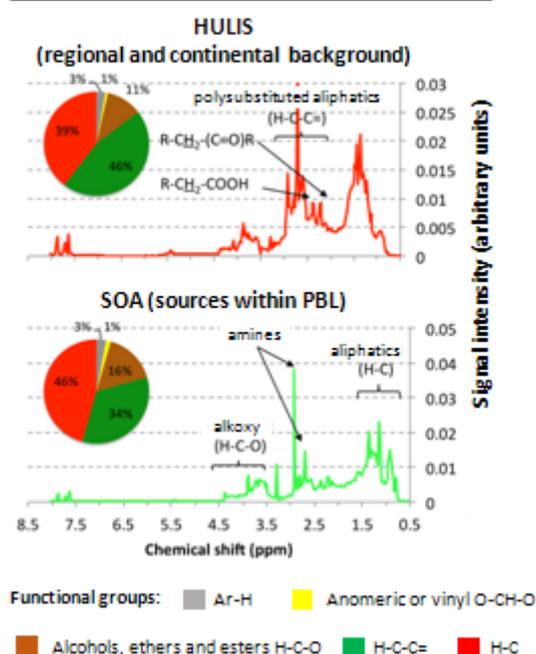


Fig. 2.10b. $^1\text{H-NMR}$ profiles of Monte Cimone factors polar organic aerosols (WSOC)

An insight into the anthropogenic/biogenic of the $^1\text{H-NMR}$ factors identified during the summer campaign is provided by the comparison of their time trends with those of molecular tracers, in this case, provided by the LC/MS analyses performed by the Leipzig Institute of Troposphere (Yoshiteru Iinuma). The LC/MS analysis detected a full range of **organosulfate tracers**, especially biogenic SOA tracers. Organosulfates in atmospheric aerosol are produced by the heterogeneous uptake of oxidized VOC onto acidic sulfate particles (Liggio et al., 2006; Surratt et al., 2007, Iinuma et al., 2007).

Organosulfates from monoterpene and isoprene are ubiquitous in the atmosphere (Stone et al., 2012; Pratt et al., 2013). In the Figure 2.11 are reported markers characterized by LC/MS during the PEGASOS campaign in San Pietro Capofiume.

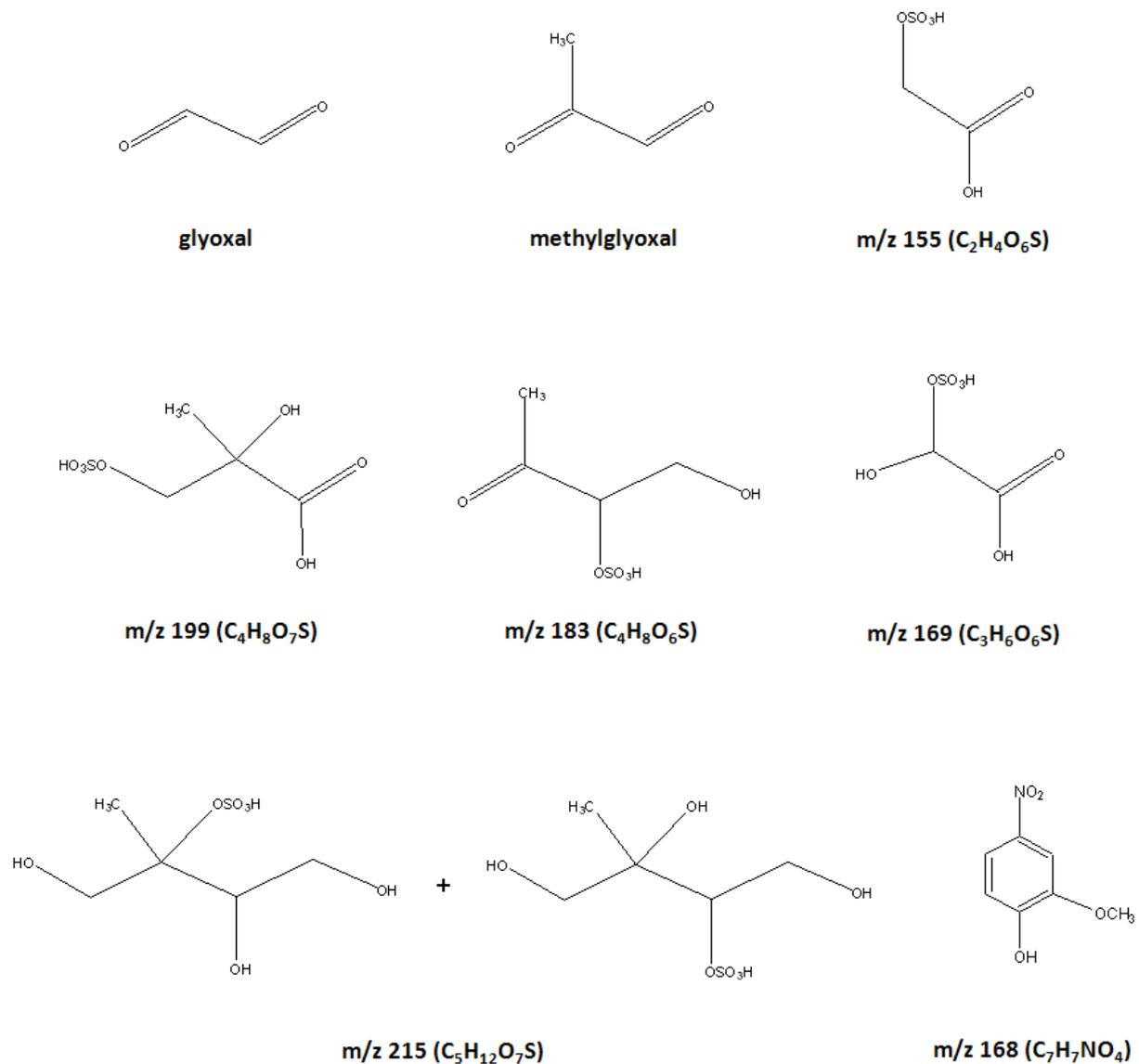


Figure 2.11. Glyoxal, methylglyoxal, organosulfates and a nitroaromatic compound of interest characterized during the PEGASOS campaign in San Pietro Capofiume during the summer 2013.

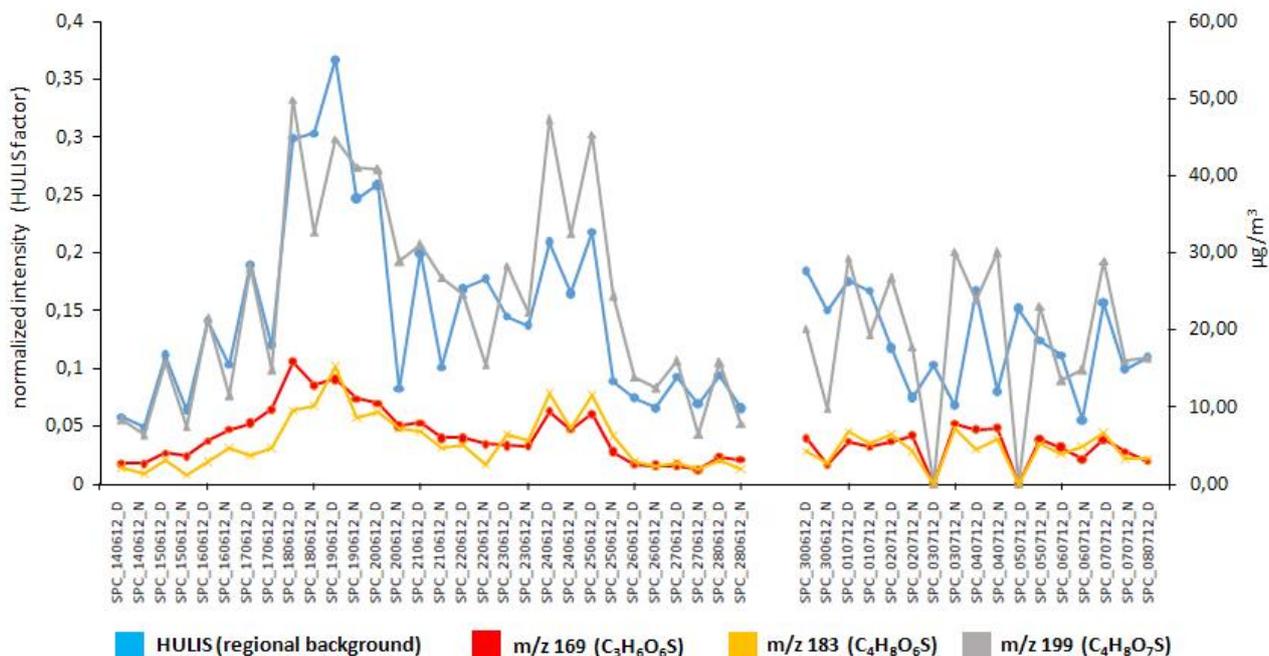


Figure 2.12. Time trends in concentrations of HULIS regional background and tracer of isoprene SOA: in San Pietro Capofiume during the PEGASOS campaign. The methylglyceric acid was analyzed by LC/MS by the Institute for Research on the Troposphere (TROPOS) in Leipzig.

The good correlation between the concentrations of some organosulfate tracers (Figure 2.12) and the time trend of the ¹H-NMR factor for HULIS (factor 2 + 4) supports a secondary origin for HULIS. It also indicates that biogenic sources provide a major contribution to polar organic compounds in the ambient aerosol in the Po Valley in summer conditions. The link between atmospheric HULIS and aged biogenic SOA is further explored in the Part II of this thesis.

2.2 PART II

CHARACTERIZING SOURCE FINGERPRINTS AND AGEING PROCESSES IN POTENTIAL AEROSOL MASS (PAM) SOA EXPERIMENTS USING ¹H-NMR ANALYSIS AND HPLC HULIS DETERMINATION

2.2.1 Overview

The source apportionment of oxygenated (water-soluble) organic compounds in ambient atmospheric particles through ¹H-NMR factor analysis techniques (see previous section) relies on the availability of comprehensive libraries of ¹H-NMR reference spectra, which allows the attribution of specific spectral profiles to distinct source types. However, the results obtained during the Po Valley experiments show that existing libraries are largely incomplete, especially for SOA classes of compounds. The reference spectra used for interpretation of ambient aerosol spectroscopic data were derived from laboratory experiments conducted in reaction chambers. These are confined artificial atmospheres of several m³ volume (10 to 250) where single (or a small number of) VOC species are injected and then oxidized by dark ozonolysis or photochemically to form SOA (Hallsquit et al., 2009). The main limitation of such laboratory setup is that aerosol particles cannot reside in the chamber forever as they deposit constantly to the walls. Therefore, SOA generation experiments in reaction chambers can be studied over time scales of a few hours up to 1 day as a maximum. However, submicron aerosol particles can accumulate in the real atmosphere for several days, hence being subjected to prolonged chemical ageing. Extending the capacity of laboratory setups to probe the chemical evolution of SOA over long time scales represents the main challenge of current laboratory research on secondary organic aerosols. During this thesis work, I contributed to the analysis of SOA samples produced by an apparatus alternative to reaction chambers, that is a flow tube reactor named "Potential Aerosol Mass (PAM)". The parent VOC is continuously injected inside the PAM and there exposed to an excess of oxidant (typically OH*). Very high oxidation rates can be reached, and the resulting SOA simulate the products of prolonged atmospheric ageing. The SOA samples were produced in the laboratories of the Davidovits research group at Boston College (<http://www.bc.edu/schools/cas/chemistry/people/faculty/davidovits.html>). I concentrated my research on the TOC, ¹H-NMR and HPLC analysis of SOA samples from isoprene oxidation. Subsequently, I took care of gathering the new experimental data and previous ones obtained at CNR-ISAC on α -pinene and naphthalene SOA and I elaborated them all together to investigate the similarities with the chemical composition of WSOC samples collected during the Po Valley summer campaign (PEGASOS experiment, see previous section). The results were collected into a paper which is currently under review on Atmospheric Chemistry and Physics ([83](http://www.atmos-chem-</p></div><div data-bbox=)

phys-discuss.net/acp-2017-91/). Since the manuscript provides all details of this research activity of my thesis, the description of Part II is provided as a copy of Zanca et al. (submitted to Atmos. Chem. Phys) as an addendum to this thesis (**Annex I**).

2.3 III PART

ORGANIC AEROSOL MASS SPECTROMETRIC MEASUREMENTS IN THE MEDITERRANEAN REGION

2.3.1 OVERVIEW

The Mediterranean Sea region — the largest of the semi-enclosed European seas — is surrounded by 22 countries, home to around 480 million people living across three continents. It is still one of the world's busiest shipping routes with about one-third of the world's total merchant shipping crossing the sea each year (<http://www.eea.europa.eu/soer-2015/countries/mediterranean>). The western Mediterranean basin is frequently exposed to high levels of air pollutants. This is due to both long-range transport from anthropized continental areas and to local sources in harbors and coastal cities. Moreover, the topography of the coasts and surrounding mountains favors the development of combined sea breeze-upslope winds with stratification of pollutants and subsidence over the coastal and marine areas during daytime in the summer (Lelieveld et al., 2002; Velchev et al., 2011). The area is influenced not only by long-range transport of continental aerosol from the north but also, due to its vicinity to North Africa, Saharan dust can frequently be observed (Kalivitis et al., 2007, <http://www.i-amica.it/i-amica/?p=4301>), making the Mediterranean Sea an area heavily impacted by aerosols. Another important source of pollution is the intensive ship traffic. The main trace gases emitted from ships are sulphur dioxide and nitrogen oxides, both precursors of secondary pollutants. NO_x-emissions from ships are projected to increase in European seas and could equal the land source by 2020, while for SO₂, a decrease in ship emissions is expected to take place in the next decade thanks to the new legislation introducing more stringent emission thresholds (Van Aardenne et al., 2013). First observations by Schembari et al. (2012) in the western Mediterranean basin provide evidence of a significant reduction of ambient SO₂ concentrations in concomitance with the adoption of the EU directive 2005/33/EC regulating the emissions of SO₂ from ships in EU harbors from January 2010. Sulfur compounds are also emitted in the atmosphere by natural sources. Marine phytoplankton produce the osmolyte dimethylsulphoniumpropionate, which undergoes enzymatic cleavage to form dimethyl sulphide (DMS). DMS is the dominant volatile Sulphur compound in ocean surface waters and is the most significant biological source of gaseous sulphur to the remote marine troposphere. After emission to the atmosphere, DMS is oxidized by the hydroxyl radical to form SO₂ and methane sulfonic acid (MSA) (Andreae et al., 1985).

The study of marine aerosols is also a major topic in the research on climate forcing. Given the very small albedo of sea surface at high solar elevation angles, the layering with scattering aerosol particles

can induce a significant reduction of the atmospheric radiative budget over tropical and subtropical marine areas. Moreover, marine aerosol can affect cloud formation and precipitation by altering the concentrations of cloud condensation nuclei (CCN) and ice nuclei (IN). Finally, the Mediterranean Sea region has been identified as one of the main **climate change hotspots** (i.e. one of the areas most responsive to climate change) due to water scarcity, concentration of economic activities in coastal areas, and reliance on climate-sensitive agriculture. Temperature IPCC projections show a probably increasing of 4-5 °C for the end of the century for some Mediterranean area (http://www.grida.no/publications/other/ipcc_tar/?src=/climate/ipcc_tar/wg1/index.htm; IPCC, 2013). For these reasons, sea areas like the Mediterranean, surrounded by important sources of aerosols, are object of international research programs on atmospheric chemistry – climate interactions (e.g., <http://charmex.lsce.ipsl.fr/>).

During my PhD, I was involved in two projects on Mediterranean aerosol research: “Air-Sea Lab”, and “Dual Use Vespucci”. The former was based on an anthropized coastal site, while the latter involved ship measurements both in harbors and off-shore:

- The project Air-Sea Lab (<http://www.isac.cnr.it/airsealab/>) that gathered several ISAC-CNR departments, aims to quantify the interplay between coastal air pollution and climate with particular focus on aerosols, clouds and near coastal boundary layer structure and dynamics, in contrasting degrees of pollution and maritime regimes. Near coast boundary layer characteristics are important for climate issues (due to the haze-cloud cooling effect) and for public health issues when air pollution (from the sea-surface, shipping and coastal industrial activity) is trapped in the boundary layer of densely populated areas.
- The project Dual Use Vespucci was set in the frame of a collaboration agreement between the CNR and Italian Navy. Aerosol and gas measurements have been carried out from 9th of May to 4th of July around the Italian coasts on Amerigo Vespucci vessel, the most famous Italian ship, during the “pre-campaign2016” for the 85th anniversary. Several ISAC groups and various on-line and off-line techniques were involved. The instrument were deployed onboard the Vespucci vessel which sailed along the coast and stopped at 11 Italian harbors (+ 1 Croatian), performing measurements in the Adriatic and Tyrrhenian seas for roughly 2 months (<https://www.cnr.it/en/navescuolavespucci-marinamilitare-cnrisc>). The scientific objectives of ISAC-CNR were contributing to filling the gap of atmospheric chemical observations in the Mediterranean basin and to gain more insight into atmospheric chemical characterization over SO₂ sources, sea spray - aerosol interactions, and anthropogenic aerosol contributes.

During both experiments, I contributed to the installation of the aerosol instrumentation, and, more importantly, I performed online aerosol chemical measurements using an Aerosol Chemical Speciation Monitor (ACSM) (see Introduction section). I joined the ship cruise in Messina, and performed measurements on board the Vespucci vessel across the Tyrrhenian Sea and docking in Trapani, Genova and La Spezia during a 3-weeks sailing campaign. I operated and checked all ISAC instruments deployed on the vessel: ACSM, Aethalometer, Thermo 49c (Ozone analyzer), OPC, Tecora Hi-vol (PM1 impactor).

The results provided new insights on the nature and composition of submicron aerosols in the Mediterranean with a focus on the sources and origin of particulate organic compounds.

2.3.2 EXPERIMENTAL

2.3.2.1 Sampling and measurements during Air-Sea Lab (April 2016)

The campaign was carried out at the Civitavecchia port and lasted for 3-weeks. The monitoring site was named “Aerolab”. Aerolab included several instruments including a black carbon (BC) monitor (Aethalometer AE33 Magee). After the calibration and in-situ checks, on-line measurements with an ACSM started from 7th to the 29th of April. All the collected data were analyzed afterwards at CNR-ISAC in Bologna, for statistical analysis and comparison with ancillary data from parallel aerosol monitors. In the Figure 2.13 a satellite view of the Civitavecchia port and surrounding area.



