NEW TECHNIQUES FOR THE MEASUREMENT OF THE PHYSICAL PROPERTIES OF ATMOSPHERIC ORGANIC AEROSOL

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Abstract

A new method for the measurement of the water solubility distribution of atmospheric organic aerosol was developed. This method is based on the extraction of organic aerosol collected on filters, using different amounts of water and measurement of the corresponding Water Soluble Organic Carbon (WSOC) concentration. The solubility distribution is then estimated using the solubility basis set. The proposed approach can quantify the solubility distribution in the $10^{-3}$-1 g L$^{-1}$ range.

The method was applied on both ambient and source-specific aerosol. 58-63% of the atmospheric urban background organic aerosol analyzed had water solubility higher than 1 g L$^{-1}$. 11% of the fresh cooking organic aerosol had water solubility higher than 0.1 g L$^{-1}$, while 80% had solubility lower than $10^{-3}$ g L$^{-1}$. The solubility of the COA increased significantly after aging. The fraction of COA with solubility greater than 0.1 g L$^{-1}$ more than doubled, increasing to 55%.

Additionally, a new method for the measurement of Henry’s law constant distribution of atmospheric organic aerosol components was developed and tested. The method is based on the separation of the OA constituents by volatility and then measurement of the water solubility distribution of each fraction. The results showed that an important fraction of the biogenic secondary organic aerosol with volatility equal to 1 μg m$^{-3}$ (about 50%) has Henry’s law constant between $4 \times 10^4$ and $4 \times 10^5$ M atm$^{-1}$. 
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Abbreviations

BBOA: Biomass Burning Organic Aerosol
BC: Black Carbon
CCN: Cloud Condensation Nuclei
CE: Collection Efficiency
COA: Cooking Organic Aerosol
HOA: Hydrocarbon-like Organic Aerosol
HR-ToF-AMS: High Resolution Time of Flight Aerosol Mass Spectrometer
IC: Ion Chromatography
L-OOA: Less Oxygenated Organic Aerosol
M-OOA: More Oxygenated Organic Aerosol
O:C: Oxygen to Carbon ratio
OA: Organic Aerosol
OC: Organic Carbon
OOA: Oxygenated Organic Aerosol
PM: Particulate Matter
PMF: Positive Matrix Factorization
POA: Primary Organic Aerosol
PTR-MS: Proton Transfer Reaction Mass Spectrometer
SMPS: Scanning Mobility Particle Sizer
SOA: Secondary Organic Aerosol
TOC: Total Organic Carbon
VOC: Volatile Organic Compound
WSOC: Water Soluble Organic Carbon
Chapter 1

Introduction
1.1 Atmospheric Aerosols

Atmospheric aerosols or particulate matter (PM) are suspended liquid or solid particles in the Earth’s atmosphere. They are characterized by their size (diameter), mass, chemical composition, physical and chemical properties and play a significant role in the physical and chemical processes occurring throughout the atmosphere.

![Figure 1.1. Schematic of the direct and indirect cooling effects of atmospheric aerosols.](image)

Atmospheric aerosols can affect the climate either direct or indirect. For example, black carbon (BC), one of the components of atmospheric PM, can absorb light and consequently has a warming effect on climate\(^1\). Particles composed of sulfates, organics, etc., can scatter solar radiation, having a direct cooling effect on climate\(^2\). Figure 1.1 shows the direct and indirect cooling effects of atmospheric aerosols.

In addition, particles can serve as cloud condensation nuclei (CCN) on which water can condense and form cloud droplets, having an indirect effect on climate. The size and the composition of the particles determine their ability to act as CCN. Thus, particles that consist of compounds with high water affinity are better CCN compared to particles with hydrophobic components. The impact of aerosols on climate forcing is still highly uncertain. Figure 1.2 illustrates the principal factors contributing to the
total radiative forcing of the Earth’s climate, including the greenhouse gases and the aerosol’s direct and indirect effect\(^3\).

**Figure 1.2.** Principal components of the radiative forcing of our planet during the last 250 years. The error bars show the range of uncertainty\(^3\).

**Figure 1.3.** Composition of atmospheric aerosol in different geographic areas\(^4\). The green color corresponds to the organic particles, the red color denotes the sulfate, the blue color the nitrate, the orange the ammonium and the purple the chloride.
The diameter of atmospheric particles ranges from a few nanometers to tens of micrometers. In general, atmospheric particles are classified in two major classes: “fine” and “coarse”, where fine particles have diameters less than 2.5 μm in diameter and particles larger than 2.5 μm are considered as coarse. The composition and size of atmospheric particles continuously changes due to reactions in the gas phase and subsequent condensation of low volatility products, evaporation, coagulation, etc. The chemical composition of atmospheric particles depends on the geographic area and on the corresponding sources. Figure 1.3 shows the composition of the atmospheric particles for different geographic regions. In general, aerosol particles emitted naturally by evaporation of water from sea spray, volcano eruptions, corrosion of materials (e.g., rocks, sand) can be found mainly in the coarse mode. Combustion emissions are almost exclusively in the fine mode.

1.2 Organic Aerosol

Organic compounds are one of the most significant components of atmospheric PM, representing 20-90% of the total aerosol mass concentration. There are tens of thousands of different chemical species in atmospheric PM and only a small fraction of them have been identified and quantified. From a source perspective, organic aerosol can be classified as primary (POA) or secondary (SOA). POA refers to the organic mass that is emitted in the particle phase. POA is directly emitted into the atmosphere from a range of combustion sources including diesel and gasoline vehicle exhaust, biomass burning, meat cooking, etc. On a global scale biomass burning is responsible for almost 90% of primary OA emissions. SOA is formed in the atmosphere when volatile organic compounds (VOCs) react with atmospheric oxidants such as ozone (O₃), hydroxyl radical (OH) or
nitrate radical ($\text{NO}_3^-$). Figure 1.4 summarizes the processes that take place in the atmosphere and lead to the formation of the SOA. These reactions form low volatility products that can condense on preexisting particles in the atmosphere. Both POA and SOA have biogenic and anthropogenic sources.

**Figure 1.4.** Schematic of the different sources of atmospheric organic aerosol and the physiochemical processes that take place in the atmosphere.

### 1.3 Water Soluble Organic Aerosol (WSOC)

The water soluble organic species present in atmospheric aerosols are usually referred to as water soluble organic carbon (WSOC). The WSOC is an operationally defined quantity, since the dissolution of a compound in water depends not only on the solubility of the compound but on the amount of water or the concentration of the solution and other extraction parameters as well.\(^7\)
The methods for the measurement of WSOC can be divided in two major classes, on-line and off-line. The on-line methods of the WSOC measurement correspond to the determination of the WSOC concentration in a high resolution of a few minutes. The off-line measurement includes sample collection on the surface of a quartz-fiber filter which is afterwards immersed in a volume of water in order to extract the water-soluble species. However, uncertainties concerning the effect of such procedures combined with the fact that there is no protocol or standard volume of water used in such extractions, can lead to differences in the measured water-soluble fraction.

1.4 Water Solubility of Organic Aerosol

The water solubility is one of the most important physical properties of atmospheric organic aerosol as it determines its ability to absorb water and also to act as CCN. Given the chemical complexity of the atmospheric OA there have been efforts to approach the complexity of the OA-water interactions by separating the OA into two fractions: water soluble and water insoluble. This simplistic approach has led to a semi-empirical definition of the Water Soluble Organic Carbon (WSOC)\(^8\). WSOC is generally operationally defined, since a variety of different off-line methods have been developed for its measurement. The wide range of solubilities and ambient concentrations of the organic compounds along with the variability of the volume of water available for their extraction can lead to different results by different methods.

1.5 Henry’s Law Constant of OA components

The Henry’s law constant \(H\) (defined here as the ratio of the aqueous-phase concentration of a compound A to its gas-phase partial pressure, \(H_A = [A_{(aq)}/p_A]\) is another important physical property of the semivolatile atmospheric organic aerosol
components that is poorly constrained. The Henry’s law constant determines the partitioning of these compounds between the gas and aqueous-phase and is important for their atmospheric lifetime (it determines their dry deposition velocity and their wet deposition rates) and it also determines to a large extent their potential for significant aqueous-phase chemical transformations. The corresponding constants for specific organic compounds that have been identified in the particulate phase vary from $10^{-4}$ to $10^{10} \text{ M atm}^{-1}$. There is no information about the distribution of Henry’s law constants for ambient OA and this creates significant uncertainty in the predictions of CTMs simulating semivolatile OA. For example, depending on the $H$ value used by the model the atmospheric lifetimes of the corresponding vapors can vary by one order of magnitude affecting significantly the predicted OA concentrations. The aqueous solubility ($S_A$ in g L$^{-1}$) together with the saturation vapor pressure ($p_A^0$ in atm) of a compound can be used to calculate its Henry’s law constant ($H_A$ in M atm$^{-1}$) using:

$$H_A = \frac{S_A}{p_A^0 \cdot MW_A}$$

(1.1)

where $MW_A$ is the molecular weight (in g mol$^{-1}$) of A. Equation (1) is an accurate approximation for all atmospheric OA components.

