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Organic aerosol molecular composition and gas–particle partitioning coefficients at a Mediterranean site (Corsica)

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ABSTRACT

Molecular speciation of atmospheric organic matter was investigated during a short summer field campaign performed in a citrus fruit field in northern Corsica (June 2011). Aimedat assessing the performance on the field of newly developed analytical protocols, this work focuses on the molecular composition of both gas and particulate phases and provides an insight into partitioning behavior of the semi-volatile oxygenated fraction. Limonene ozonolysis tracers were specifically searched for, according to gas chromatography–mass spectrometry (GC–MS) data previously recorded for smog chamber experiments. A screening of other oxygenated species present in the field atmosphere was also performed. About sixty polar molecules were positively or tentatively identified in gas and/or particle phases. These molecules comprise a wide range of branched and linear, mono and di-carbonyls (C_3–C_7), mono and di-carboxylic acids (C_3–C_{18}), and compounds bearing up to three functionalities. Among these compounds, some can be specifically attributed to limonene oxidation and others can be related to α- or β-pinene oxidation. This provides an original snapshot of the organic matter composition at a Mediterranean site in summer. Furthermore, for compounds identified and quantified in both gaseous and particulate phases, an experimental gas/particle partitioning coefficient was determined. Several volatile products, which are not expected in the particulate phase assuming thermodynamic equilibrium, were nonetheless present in significant concentrations. Hypotheses are proposed to explain these observations, such as the possible aerosol viscosity that could hinder the theoretical equilibrium to be rapidly reached.

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Introduction

The formation of organic particulate matter in the earth's atmosphere through gas-to-particle transfer during atmospheric oxidation of volatile organic compounds (VOC), namely secondary organic aerosol (SOA) formation, is involved in both air quality and climate issues (IPCC 2007; Hallquist et al. 2009). However, despite substantial advances during the last decade (Donahue et al. 2006; Tsimpidi et al. 2010; Valorso et al. 2011; Couvidat et al. 2012), significant efforts are still currently provided in modeling studies to take into account the gas/particle partitioning behavior of the semi-volatile fraction of the secondary organic matter. Understanding the processes involved in these gas/particle equilibriums is indeed crucial for a better assessment of SOA yields, SOA chemical composition and thus SOA's influence on climate and health. SOA growth is usually described by absorption into the organic phase of the aerosols of semi- and non-volatile secondary species formed in the gas phase by atmospheric oxidation of precursor VOC (Odum et al. 1996; Seinfeld and Pankow 2003; Asher and Pankow 2006). Nevertheless, SOA formation and aging also involve chemical processes into the particle phase (Graber and Rudich, 2006; Healy et al. 2008; Kroll and Seinfeld, 2008; Monks et al. 2009) or at the gas–particle interface (Rudich et al. 2007, George and Abbatt 2010). This results in continuous modifications of SOA chemical composition and physico-chemical properties, influencing in turn the partitioning of the semi-volatile species (Healy et al. 2008). Such phenomena have to be evidenced and characterized in real atmospheric conditions.

In order to describe this multiphase chemistry and take gas/particle partitioning phenomena into account, a new analytical approach has recently been developed by Rossignol et al. (2012). It involves the simultaneous collection of both gaseous and particulate phases onto solid supports (adsorbent and filter), which are subsequently analyzed by thermal desorption coupled with gas chromatography and mass spectrometry (TD–GC/MS). Compared to previous works (Temime et al. 2007), this technique allows a rather easy detection of carbonyl compounds on the one side, and hydroxyl and carboxyl species, on the other side, using solid support derivatization procedures.

The present study, performed on a rural site of a Mediterranean island, Corsica, focused on the detection of limonene oxidation products by means of this new analytical method and relies for this purpose on a parent study performed in smog chamber experiment that involved the same new technique (Rossignol et al. 2012). A screening of other oxygenated species present in the field atmosphere was also performed in order to chemically characterize the collected organic matter as much as possible. One of the main objectives was to provide gas/particle partitioning coefficients of identified species under real conditions and compare them to theoretical values currently used in models to provide insight into the behavior of semi-volatile oxygenated compounds that are potentially influenced by still unaccounted specific processes.

1. Experimental

1.1. Sampling location and periods

The sampling site is a citrus field of around 30 ha belonging to the French National Institute for Agricultural Research (INRA). It is located in Corsica (France, Fig. S1) in a woody environment between Cervione and San Giuliano, small villages of 1600 and 600 inhabitants respectively, at 2 km from the eastern coast (9.5339744°E,42.2813633°N). The field is composed of a wide variety of citrus trees, including lemon, oranges, tangerine, citron, clementine, *etc*. It is surrounded by other tree species, like pine, implying the emission of wide range of biogenic VOC including limonene (Kesselmeier and Staudt 1999). This paper presents a snapshot of the atmospheric chemical composition as measured on June 23, 2011, as only two samples were taken during two consecutive periods, from 1 pm to 5 pm UTC and from 7 pm to 12 pm UTC. Nevertheless, these two samples were extremely useful to illustrate the analytical power of the protocol developed by Rossignol et al. (2012) and so, to provide an interesting insight on the physico-chemical behavior of oxidized organic atmospheric species. For these two sampling periods, low level (100 m) Hysplit back-trajectories (Draxler and Rolph 2014; Rolph 2014) provided with the Global Data Assimilation System (GDAS) meteorology fields from US National Weather Service at a resolution of 0.5° show that air masses were coming south-south-east, traveling in the boundary layer above Tyrrhenian Sea with no off-land contamination for more than 48 hr. Remarkably, the air masses that arrived on the sampling site from 1 pm to 5 pm had reached the Corsica coast from 30 min to 1.5 hr before, whereas the air masses that arrived on the sampling site from 7 pm to 12 pm had reached the coast from 2 to 5 hr before, possibly inducing differences in air masses chemical composition. Furthermore, higher level back-trajectories (500 m) show an even longer above-land transit for the evening air-masses. Globally, this indicates that both air masses sampled include a significant aged component with a very low fine aerosol loading while the second sample has probably been under a much stronger influence of in-land sources passing over fields and typical Mediterranean forest (with no major urbanized area).

1.2. Instrumentation for key parameters measurement

A weather station monitored temperature, relative humidity, wind speed and wind direction. Ozone concentration was measured by a 49i absorption ozone analyzer (49i, Thermo Electron Corporation, USA). $PM_{2.5}$ mass concentration was monitored with a Tapered Element Oscillating Microbalance (TEOM) (series 1400a, Rupprecht & Patashnick Co., USA) mounted with an Filter Dynamics Measurement System (FDMS) (series 8500, Rupprecht & Patashnick Co., USA). An optical particle counter (Grimm 1.108, Grimm Technologies, Germany) was used in parallel to estimate $PM_{2.5}$ and PM_1 mass concentrations, using a proportionality factor of 1 (taking into account the aerosol's density, refraction index and shape) to convert volume concentrations into mass concentrations. Limonene concentration was measured by an on-line gas