Figure 2.13. Satellite view (from Google Maps) of the Civitavecchia port and surrounding area. In the North-East of this map the coal power plant Torrevaldaliga Nord, in the middle-South of the port the cargo, cruises and car-ferry docks. The Aerolab is located in the center of the port, nearby principal docks.

2.3.2.2 Dual Use Vespucci (May - July 2016)

During the two-months ship campaign, in a joint experiment involving CNR-ISAC and the University of Bari, on-line chemical composition of the fine fraction of PM₁ was measured by ACSM on a half hourly basis. Other on-line techniques were deployed on Vespucci: an Aethalometer Magee E33 for the black carbon (BC) measurements, an “Ozono Tei 49c” for measurements of ozone, an Optical Particle Counter (OPC) for aerosol size distribution, and a Tecora Hi-vol (PM₁ impactor, 500l/min, 24h samples).

Figure 2.15 shows the ACSM installed below deck, in the vessel prow, and the Italian Navy Amerigo Vespucci vessel. Figure 2.16 reports the route of the Italian Navy during the *Pre campagna 2016*.



Figure 2.15. On the left the ACSM installed below deck, in the vessel prow, and on the right the Italian Navy Amerigo Vespucci vessel (picture at the port of Messina).

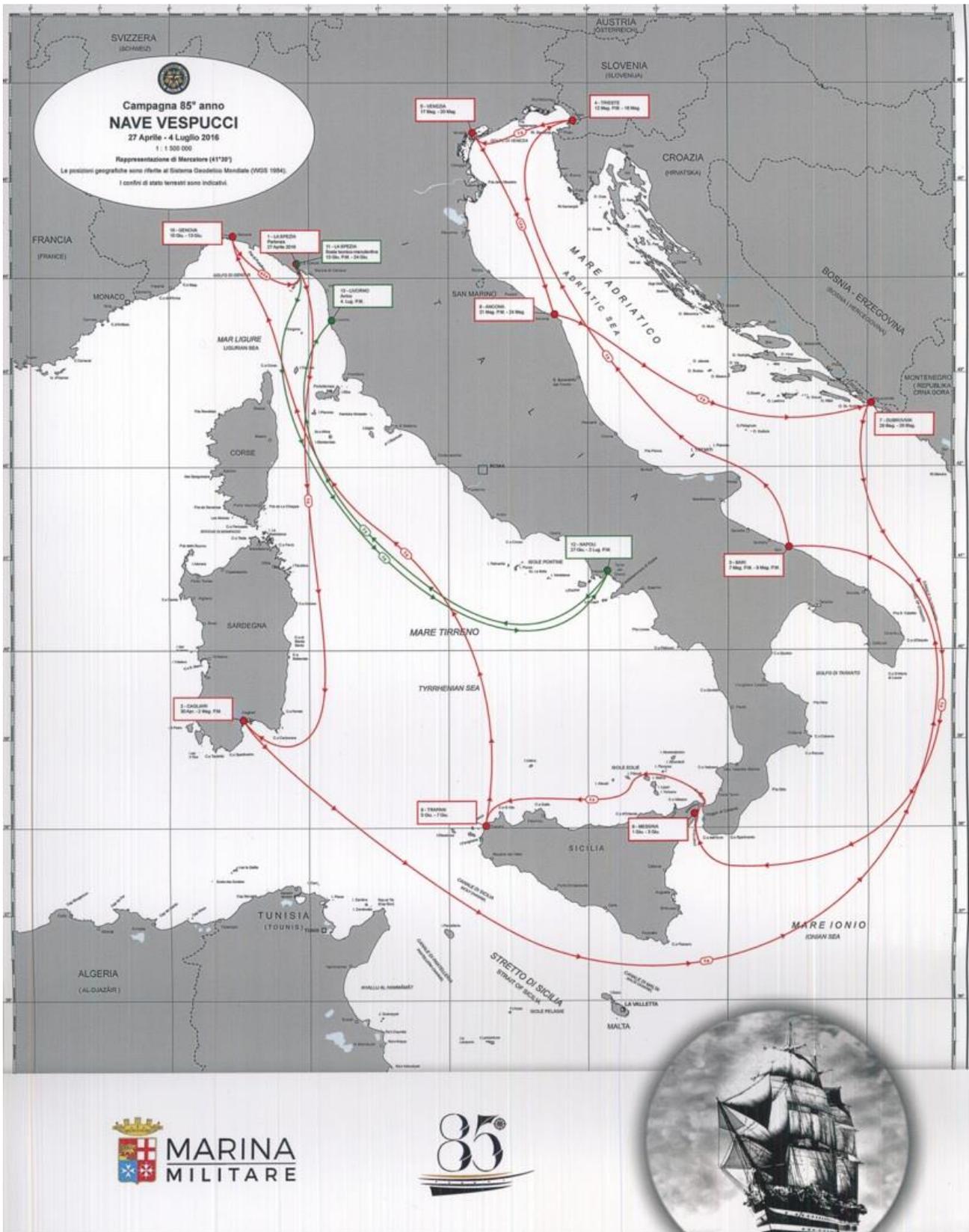


Figure 2.16. Map of Amerigo Vespucci cruise legs during the “Pre Campagna 2016” started the 27th of April from La Spezia and ended in Livorno the 4th of July. The ISAC-CNR instruments were installed in Bari port and operated till the end of the Pre Campagna 2016.

2.3.2.3 ACSM

The quadrupole-ACSM used for this study took part to the international intercomparison leaded by ACMCC, Aerodyne and ADDAIR in Paris in 2016 for the European ACTRIS program. All ACSM settings were dealt with Aerodyne team, to perform the optimize parameters, according to that intercomparison and to Aerodyne protocols. The aerodynamic lens system of each instrument was aligned according to the protocols described in AMS and ACSM previous publications (Jayne et al., 2000; Ng et al., 2011a) to ensure that the particle beam was well centered on the particle vaporizer and all voltages were tuned for best instrument performance and data quality before calibrating. Several further operations were performed on each ACSM before calibration and consisted in harmonizing software versions (data acquisition and processing), detector gain, and data acquisition parameters (scan rate, number, time duration and $m=z$ coverage for each scan).

During the campaign, Q-ACSMs were operated from mass-to-charge ($m=z$) 12–148 with a scan speed of 200 ms amu^{-1} and 28 cycles of ambient and filter scans (30 minutes per acquisition), collection efficiency (CE) = 0.5. The sampling time of all measurements presented here is expressed in coordinated universal time (UTC). The mass-to-charge calibration of the quadrupole was performed using two calibration points, the N_2 peak corresponding to the air-beam (AB) signal used to normalize the measurements with respect to drifts in instrument measurement sensitivity and sampling flow rate, and the internal naphthalene ($\text{C}_{10}\text{H}_8^+$) standard peak until they are centered at their nominal mass values ($m=z$ 28 and 128, respectively) during $m=z$ scans. These signals are also used to determine the relative ion transmission (RIT) efficiency (Crenn et al., 2015).

Multilinear engine (ME-2) algorithm (Paatero, 1999) implemented within the new toolkit SoFi (Source Finder) developed by Canonaco et al. (2013) at Paul Scherrer Institute, is used for the organic aerosol source apportionment from ACSM data (Canonaco et al., 2013; Ulbrich et al. 2009).

The analysis and input error matrix calculations are performed following the procedures described in Canonaco et al. (2013). Several criteria are employed to determine the optimum number of factors: the scaled residuals are examined carefully, the mass fractions and diurnal cycles of each factor are evaluated and compared, time series are compared to external markers, and factor spectra are compared to reference mass spectra from the AMS MS database (Ulbrich et al. 2009). A full description of factor analysis methods applied to atmospheric datasets is reported by Canonaco et al. (2013).

2.3.2.4 Back-trajectory calculation

Air mass back trajectories are a useful tool when studying the aerosol composition as a function of the air mass history. Back trajectories for were calculated by the HYSPLIT model (HYbrid Single-

Particle Lagrangian Integrated Trajectory, version 4) (Stein et al.; 2015; Rolph, 2017) (https://ready.arl.noaa.gov/HYSPLIT_traj.php). A full description of HYSPLIT procedure applied to atmospheric datasets is reported by Stein et al. (2015).

In addition, Civitavecchia polar plots (Figure 2.20) for the AIR-SEA Lab campaign are on courtesy of Gian Paolo Gobbi and Luca Di Liberto (CNR-ISAC, Rome).

2.3.2.5 Ion chromatography

A high-volume sampler (Tecora Echo Hivol – equipped with Digitel PM1) operating at a constant nominal flow of 500 l/min was instead employed at on Vespucci vessel to collect PM1 on 15 cm quartz-fiber filters (Whatman). Two ion chromatographs (Dionex ICS_2000) were used to determine the water-soluble ionic compounds in filter samples of high-volume sampler. The procedure is reported in the section *2.1.2.5 Ion Chromatography*.

2.3.3 RESULTS

2.3.3.1 ACSM measurements at the harbor of Civitavecchia

The harbor of Civitavecchia, being the Port of Rome (<http://www.civitavecchiaport.org/>), hosts a significant traffic of cruises, ferries and cargos. An active coal power plant, “Torrevaldaliga Nord” is located nearby the port area (https://it.wikipedia.org/wiki/Centrale_termoelettrica_di_Torrevaldaliga_Nord) and a diesel tank engine operates in the port for vehicles transportation, in addition to common anthropogenic sources for urban sites, as vehicle traffic and heating systems.

An evaluation of PM1 chemical composition was obtained by examining the ACSM data (organics, sulfate, nitrate, ammonium, chloride) together with black carbon (BC) concentrations estimated by the Aethalometer. The BC concentration added up to the concentrations of non-refractory compounds determined by ACSM accounts for the majority of the of PM1 mass. Figure 2.17 presents the time trend of the main sub-micron aerosol components measured during the campaign by ACSM. Sub-micron aerosol at the Civitavecchia harbor was mainly composed of organic compounds (42%), sulfate (20%) and BC (19%), followed by ammonium (7%), nitrate (5%) and chloride (1%).

The organic fraction was apportioned into source contributions by Positive Matrix Factorization (PMF). The organic aerosol components from PMF analysis were identified by their mass spectra, in comparison with literature data (Crippa et al., 2013; Ulbrich et al., 2009), and by analyzing their diurnal cycles. A five-factor solution was selected as the most reliable, with organic aerosol apportioned into the following components. Oxidized organic aerosol (OOA) represents the majority

of PM1 analyzed, about the 51%, and comprises the products of gas-to-particle conversion processes and organic aerosol ageing. Hydrocarbon-like organic aerosol (HOA), representative of traffic emission and fossil fuel combustion in general, is about 20%, biomass burning organic aerosol (BBOA) is 7%, cooking organic aerosol (COA), associated to food preparation activities, 10%. The rest of organic aerosol mass was attributed to a fraction similar to HOA but with higher mass fragments, named hHOA (heavy HOA).

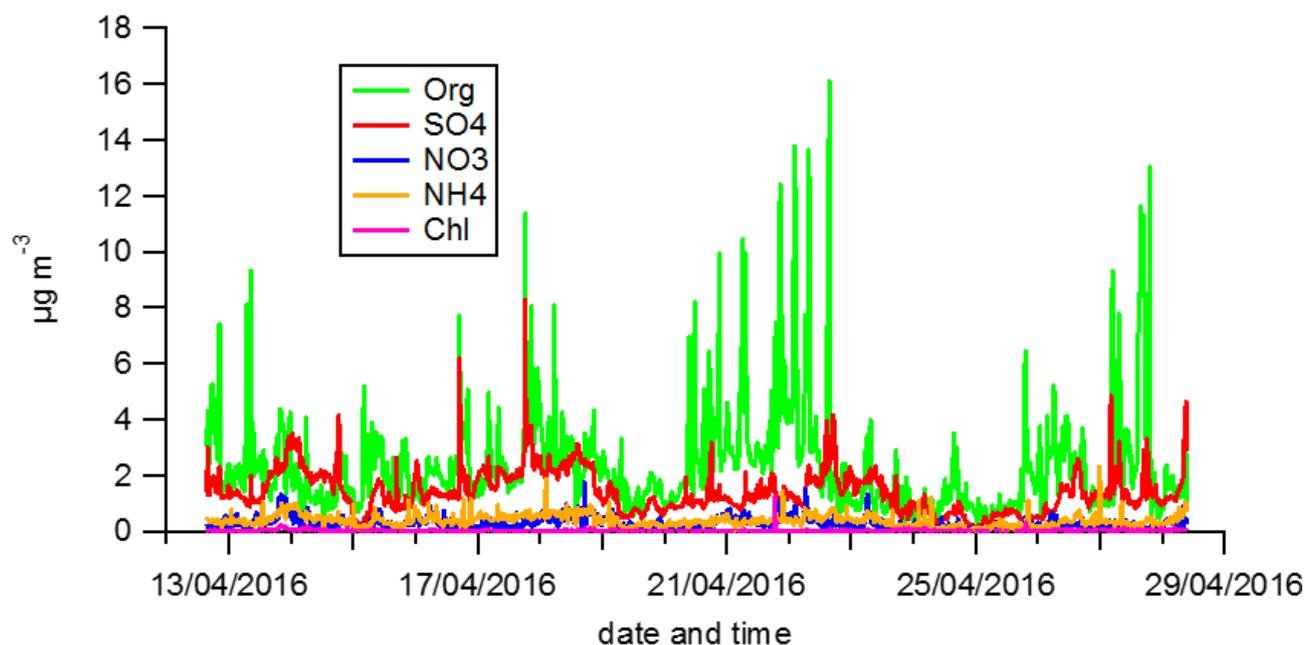


Figure 2.17. Time trend of principal organic components of PM1 measured by ACSM in Civitavecchia port during the Air-Sea Lab campaign. (The nomenclature *Org*, *SO4*, *NO3*, *NH4* and *Chl* and related colors are currently in use and adopted by the AMS users community, even if abbreviations are not “chemically” correct <http://www.aerodyne.com/products/aerosol-mass-spectrometers>).

The ACSM results showed that ammonium nitrate and several of the organic fractions identified by positive matrix factorization (PMF) followed diurnal variations, while ammonium sulfate and the most oxidized fraction of particulate organic compounds (OOA) showed no variations, pointing to components well mixed in the lower troposphere and therefore not linked to local sources in Civitavecchia port. Average contributions of the main aerosol species and PMF organic fractions are reported below in Figure 2.18.

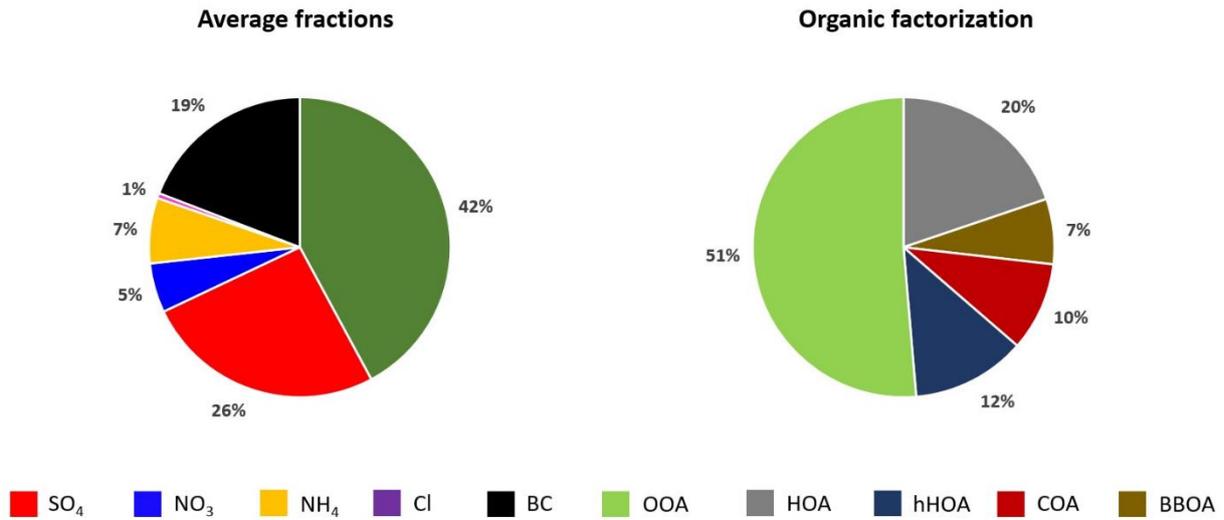
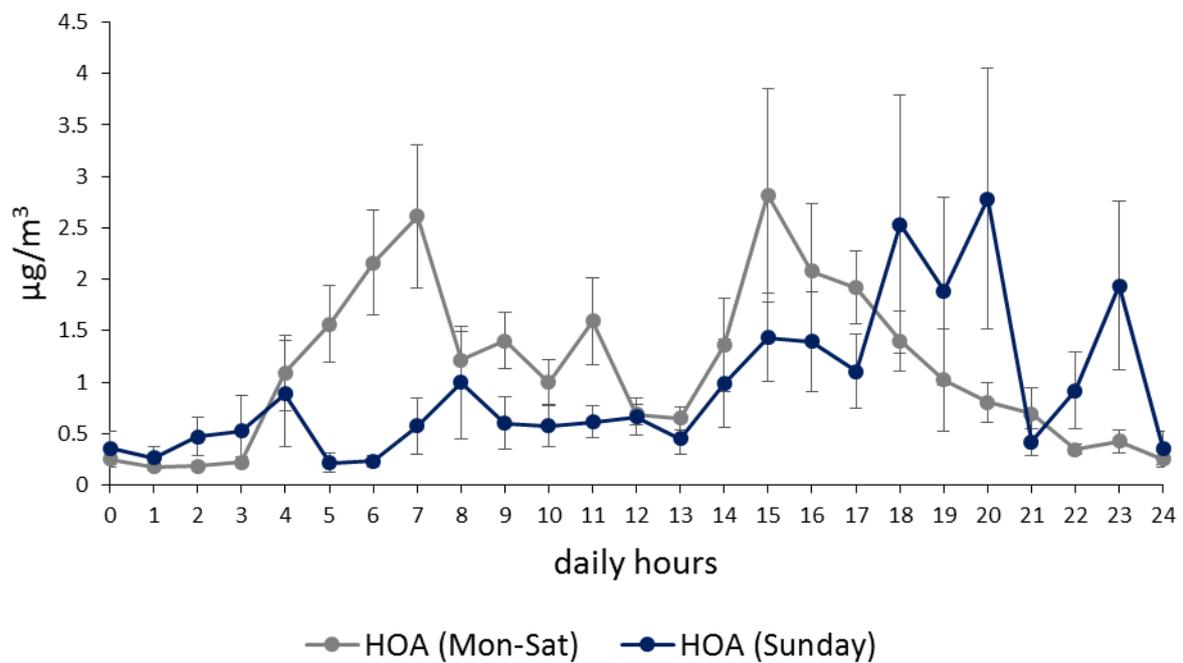


Figure 2.18. Average PM composition during the Civitavecchia AIR-SEA Lab campaign. Apportioned PM mass into organic matter, sulfate, nitrate, ammonium, chloride, black carbon is reported in the pie chart on the left. Distribution of ACSM organic fractions (OOA, HOA, hHOA, COA, BBOA) on the right chart.