1.6. References


Chapter 2

Development of a Method for the Measurement of the Water Solubility Distribution of Atmospheric Organic Aerosol*

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2.1 Introduction

Fine atmospheric aerosol (PM$_{2.5}$) has adverse effects on human health contributing to respiratory and cardiovascular illnesses$^{1,2}$. In addition, atmospheric aerosols affect the global climate directly either by scattering$^3$ or by absorbing solar radiation$^4$. They also have an indirect effect on climate, acting as cloud condensation nuclei (CCN)$^5$. Organic aerosol (OA) is one of the most important components of the fine atmospheric particulate matter$^6$. Its contribution to the PM$_{2.5}$ mass may reach more than 50%$^7$. However, its chemical composition and physical properties remain uncertain$^8,9$. OA consists of thousands of compounds but only a small fraction of them has been identified and quantified$^{10}$.

Primary organic aerosol (POA) components tend to be less water-soluble than secondary ones$^{11-13}$. The water soluble organic compounds usually represent an important part of the total OA$^{14,15}$. The WSOC fraction influences the water uptake ability and the CCN activity of the atmospheric fine aerosol$^{16}$. Although there have been a lot of laboratory and field measurements of WSOC, the corresponding measurement approaches still remain semi-empirical as they depend on many parameters (e.g., air sampling flow rate, water volume used for the extraction etc.) making the interpretation of their results challenging$^{14,17}$.

Psichoudaki and Pandis$^{18}$ presented a theoretical analysis of the existing WSOC measurement approaches. They proposed a single parameter, $P$, to describe all the measurement method variables. The $P$ parameter (cm$^3$ m$^{-3}$) is proportional to the water volume used for the extraction ($V_w$ in cm$^3$) and inversely proportional to the sample volumetric flow rate ($Q$ in cm$^3$ min$^{-1}$), the fraction of the filter’s surface used for the analysis ($f$) and the sampling time ($\Delta t$ in min):

$$ P = \frac{V_w}{f Q \Delta t} \tag{2.1} $$
The $P$ parameter, describes the quantity of the solvent (water) used for the WSOC analysis per volume of air sampled\textsuperscript{18}. They suggested that the measured WSOC concentration increases when $P$ increases.

Riipinen et al.\textsuperscript{19} estimated that atmospheric OA components in the solubility range 0.1-100 g L\textsuperscript{-1} act partially as CCN. They suggested that compounds with solubility higher than 100 g L\textsuperscript{-1} are completely soluble during cloud formation, while compounds with solubility less than 0.1 g L\textsuperscript{-1} should be considered practically as insoluble for atmospheric purposes.

Although the theoretical analysis of Psichoudaki and Pandis\textsuperscript{18} was a first step towards improvement of WSOC quantification their work was purely theoretical and has not been confirmed by measurements. The first objective of this work is to verify their prediction that WSOC increases significantly as $P$ increases. The second objective is to take advantage of the WSOC dependence on $P$ in order to estimate the OA water solubility distributions.

\section*{2.2 Experimental Description}

\subsection*{2.2.1 Measurement of WSOC}

Aerosol samples were collected on quartz fiber filters. The filters were preheated at 500°C for 24 hours in order to remove any organic impurities. A high-volume PM\textsubscript{2.5} sampler (Tisch Environmental) was used for the sample collection, operating at a flow rate 0.22 m\textsuperscript{3} min\textsuperscript{-1}. The sampling time varied from a few hours to several days depending on the concentration of organic compounds and the desired value of the $P$ parameter.

All the sample analysis took place in a laminar fume hood in order to avoid contamination of the samples. The glass bottles, Pasteur pipettes, and syringes used
were first cleaned with acetic acid and purified water. After cleaning they remained in an oven at 500°C for 24 hours, so that all organic compounds were removed.

Punches (1.13 cm² area) were removed from the filter. The number of the punches depended on the desired $P$ value: 5 for $P=0.01$ cm³ m⁻³, 2 for $P=0.1$ cm³ m⁻³ and 1 for $P$ higher than 1 cm³ m⁻³. After the punches were placed in glass bottles ultrapure water was added. The amount of the needed water was calculated using the definition of the $P$ parameter (Equation 2.1) as:

$$V_w = PQf\Delta t$$ (2.2)

Four different $P$ values were used in these experiments: 0.01, 0.1, 1 and 10 cm³ m⁻³. The glass bottles with the filter punches and the water were then placed in a sonicating bath (Ultrasonic Laboratory Bath, Elmasonic S150) for 45 minutes. The sonication was followed by hand shaking and rinsing of the bottle walls with 12-20 cm³ of water. Afterwards, the liquid sample was filtered through a 0.45 μm pore size PTFE filter for insoluble particles and filter debris removal, using a glass syringe¹⁹,²⁰. The PTFE filters had been preheated at 70°C for 15 minutes. The final volume of the liquid sample was recorded. Finally, the glass bottle was sealed with parafilm and was connected to a Total Organic Carbon (TOC) analyzer (Portable TOC, Sievers 900, GE) for the WSOC measurement. The TOC level (blank level) of the ultrapure water was also measured after each sample.

### 2.2.2 Additional Instrumentation

A Lab OC-EC Aerosol analyzer (SUNSET Laboratory Inc.) was employed to measure the total organic carbon (OC) and elemental carbon (EC) of the same aerosol samples applying the EUSAAR2 protocol²¹.
A High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc), monitored the chemical composition of the non-refractory (NR) PM$_1$ particles$^{22}$. The HR-ToF-AMS was operated in the V-mode with a 3-minute sampling time. The voltage of the filament was 70 eV and the vaporizer temperature was 600 °C.

The ozone that needed for the aging experiments purposes was generated by an electrical discharge generator (AZCO, model HTU-500ACPS) and its concentration was monitored using a continuous ozone analyzer (Dasibi 1008-PC).

An ion chromatography system (Metrohm 761 Compact IC) was used to measure the sulfate and other ion concentration. For the analysis purposes parts of the filters were used. The collected aerosol, on those parts, was extracted in ultrapure water. The corresponding solutions were injected in the system and the ion concentration was measured.

### 2.2.3 Sampling Details

Ambient measurements were performed at the Institute of Chemical Engineering Sciences (ICE-HT) in Patras, Greece (latitude 38.298°, longitude 21809°). Ambient samples were collected during three different periods: 13:40 on November 15 to 16:40 on November 17 of 2016 (Period 1), 14:15 on November 17 to 15:25 on November 18 of 2016 (Period 2) and 15:50 on March 30 to 15:00 on April 1 of 2015 (Period 3). For Periods 1 and 2, the sampling time was about 24 hours, while for Period 3 the corresponding sampling time was about 48 hours.

Cooking experiments were conducted in the Laboratory of Air Quality Studies of the ICE-HT. For the two meat cooking experiments, souvlakia of pork meat were grilled using charcoal. The corresponding meat cooking emissions were injected into
an 8 m³ Teflon (PTFE) smog chamber pre-filled with clean air. The HR-ToF-AMS sampled the COA emissions from the chamber, while the Tisch sampler was sampling directly above the source of COA. More information is provided in Kaltsonoudis et al.23. For the COA measurements, the sampling period was about 1 hour.

Cooking experiments were also conducted in the laboratory of the Center for Atmospheric Particle Studies (CAPS), in Carnegie Mellon University. The smog chamber is a 10 m³ Teflon reactor (Welch Fluorocarbons) inside a temperature controlled room. Beef burgers (25% fat) were cooked on a grill using charcoal. The COA was injected into the smog chamber using two ejector diluters (Dekati, Finland) in parallel. The chemical aging of COA was initiated by injecting ozone one hour after the COA injection. The aging process lasted 5-6 hours. Again, the HR-ToF-AMS sampled the COA emissions from the chamber. Fresh and aged particles were collected on quartz filters (47 mm diameter, Pall Life Sciences) for about 1 h with a sampling flow rate of 20 L min⁻¹. The fresh particles were collected just after the COA injection and the aged particles were collected about 1 h after the ozone injection.