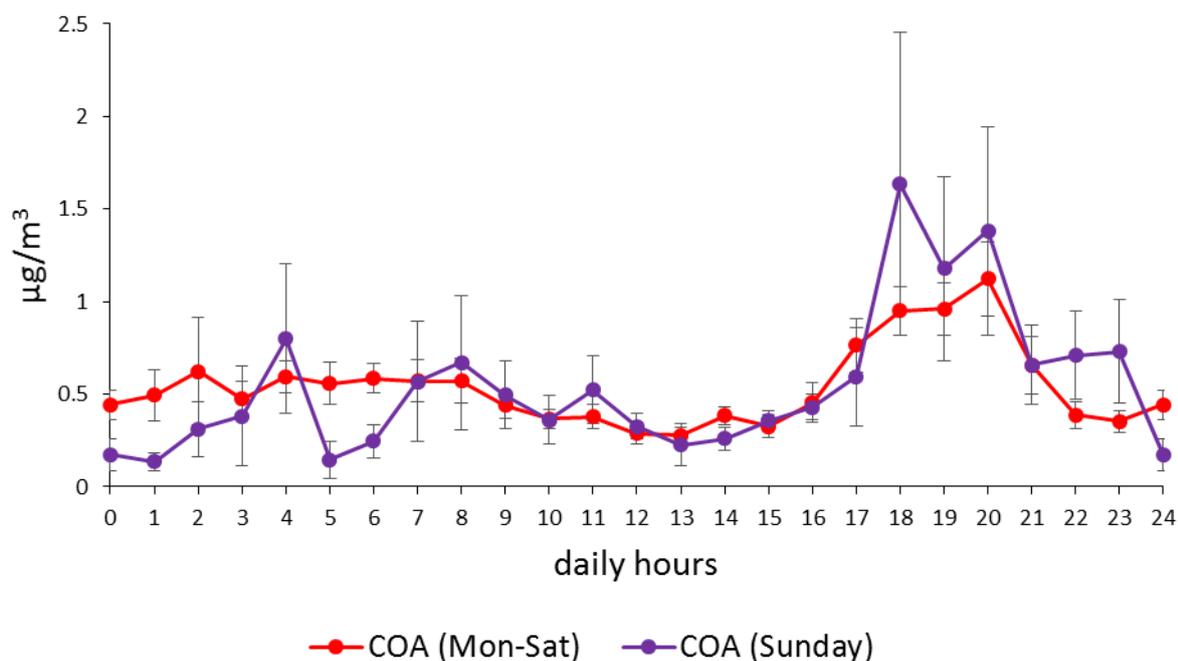


Figure 2.19. Daily trend of 2 ACSM factors during the week (Monday to Saturday) and on Sunday. HOA (Hydrocarbon-like Organic Aerosol): primary from fossil fuel combustion (traffic, ships...) and COA (Cooking Organic Aerosol). Time recorded was in UTC (Coordinated Universal Time) (local time: UTC+2).

The blue line in the Figure 2.19 shows the HOA daily trend, with peaks during early morning (5-8am UTC+2) and in the afternoon (2-5pm UTC+2), which coincide with the morning and afternoon traffic rush hours. During weekdays, traffic activities are higher than on Sunday: traffic related to workers, loading and unloading of vehicles from cargos and car ferries, arrival/departure of boats with correlated loading/unloading activities. On the other hand, port activities are reduced at a minimum on Sunday, and the HOA factor contribute is lower, with only the afternoon rush hour evident, likely related to the city traffic.

Crossing chemical data with wind speed and direction, a polar distribution of concentrations was generated (Figure 2.20) that broadly identifies the spatial origin of the isolated organic aerosol components. The major contribution to HOA comes from the direction of the docks, where cruises and car ferries operate, even though a contribution from emissions in the city area is also likely, particularly during the day.

In the Figure 2.19 the daily trend of COA factor, “Cooking Organic Aerosol”, shows similar patterns between weekdays and the weekend. The highest values are detected during the evening. The polar

plots (Fig. 2.20) for COA suggest that the most probable sources are, cooking activities onboard cruise ships anchored in the Civitavecchia port or in nearby commercial activities.

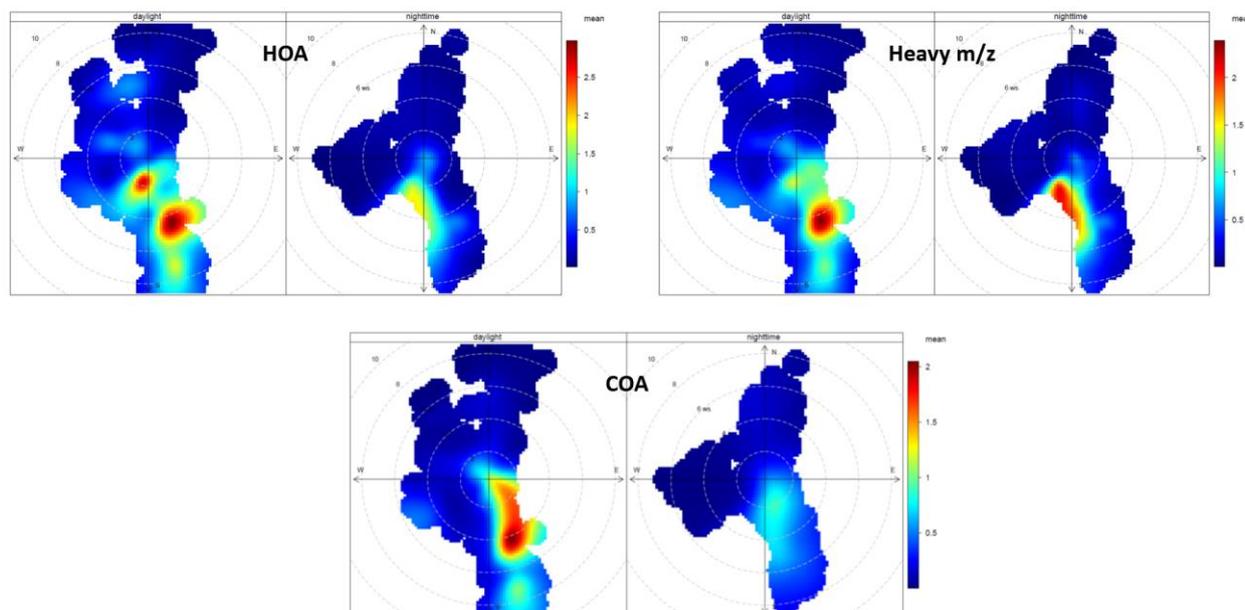


Figure 2.20. Polar plots for HOA, heavy m/z and COA sources profiles depending on wind data of the sampling site. The intersection of the axes indicates the Aerolab. The reddish is the area, the most probable source is located there, calculated by wind data and back trajectories.

Finally, the diurnal trend of hHOA is very similar to that of HOA pointing to similar sources. The mass fragments dominant in the hHOA spectrum (m/z 63-65, 74-76, 91, 95, 97, 105, ...) are consistent with the fragmentation of polysubstituted polycyclic aromatic hydrocarbons PAHs in electron impact mass spectrometers, according to recent literature (Bruns et al., 2015; Dzepina et al., 2007; Herring et al., 2015). This suggests that this component could represent a second type of primary organic aerosol from combustion, with a potentially high PAHs contribution, maybe related to combustion of heavier oils than common car fuels (e.g., ship fuel). In summary, all HOA, hHOA and COA factors could be related to sources located nearby the measurement site. According to the examination of the ACSM factor contributions along with wind direction data, the most likely sources are the activities conducted at the ferry docks (ferry operations, load and unload of goods, traffic of boarded vehicles).

2.3.3.2 Ship measurements with an ACSM onboard the Vespucci navy vessel – Dual Use Vespucci

The study has provided information about the sources of aerosol collected in open sea and in several ports during the campaign in the Mediterranean around Italian coasts. Source apportionment was conducted using chemical characterization, correlation analysis and PMF receptor modelling. A main scope of the analysis was to quantify and characterize background aerosol in the Mediterranean basin, i.e., the concentration and composition of aerosols outside the direct influence of plumes of aerosol transported from the continent.

The time trend of ACSM dataset (plus BC mass concentration derived from the aethalometer) is reported in Figure 2.21. The measurements took place mainly in harbor areas (Bari, Trieste, Venezia and Ancora) until the 15th of May, with only a small transect in the Adriatic Sea. During the second part of the campaign, measurements were performed in harbors (Messina, Trapani, Genova, La Spezia and Napoli) as well as offshore Sicily and across the Tyrrhenian and Ligurian seas.

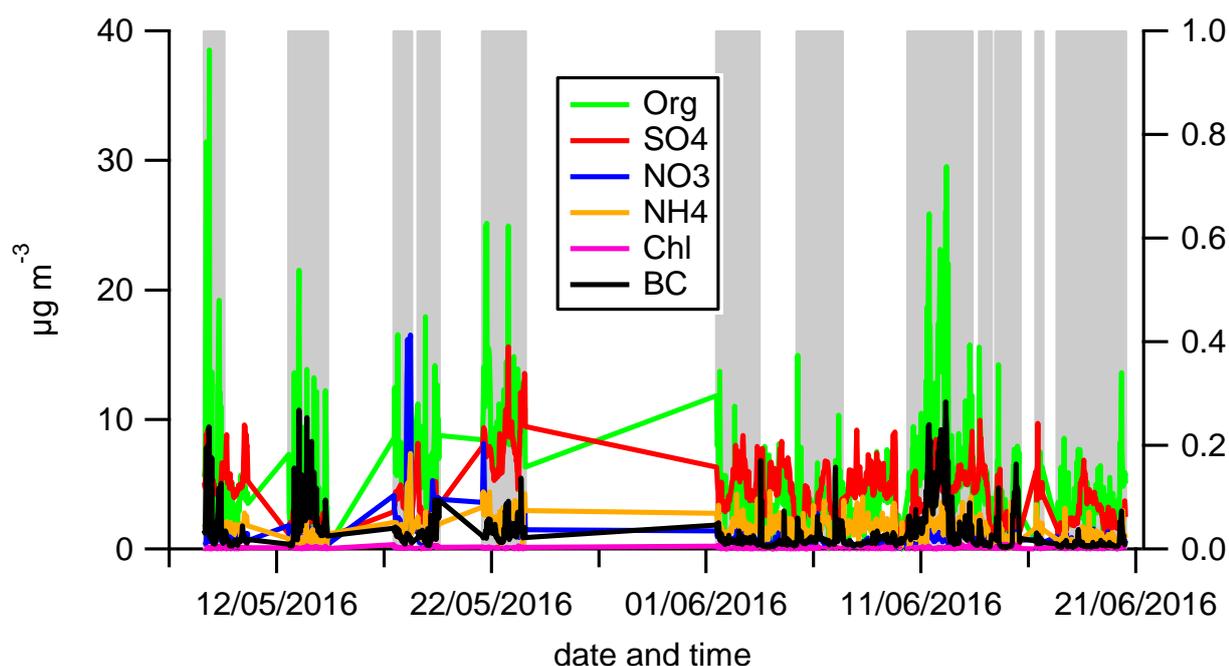


Figure 2.21. Time trend of ACSM measurements added with BC ones by aethalometer during the Dual Use Vespucci campaign. Port measurements are reported in shaded area.

The measurements performed during the open sea transects were particularly useful in attempting a characterization of background aerosol particles in the Mediterranean. To this aim, all possible sources of contaminations must be subtracted. The same ship was a source of contaminants, especially for organic aerosols. The ship contaminations in the organic signal were then isolated by factor

analysis. Two main local contamination sources were identified: COA (cooking organic aerosol) and CSOA (cigarette smoke organic aerosol) (Crippa et al., 2013). The contribution of COA to organic aerosol mass can be clearly identified by its diurnal trend (Figure 2.22) showing a pronounced peak between 8 am and 10 am UTC time (which corresponds to 10-12 am local time). A second peak can be seen around 5 pm (UTC time, hence 7 pm local time). The cigarette smoke factor, CSOA, was identified by comparison with reference spectra in the literature (Struckmeier et al., 2016). The location of the ACSM inlet on the ship prow, close to kitchen vents and accessed by the crew, explains why COA and CSOA were actively samples by the ACSM. These sources of contamination were removed from the organic signal acquired by the ACSM and the filtered data are summarized below. According to PMF results, organic aerosol measured during the campaign (upon correction for contaminations) could be apportioned into two main factors: HOA and OOA. HOA (hydrocarbon like organic aerosol) is a primary fraction of organic aerosol resulting from the combustion of fossil fuels (He et al., 2011; Ulbrich et al., 2009). OOA (oxygenated organic aerosol) instead traces secondary organic compounds (SOA) (Ulbrich et al., 2009). HOA accounts for 21% of the total organic PM1 and OOA for 79%, when considering the whole dataset including port and open sea measurements.

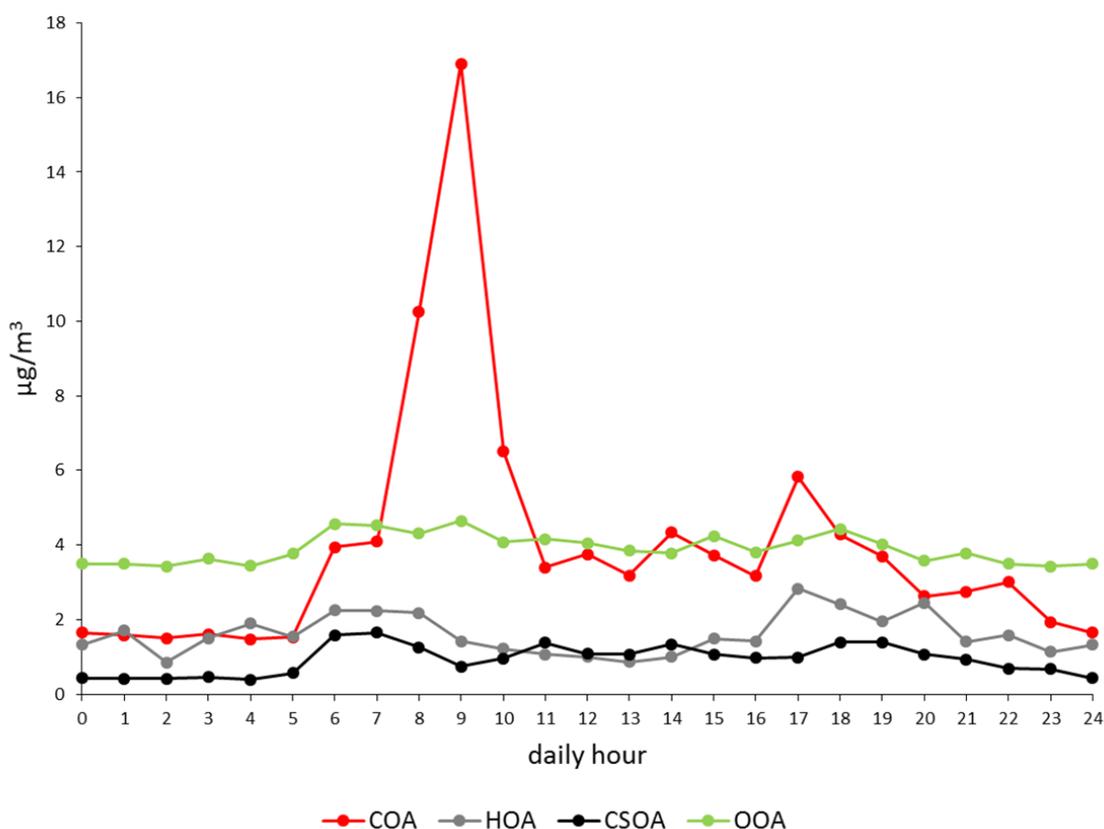


Figure 2.22. Daily trend of ACSM factors on Vaspucchi vessel. COA = cooking organic aerosol and CSOA = cigarette smoke organic aerosol were identified by literature reference data. Time is in UTC.

The average aerosol chemical composition for all cruise transects and port measurements is represented by pie charts in Fig. 2.23. Sulfate, nitrate, ammonium, chloride species from direct ACSM measurements and PMF organic factors HOA (hydrocarbon-like organic aerosol) and OOA (oxidized organic aerosol) were integrated with BC (black carbon) from aethalometer measurements to provide a comprehensive picture of sub-micron aerosol composition. Clearly, sulfate is the dominant chemical species. The sulfate and ammonium contributions are higher in open sea, whereas nitrate increases in port area, in agreement for its anthropogenic nature (whereas sulfate is contributed by biogenic sources from DMS oxidation).

The OOA concentrations are similar for all the ship transects, and also similar between harbors and open sea areas. These observations indicate that SOA in the central Mediterranean are formed at regional scale and the contributions from local sources at coastal sites is insignificant. The primary component HOA, instead, mostly influenced by fossil fuel combustion sources, is higher in the ports, therefore significantly impacted by local sources. The same conclusion can be given for the behavior of black carbon. These findings are in agreement with the observations performed during the Air-Sea Lab campaign in Civitavecchia.

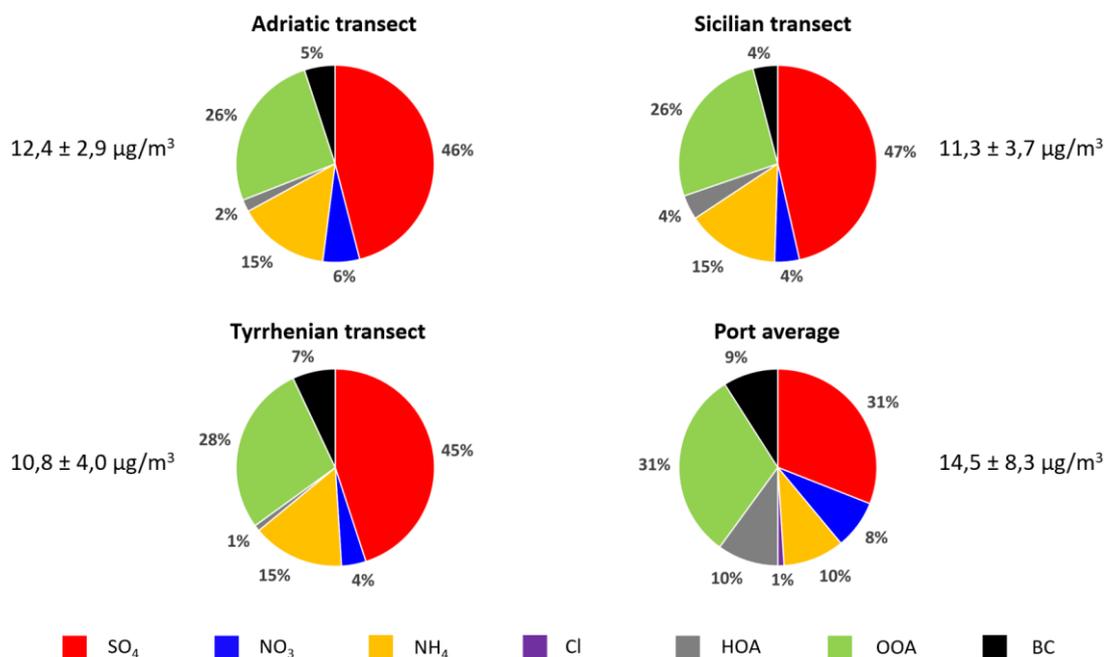


Figure 2.23. Pie charts of chemical composition and PMF factors for all cruise transects and the port average in percentage. Sulfate, nitrate, ammonium, chloride and PMF factors HOA, OOA and BC.

The difference between port and open sea concentrations is mainly driven by primary species (HOA, BC), but also nitrate aerosols (Figure 2.24). On average, PM1 mass is only 22% lower over the open sea than in ports. This means that the Mediterranean sea is characterized by a high background aerosol concentration deriving from diffuse anthropogenic (but also biogenic) sources in and around the basin.

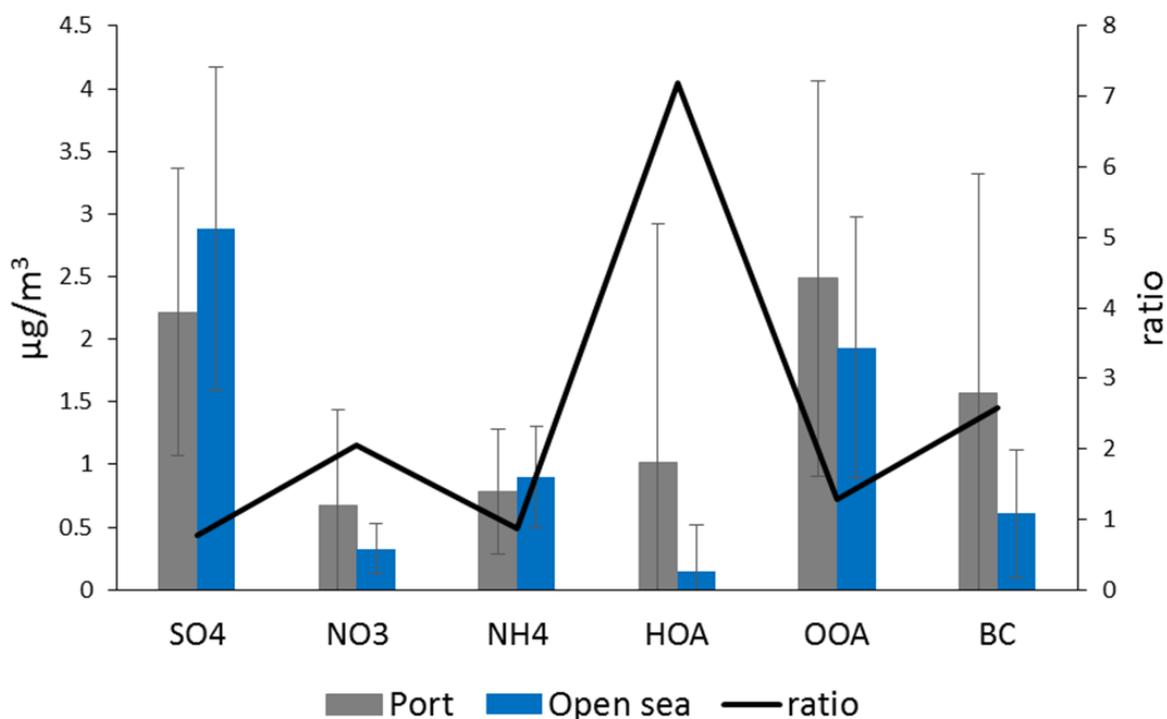


Figure 2.24. Diagram of chemical composition and PMF factors for all cruise transects and the port average with relative ratio. Principal chemical species: sulfate, nitrate, ammonium, and PMF factors: HOA, OOA and BC.

An estimation of the HOA/BC and HOA/OOA ratios is reported in Table 2.5. These ratios are indicative of the organic aerosol atmospheric age: higher HOA/BC is associated with fresher aerosol, observed closer to primary sources. The same for the HOA/OOA ratio. Adriatic and Tyrrhenian transects show lower values for both ratios compared to the Sicilian transect. The Sicilian route was characterized by ship traffic during the analysis at the beginning of June. As expected, HOA/BC and HOA/OOA ratios are much higher for the port average, where measurements were performed very close to intense primary sources. The Tyrrhenian transect shows the lowest ratios, in agreement with the back-trajectory analysis (Figure 2.25). Figure 2.25 shows that air masses sampled during the

Adriatic transect passed over the Italian peninsula just before reaching the open sea, enriching in primary species (like HOA and BC). Over the Tyrrhenian Sea, the circulation from West allowed the sampling of air masses that have traveled for more time over the open sea before being sampled, therefore with a lower contribution of primary anthropogenic sources from the continent. Furthermore, the synoptic circulation during the Tyrrhenian transect favored stagnation, which facilitates organic aerosol atmospheric processing, which lead to enhanced HOA depletion and OOA formation.

	Adriatic Sea	Sicilian Sea	Tyrrhenian Sea	Port average
HOA / BC	0,25	0,69	0,10	0,77
HOA / OOA	0,10	0,19	0,04	0,57

Table 2.5. Rates of HOA/BC and HOA/OOA for all open sea transects and the port average.

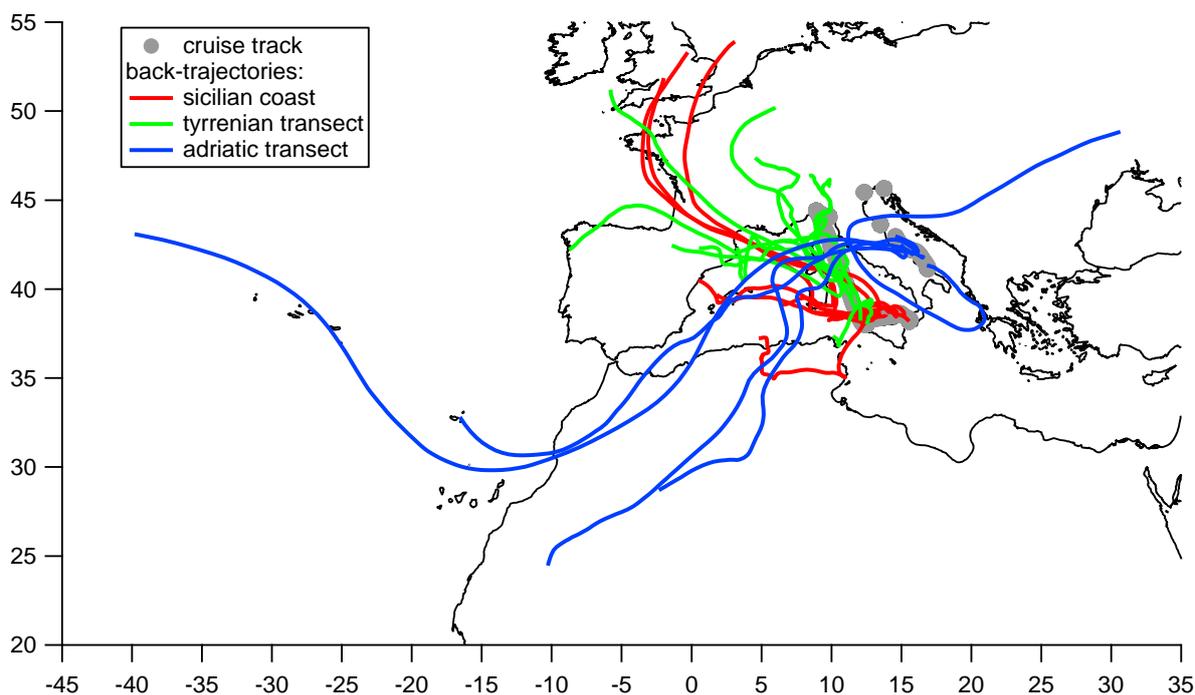


Figure 2.25. Wind masses back trajectories map of the “Pre campagna 2016”. (http://www.arl.noaa.gov/HYSPLIT_info.php)

Interestingly, higher average concentrations of sulfate were observed over the open sea than in ports. The difference between open sea and port measurements is about 20% ($2.42 \mu\text{g m}^{-3}$ vs $1.95 \mu\text{g m}^{-3}$) suggesting an open sea source of sulfate. This source may be from ship emissions or biogenic

emissions. Recent researches estimate the biogenic sulfate contribution to be $35\pm 5\%$ (Bove et al., 2016) and 26% (Schembari et al., 2012) during the summer season in the central and western Mediterranean sea. Based on the temperature dependent ratio between biogenic sulfate and MSA observed by Bates et al. (1992) and on the concentrations of sulfate and MSA from our offline analyses, estimated biogenic sulfate contribution during the Vespucci cruise is 20-30% of the total sulfate (with average air temperatures during the campaign of 17-19°C). These preliminary findings suggest that the excess of sulfate aerosols in open sea areas with respect to the coasts is likely of biogenic origin more than from ship emissions.

3. FINAL REMARKS

Anthropogenic atmospheric aerosols impact air quality and exert a forcing on the climate system. My research work has implications for both environmental challenges.

Efficient control of air quality and related health effects requires a comprehensive understanding of the identity, sources, atmospheric interactions, and sinks of hazardous pollutants. In this context, my doctoral work and this thesis contribute to: a) discriminate the contributions of specific pollution sources to ambient PM₁ levels using chemometric techniques; and to b) characterize the formation of biogenic secondary organic aerosols in laboratory experiments. The scientific findings discussed in the present thesis contribute to the body of knowledge on atmospheric composition emerging from current European research, upon which the evaluation of new regulatory actions for air quality control can be undertaken.

In respect to the climate impacts, it is worth reminding that the concept of climate forcing requires an assessment of the anthropogenic contribution to climate-forcing agents with respect to the natural background. My doctoral work and thesis present original aerosol source apportionment data, and contribute to the development of experimental techniques aimed to assess the anthropogenic vs. natural fractions of atmospheric aerosol particles. Specifically, the aerosol measurements and source apportionment studies performed during the second part of my thesis at coastal stations and during a research cruise provide new data on aerosol sources and composition at a major climate hotspot, the Mediterranean basin.

Overall, the spectroscopic methods employed in this study, ACSM and ¹H-NMR (the latter often assisted by chromatographic methods), proved to be able to overcome the main drawbacks of the methodologies relying solely on molecular tracer analysis, and could be profitably used for the identification of the primary and secondary fractions of organic PM (POA and SOA). In particular, during the ship campaign and the measurements in harbor areas, the ACSM observations were able to distinguish the contribution of local pollution sources to organic aerosols (mainly POA) from the background PM concentrations (rich of SOA) which are virtually constant between coastal and off-shore areas. Also the ¹H-NMR analysis carried out on the Po Valley samples were able to discriminate diverse contributions to oxygenated organic aerosols concentrations encompassing biomass burning POA, and various SOA types. The interpretation of the ¹H-NMR SOA factor profiles, however, is dependent on the availability of reference spectra libraries, which in turn must be provided by dedicated laboratory experiments, but are currently incomplete. The relatively short residence time of SOA in traditional reaction chamber experiments poses limits to the ability of laboratory experiments to simulate the chemical ageing of SOA in the atmosphere. However, the new findings

based on the employ of flow tube reactors (“potential aerosol mass”, PAM) proved to be able to reproduce SOA with spectral fingerprints overlapping those of ambient aged OA particles, typically associated to the so-called “humic-like substances” (HULIS) which account for the majority of SOA in continental rural areas in summertime.

In conclusion, my doctoral work provides examples of the usefulness of a combination of multiple chemical methods and techniques for addressing source apportionment problems during field and laboratory experiments. At the moment, none of the individual analytical techniques possesses all requirements for organic source apportionment, accounting for both primary and secondary sources. Nonetheless, suitable combinations of on-line and off-line techniques, laboratory experiments and meteorological datasets, allow to achieve a significant amount of information on particulate matter source apportionment. Expertise in analytical techniques and team working are of paramount importance for deeper researches on the big topic of air pollution and climate change.

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LIST OF FREQUENTLY USED ABBREVIATIONS

¹H-NMR = Proton-Nuclear Magnetic Resonance Spectroscopy
AEC = Anion-Exchange Chromatography
ACSM = Aerosol Chemical Speciation Monitor
AMS = Aerosol Mass Spectrometer
BB = Biomass Burning
BBOA = Biomass Burning Organic Aerosol
BB-POA = Biomass Burning – Primary Organic Aerosol
BB-SOA = Biomass Burning – Secondary Organic Aerosol
BB-SOA_Aq = Biomass Burning – Secondary Organic Aerosol _ Aqueous phase
BB-SOA_not-aq = Biomass Burning – Secondary Organic Aerosol _ not-aqueous phase
nonBB-SOA = non Biomass Burning – Secondary Organic Aerosol
BC = Black Carbon
CCN = Cloud Condensation Nuclei
COA = Cooking Organic Aerosol
CSOA = Cigarette Smoke Organic Aerosol
Da = Aerodynamic Particle diameter
DEA = Diethylamine
DMS = dimethyl sulphide
DMPS = Differential Mobility Particle Sizer
EC = Elemental Carbon
FA = Factor Analysis
FTIR = Fourier Transform Infrared spectroscopy
GC/MS = Gas Chromatography coupled with Mass Spectroscopy
hHOA = heavy Hydrocarbon-ike Organic Aerosol
HMSA = Hydroxy-MethaneSulfonic Acid
HOA = Hydrocarbon-like Organic Aerosol
HPLC = High Performance Liquid Chromatography
HULIS = Humic-Like Substances
IC = Ion Chromatography
IN = Ice Nuclei
IVOC = Intermediate Volatile Organic Compound
IPCC = Intergovernmental Panel On Climate Change; <http://www.ipcc.ch/>

LC/MS = Liquid Chromatography coupled with Mass Spectroscopy
MCR-ALS = Multivariate Curve Resolution-Alternating Least Squares
MMA = Monomethylamine
MSA = MethaneSulfonic Acid
MW = Molecular Weight
m/z = mass to charge ratio
OA = Organic Aerosol
OM = Organic Matter
OOA = Oxygenated (or Oxidized) Organic Aerosol
PAD = Pulsed Amperometric Detection
PAHs = Polycyclic Aromatic Hydrocarbons
PCA = Principal Component Analysis
PEGASOS = Pan-European Gas-AeroSOI-climate interaction Study
PILS = Particle Into Liquid Sampler
PM = Particulate Matter
PMF = Positive Matrix Factorization
POA = Primary Organic Aerosol
SMPS = Scanning Mobility Particle Sizer
SA = Source Apportionment
SOA = Secondary Organic Aerosol
SPC = San Pietro Capofiume
SV-OOA = semi-volatile OOA
TC = Total Carbon
TOC = Total Organic Carbon
TD-PTR-MS = Thermo-Desorption Proton-Transfer-Reaction Mass Spectrometer
TMA = Trimethylamine
TMCS = trimethylchlorosilane (GC/MS internal standard)
TOC = Total Organic Carbon
TSP-d₄ = sodium 3-(trimethylsilyl)-2,2,3,3-d₄-proponiate (NMR internal standard)
VOC = Volatile Organic Compound
WSOC = Water Soluble Organic Carbon

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ANNEX 1

Characterizing source fingerprints and ageing processes in laboratory-generated secondary organic aerosols using proton-nuclear magnetic resonance (¹H-NMR) analysis and HPLC HULIS determination.

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Abstract. The study of secondary organic aerosol (SOA) in laboratory settings has greatly increased our knowledge of the diverse chemical processes and environmental conditions responsible for the formation of particulate matter starting from biogenic and anthropogenic volatile compounds. However, characteristics of the different experimental setups and the way they impact the composition and the timescale of formation of SOA are still subject to debate. In this study, SOA samples were generated using a Potential Aerosol Mass (PAM) oxidation flow reactor using α -pinene, naphthalene and isoprene as precursors. The PAM reactor facilitated exploration of SOA composition over atmospherically-relevant photochemical aging time scales that are unattainable in environmental chambers. The SOA samples were analyzed using two state-of-the-art analytical techniques for SOA characterization - proton nuclear magnetic resonance (¹H-NMR) spectroscopy and HPLC determination of humic-like substances (HULIS). Results were compared with previous Aerodyne aerosol mass spectrometer (AMS) measurements. The combined ¹H-NMR, HPLC, and AMS datasets show that the composition of the studied SOA systems tend to converge to highly oxidized organic compounds upon prolonged OH exposures. Further, our ¹H-NMR findings show that only α -pinene SOA acquire spectroscopic features comparable to those of ambient OA when exposed to at least 1×10^{12} molec OH /cm³*s OH exposure, or multiple days of equivalent atmospheric OH oxidation. Over multiple days of equivalent atmospheric OH exposure, the formation of HULIS

is observed in both α -pinene SOA (maximum yield = 16%) and in naphthalene SOA (maximum yield = 30%), providing evidence of the formation of humic-like polycarboxylic acids in unseeded SOA.