2.3. Data Analysis

2.3.1 HR-ToF-AMS data

The HR-ToF-AMS data were analyzed using the data analysis software SQUIRREL v1.56D and PIKA v1.15D24, within Igor Pro 6.34A (Wave Metrics). The HR-ToF-AMS collection efficiency (CE) was assumed to be equal to unity, in all cases. For the elemental ratios the method of Canagaratna et al.25 was used. Positive Matrix Factorization (PMF) analysis26,27 was applied, using as inputs the HR OA mass spectra, for the identification of the various OA sources.
2.3.2 TOC analyzer data

The WSOC concentration of each sample was calculated by subtracting the concentration of the corresponding blank value. The WSOC concentration was calculated by:

\[
\text{WSOC (\(\mu g m^{-3}\))} = \frac{((\text{TOC})_{\text{meas}} - [\text{TOC}]_{\text{blank}})}{f \cdot Q \cdot \Delta t} \cdot V_{\text{sample}} \cdot \rho_w
\] (2.3)

where \((\text{TOC})_{\text{meas}}\) is the sample TOC concentration in ppm, \((\text{TOC})_{\text{blank}}\) is the concentration of the corresponding TOC concentration of ultrapure water in ppm, \(\rho_w\) is the density of water in kg \(m^{-3}\) and \(V_{\text{sample}}\) is the final sample volume of the liquid sample used for the WSOC analysis, in cm\(^3\).

2.3.3 Calculation of the Solubility Distributions

Following the approach of Psichoudaki and Pandis\(^{18}\), we assume that the organic components form a pseudo-ideal solution in the particle phase. According to their analysis, the fraction of a component \(A\), \(f_A\), that will be extracted in water is given by:

\[
f_A = \frac{P \cdot S_A}{P \cdot S_A + C_{OA}(1 - f_{\text{wsoc}})}
\] (2.4)

where \(S_A\) is the saturation concentration of \(A\) in the aqueous phase, \(f_{\text{wsoc}}\) is the fraction of the water-soluble compounds in the solution, \(C_{OA}\) is the total concentration of all organic compounds collected on the filter and \(C_{OA}(1 - f_{\text{wsoc}})\) is the concentration of the organics that will remain in the organic phase of the aerosol. In this case, the fraction of a compound that will be measured as WSOC depends on (a) the total concentration of the organic compounds not dissolved in the water during the extraction, (b) the solubility of the compounds, and (c) the \(P\) parameter. Using this simplified model each
value of the $P$ parameter corresponds to a specific range of solubility that is extracted (Figure 2.1). For example, a $P$ value equal to 0.01 cm$^3$ m$^{-3}$ corresponds to OA components with water solubility above 1 g L$^{-1}$, $P=0.1$ cm$^3$ m$^{-3}$ to those with solubility above 0.1 g L$^{-1}$ etc.$^{18}$.

**Figure 2.1** Solubility ranges of various organic compound classes found in atmospheric aerosols and predicted solubility range for full extraction of a compound by the ideal organic solution model for different $P$ parameter values. The vertical lines above the figure indicate the thresholds above which organic compounds are fully extracted for typical OA concentrations. The horizontal lines represent the corresponding solubility ranges.

Therebefore the fraction of the OA that corresponds to each solubility range can be calculated taking the difference of the corresponding fractions. For example, the fraction of the OA with solubility between 0.1 and 1 g L$^{-1}$ can be estimated by subtracting the fraction that dissolved in water at $P=0.01$ cm$^3$ m$^{-3}$ (solubility above 1 g L$^{-1}$) from that which dissolved at $P=0.1$ cm$^3$ m$^{-3}$ (solubility above 0.1 g L$^{-1}$). Since
the sum of the OA mass fractions is equal to unity, the least water soluble organic aerosol mass fraction can also be calculated by subtracting the previously estimated fractions from unity. As an example, let us assume that one is using two \( P \) values: 0.01 and 0.1 cm\(^3\) m\(^{-3}\). Then from the corresponding measurements one can estimate the solubility distribution with three bins: solubility less than 0.1 g L\(^{-1}\), between 0.1 g L\(^{-1}\) and 1 g L\(^{-1}\) and above 1 g L\(^{-1}\).

The proposed method can measure the water solubility distribution in the range from 10\(^{-3}\) to 1 g L\(^{-1}\). For water solubility higher than 1 g L\(^{-1}\), \( P \) values lower than 0.001 cm\(^3\) m\(^{-3}\) are necessary. These require use of tiny amounts of water and will probably lead to incomplete water-soluble OA extraction, as the low water volume might not even cover the filter completely and even highly soluble compounds might not be extracted. On the other hand, for solubility values lower than 10\(^{-3}\) g L\(^{-1}\), \( P \) values higher than 10 cm\(^3\) m\(^{-3}\) should be used, requiring large amounts of ultrapure water for the extract. These result in aqueous solutions with organic compound concentration lower than the TOC detection limit. Riipinen et al.\(^1\) suggested that the critical solubility range for CCN studies can be up to 100 g L\(^{-1}\). This requires \( P \) values as low as 10\(^{-4}\) cm\(^3\) m\(^{-3}\) for 24-hr sample collection, using a 220 L min\(^{-1}\) flowrate, which is quite difficult to achieve. In order to attain such low \( P \) values, the sampled air volume should be very high. This can be accomplished using very long sampling times such as 10 days or more, with high sampling flowrates.

2.4 Results

2.4.1. Ambient Organic Aerosol Characterization

(a) Ambient organic aerosol (Periods 1 and 2). During Periods 1 and 2 the average temperature and relative humidity (RH) were 13°C and 72-75% respectively (Figure
2.2). For Period 1, the temperature varied from 10 to 16°C, while the RH was between 53 and 92%. For Period 2 the varied between 10 and 18°C, and the RH between 49 and 87%.

Figure 2.2. Temperature and RH variation during the two filter collection periods. Shaded areas depict the two periods during which samples were collected. The data correspond to 1-hour averages.

Figure 2.3. Time series of the concentrations of the ambient PM$_1$ components, measured by the AMS. The shaded areas correspond to the two filter collection periods. The CE was assumed to be 1. The data shown correspond to 1-hour averages.
During Period 1, the ambient OA concentration varied from 0.4 to 2.2 μg m$^{-3}$, while during Period 2, between 1.7 and 4.3 μg m$^{-3}$ (Figure 2.3). For Period 1, the average OA mass concentration was 1.2 μg m$^{-3}$, ammonium was 0.3 μg m$^{-3}$, sulfate was 1 μg m$^{-3}$, nitrate was 0.1 μg m$^{-3}$, and chloride was 0.01 μg m$^{-3}$. During Period 2, the average OA was 2.5 μg m$^{-3}$, ammonium was 0.4 μg m$^{-3}$, sulfate was 1.5 μg m$^{-3}$, while nitrate and chloride were 0.2 μg m$^{-3}$ and 0.01 μg m$^{-3}$ respectively. During the first filter collection period, the average O:C and H:C ratios were 0.6 and 1.5 correspondingly. For Period 2 the average O:C ratio was 0.7, while the H:C was 1.5 (Figure 2.4).

![Figure 2.4](image) O:C and H:C ratios as a function of time. The shaded areas correspond to the two sampling periods. The averaging time was 1 hour.

The PMF analysis (APPENDIX II) showed the existence of three factors: more oxidized OOA (M-OOA), less oxidized OOA (L-OOA) and hydrocarbon-like/cooking OA (HOA/COA) (Figure 2.5). Both M-OOA and L-OOA factors were related to
secondary OA likely transferred to Patras from other areas. The HOA/COA factor corresponds to primary OA, emitted by transportation and cooking activities.

For Period 1, 26% of the total OA was M-OOA, 57% was L-OOA and 17% was HOA/COA. For Period 2, the M-OOA contributed 53%, L-OOA represented 29% and HOA/COA was 18% (Figure 2.6).

Figure 2.5. Mass spectra of the three PMF factors for sampling Periods 1 and 2.
Figure 2.6. Time series of the 3 factors, as they were calculated by the PMF analysis of the AMS data (1-hour averages and CE=1). The black line denotes the M-OOA, the red line the L-OOA, and the blue line corresponds to the combination of hydrocarbon-like and cooking OA (HOA/COA).