1 Introduction

Organic aerosol (OA) constitutes a large proportion of ambient particulate matter, affecting the Earth's radiation balance, cloud formation and human health (Hallquist et al., 2009). Understanding and simulating the concentration and composition of OA particles is one of the major challenges of modern atmospheric chemistry. In the mid 2000's, the discovery of a dominant fraction of oxidized organic compounds over primary organic compounds outside urban areas (Zhang et al., 2007; Jimenez et al., 2009), together with the understanding that the ambient organic aerosol concentrations were systematically under-predicted by existing chemical transport models (Heald et al., 2005), led to a reevaluation of the treatment of secondary organic aerosol (SOA) formation processes in chemistry and climate models. Since the model-measurement gap is mostly overcome by subjecting the particles to "oxidative aging", understanding the nature of ageing processes has become a primary objective of new generation SOA studies. Experimental findings showing the existence of highly-oxidized SOA molecular tracers with a high oxygen-to-carbon (O/C) ratio (Szmigielski et al., 2007) and molecular structures that are chemically distinct from 1st and 2nd generation oxidation products of the same precursors (Jenkin et al., 2000) provided indirect confirmation of still unknown chemical processes forming highly oxidized, low-volatility compounds.

The first formulations of SOA ageing into models were based on the chemistry of saturated hydrocarbon oxidation by OH, for which a step-by-step process with a slow, progressive increase of the oxidation state, along with a decrease in volatility, can be proposed (Robinson et al., 2007). The duration of such processes clearly exceeds the residence time of SOA in traditional environmental chamber experiments with equivalent atmospheric ageing times of less than 1 day. These limitations led to the emergence of oxidation flow reactors that are capable of higher integrated oxidant exposures, including the Potential Aerosol Mass (PAM) oxidation flow reactor (Kang et al., 2007; Lambe et al., 2011) and related techniques (Hall IV et al., 2013; Keller and Burtscher, 2012; Slowik et al., 2012). Recent studies suggest that flow reactor-generated SOA particles have similar composition to SOA generated in chambers (Lambe et al., 2015; Bruns et al., 2015). Modeling work further suggests that flow reactors simulate tropospheric oxidation reactions with minimal experimental artifacts (Li et al., 2015; Peng et al., 2015, 2016). Recent applications of oxidation flow reactors in field measurements showed that the maximum yields of SOA were attained at approximately 2-3 days of equivalent atmospheric OH oxidation; at higher photochemical age, SOA yields decrease substantially (Tkacik et al., 2014; Ortega et al., 2016; Palm et al., 2016). Such

observations demonstrate the influence of fragmentation reactions in which oxidation leads to C-C bond cleavage with the production of highly volatile products (Kroll et al., 2009; Chacon-Madrid and Donahue 2011; Lambe et al., 2012).

The idea of a slow, multi-generation SOA ageing was recently challenged by recent findings from reaction chamber experiments employing modern chemical ionization mass spectrometric methods. For example, it was found that oxidized gaseous compounds with O/C > 0.7 form readily upon VOC oxidation (Ehn et al., 2012, 2014; Krechmer et al., 2015; Rissanen et al., 2014) and that even the chemical tracers of “aged” SOA can be in fact produced among 2nd generation oxidation products (Müller et al., 2012). The quantification of highly oxidized SOA compounds in reaction chambers is challenging because of significant vapor and particle wall losses (Zhang et al., 2014; Krechmer et al., 2016), but these findings suggest that SOA ageing can be much faster than previously thought (Hodzic et al., 2016). As a result of the diverse implementations of SOA schemes in models, the quantification of SOA production and concentration in the atmosphere is still highly uncertain: a recent intercomparison between 20 state-of-the-art global models showed that the estimated SOA annual production rates differ of one order of magnitude (Tsigaridis et al., 2014). These results call for more experimental observations for constraining the existing SOA parameterizations.

The present study focuses on laboratory production of SOA from three different precursors using a PAM reactor. The novel feature of this work is our application of two off-line analytical techniques that provide valuable insight in regards to SOA composition yet are rarely employed for SOA characterization. The first technique, ¹H-NMR spectroscopy, is a universal technique in organic chemistry. It was used to confirm the molecular structures of many SOA tracers (Finessi et al., 2014) or for following SOA reaction products in aqueous solution (Yu et al., 2011). The few examples of ¹H-NMR spectroscopy on SOA complex mixtures (Cavalli et al., 2006; Baltensperger et al., 2008; Bones et al., 2010) indicate that the technique can be very specific for distinguishing different biogenic and anthropogenic SOA systems. The present study is the first application of ¹H-NMR spectroscopy to SOA samples produced from the OH oxidation of biogenic and anthropogenic SOA. The acquisition of ¹H-NMR fingerprints for fresh and aged biogenic and anthropogenic SOA can be useful also for interpreting factor analysis results obtained on a timeline of NMR spectra of ambient aerosol extracts (e.g., Paglione et al. 2014a). The second technique is a HPLC set-up for the determination of humic-like substances (HULIS). HULIS have been observed in ambient organic aerosol for nearly two decades (Havers et al., 1998; Limbeck et al., 2003), but their formation pathways aside from production in biomass burning plumes remain unclear (Graber and Rudich 2006). It is well-known that high-molecular weight oxygenated organic compounds readily form by heterogeneous reactions (Limbeck et al., 2003) or by gas-to-particle conversion (Kalberer et al.,

2006), but there is little evidence for their identification with HULIS in ambient aerosols (especially if we base the definition on the chromatographic behavior, as in Baduel et al., 2009).

Here we focus on SOA systems generated from three distinct precursors: isoprene, α -pinene and naphthalene. Naphthalene is used as proxy for anthropogenic aromatic intermediate volatility organic compounds (IVOCs). Alpha-pinene is the most studied biogenic monoterpene due to its global importance as a biogenic SOA precursor (e.g. Pye et al., 2010), while isoprene is the most abundant biogenic VOC, accounting for 44% of global emissions (Guenter et al., 1995). The discovery of isoprene SOA is relatively recent (Claeys et al. 2004). In the presence of acidic wet aerosols, SOA originates from the heterogeneous uptake of isoprene epoxides (“IEPOX channel”, Lin et al., 2012). Since aerosol water and acidity are primarily determined by anthropogenic mineral acids, the formation of SOA from isoprene appears to be very much controlled by anthropogenic emissions. On the other hand, recent experiments conducted at very low nitrogen oxide (NO) concentrations, and in the absence of seed aerosols, showed that SOA can still form from isoprene (“non-IEPOX” SOA, Krechmer et al., 2015). Such aerosols are more representative of the preindustrial world and their characterization is of paramount importance for understanding the climate radiative forcing of SOA at the global scale. Our results, obtained in the PAM reactors in absence of NO_x, are representative for non-IEPOX isoprene SOA.

2 Experimental methods

2.1 PAM oxidation flow reactor

The PAM oxidation flow reactor is a horizontal 13L glass cylindrical chamber that is 46 cm long x 22 cm ID. Carrier gas flows of 8.5 liter per minute (lpm) N₂ and 0.5 lpm O₂ were used, with 8.5 lpm of flow pulled through the reactor and 0.5 lpm of excess flow removed prior to the reactor. Other experimental details are fully described in Lambe et al. (2011). In this study, the PAM reactor was connected to a Scanning Mobility Particle Sizer (SMPS), an Aerodyne time-of-flight aerosol mass spectrometer (AMS), and a filter holder equipped with 47 mm (prebaked) quartz-fiber filters. SOA concentrations calculated from SMPS and/or AMS measurements averaged over filter collection times provided an estimate of the organic matter loading on the filters.

During the first set of experiments, α -pinene and naphthalene SOA samples were generated at multiple ageing states, by varying the UV actinic flux inside the reactor through changing the voltage applied to the lamps (Table 1). A total of five α -pinene and five naphthalene SOA samples were obtained (collection time between 3 and 20 h), with integrated OH exposures varying between 2×10^{11} and 2×10^{12} molecules/cm³*s, corresponding to a photochemical age of 1.5 to 15 days assuming a 24-hour average OH concentration of 1.5×10^6 molec cm⁻³ (Mao et al., 2009).

During the second set of experiments, isoprene SOA samples were generated in the reactor (Table 2). Due to the lower yields of SOA produced by isoprene oxidation, samples were collected at OH exposure of approximately 8×10^{11} molec cm^{-3} sec (corresponding to a photochemical age of 6 days) at which the maximum SOA yield is obtained (Lambe et al., 2015). The collection time was varied between 2 and 18 h.

2.2 Extraction and off-line sample characterization

Each filter was extracted with 5 mL of deionized ultra-pure water (Milli-Q) in a mechanical shaker for 1 h and the water extract was filtered on PTFE membranes (pore size: 0.45 μm) in order to remove suspended particles. The water extracts were dried by rotary evaporator and were then re-dissolved in 2.15 mL of D_2O : 0.65 mL for proton-nuclear magnetic resonance ($^1\text{H-NMR}$) characterization (Decesari et al., 2000), and 1.5 mL for HPLC analysis and total organic carbon (TOC) analysis (Mancinelli et al., 2007). Tests of extraction using methanol instead of water were carried out on three isoprene SOA samples. The $^1\text{H-NMR}$ spectra of methanol extracts were completely consistent with those obtained for the other three analyzed in deuterated water (Fig. S1), indicating that there were no specific classes of water-insoluble compounds in the isoprene SOA under the conditions used in this study. The following discussion will focus on the water-soluble fraction for which spectroscopic and chromatographic data were obtained for all three SOA systems.

2.3 NMR spectroscopy

The $^1\text{H-NMR}$ spectra were acquired at 600 MHz with a Varian 600 spectrometer in a 5 mm probe with 0.65 mL of each sample re-dissolved in D_2O . Sodium 3-trimethylsilyl-(2,2,3,3- d_4) propionate (TSP- d_4) was used as the referred internal standard. A buffer of potassium deuterated formate/formic acid (pH~3.8) was used in the second series of experiments (isoprene SOA) to stabilize the chemical shift of hydrogen atoms in acyl functional groups, while the extracts obtained during the first experiments (α -pinene and naphthalene) were analyzed unbuffered. $^1\text{H-NMR}$ spectroscopy of low-concentration samples in protic solvents provides the speciation of hydrogen atoms bound to carbon atoms (H-C). On the basis of the range of frequency shifts (the chemical shift, in ppm) in which the NMR resonances occur, they can be attributed to different H-C containing functional groups (Paglione et al. 2014a).

2.4 HPLC-UV-TOC method

HULIS were determined using the ion exchange chromatographic method described by Mancinelli et al. (2007). A HPLC system (Agilent Model 1100) with gradient elution was used. The subsequent elution of chemical compounds bearing zero, one, two or more than two ionized groups per molecule (mainly carboxylate ions at pH 7) is monitored by an UV detector at 260 nm. Downstream of the detector, a fraction collector is programmed to sample separately “neutral compounds” (NC), “monocarboxylic acids” (MA), “dicarboxylic acids” (DA), and “polycarboxylic acids” (PA) or HULIS. The amount of WSOC recovered in each fraction is determined off-line by TOC analysis using an Analytik-Jena multi analyzer N/C (model 2100). The full HPLC-UV-TOC analytical protocol is reported in the Supplementary material. Further information on the nature of the chemical classes separated by the HPLC method based on elution tests of standard compounds, including discussion of possible misclassification, is reported by Decesari et al. (2005).

3.1 Results: ^1H -NMR results

3.1.1 NMR fingerprints of fresh and aged α -pinene SOA

Figure 1 shows the ^1H -NMR spectra of α -pinene SOA with increasing photochemical age. The first spectrum corresponding to a “low” SOA oxidation level is similar to reported NMR spectra of environmental chamber-generated α -pinene ozonolysis (Cavalli et al., 2006). However, the NMR fingerprint of α -pinene SOA evolves rapidly with further oxidation steps. A clear, progressive disappearing of 1st generation oxidation products (pinic and pinonic acid) with increasing O/C ratio can be observed. In the NMR spectra corresponding to a “medium” SOA oxidation level, the resonances at ~ 1 ppm of chemical shift, arising from one of the two gem-methyls of α -pinene, have almost disappeared. This indicates that α -pinene SOA composition evolves rapidly towards more highly-oxidized molecular structures with little resemblance to 1st generation oxidation products. At “medium” and “high” oxidation levels, the unsubstituted alkyl groups of the SOA mixture give rise to a broad Gaussian band between 1.1 and 1.8 ppm of chemical shift with a maximum at 1.4 – 1.5 ppm. The middle point position showing a slight deshielding with respect to a purely alkylic chain (~ 1.3 ppm for fatty acids) indicates the presence of electronegative groups (such as oxygen atoms) in beta or gamma position with respect to these alkyl groups. The band between 1.9 and 3 ppm, attributable to C-H groups of acyl groups (HC-C=O), also shows a transition towards structures containing more deshielded H atoms. In all cases, the most conspicuous band in this spectral region is found at 2.2 – 2.3 ppm of chemical shift, which corresponds to acetyl and acyl groups of aliphatic compounds with a low O/C ratio, like pinonic acid ($\text{R-CH}_2\text{-C=O}$ and $\text{CH}_3\text{-(C=O)-R}$, where R is mainly a $\text{C}_x\text{H}_{2x+1}$ radical). Such band persists in all SOA samples, but an additional band between 2.5 and 2.9 ppm is observed in the two samples with the highest O/C ratio, indicating that the aliphatic

groups become more and more substituted by electronegative groups: the keto and carboxylic groups become spaced by no more than two methylene (or methyns) groups ($x(\text{C}=\text{O})\text{-CH-CH-(C}=\text{O})\text{X}$, where X is a generic substituent). Finally, the NMR resonances in the third important aliphatic region of alcoxyl groups (CH-O), between 3.3 and 4.2 ppm of chemical shift, are always relatively small, with peak intensity at intermediate photochemical age. SOA species that contribute to NMR resonance in this region may be correlated with semivolatile, highly functionalized species that contribute to maximum SOA yields observed at intermediate OH exposures (Lambe et al., 2015).

Overall, the NMR fingerprint of α -pinene SOA is highly dependent on photochemical age, with a sharp change already at medium ageing. The most oxidized samples show spectral features that have lost any clear similarity with those of SOA sampled in reaction chambers experiments without ageing (Cavalli et al., 2006).

3.1.2 NMR fingerprints of fresh and aged naphthalene SOA

The $^1\text{H-NMR}$ spectra of naphthalene SOA samples with increasing O/C ratio are presented in Figure 2. The extract of the least-oxidized sample (on the top) shows broad resonances between 0 and 3 ppm probably due to the effect of colloidal hydrophobic material in solution. Despite such artifact, all spectra of fresh and moderately aged SOA show clear signals from aromatic structures (region at chemical shift from 6.5 to 8.5 ppm) and alkenes (approximately between 5 and 7 ppm). The HNMR spectra of naphthalene SOA are very different than HNMR spectra of SOA produced from the OH oxidation of one-ring aromatic VOCs (Baltensperger et al., 2008), which have mostly aliphatic groups originating from ring opening reactions. Our data are in agreement with molecular speciation studies (Lee and Lane 2009), indicating that naphthalene is oxidized to form 1- or 2-ring aromatic compounds such as naphthol, and substituted benzoquinones, cinnamic acid, and phthalic acid (Chhabra et al., 2015). The chemical shift range of the main aromatic band, between 7.4 and 8.1 ppm, indicates that aromatic rings are substituted prevalently by electron-withdrawing groups, such as carbonyl and carboxyls. At moderate ageing states, a small band at 6.9 – 7.1 ppm indicates the formation of phenolic structures. The HNMR spectra of fresh naphthalene SOA show several singlets in the aromatic region, indicating a diversity of individual compounds occurring in relatively high concentrations, while moderately aged SOA show mainly the two singlets of phthalic acid. All spectra contain signals at lower chemical shifts with respect to the aromatics, mainly between 3.5 and 6.0 ppm (with the interference of the partly suppressed peak of water in the middle): several functional groups can give rise to these bands, including alkoxy-, peroxy-, esters, hemiacetals and acetals, and vinyls.

The spectrum of the most aged sample (NAPTH 1), which is also the one with the lowest SOA concentration, shows an interference from α -pinene SOA in the aliphatic region. This feature is likely due to experimental setting contamination from a previous α -pinene SOA experiment. Despite the low naphthalene SOA concentration, a broad aromatic band between 6.5 and 8.5 ppm and the same signals found between 3.5 and 6.0 ppm seen in the samples with a medium O/C ratio are still visible in this most aged naphthalene SOA spectrum. Unlike α -pinene SOA, there is no clear trend in the formation/disappearance of aromatic and aliphatic bands with ageing, and overall the $^1\text{H-NMR}$ fingerprint of naphthalene SOA appears less sensitive to variations in the OH exposure compared to the α -pinene SOA.

3.1.3 NMR fingerprints of non-IEPOX isoprene SOA

The samples of isoprene SOA were obtained from the same OH exposure (corresponding approximately to a “medium” exposure in the α -pinene and naphthalene experiments) and differed only for collection time and sample quantity loaded on the filter. The isoprene SOA $^1\text{H-NMR}$ spectra profiles were all very similar (an example is provided in Figure 3). The comparison with literature data (Budisulistiorini et al. 2015) led to the unambiguous identification of 2-methyltetrols, responsible for the two singlets at 1.12 ppm (methyl H atoms of methylerythritol) and 1.13 ppm (methyl H atoms of methylthreitol) and for a series of multiplets between 3.4 and 3.9 ppm in a clear pattern. Methylerythritol is slightly more abundant (on average 55% of the sum of the two) than methylthreitol. The two methyltetrols account for 65% of the total $^1\text{H-NMR}$ signal, the rest being characterized by broad background signal with very few sharp resonances, indicating that the isoprene SOA samples are composed mainly of methyl-tetrols together with a significant amount of mass composed of a very complex mixture of products. The unresolved background resonances are located below the peaks of the methyltetrols, suggesting that the complex mixtures (which can include also oligomeric species) encompass molecular species (or monomers) similar to methyltetrols (at least in their C-H backbone). However, the range of chemical shifts of the background bands characterize molecular species with more electronegative groups (leading to more de-shielded H atoms) than methyltetrols: the band of methyl protons extends to 1.7 ppm (respect to 1.12-1.13 of methyltetrols) and the band of alcoxyl groups (HC-O) extends to 4.3 ppm. The results of Liu et al. (2016), indicating that non-IEPOX isoprene SOA include peroxide-equivalents of methyltetrols, are in agreement with these findings. However, Liu et al. (2016) do not report the presence of carboxylic or keto groups, while our data clearly indicate that these (and/or other acyl groups) are found in the unresolved mixtures of non-IEPOX isoprene SOA, and are responsible for the signal band between 2.0 and 2.6

ppm. Still, this band is much less intense than that of alcoxyls, which is opposite to what observed for α -pinene SOA where acyls are by far the main oxygenated aliphatic functional group. Thus, $^1\text{H-NMR}$ spectroscopy provides distinct fingerprint for isoprene and monoterpene SOA.

3.2 HPLC results

The HPLC analysis of fresh α -pinene SOA extracts show the presence of compounds unretained by ion-exchange columns (neutral compounds) or weakly retained (mono- and di-acids) with a small contribution from compounds having a high retention factor (polyacids, PA, or HULIS), in agreement with previous results obtained from α -pinene SOA samples generated in environmental chamber experiments (unpublished data). The HULIS content increases only moderately with ageing, while the yield/fraction of di-acids increases significantly with respect to mono-acids and neutral/basic compounds (Figure 4). With increasing photochemical age, the total organic carbon (TOC) mass fractions of mono-acids, di-acids and HULIS increase from 20% to 34% and 7% to 16%, respectively, whereas the mass fraction of neutral compounds decreases from 19% to 9%. These results are in qualitative agreement with the known chemistry of α -pinene SOA, in which mono- and dicarboxylic acids are the most characteristic condensable 1st generation products (Jenkin et al., 2000; Jaoui and Kamens 2001) while tricarboxylic acids such as 3-methyl-1,2,3-butanetricarboxylic acid or pinyl-diaterpenyl ester (Szmigielski et al., 2007; Yasmeeen et al., 2010) are present in lesser amounts and can contribute the observed concentrations of HULIS in this study.

The HPLC fractionation of naphthalene SOA (Figure 5) shows that fresh samples are characterized by a mixture of neutral compounds and mono- and di-acids, completely consistent with the molecular compositions reported in the literature (Lee and Lane 2009). However, a net increase in acidic compounds with photochemical age can be clearly observed. The HULIS content, initially small, increases substantially and progressively with ageing. With increasing photochemical age, the TOC mass fraction of mono- and di-acids decreases from 33% to 18% and the fraction of PA/HULIS increases from 11% to 30%. This is the first evidence of HULIS formation (determined with the ion-exchange method) in laboratory-generated SOA. The formation of polyacidic molecules with three or more carboxylic groups implies the opening of the second aromatic ring in the naphthalene precursor backbone, and/or oligomerization reactions. In both cases, products of such oxidation reactions cannot be explained by current naphthalene SOA molecular speciation studies (e.g. Kautzman et al., 2010).

Finally, the HPLC analysis of isoprene SOA shows that neutral compounds (NC) were dominant in all sample extracts (Figure 6). NC accounted for 59% of the TOC content of the sum of the HPLC fractions. The second most abundant fraction (34%) are the mono-acids, while diacids accounted for

a much smaller fraction of TOC, and to polyacids were almost absent (ca. 1% of the TOC). The dominance of NC is consistent with the high yield methyltetrols and their analogues (see Section 3.1.3). Assuming that the distribution of NMR functional groups approximately reflects their carbon content, methyltetrols (accounting for 65% of the total NMR signal) can account for the whole of the HPLC neutral compounds, and, as a corollary, the complex mixtures of products detected by unresolved bands by NMR spectroscopy correspond to the mono- and di-acids in HPLC. As already noticed in the previous section, the NMR analysis shows indeed the occurrence of acyl groups which indicate/support the presence of carboxylic acids. We cannot exclude, however, possible misclassification of some neutral compounds into the monoacid fraction, as already observed for some dicarbonyls (Decesari et al. 2005).

4 Discussion and conclusions

In this section, the NMR and HPLC results obtained for the isoprene, α -pinene and naphthalene SOA systems are compared with ambient OA samples. First, we investigated the similarity between the ^1H -NMR spectral profiles of SOA with those “typical” of ambient non-biomass-burning WSOC. For this purpose we used one sample of PM_{10} from the rural Po Valley in summertime, collected during the 2012 PEGASOS field campaign (Sandrini et al., 2016). The PEGASOS and laboratory SOA spectra were binned to 400 points in order to remove the variability in chemical shifts due to, e.g., different pH conditions during the analyses of the samples. Figure 7 shows the correlation between the SOA spectra and the reference spectrum of ambient WSOC. There is a good correlation ($0.62 < r < 0.92$) between the NMR spectra of α -pinene SOA, at all oxidation levels, with the spectrum of the PM_{10} sample, whereas a low correlation is found for the isoprene SOA ($0.26 < r < 0.30$); the naphthalene SOA spectra exhibit zero or negative correlations ($-0.15 < r < -0.02$). This result is somewhat expected if we consider that ambient water-soluble aerosols are characterized by acyl functional groups (HC-C=O) in higher concentrations with respect to alcoxyl groups (HC-O) and by a smaller aromatic content (Decesari et al., 2007), with a functional group pattern that is well reproduced by α -pinene SOA and not by non-IEPOX SOA and by naphthalene SOA. Clearly, naphthalene SOA *alone*, with hydrogen-to-carbon (H/C) ratio less than 0.9 due to relatively high aromatic content (Lambe et al. 2011, 2015), does not mimic ambient OA *bulk* composition. It should be noted, however, that naphthalene and other polyaromatic hydrocarbons are co-emitted with many other anthropogenic IVOCs and VOCs including aliphatic compounds in the real atmosphere; therefore the contribution of naphthalene SOA could be simply masked by the contribution of aliphatic IVOC SOA in the ^1H -NMR spectra of ambient WSOC. When limiting the correlation analysis of Figure 7 to the aromatic and vinyl region of the spectra (> 6 ppm), Pearson r coefficients

of 0.49 to 0.58 are found between the naphthalene SOA and the ambient WSOC spectra, while small values (between -0.2 and 0.4) are found for the α -pinene and isoprene SOA. This result suggests that SOA produced from naphthalene or similar precursors, including many other ring-retaining oxidation products (Section 3.1.2) can explain the presence of aromatic moieties in ambient water-soluble aerosols in areas not affected by biomass burning emissions.

When considering the full spectral range, the H-NMR spectra of α -pinene SOA most closely mimic the functional group distributions of the ambient WSOC sample obtained in PEGASOS. Interestingly, similarity between H-NMR spectra of α -pinene SOA and Po Valley WSOC increases with increasing photochemical age. For the most oxidized α -pinene SOA samples, the functional group composition, characterized by polysubstituted aliphatic compounds rich of acyls (carboxylic or keto groups), overlaps well with that of ambient WSOC. A good fit between α -pinene SOA and ambient WSOC mass spectral features is already achieved at medium oxidation conditions, in agreement with the results of Lambe et al. (2011) showing that the correlation between the AMS spectra of PAM-generated α -pinene SOA with the spectra of ambient OOA increases up to an exposure of 1×10^{12} OH molec $\text{cm}^{-3} \cdot \text{s}$ and remains rather stable afterwards. These results suggest that NMR-traced ageing processes reflect the same chemical mechanisms already studied using high-resolution AMS techniques. However, the correlation coefficients shown in Figure 7 for the NMR spectra of α -pinene vs. ambient WSOC ($r^2 = 0.39$ to 0.84) are smaller than those between the HR-ToF-AMS spectra of PAM-generated SOA vs. ambient OOA ($r^2 = 0.7$ to 0.9) (Fig. 9 in Lambe et al., 2011). Apparently, the AMS features of ambient OA are more easily reproduced by PAM experiments than the NMR composition, or, in other words, NMR spectroscopy exhibits a greater selectivity for the OA components than AMS. Specifically, ^1H -NMR spectroscopy was able to resolve significant changes in composition of α -pinene SOA with photochemical ageing in great detail, especially at an OH exposure of $\sim 1.1 \times 10^{12}$ molec OH / $\text{cm}^3 \cdot \text{s}$ equivalent to multiple days of atmospheric ageing.

A comparison of fresh and aged SOA with ambient WSOC samples with respect to the HPLC fraction distributions is reported in Figure 8. The distribution of neutral vs. acidic classes of compounds in ambient WSOC refers to average of the samples collected at a rural background station at Cabauw in the Netherlands (Paglione et al. 2014b). The HULIS contribution in these samples varied between 15 and 20%, in line with previous results obtained in the Po Valley (Mancinelli et al., 2007), but lower than in biomass burning aerosol samples (Decesari et al., 2006). The α -pinene SOA generated in the PAM reactor at high photochemical age are characterized by a HULIS amount similar to that of Cabauw samples, while the polyacidic content of aged naphthalene SOA is higher than in the ambient samples. These results demonstrate that laboratory experiments of SOA formation can generate

complex mixtures of products with the same chromatographic properties of HULIS provided a sufficient extent of photochemical aging using the PAM reactor or related techniques. The HULIS fraction of WSOC is in fact proportional to the AMS f44 for SOA (integrated over the filter sampling times) (Figure 9) irrespectively of precursor type. Therefore, the formation of polycarboxylic acids determined by the HPLC technique follows the same positive trend in concentrations of the AMS proxy for C(O)OH groups with increasing OH exposure. This is in contrast with the numerous observations of rapid formation of SOA oligomers during reaction chamber experiments (Kalberer et al., 2006; Reemtsma et al., 2006), indicating that oligomers do not account for chromatographically-defined HULIS. A survey of the laboratory studies on the formation of humic material in secondary aerosol shows that evidence for the formation of polycarboxylic acids comes from the reaction of phenolic compounds in the presence of particulate water (Hoffer et al., 2004), while little is known for unseeded, dry gas-to-particle formation experiments. With the exception of the very preliminary data reported by Baltensperger et al. (2008), our results – to our best knowledge – are the first showing the occurrence of HULIS *sensu strictu* in monoterpene and aromatic hydrocarbon SOA, and these HULIS are clearly shown to be a product of photochemical ageing.

In conclusion, we observed that OA ageing reactions in the PAM reactor produces water-soluble compounds of high complexity but with spectroscopic and chromatographic properties that converge towards those characteristic of ambient OA. Specifically, a good correlation between ambient HPLC/HNMR samples and aged α -pinene SOA was observed in respect to HULIS content and NMR functional group distribution, while aged aromatic IVOC SOA show clear potential for HULIS formation. The isoprene SOA samples do not show compositional features with a clear overlap with those of ambient WSOC obtained in the Cabauw and Po Valley samples that are representative of continental polluted atmospheres, but should serve as useful reference spectra for future studies/environments impacted by non-IEPOX isoprene SOA.

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Tables

Sample	Oxidation level	PAM Lamp voltage (V)	OH Exposure (molec/cm ³ *s)	Collection Time (h)	average AMS OM concentration (RIE*CE=1.4) (µg/m ³)	OM on filter based on AMS (RIE*CE=1.4) (µg)
<i>α-pinene</i>						
Pin#1	High (f44 = 0.24)	110	2.10x10 ¹²	18.5	46.1	384
Pin#2	Med. (f44 = 0.11)	75	1.10x10 ¹²	3.2	151.6	221
Pin#3	Med.	75	1.10x10 ¹²	20.2	14.1	129
Pin#5	Low	30	2.00x10 ¹¹	20.5	7.5	69
Pin#6	Low (f44 = 0.05)	30	2.00x10 ¹¹	7.1	50.3	161
<i>Naphthalene</i>						
Nap#1	High f44 = 0.30)	110	2.10x10 ¹²	19.7	31.3	277
Nap#2	Med. (f44 = 0.19)	75	1.10x10 ¹²	7	55.3	174
Nap#3	Low (f44=0.084)	30	2.00x10 ¹¹	6.6	16.9	50
Nap#4	Med (f44 = 0.20)	75	1.10x10 ¹²	6.6	42.9	127
Nap#5	Low (f44 = 0.074)	30	2.00x10 ¹¹	15.8	34.7	246
<i>blanks</i>						
Blk#1		110	2.10x10 ¹²	6.1	0	0
Blk#2		110	2.10x10 ¹²	23.2	0	0
Blk#3		110	2.10x10 ¹²	6.1	0	0

Table 1. PAM experimental conditions for naphthalene and *α-pinene* SOA ageing studies.

Sample	Oxidation level	PAM Lamp voltage (V)	OH Exposure (molec/cm ³ *s)	Collection Time (h)	average AMS OM concentration (RIE*CE=1.4) (µg/m ³)	OM on filter based on AMS (RIE*CE=1.4) (µg)
<i>Isoprene</i>						
Iso#1	Med (f44 = 0.046)	60	7.8*10 ¹¹	3.7	409	651
Iso#2	med	60	7.8*10 ¹¹	2.8	575	700
Iso#3	Med (f44 = 0.039)	60	7.8*10 ¹¹	2.2	678	656
Iso#4	Med (f44 = 0.037)	60	7.8*10 ¹¹	2.9	551	684
Iso#5	Med (f44 = 0.040)	60	7.8*10 ¹¹	16.1	685	4959
Iso#6	Med (f44 = 0.066)	60	7.8*10 ¹¹	3.9	767	1280
Iso#7	Med (f44 = 0.059)	60	7.8*10 ¹¹	3.8	593	986
<i>Blanks</i>						
Blk#1		60	7.8*10 ¹¹	15.9	0	0
Blk#2		60	7.8*10 ¹¹	3.1	0	0
Blk#3		60	7.8*10 ¹¹	16.3	0	0

Table 2 PAM experimental conditions for isoprene SOA ageing studies.

Figures

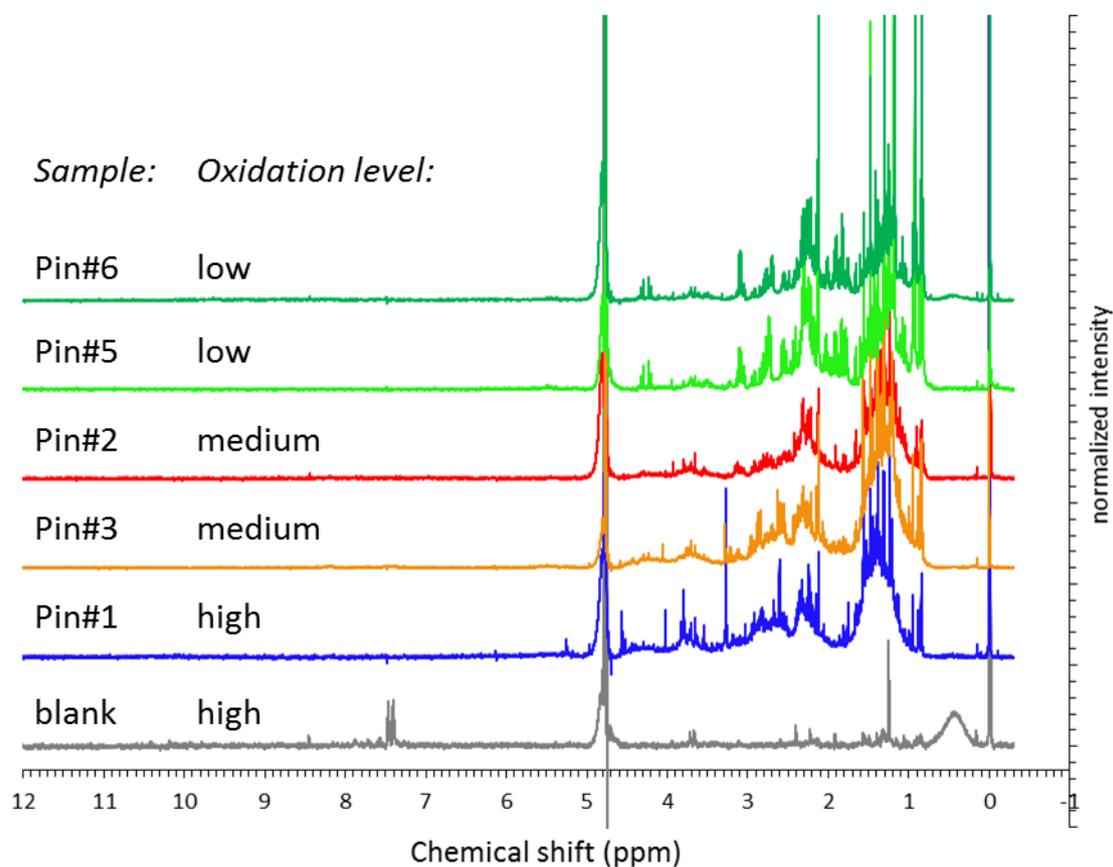


Figure 1. $^1\text{H-NMR}$ spectra of α -pinene SOA as a function of increasing photochemical age in the Potential Aerosol Mass (PAM) oxidation flow reactor. The sharp singlet at zero ppm represents the internal standard ($Tsp-d_4$), while the broad peak at 4.8 ppm is the – partly instrumentally suppressed – H_2O peak. The sharp singlets between 0.9 and 2.2 ppm in the fresh SOA samples (Pin#5 and Pin#6) are genuine bands of the samples and were identified as methyl groups of pinic and pinonic acid.