In these measurements, which corresponded to long sampling periods, low OA concentrations and high flowrate values, the chosen $P$ parameters were 0.01, 0.1 and 1 cm$^3$ m$^{-3}$. The measured WSOC at different $P$ values during the two periods is given in Figure 2.7(a-b). The concentration of the OC, as expected, exceeded the concentration of WSOC in all cases. The concentration of WSOC increased when higher values of the $P$ parameter were used, confirming the predictions of Psichoudaki and Pandis (2013). During Period 1, WSOC increased from 1.5 to 2.4 μg m$^{-3}$ when $P$ increased from 0.01 to 1 cm$^3$ m$^{-3}$ in these samples. During Period 2, for the same increase of $P$, WSOC increased from 2 to 2.7 μg m$^{-3}$ (Table I).
Figure 2.7. WSOC and OC concentration as a function of P parameter for (a) Period 1, (b) Period 2, and (c) Period 3. Different axes are used.

The estimated solubility distributions of the ambient OA are shown in Figure 2.8. During Period 1, 58% of the collected OA had water solubility higher than 1 g L\(^{-1}\), while during Period 2 the corresponding percentage was 63%. PMF analysis showed that during the two periods approximately 80% of the total OA was oxidized OOA. This is consistent with the high mass fractions of the OA distributed in solubility ranges higher than 1 g L\(^{-1}\), since SOA tends to be quite water soluble\(^7\). The estimated solubility distributions for the two periods were in general quite similar. The mass fraction values corresponding to water solubility less than 0.01 g L\(^{-1}\) were equal to 8% and 14% during
Periods 1 and 2, respectively. For comparison, the fresh primary OA was estimated to contribute 17% and 18% to the total OA during these two periods.

![Diagram](image)

**Figure 2.8.** (a) Water solubility distributions of ambient organic aerosol for the two filter collection periods, (b) water solubility distribution of ambient aerosol influenced by biomass burning emissions (Period 3) and (c) water solubility distributions of cooking organic aerosol for Experiments 1 and 2.

**(b) Ambient Aerosol influenced by biomass burning emissions (Period 3).** The average temperature during the third sampling period was 13.2°C and the average RH was 72% (Figure 2.9). There were periods of high OA concentrations due to biomass burning and local off-road vehicles emissions in nearby construction (Figure 2.10). The average
total mass PM$_1$ concentration was 3.8 μg m$^{-3}$, while the average OA mass concentration was 2.3 μg m$^{-3}$.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2_9.png}
\caption{Atmospheric temperature and RH range during the sampling period March 30 to April 1 of 2015 (Period 3). The temperature varied from 9.6 to 18.3o C, while the RH was between 91% and 44%. The averaging time was 1-hour.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig2_10.png}
\caption{Mass concentration of ambient PM1, components measured by the AMS during the sampling period March 30 to April 1 of 2015 (CE=1). The average OA was 2.3 μg m$^{-3}$, sulfate 1.02 μg m$^{-3}$, ammonium 0.36 μg m$^{-3}$, nitrate 0.10 μg m$^{-3}$ and chloride was 0.04 μg m$^{-3}$. The data correspond to 3-minute averages.}
\end{figure}
The O:C ratio varied from 0.22 to 0.96 with an average value equal to 0.57. The H:C ratio was between 1.40 and 1.90, with an average equal to 1.63 (Figure 2.11).

Figure 2.11. O:C and H:C as a function of time during Period 3 (March 30 to April 1 of 2015). The averaging time was 1 hour.

The PMF analysis revealed 4 distinct OA sources (Figure 2.12); 31.5% of the total OA was L-OOA, 23.6% was M-OOA, 13.4% was HOA and 31.5% was biomass burning OA (BBOA) (Figure 2.13). The HOA peaks were associated with construction activities, while the BBOA factor was related to emissions from the burning of olive trees branches.29
Figure 2.12. AMS mass spectra of the four PMF factors for the sampling period March 30 to April 1 of 2015 (Period 3).

The $P$ parameters used, as in the previous ambient measurements, were 0.01, 0.1 and 1 cm$^3$ m$^{-3}$. The measured WSOC concentration increased from 1 μg m$^{-3}$ to 1.5 μg m$^{-3}$ as the $P$ increased from 0.01 to 1 cm$^3$ m$^{-3}$ (Figure 2.7 and Table II). The estimated solubility distribution is shown in Figure 2.8. Approximately, 59% of the aerosol had water solubility higher than 1 g L$^{-1}$, while 12% of the OA had solubility lower than 0.01 g L$^{-1}$. The remaining 29% of the total OA had intermediate solubility concentrations. According to the PMF results, over 55% of the total OA was oxidized OA, which is likely related to the high-water solubility mass fraction. The HOA, which
represented 13.4% of the total OA, is quite consistent with the OA mass fraction corresponded to water solubility lower than 0.01 g L$^{-1}$. The biomass burning emissions contributed significantly to the total OA during this period. The water solubility distribution indicates that a lot of these compounds may have water solubility values between 0.01 and 1 g L$^{-1}$, as BBOA tends to be more water soluble than HOA$^{30}$.

**Figure 2.13.** Time series of the 4 factors, extracted by the PMF analysis during Period 3 (March 30 to April 1 of 2015). The black line corresponds to the M-OOA, the red line stands for the L-OOA, the green line refers to the HOA, and the magenta line denotes the BBOA. The data correspond to 3-min averages (CE=1).

### 2.4.2 Fresh Cooking Organic Aerosol Characterization

During the COA experiments the organic aerosol represented 99% of the total PM$_1$ mass concentration. The initial concentrations of the COA in the smog chamber were around 400 μg m$^{-3}$. The initial O:C ratio was 0.10 in both experiments. To verify that the vast majority of the aerosol sampled by the high-volume sampler was indeed COA (and not ambient aerosol) we used the OC to sulfate ratio of the samples. This ratio was around 1 for ambient aerosol in Patras. In the two collected samples, it was
6600 and 21000 respectively. This confirms that we collected COA with negligible influence of ambient aerosol.

![Figure 2.14. WSOC and OC concentration of Cooking Organic Aerosol for (a) Experiment 1 and (b) Experiment 2, for different P parameter values.](image)

For both meat cooking experiments, the OA mass concentration was high, the sampling time was short and $P$ values between 0.1 and 10 cm$^3$ m$^{-3}$ were used. For Experiment 1, the concentration of the WSOC increased from 20.5 μg m$^{-3}$ to 37.5 μg m$^{-3}$ when $P$ increased from 0.1 to 10 cm$^3$ m$^{-3}$, while for Experiment 2 the concentration of WSOC increased from 15.2 μg m$^{-3}$ to 30.4 μg m$^{-3}$ for the same $P$ increase (Figure 2.14 and Table I1). The WSOC/OC ratio for $P=0.1$ cm$^3$ m$^{-3}$ was equal to 0.11 for both experiments. This indicates that OA from meat cooking emissions has, as expected, low water solubility. The solubility distributions of the COA for the two experiments are shown in Figure 2.8. In both experiments, about 80% of the OA has solubility lower
than $10^{-3}$ g L$^{-1}$, while only 11% of the COA has solubility higher than 0.1 g L$^{-1}$. Around 10% of the COA had water solubility in the $10^{-3}$–0.1 g L$^{-1}$ range.

### 2.4.3 Aged Cooking Organic Aerosol Characterization

Figure 2.15 shows the mass concentration of the OA, and the ozone concentration during the experiment. The initial concentration of the COA in the smog chamber were around 250 μg m$^{-3}$.

![Figure 2.15](image)

**Figure 2.15.** OA mass, BC and ozone concentration during the experiment. The green line corresponds to the OA and the blue line corresponds to the ozone concentration. The grey areas correspond to the two filter collection periods.

After the aging, the concentration was about 100 μg m$^{-3}$. The initial O:C ratio was stable at 0.10. The O:C ratio increased to 0.20 and stabilized again as shown in Figure 2.16.
Figure 2.16. O:C as a function of the hour of the experiment. The blue line corresponds to the ozone injection.

The PMF analysis showed the existence of two distinct factors; the fresh COA and the aged COA. Figure 2.17 illustrates the two factor mass spectra for the COA experiment.

Figure 2.17. Mass spectra of the two factors for the COA experiment. The black bars correspond to the fresh OA, while the red bars correspond to the aged OA.
For the measurement of the WSOC two values of $P$ were used; 0.1 and 1 cm$^3$ m$^{-3}$. The measured WSOC concentration of the fresh COA increased from 15 $\mu$g m$^{-3}$ to 22 $\mu$g m$^{-3}$ as $P$ increased from 0.1 to 1 cm$^3$ m$^{-3}$ (Figure 2.18). For the aged cooking organic aerosol, the WSOC increased from 14 to 16 $\mu$g m$^{-3}$ for the same $P$ increase.