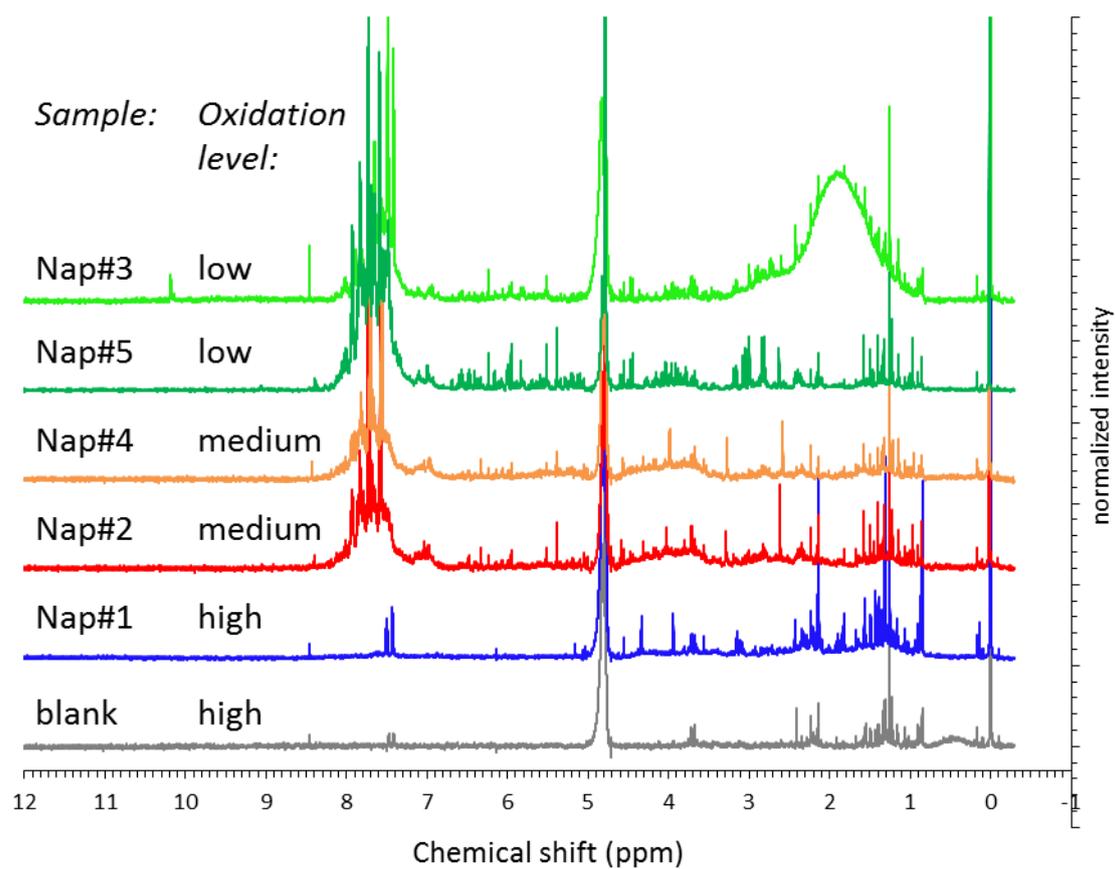


Figure 2. $^1\text{H-NMR}$ spectra of naphthalene SOA as a function of increasing photochemical age in the PAM reactor. The sharp singlet at zero ppm represents the internal standard (Tsp-d4), while the broad peak at 4.8 ppm is the – partly instrumentally suppressed – HDO peak.

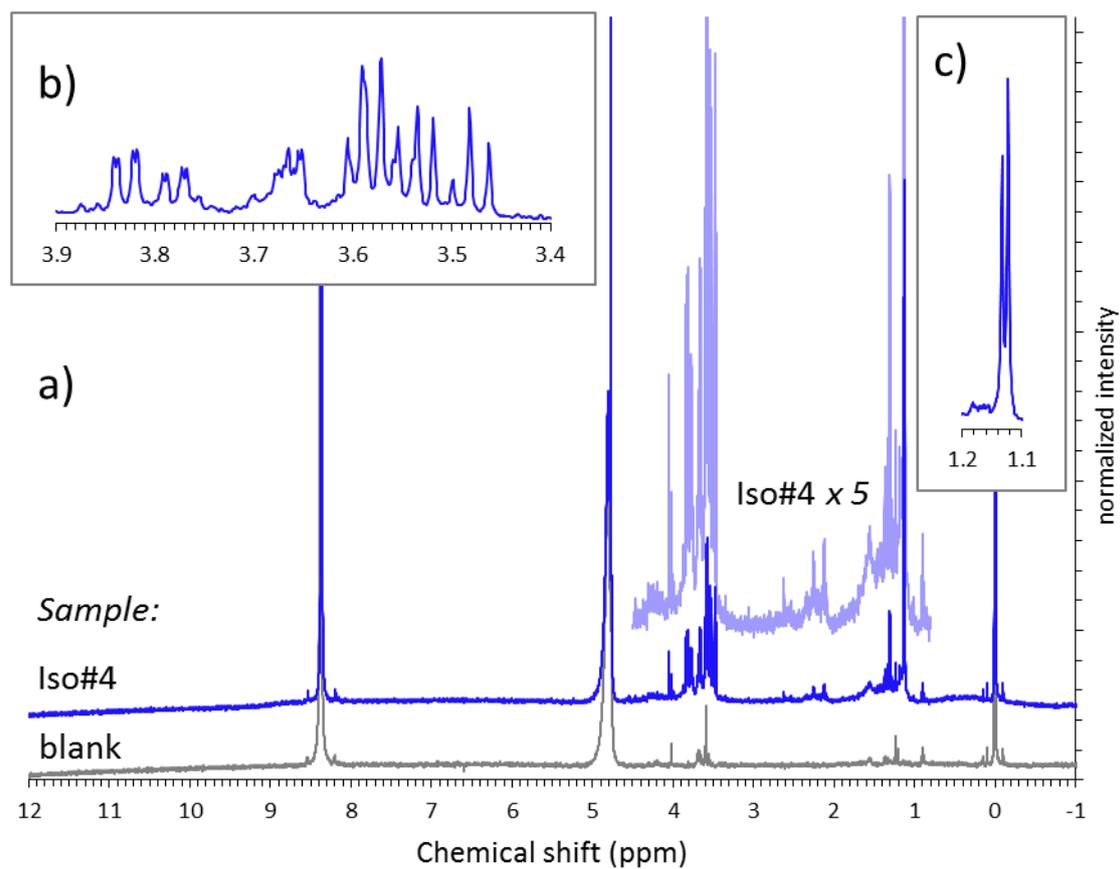


Figure 3. Panel a: ¹H-NMR spectrum of isoprene SOA generated in the PAM reactor at an OH exposure of $8 \cdot 10^{11}$ molec cm^{-3} sec. The bottom trace shows the same spectrum with enlarged the broad background bands. Panel b and c show the methyltetrols resonances between 3.4 and 3.9 ppm and 1.12-1.13 ppm, respectively

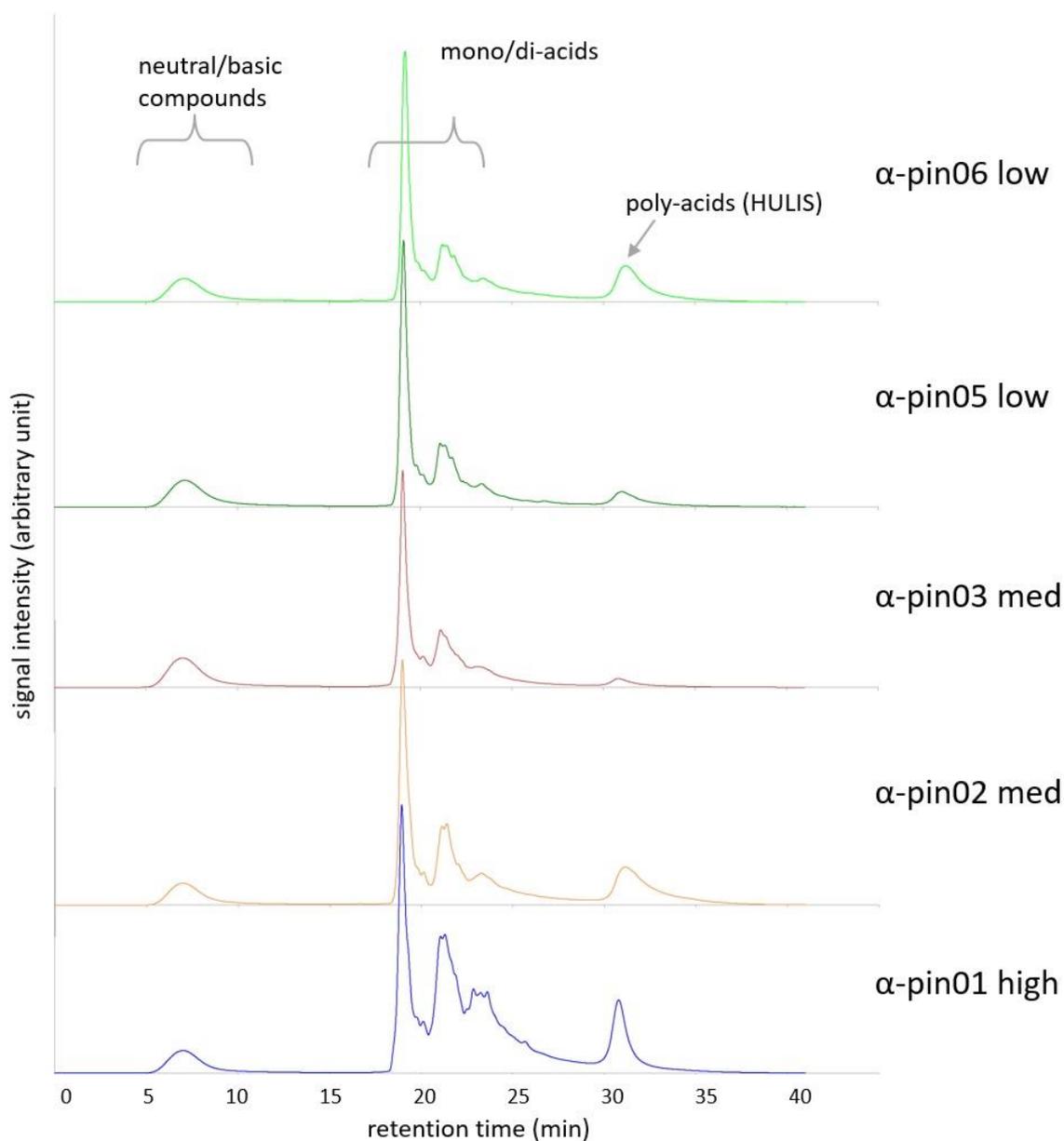


Figure 4. HPLC chromatograms of α -pinene SOA water extracts. Chromatographic features are grouped into neutral, mono-/di-carboxylic acid, and polycarboxylic acid classes based on their affinity for the column phase. Sample identifications are provided in Table 1.

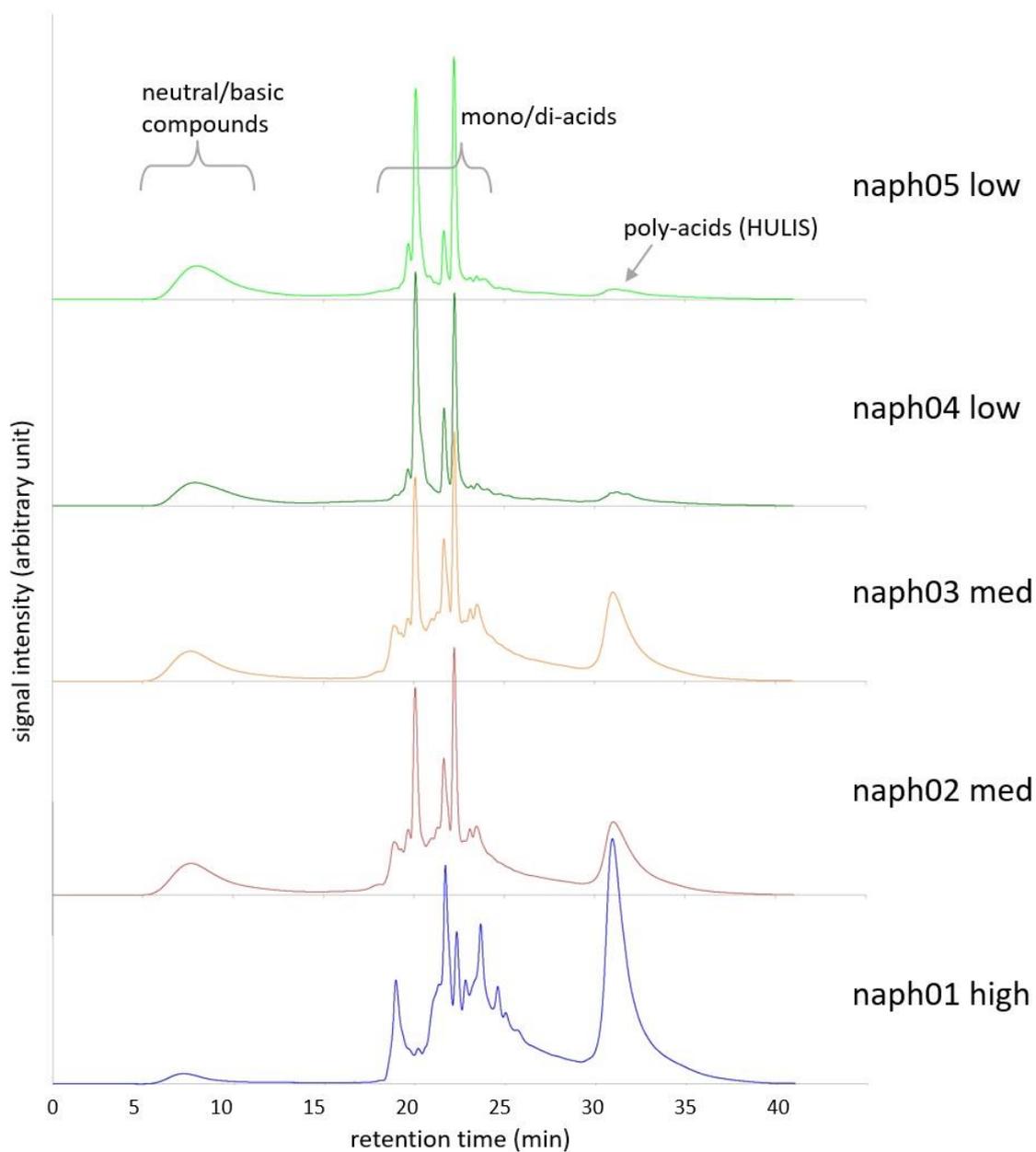


Figure 5. HPLC chromatograms of naphthalene SOA water extracts. Chromatographic features are grouped into neutral, mono-/di-carboxylic acid, and polycarboxylic acid classes based on their affinity for the column phase. Sample identifications are provided in Table 1.

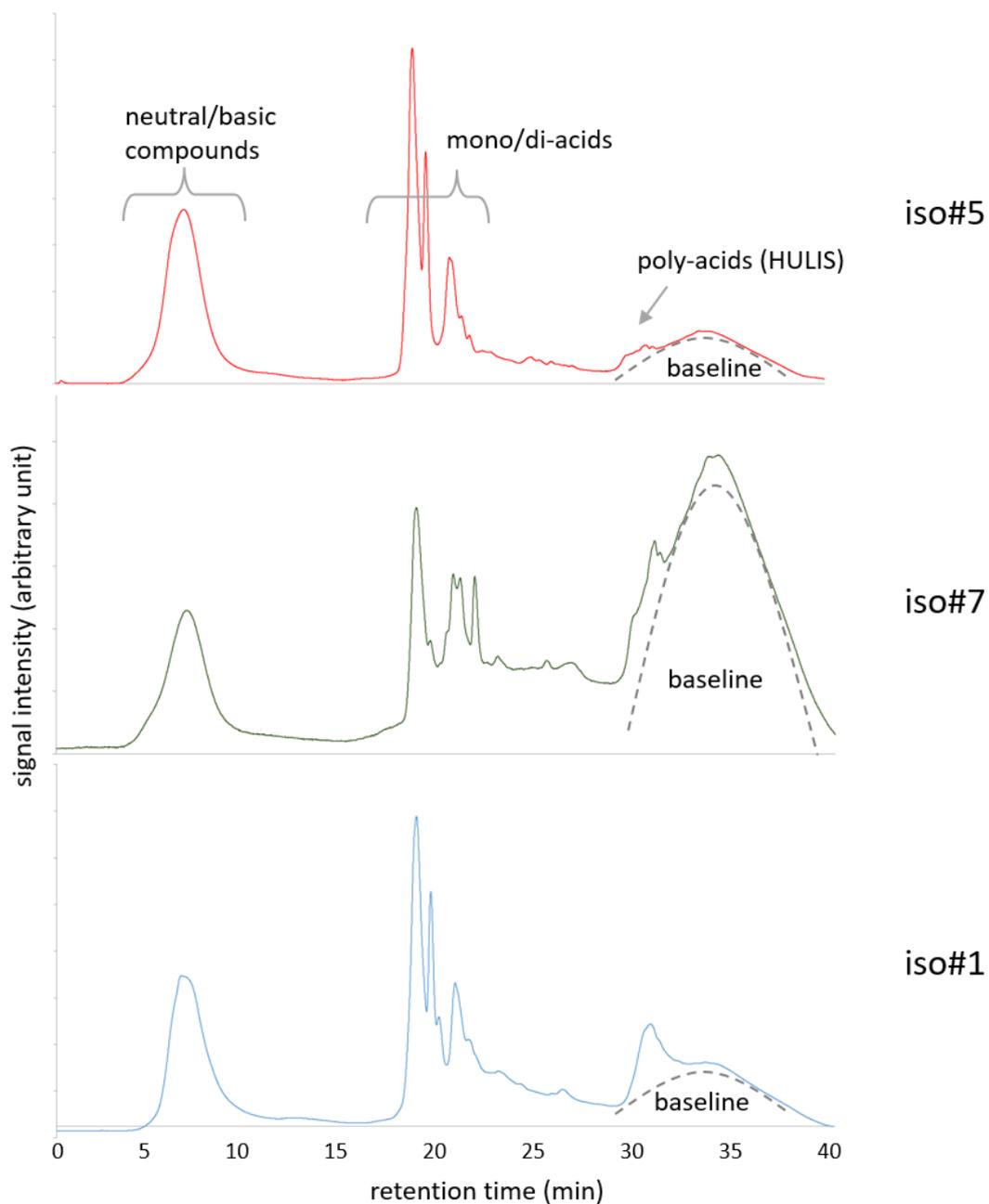


Figure 6. HPLC chromatograms of isoprene SOA water extracts. Chromatographic features are grouped into neutral, mono-/di-carboxylic acid, and polycarboxylic acid classes based on their affinity for the column phase. Sample identifications are provided in Table 2.