**Figure 2.18.** WSOC and OC concentration as a function of $P$ parameter for (a) fresh and (b) oxidized via ozone COA.

The estimated solubility distribution is shown in Figure 2.19. The majority of the fresh COA (76%) had water solubility less than 0.1 g L$^{-1}$. 63% of the fresh COA had solubility less than 0.01 g L$^{-1}$, while 13% was between 0.01 and 0.1 g L$^{-1}$. The remaining 24% had a solubility equal to or greater than 0.1 g L$^{-1}$. The solubility of the COA increased significantly after aging. The fraction of COA with solubility greater than 0.1 g L$^{-1}$ more than doubled, increasing to 55%. The increase in solubility was
consistent with the observed increase in the O:C ratio, indicating that the aging process of COA increases solubility.

![Solubility distributions of fresh COA (a) and oxidized via ozone COA (b)](image)

**Figure 2.19.** Solubility distributions of a) fresh and b) oxidized via ozone COA.

### 2.5 Discussion

In this work, a new experimental method for the WSOC measurement was developed. Instead of a single measurement, the WSOC concentration was measured as a function of the $P$ parameter as proposed by Psichoudaki and Pandis. The OA concentration, the sampling time and the sampler flowrate are important indicators of the $P$ values that should be used. In general, for high OA concentration (e.g. $> 30$ µg m$^{-3}$) or small sampled air volume (less than 1 m$^3$), $P$ values higher than 0.1 cm$^3$ m$^{-3}$
should be used to attain successful OA extraction. On the other hand, for lower OA concentration or long sampling times (a few days or more), \( P \) values smaller than 0.01 cm\(^3\) m\(^{-3}\) should be chosen.

The WSOC concentration increased as \( P \) increased. For the ambient OA experiments, a \( P \) parameter increase from 0.1 to 1 cm\(^3\) m\(^{-3}\) corresponded to a 40-50\% WSOC increase, while for the COA experiments WSOC increase approached high values (90\%). The proposed method can indeed show the differences in solubility distributions between a highly-processed aerosol and the fresh OA from a source.

For the aging COA experiment, most of the fresh COA had water solubility less than 0.1 g L\(^{-1}\). After aging the COA fraction with water solubility greater than 0.1 g L\(^{-1}\) increased more than 2 times.

The ambient measurements suggested that the mass fractions that corresponded to the the different solubility ranges are roughly consistent with the PMF factors determined during the analysis of the HR-ToF-AMS data. Most of the OOA appears to have water solubility above 1 g L\(^{-1}\), while the HOA and COA less than 0.01 and 0.001 g L\(^{-1}\) respectively. The BBOA seems to have mostly intermediate solubility in water, between 0.01 and 1 g L\(^{-1}\).

### 2.6. References


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Chapter 3

Development of a method for the measurement of Henry’s law constant distribution of atmospheric organic aerosol
3.1 Introduction

The Henry’s law constant, \( H \), is one of the most important physical properties of atmospheric organic aerosol components. The Henry’s law constant is essentially an air-water partitioning coefficient which can be, in principle at least, determined by measurement of the concentrations of a pollutant in both phases\(^1\). It determines to a large extent the lifetime of the semi-volatile organic aerosol components and its intermediate volatility precursors as compounds with high \( H \) are removed rapidly both by wet and dry deposition.

The Henry’s law coefficient values of the thousands of complex atmospheric organic compounds are mostly unknown\(^2\)\(^\text{-}\)\(^6\). Most atmospheric models use just one value in order to describe the Henry’s law constant of all oxidized organic aerosol components and precursors. The corresponding values used in different models vary by several orders of magnitude.

We propose a new method for the measurement of Henry’s law constant of atmospheric OA components, which is based first on their separation by volatility and then measurement of the water solubility distribution of each fraction. The advantage of this method is that a distribution of the Henry’s law constant is measured for the first time.

3.2 Measurement of Henry’s Law Constant Distribution

The Henry’s law constant of ambient OA component \( A \), \( H_A \) in \( \text{M atm}^{-1} \), can be estimated as the ratio of its aqueous-solubility to its saturation concentration:

\[
H_A = \frac{S_A}{p_A^o \cdot MW_A}
\]  

(3.1)

where \( S_A \) (in g L\(^{-1}\)) is the aqueous solubility of \( A \), \( p_A^o \) (in atm) is the saturation vapor pressure of the compound, and \( MW_A \) is its molecular weight (in g mol\(^{-1}\)).
In our technique, we combine separation of the OA by volatility using a thermodenuder (TD) and then measurement of the water solubility distribution of each fraction using the method outlined in Chapter 2. We use 3 temperature steps in the TD starting with ambient and going up to a temperature at which around 20% has not evaporated in the TD. For each temperature the corresponding OA is collected on a separate quartz filter, with the sampling controlled by the same computer and software (Labview) that controls the TD operation (Figure 3.1). The HR-ToF-AMS is monitoring the aerosol composition throughout the experiment. Each filter is then cut in pieces and the pieces are used for the determination of the corresponding solubility distribution.

![Figure 3.1. Schematic of the measurement system for the Henry’s law constant estimation.](image)

Figure 3.1 is a schematic of the experimental setup. The aerosol sample passes through a TD, where it is separated by volatility and then it is collected on filters, which are used for the determination of the water solubility distribution of each fraction. The SMPS and the AMS are used for the continuous determination of the chemical composition of the aerosol sampled.
3.2.1 Calculation of Henry’s Law Constant

Using the ideal gas law, the saturation vapor pressure (in atm) for a compound A \( (p_A^0) \), can be written as:

\[
p_A^0 = \frac{C_A^*RT}{MW_A}
\]

(3.2)

where \( C_A^* \) is the gas-phase saturation concentration of the compound (in g L\(^{-1}\)), \( R \) is the ideal gas constant (in atm L mol\(^{-1}\) K\(^{-1}\)), \( T \) is the temperature (in K) and \( MW_A \) is its molecular weight (in g mol\(^{-1}\)).

Combining Equations (3.2) and (3.1) the Henry’s law constant can be calculated by:

\[
H_A = \frac{S_A}{C_A^* \cdot R \cdot T}
\]

(3.3)

The Henry’s law constant can be thus calculated based on the solubility \( (S_A) \) and the effective volatility \( (C_A^*) \).

3.2.2 Water Solubility Distribution Calculation

The measurement of the solubility distributions is based on the method described in Chapter 2. The measurement of Water Soluble Organic Carbon (WSOC) in atmospheric aerosol is usually carried out by sample collection on filters, extraction in ultrapure water, filtration, and measurement of the total organic carbon. We showed in Chapter 2 that the sampling and extraction of WSOC can be described by a single parameter, \( P \), expressing the ratio of water used per volume of air sampled on the analyzed filter. Varying the \( P \) parameter, organics of different aqueous solubility are extracted from the aerosol sample and included in the measured WSOC. By taking advantage of this, we can measure the WSOC of the same aerosol sample using different \( P \) values.
For each TD operating temperature one sample is collected and the corresponding solubility distribution of the collected OA fraction is measured. Two $P$ values are used for each TD operation temperature (each sample).

### 3.2.3 Volatility Distribution Calculation

The volatility of OA can be measured in principle with a thermodenuder (TD). Figure 3.2 shows a schematic of the TD developed by our group\(^7\). The TD heats the aerosol sample, removes the evaporated material (usually by adsorption on activated carbon) and cools the remaining aerosol back to ambient temperature so that it can be characterized by other techniques. The TD can also be viewed as a volatility separator: it allows compounds with volatility lower than a threshold to go through the instrument. Coupling of a TD with the HR-ToF-AMS and the SMPS allows measurement of the fraction of the OA that evaporates at a given temperature (together with the chemical characteristics of this less volatile fraction).

![Schematic of the main parts and processes that take place in a thermodenuder.](image)

**Figure 3.2.** Schematic of the main parts and processes that take place in a thermodenuder.
While the TD technique is straightforward and can provide the fraction of OA evaporated as a function of temperature (a thermogram), it remains a semi-quantitative tool. As a result, challenges in the TD measurement interpretation include the dependence of the evaporated OA fraction not only on the OA volatility distribution but also on the residence time in the instrument, the size distribution of the OA, and the potential resistances to mass transfer. An aerosol dynamics model is needed for the interpretation of the TD results.

The Karnezi et al. (2014)\textsuperscript{8} algorithm is used for the estimation of the OA volatility distributions based on the TD measurements. The algorithm uses as inputs the thermogram which is the mass fraction remaining of the sample after passing through the TD for different temperatures, the initial OA concentration, the density of the sample, the volatility bins, the length of the heating section of the TD and the residence time. It solves differential equations for particle mass and gas phase concentrations (Appendix II). It calculates the mass fraction of the OA that corresponds to each volatility distribution bin (volatility distribution) at 298 K, the effective vaporization enthalpy and the mass accommodation coefficient.

\textbf{3.2.4 Combination of Measurements}

After the measurement of the volatility and solubility distributions, the combination of the results is used to calculate the Henry’s law constant distribution for each volatility bin and the total OA.

We define as $H_{ij}$ the Henry’s law constant of solubility bin $i$ and volatility bin $j$ and as $x_{ij}$ the contribution of each solubility bin $i$ to each volatility bin $j$. Please note that the sum of $x_{1j}$, $x_{2j}$, …, etc. gives the OA mass fraction of the volatility bin $j$, $x_{j}$. The contribution of each solubility bin to each volatility bin ($x_{ij}$) does not change with the
temperature as it is a physical property of the OA. The mass balances that correspond to each bin and to each temperature and the corresponding constraints are:

\[
\sum_{j=1}^{n} V_j(T) x_{ij} = S_i(T) \quad i = 1, k \quad (3.4)
\]

\[
\sum_{i=1}^{k} x_{ij} = 1 \quad j = 1, n \quad (3.5)
\]

\[
\sum_{i=1}^{k} S_i(T) = 1 \quad (3.6)
\]

\[
\sum_{j=1}^{n} V_i(T) = 1 \quad (3.7)
\]

\[
0 \leq x_{ij} \leq 1 \quad (3.8)
\]

where \( k \) is the number of solubility distribution bins, \( n \) is the number of volatility distribution bins, \( V_j(T) \) is the mass fraction of bin \( j \) of the volatility distribution for temperature \( T \), \( S_i(T) \) is the mass fraction of bin \( i \) of the solubility distribution at temperature \( T \) and \( x_{ij} \) is the contribution of solubility bin \( i \) to the volatility bin \( j \).

Equation (3.4) describes the mass balances of the system; the mass fraction of each solubility bin (right side of the equation) should be equal to the sum of the mass fractions of each volatility bin times the contribution of that solubility bin to each volatility bin (left side of the equation). The constraints are given by Eq. (3.5) - (3.7); the sum of the mass fractions of all the volatility bins and the sum of the mass fractions of all the solubility bins have to be equal to unity. Eq. (3.8) restricts the fractional contribution of each solubility bin to each volatility to be between 0 and 1.

For the calculation of the contribution of each solubility bin to each volatility bin, we calculate the OA volatility distributions in the other TD operating temperatures using the modified Karnezi et al.\(^8\) algorithm. For each TD operating temperature, the
corresponding volatility and solubility distributions are used for the calculation of the corresponding mass balances. We solve this problem using a simple algorithm (Appendix III) in order to calculate the contributions of each solubility bin to each volatility bin.

Figure 3.3. Example of the calculation of the contribution of each solubility bin to each volatility bin for a temperature equal to 25°C. (a) Solubility distribution of OA. The \( S(25)_1 \), \( S(25)_2 \) and \( S(25)_3 \) correspond to the mass fractions of OA in the solubility bins 1, 2 and 3 respectively. (b) Volatility distribution of OA. The \( V(25)_1 \), \( V(25)_2 \) and \( V(25)_3 \) correspond to the mass fraction of OA in volatility bins 1, 2 and 3 respectively.

For example, let us assume that we have an OA solubility distribution with 3 bins; \(<0.001, 0.001-0.01, \text{and } >0.01 \text{ g L}^{-1}\) and a corresponding volatility distribution with three bins; 1, 10 and 100 \( \mu \text{g m}^{-3}\) as shown in Figure 3.3. Each volatility bin will include contributions of all the solubility bins. These are the \( x_{ij} \) variables in our problem. The fraction of the OA, for example, with solubility lower than 0.001 \( \mu \text{g m}^{-3}\) would be the sum of the contributions of this solubility bin to each volatility bin (1, 10, 100) times the OA mass fraction represented by the corresponding volatility bins. Therefore, the mass balance for the first solubility bin using Eq. (3.4) will be:
\[ V(25)_1 x_{11} + V(25)_2 x_{12} + V(25)_3 x_{13} = S(25)_1 \quad (3.9) \]

\[ 0.24 x_{11} + 0.28 x_{12} + 0.48 x_{13} = 0.1 \quad (3.10) \]

where \( V(25)_i \) is the OA mass fraction of the volatility bin 1 (1 \( \mu \text{g m}^{-3} \)), \( V(25)_2 \) is the OA mass fraction of the volatility bin 2 (10 \( \mu \text{g m}^{-3} \)), \( V(25)_3 \) is the OA mass fraction of the volatility bin 3 (100 \( \mu \text{g m}^{-3} \)), \( x_{1i} \) is the contribution of solubility bin 1 (<0.01 \( \text{g L}^{-1} \)) to the volatility bin 1 (1 \( \mu \text{g m}^{-3} \)), \( x_{12} \) is the contribution of solubility bin 1 (<0.001 \( \text{g L}^{-1} \)) to the volatility bin 2 (10 \( \mu \text{g m}^{-3} \)), \( x_{13} \) is the contribution of solubility bin 1 (<0.001 \( \text{g L}^{-1} \)) to the volatility bin 3 (100 \( \mu \text{g m}^{-3} \)) and \( S(25)_j \) is the OA mass fraction of the solubility bin 1 (<0.001 \( \text{g L}^{-1} \)).

After the calculation of the contribution of each solubility bin to each volatility bin \((x_{ij})\), we can calculate the Henry’s law constant distribution for each solubility bin \(i\) and volatility bin \(j\) using Eq. (3.3) as:

\[ H_{ij} = \frac{10^9 \cdot S_i}{C^*_j \cdot R \cdot T} \quad (3.11) \]

where \( H_{ij} \) (in M atm\(^{-1}\)) is the Henry’s law constant bins that correspond to the solubility bin \(i\) and the volatility bin \(j\), \( S_i \) (in g L\(^{-1}\)) is the solubility of the solubility bin \(i\), \( C^*_j \) (in \( \mu \text{g m}^{-3} \)) is the effective volatility of the volatility bin \(j\), \( n \) is the number of the solubility distribution bins, \( k \) is the number of the volatility distribution bins, \( R \) (in atm L mol\(^{-1}\) K\(^{-1}\)) is the ideal gas constant and \( T \) (in K) is the temperature.

The mass fractions that correspond to each \( H_{ij} \) value will be equal to the contributions \((x_{ij})\) of the corresponded solubility and volatility bins. In our example, for the volatility bin 1 (1 \( \mu \text{g m}^{-3} \)), a Henry’s law distribution with three bins can be calculated using the corresponding three solubility bins. The mass fractions that
correspond to the first second and third bin of the $H$ distribution will be $x_{11}$, $x_{21}$ and $x_{31}$ respectively.

An average Henry’s law constant $H_j$ can also be calculated for each volatility bin $j$ as:

$$H_j = \frac{10^9 \cdot \sum_{i=1}^{n}(x_{ij} \cdot s_i)}{C^*_j \cdot R \cdot T} \quad (3.12)$$

### 3.3 Experimental Procedure

#### 3.3.1 Experimental Setup

The proposed method for the measurement of the Henry’s law constant distribution was tested in experiments of ozonolysis of a-pinene. The experimental setup is shown in Figure 3.4. The experiment took place in the Laboratory of Air Quality Studies (LAQS) in FORTH/ICE-HT. Approximately 2 μl of a-pinene were injected in the 10 m³ smog chamber that was prefilled with pure air. After the a-pinene concentration stabilized we injected 350 ppb of ozone using an ozone generator.

![Figure 3.4. Schematic of the experimental setup that was used in the experiments.](image-url)
For the measurement of the gas phase concentration of organics we used a proton transfer mass spectrometer (PTR-MS) and an ozone monitor (Teledyne, model 300E) for the ozone concentration. The sampling flowrate of the ozone monitor was 1 L min$^{-1}$. The PTR-MS sampled continuously in the selected mass scan mode (23–42 masses were selected) with a total sample time of 6–10 s. A Teflon filter (Whatman PTFE 0.2 µm) was installed before the inlet tube in order to minimize the particles entering the instrument. The inlet tube was at 60°C and the same temperature was used for the reaction chamber. The drift tube pressure was 2.2 mbar and the voltage applied was 600 V.