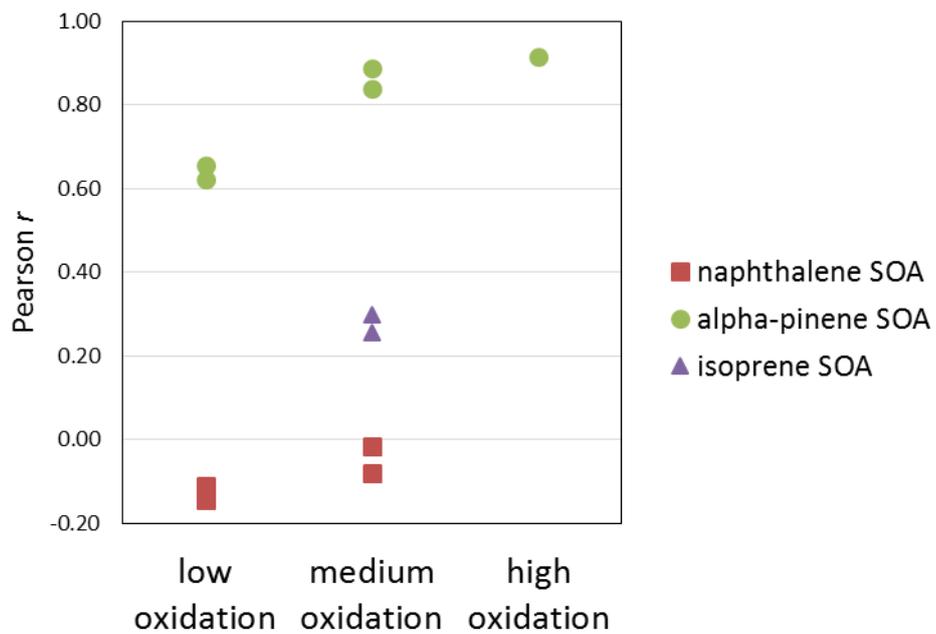


Figure 7. Pearson correlation coefficient between H-NMR spectra of PAM-generated SOA and ambient PEGASOS WSOC.

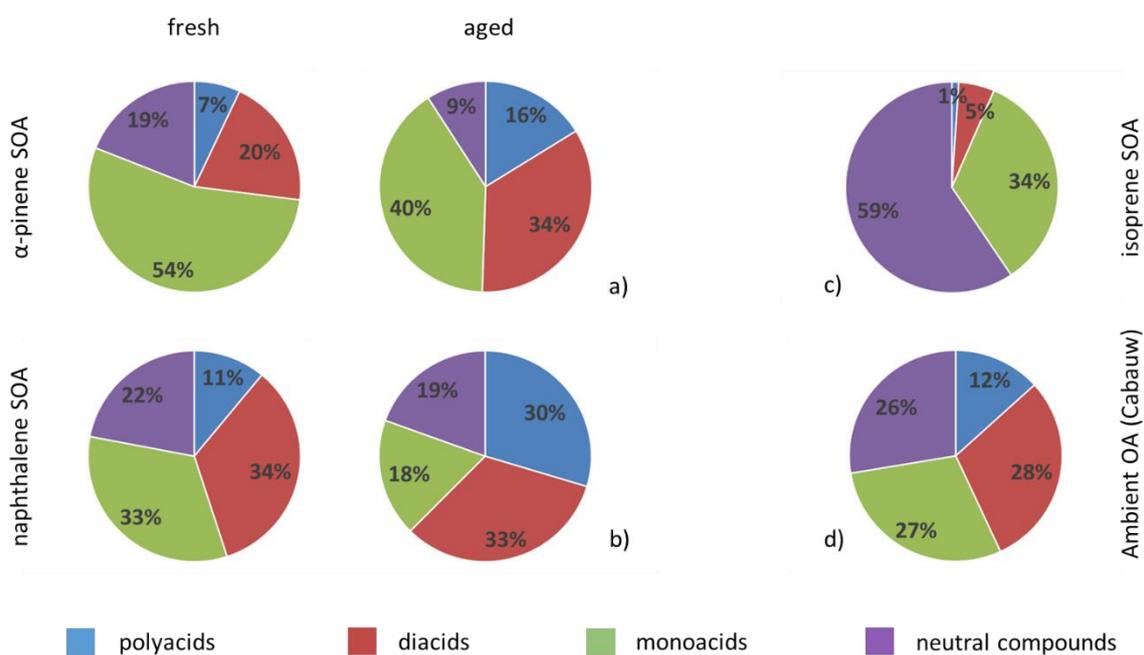


Figure 8. Distribution of HPLC fractions (total recovered TOC content = 100%) for α -pinene SOA (panel a), naphthalene (panel b), isoprene (panel c), and for ambient OA sampled in Cabauw Netherlands (panel d).

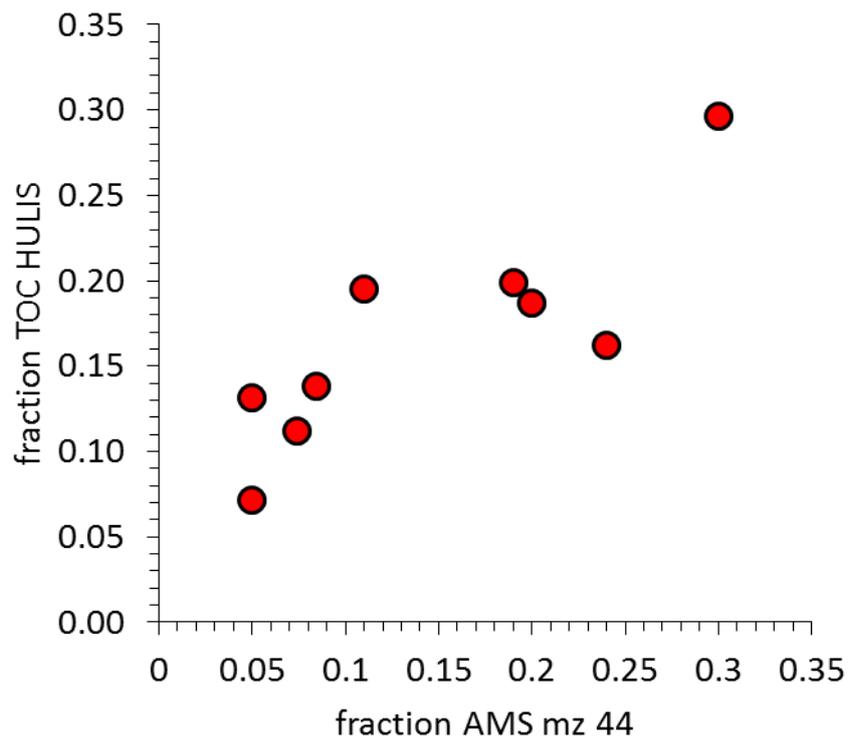


Figure 9. Correlation plot between the AMS f_{44} of SOA and the HULIS fraction of HPLC-eluted WSOC.

Supplement

Characterizing source fingerprints and ageing processes in laboratory-generated secondary organic aerosols using proton-nuclear magnetic resonance (¹H-NMR) analysis and HPLC HULIS determination.

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Content:

- Supporting information on source and nature of ambient OA samples.
- NMR spectroscopic data for non-aqueous components of isoprene SOA.
- HPLC fraction distributions for all α -pinene and naphthalene SOA samples.

Origin of ambient samples

The Po Valley samples discussed in Section 4 were collected in San Pietro Capofiume (SPC), a rural site located in the south-eastern sector of the Valley, during the PEGASOS campaign of summer 2012 (Rosati et al., *Atmos. Chem. Phys.*, 16, 7295-7315, 2016). Aerosol particles with ambient aerodynamic diameter $< 1 \mu\text{m}$ were sampled on pre-washed and pre-baked quartz-fiber filters (Whatman, 9 cm size) using a high-volume sampler (model Echo Hivol, Tecora) at a constant nominal flow of 500 l/min located at ground level. Two filters per day were sampled (change at 9 AM and 6 PM local time). Each filter was extracted with 5mL of deionized ultra-pure water (Milli-Q) in a mechanical shaker for 1 hour and the water extract was filtered on PTFE membranes (pore size: $0.45 \mu\text{m}$) in order to remove suspended particles. The water extracts were dried by rotary evaporator and were then re-dissolved in 2.15mL of D_2O . An aliquot (0.65mL) was used for proton-nuclear magnetic resonance ($^1\text{H-NMR}$) characterization, while a second aliquot (1.5mL) was kept for HPLC analysis and total organic carbon (TOC) analysis. The NMR aliquot was mixed with sodium 3-trimethylsilyl-(2,2,3,3- d_4) propionate (TSP- d_4) as internal standard, and with a buffer of potassium formate/formic acid (pH~3.8). The $^1\text{H-NMR}$ spectra were acquired at 600MHz with a Varian 600 spectrometer in a 5mm probe. The sample SPC_020712_D was used for comparison with the spectroscopic data of the SOA samples (Figure 7 of the manuscript). The $^1\text{H-NMR}$ spectrum of sample SPC_020712_D is shown in Figure S1.

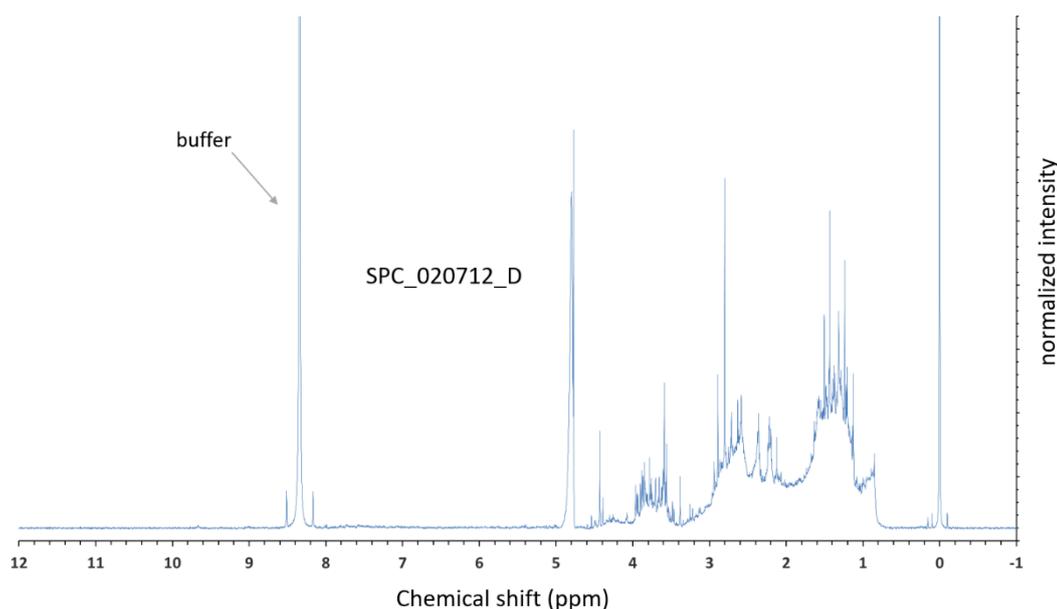


Figure S1. $^1\text{H-NMR}$ spectrum of sample SPC_020712_D (after water-extraction) collected in San Pietro Capofiume, a rural site nearby Bologna. Sampling time was 9:00-20:30 (local time).

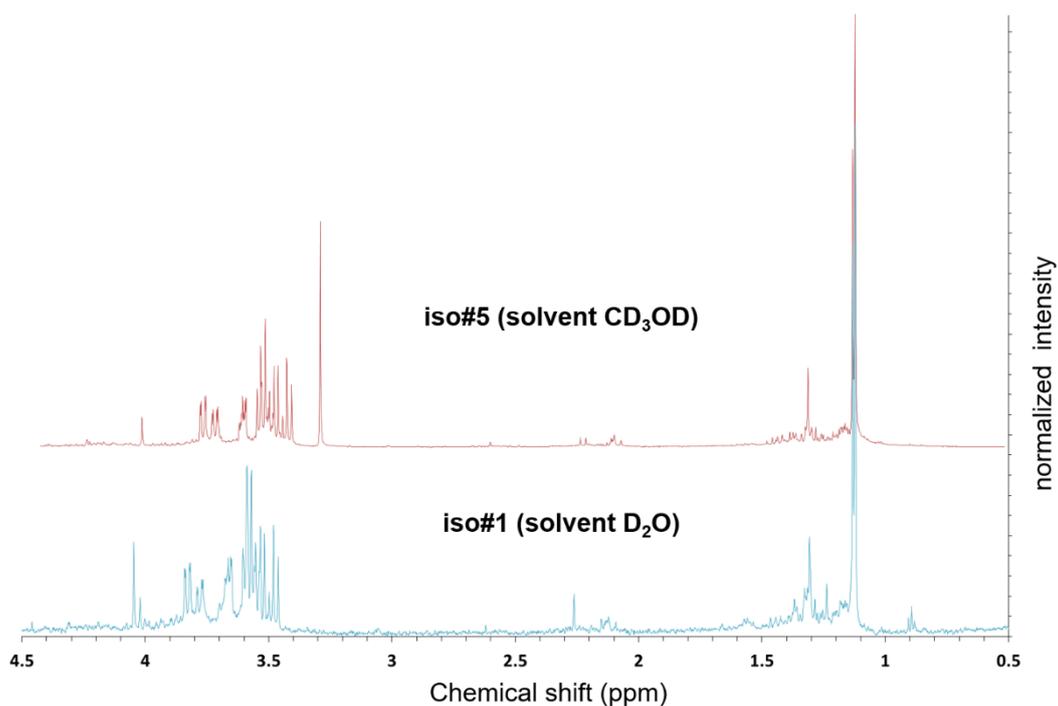


Figure S2. H-NMR spectra (600 MHz) of two isoprene SOA generated with the PAM flow reactor, iso#1 (H-NMR solvent: D₂O) and iso#5 (H-NMR solvent: CD₃OD) samples.

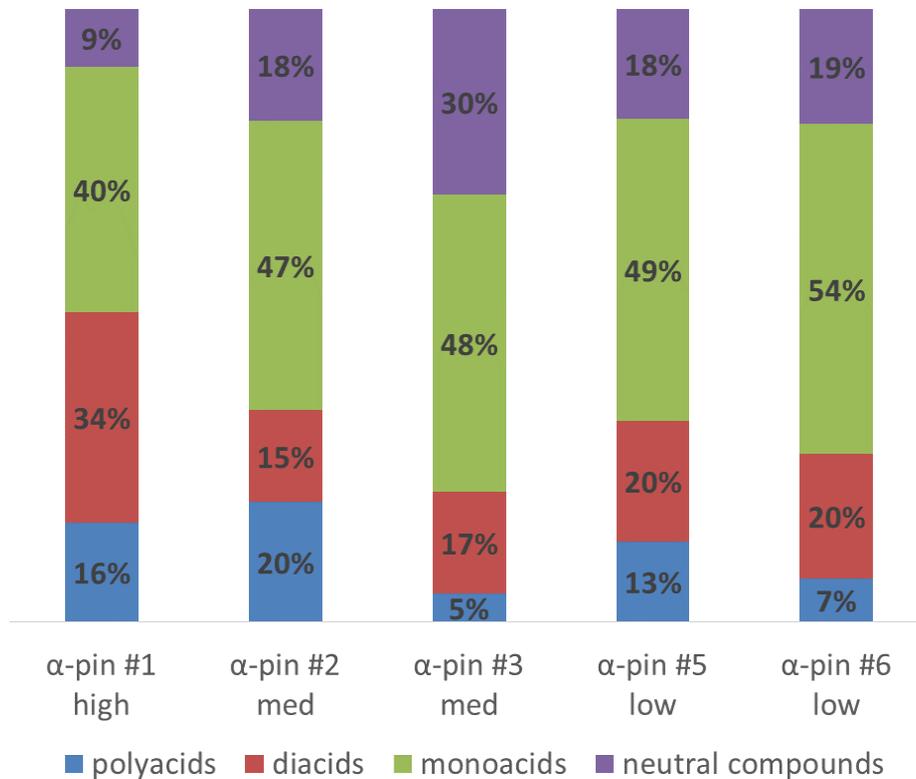


Figure S3. WSOC fractions analyzed by HPLC-TOC for various α-pinene SOA samples generated with the PAM.

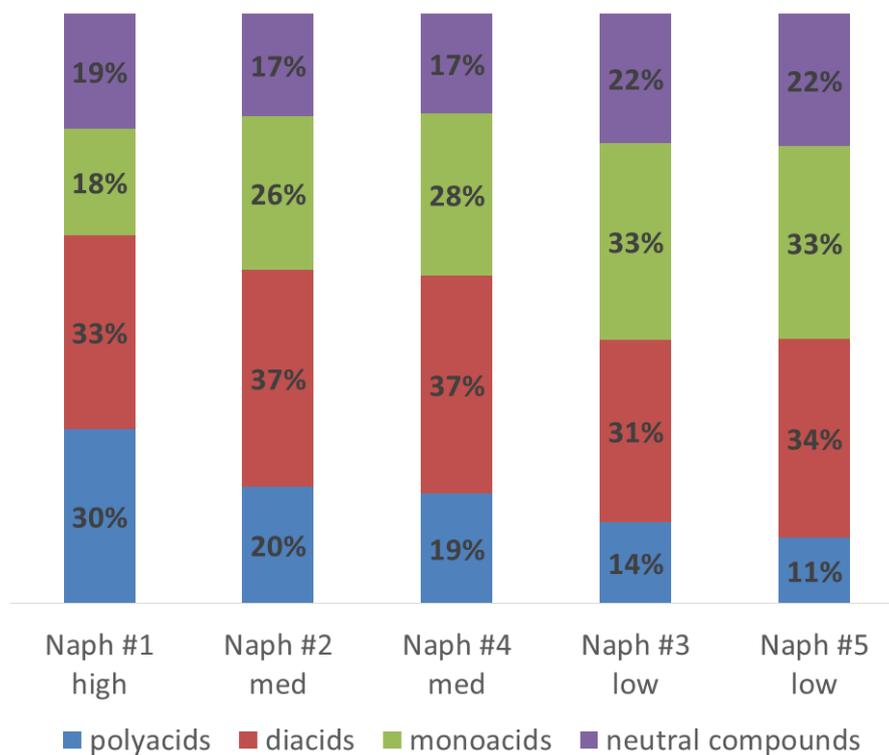


Figure S4. WSOC fractions analyzed by HPLC-TOC for various naphthalene SOA samples generated with the PAM.