The experimental setup that was described in Chapter 3.2 was used for the characterization of the particle phase. The TD was operated in 3 temperatures (25, 50 and 100°C). The centerline residence time was 3 s. The SMPS and the HR-ToF-AMS provided continuous information about the chemical composition of the OA. The size-resolved chemical composition of the aerosol was monitored using a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) from Aerodyne Research Inc. (DeCarlo et al., 2006). The HR-AMS measures only the non-refractory PM$_1$ species. The vaporizer temperature was set at 600°C and the tungsten filament for electron ionization was run at an accelerating voltage of 70 eV was operated in the V-mode with a 3 min sampling time. The voltage of the filament was 70 eV and the vaporizer temperature was 600 °C. The SMPS (classifier model 3080, DMA model 3081, CPC model 3775, TSI) operated at a sheath flow rate of 3 L min$^{-1}$ and a sample flow rate of 0.3 L min$^{-1}$. The SMPS measured the number size distribution in the 10–700 nm range.

The part of the OA that did not evaporate was collected on quartz filters as shown in Figure 3.4. The sampling period was 1 hr for each filter and the flowrate was
5 L min\(^{-1}\). After the filter collection, the solubility distributions were calculated using the method described in Chapter 2. The \(P\) parameter values that were used for the calculation of the amount of the ultra-pure water that needed in order to extract the OA were 1 and 10 cm\(^3\) m\(^{-3}\).

### 3.4 Results

#### 3.4.1 OA Mass Concentration

The mass concentration of the OA in the chamber and after the TD is shown in Figure 3.5. Approximately 110 µg m\(^{-3}\) of OA were created from the reaction of the 14 ppb of a-pinene with 15 ppb of ozone. The mass concentration during the three TD operation temperatures is shown in the grey areas of Figure 3.5. As expected the higher the TD operation temperature the lower the mass fraction of OA remaining after the TD.
Figure 3.5. Mass concentration of OA as a function of time. The blue line corresponds to the time of the ozone injection and the red to the time of the α-pinene injection. The grey areas correspond to the three filter collection periods (1 filter for each temperature). A CE equal to 1 is assumed. The data correspond to 3 min averages.

3.4.2 Estimation of OA Volatility Distributions

The mass fraction remaining (MFR) was calculated for each of the three temperatures using the ratio of the fraction that did not evaporate to the total OA concentration at that time. The data were corrected for the particle losses inside the TD. Figure 3.6 shows the MFR in the three TD operation temperatures. Approximately, at 50°C about 77% of the total OA remains in the particle phase, while at 100°C the corresponding percentage is about 42%.
Figure 3.6. Thermogram of the experiment. The black dots correspond to the measured MFR for each temperature while the red line corresponds to the MFR calculated by the Karnezi et al.\textsuperscript{8} algorithm.

The volatility distributions were calculated using the Karnezi et al. (2014)\textsuperscript{8} algorithm. A vaporization enthalpy equal to 30 kJ mol\textsuperscript{-1} and an accommodation coefficient equal to 1 were assumed. Three volatility bins were chosen; 1, 10, 100 μg m\textsuperscript{-3}. Figure 3.6 shows that the calculated MFR is as expected in good agreement with the experimental data. The estimated volatility distribution is shown in Figure 3.7. 24% of the total OA had volatility equal to 1 μg m\textsuperscript{-3}, 28% equal to 10 μg m\textsuperscript{-3} and 48% equal to 100 μg m\textsuperscript{-3}.

The estimated contributions of each volatility bin to the remaining OA at each temperature is given in Figure 3.8. The mass fractions of each bin were calculated as a function of temperature by the TD model. At higher TD operating temperatures, the
mass fraction of the less volatile OA increases while the contribution of the C*=100 μg m⁻³ decreases to less than 8% at 100°C.

**Figure 3.7.** Volatility distribution of OA for the a-pinene ozonolysis experiment.

**Figure 3.8.** Contribution of the different surrogate compounds to the remaining OA after the TD as a function of temperature. The blue color corresponds to OA with saturation concentration equal to 100 μg m⁻³, the red to 10 μg m⁻³ and the green to 1 μg m⁻³.
3.4.3. Solubility Distributions

Three samples were collected on quartz filters, and the corresponding solubility distributions were measured using the method described in Chapter 2. Figure 3.9 shows the three solubility distributions for the three TD operation temperatures. For example, at 25°C (all of the OA), over 70% of the OA had solubility higher than 0.01 g L⁻¹, 20% had solubility between 0.001-0.01 and 10% less than 0.001 g L⁻¹. These results suggest the solubility distribution shifted towards lower values as the TD temperature increased over 50°C.

Figure 3.9. Solubility distributions of OA at the three TD operating temperatures: (a) Solubility distributions of OA at 25°C; (b) Solubility distributions of OA at 50°C; and (c) Solubility distributions of OA at 100°C.
3.4.4 Henry’s law constant distribution

The Henry’s law constant distribution of the OA was calculated using the method described in Section 3.2.4. The mass balances corresponding to Eq. (3.4) using the known volatility and unknown solubility distributions for the three TD temperatures are:

\[ 0.24 x_{11} + 0.28 x_{12} + 0.48 x_{13} = 0.1 \]  
\[ 0.24 x_{21} + 0.28 x_{22} + 0.48 x_{23} = 0.2 \]  
\[ 0.24 x_{31} + 0.28 x_{32} + 0.48 x_{33} = 0.7 \]  
\[ 0.30 x_{11} + 0.33 x_{12} + 0.27 x_{13} = 0.1 \]  
\[ 0.30 x_{21} + 0.33 x_{22} + 0.27 x_{23} = 0.1 \]  
\[ 0.30 x_{31} + 0.33 x_{32} + 0.27 x_{33} = 0.8 \]  
\[ 0.52 x_{11} + 0.41 x_{12} + 0.07 x_{13} = 0.1 \]  
\[ 0.52 x_{21} + 0.41 x_{22} + 0.07 x_{23} = 0.3 \]  
\[ 0.52 x_{31} + 0.41 x_{32} + 0.07 x_{33} = 0.6 \]  

\[ x_{11} + x_{21} + x_{31} = 1 \]  
\[ x_{12} + x_{22} + x_{32} = 1 \]  
\[ x_{13} + x_{23} + x_{33} = 1 \]  

\[ 0 \leq x_{ij} \leq 1 \]

where \( x_{ij} \) is the contribution of each solubility bin \( i \) (<0.001, 0.001-0.01, and >0.01 g L\(^{-1}\)) to each volatility bin \( j \) (1, 10 and 100 \( \mu \)g m\(^{-3}\)).
The above system of equations together with the following constraints was solved using the MATLAB linear least squares algorithm *lsqlin*. Table 3.1 shows the calculated contributions \((x_{ij})\) of each solubility bin to each volatility bin.

**Table 3.1.** Contributions \((x_{ij})\) of each solubility bin \(i\) to each volatility bin \(j\).

<table>
<thead>
<tr>
<th></th>
<th>(x_{11})</th>
<th>(x_{12})</th>
<th>(x_{13})</th>
<th>(x_{21})</th>
<th>(x_{22})</th>
<th>(x_{23})</th>
<th>(x_{31})</th>
<th>(x_{32})</th>
<th>(x_{33})</th>
</tr>
</thead>
<tbody>
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<td>0.18</td>
<td>0</td>
<td>0.13</td>
<td>0.54</td>
<td>0</td>
<td>0.03</td>
<td>0.28</td>
<td>1</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Figure 3.10 shows the effective Henry’s law constant distribution for the three volatility bins of the volatility distribution. For the lower volatility material \((C^*=1 \, \mu g \, m^{-3})\) 72% of the mass had \(H<4x10^5\) M atm\(^{-1}\). The remaining 28% had higher \(H\) values but our measurements cannot determine how high these values are. For the \(C^*=10 \, \mu g \, m^{-3}\) OA, our technique in this case provides relatively limited information: all of it has \(H\) more or equal to \(4x10^4\) M atm\(^{-1}\). Finally, for the more volatile OA with \(C^*=100 \, \mu g \, m^{-3}\) 16% had \(H\) less or equal than \(4x10^3\) M atm\(^{-1}\). Once more our current measurements cannot provide better constraints for the remaining 84%, other than provide a lower limit for the corresponding value.

In general compounds with Henry’s law constants higher than \(10^6\) M atm\(^{-1}\) have fast wet and dry deposition rates, while compounds with \(H\) lower than \(10^4\) M atm\(^{-1}\) have relatively slow removal rates. Our results show that the majority of OA from the ozonolysis of a-pinene with volatility 1 \(\mu g \, m^{-3}\) have intermediate deposition rates, while the majority of the corresponding OA with volatilities higher than 10 \(\mu g \, m^{-3}\) has the potential to have fast wet and dry deposition rates. However, we cannot constrain well the behavior of this material at this stage.
Figure 3.10. Henry’s law constant distribution for the different volatility bins: (a) $C^* = 1 \, \mu g \, m^{-3}$; (b) $C^* = 10 \, \mu g \, m^{-3}$; (c) $C^* = 100 \, \mu g \, m^{-3}$.

The Henry’s law constant distribution of the total OA was also estimated assuming that the solubility distribution’s bins were equal to $10^{-4} \, g \, L^{-1}$, $10^{-3} \, g \, L^{-1}$ and $10^{-2} \, g \, L^{-1}$ instead of $< 10^{-3} \, g \, L^{-1}$, $10^{-3}-10^{-2}$ and $10^{-2} \, g \, L^{-1}$. This is a crude simplification but allows a preliminary analysis of the behavior of the total OA in this system. For the
calculation of the average $H_i$ for each volatility bin Eq. (3.12) was used. Figure 3.11 shows the $H$ distribution for the total OA. Approximately, about 50% of the OA had effective $H = 3.5 \times 10^3$ M atm$^{-1}$, 30% $H = 4 \times 10^4$ M atm$^{-1}$ and 20% had $H = 1.4 \times 10^5$ M atm$^{-1}$. In this case it seems that most of the total OA had effective $H$ around $3.5 \times 10^3$ M atm$^{-1}$. However, the actual distribution is probably a lot wider than the above. Additional development of the experimental approach is needed to capture better especially the right tail of this distribution and especially for the more volatile OA components and precursors.

**Figure 3.11.** Effective Henry’s law constant distribution of OA of a-pinene ozonolysis at 25°C.

### 3.5 Conclusions

A new method for the measurement of Henry’s law constant was developed and tested. The method is based on the combination of the method for the measurement of the solubility distribution using filters and the method for calculation of the volatility distribution using a TD and Karnezi et al. (2014)$^8$ algorithm.
The method was tested in laboratory experiments which included studying of the products of dark ozonolysis of a-pinene. The volatility distribution suggested that most of the measured OA tend to have volatilities higher than 100 μg m$^{-3}$. The solubility distribution showed that the products of ozonolysis of a-pinene tend to be water soluble; most of the OA (>60%) had solubility higher than 0.01 g L$^{-1}$.

The Henry’s law constant distribution of the products of the ozonolysis of a-pinene was calculated for the first time. For each volatility bin a Henry’s law constant distribution was measured. For the lower volatility material ($C*=1$ μg m$^{-3}$) 72% of the mass had $H<4\times10^5$ M atm$^{-1}$. the $C*=10$ μg m$^{-3}$ OA has $H$ more or equal to $4\times10^4$ M atm$^{-1}$. Finally, 16% of the more volatile OA with $C*=100$ μg m$^{-3}$ had $H$ less or equal than $4\times10^3$ M atm$^{-1}$.

While our measurements constrained relatively well the OA with the lower $H$ values, they provide only lower limits for the components with the higher $H$. This is an area in which significant improvement is needed in future work. However, our results are still valuable, and a significant step forward compared to the current state of knowledge. For example, we were able to show that roughly half of the OA has a Henry’s law constant less or equal than $3.5\times10^3$ M atm$^{-1}$ and therefore the atmospheric removal of the corresponding vapors will be relatively slow.

3.6. References


(2) Lincoff, A. H., Gossett, J. M.: The determination of Henry’s law constants for volatile organics by equilibrium partitioning in closed systems. In: Gas Transfer


Chapter 4

Conclusions

and

Future work
4.1 Conclusions

A new experimental method for the measurement of the Water Solubility Distribution of atmospheric organic aerosol was developed. The WSOC concentration was measured as a function of the $P$ parameter as proposed by Psichoudaki and Pandis (2013).

The ambient measurements showed that the higher mass fraction of the OA had water solubility higher than 1 g L$^{-1}$, while the POA had solubility lower than 0.1 g L$^{-1}$.

Only around 10% of the cooking OA from souvlakia had solubility higher than 0.1 g L$^{-1}$. Around 80% of the OA had solubility lower than 0.001 g L$^{-1}$ was about 80%.

The cooking OA from burgers became more water soluble after reacting with ozone. The fraction with solubility more than 0.1 g L$^{-1}$ increased from 24% to 55%.

A new experimental method for the Measurement of the Henry’s Law Constant Distribution was developed, combining two methods for the measurement of the solubility and the volatility distributions.

The Henry’s law constant distribution of OA of ozonolysis of a-pinene showed that an important percent of the OA (50%) with volatility equal to 1 μg m$^{-3}$ had Henry’s law constants between $4\times10^4$ and $4\times10^5$ M atm$^{-1}$, while most of OA with volatility higher than 10 μg m$^{-3}$ had $H$ higher than $10^3$ M atm$^{-1}$.

4.2 Future work

In this work a vaporization enthalpy equal to 30 kJ mol$^{-1}$ was assumed in order to calculate the volatility distribution of OA of a-pinene ozonolysis. Recent studies have been shown that this value may be quite higher. A sensitivity analysis should be performed in order to study the system’s behavior when higher vaporization enthalpy values are used.
For these experiments the sampling time of the filters was 1 h and the flow rate was 5 L min\(^{-1}\). These conditions necessitate the use of small amounts of water for the OA extraction and restrict the solubility range that can be measured. Very water soluble components cannot be separated from the just soluble ones. Higher sampling flow rates would lead to low residence times of the OA through the TD and therefore limit the volatility range that can be characterized. This problem could be overcome by using a much longer heating section of the TD or more than one TDs in series. Another possible way to measure the mass fraction of OA with solubility higher than 1 g L\(^{-1}\) is the introduction of CCN measurements and the connection of the solubility distributions with these measurements. For this purpose, multiple experiments using different supersaturation values should be done which include the simultaneous measurement of the solubility distribution and the activation diameters of the OA.

Further testing of the method for the measurement of Henry’s law constant distribution should also be done using more VOCs like β-caryophyllene, limonene, isoprene, etc. We can also measure the Henry’s law constant distribution of different primary OA components like ambient hydrocarbon-like OA (HOA), cooking organic aerosol (COA), biomass burning OA (BBOA).
Algorithm for the calculation of the contribution of each solubility bin to each volatility bin.

clear
clc

% x = lsqlin(C,d,A,b)
% x = lsqlin(C,d,A,b,Aeq,beq,lb,ub)
% x = lsqlin(C,d,A,b,Aeq,beq,lb,ub,x0,options)
% x = lsqlin(problem)
% [x,resnorm,residual,exitflag,output,lambda] = lsqlin(__)

%  x11  x12  x13  x21  x22  x23  x31  x32  x33
C = [0.24 0.28 0.48 0.00 0.00 0.00 0.00 0.00 0.00;  % Eq1
     0.00 0.00 0.00 0.24 0.28 0.48 0.00 0.00 0.00;  % Eq2
     0.00 0.00 0.00 0.00 0.00 0.00 0.24 0.28 0.48;  % Eq3
     0.30 0.33 0.37 0.00 0.00 0.00 0.00 0.00 0.00;  % Eq4
     0.00 0.00 0.00 0.30 0.33 0.37 0.00 0.00 0.00;  % Eq5
     0.00 0.00 0.00 0.00 0.00 0.00 0.30 0.33 0.37;  % Eq6
     0.52 0.41 0.07 0.00 0.00 0.00 0.00 0.00 0.00;  % Eq7
     0.00 0.00 0.00 0.52 0.41 0.07 0.00 0.00 0.00;  % Eq8
     0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.52 0.41 0.07];  % Eq9

d = [ 0.3;
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     0.6;
     0.1;
     0.2;
     0.7;
     0.2;
     0.4;
     0.5];

A = [];
b = [];

Aeq = [1 0 0 1 0 0 1 0 0;
       0 1 0 0 1 0 0 1 0;
       0 0 1 0 0 1 0 0 1];

beq = [ 1;
        1;
1];

lb = [0 0 0 0 0 0 0 0];
ub = [1 1 1 1 1 1 1 1];

options = optimoptions('lsqlin','Algorithm','interior-point','Display','iter');

x0 = [0 0 0 0 0 0 0 0];

x0 = [1 1 1 1 1 1 1 1];

x = lsqlin(C,d,A,b,Aeq,beq,lb,ub,x0,options)