Determining polarity distribution of atmospheric water-soluble organic matter

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**Determining Polarity Distribution of Atmospheric Water-Soluble
Organic Matter**

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SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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Determining Polarity Distribution of Atmospheric Water-Soluble Organic Matter

Wen-Chien Lee

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological University in partial fulfilment of
the requirement for the degree of Doctor of Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Authorship Attribution Statement

This thesis contains material from 2 papers published in the following peer-reviewed journal in which I am listed as an author.

Chapter 2 is published as

Kuwata, M., and Lee, W.-C.: 1-octanol-water partitioning as a classifier of water soluble organic matters: Implication for solubility distribution, *Aerosol Sci. Technol.*, 51, 602-613, 10.1080/02786826.2017.1283004, 2017. The contributions of the co-authors are as follows:

- Mikinori Kuwata designed the research and wrote the manuscript
- Wen-Chien Lee planned and performed experiments and analyzed the data
- Wen-Chien Lee rewrote the manuscript as Chapter 2 of the thesis

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The contributions of the co-authors are as follows:

- Wen-Chien Lee and Mikinori Kuwata designed the research
- Wen-Chien Lee performed experiments and wrote the manuscript under the supervision of Mikinori Kuwata
- Jing Chen and Sri Hapsari Budisulistiorini provided critical comments on the manuscript
- Masayuki Itoh and Satomi Shiodera collected biomass samples in Indonesia and provided editorial comments on the manuscript

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Date

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Abstract

Organic matter (OM) accounts for a significant fraction of submicron particulate in the atmosphere. The impact of OM on climate and human health is largely contributed by the water-soluble OM (WSOM). Interplay of WSOM and water leads to hygroscopic growth and cloud formation processes. Magnitude of the organic hygroscopicity can be determined by the polarity distribution of WSOM, yet experimental method to systematically examine the relationship is not available. This thesis presents a novel framework to classify WSOM according to its 1-octanol–water partition coefficient (K_{OW}), which often serves as a metric of polarity and water solubility. Fractionization of OM by the K_{OW} approach offers information about the degree of oxidation, which has been viewed as a critical indicator in governing the thermodynamic properties of OM. A theoretical method was developed to classify WSOM by varying the volume ratio of 1-octanol and aqueous phases and extraction steps. An inversion algorithm was further developed to derive K_{OW} distribution of WSOM. The method was verified by OM from proxy of biomass burning particles, and applied to Indonesian biomass burning particles. Optical and chemical characteristics of the extracted WSOM were measured by UV–visible spectrophotometer, spectrofluorometer, and aerosol mass spectrometer. Deconvolution methods including positive matrix factorization, parallel factor analysis, and least-squares analysis were applied to the measured spectra, categorizing WSOM into three classes. The highly polar fraction of WSOM ($\log K_{OW} < 0$) is dominated by highly oxygenated species; the marginally polar fraction ($0 \leq \log K_{OW} \leq 1$) likely contains aromatic compounds; while the least polar fraction ($\log K_{OW} \geq 1$) mostly consists of hydrocarbon-like species. Comparison with hygroscopicity measurements indicates that only WSOM in the highly polar fraction ($\log K_{OW} < 0$) can significantly contribute to water uptake.

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Abbreviations

AMS	Aerosol mass spectrometer
CCN	Cloud condensation nuclei
CIMS	Chemical ionization mass spectrometry
CPC	Condensation particle counters
DMA	Differential mobility analyzer
EEM	Excitation-emission matrix
EPI	Estimations programs interface
FTIR	Fourier-transform infrared spectroscopy
GC/MS	Gas chromatography/mass spectrometry
HEPA filter	High-efficiency particulate air filter
HGF	Hygroscopic growth factor
HMW	High molecular weight
HOA	Hydrocarbon-like organic aerosol
HPLC	High-performance liquid chromatography
HTDMA	Humidified tandem differential mobility analyzer
HULIS	Humic-like substances
LC/MS	Liquid chromatography/mass spectrometry
LLPS	Liquid-liquid phase separation
NMR	Nuclear magnetic resonance
NNLS	Nonnegative least-squares
OM	Organic matter
OOA	Oxygenated organic aerosol
PARAFAC	Parallel factor
PILS	Particle into liquid sampler
PM	Particulate matter
PMF	Positive matrix factorization
RES	Residual
RH	Relative humidity
SOA	Secondary organic aerosol
SPE	Solid phase extraction
STWOM	Smoothed-Twomey
ToF-ACSM	Time-of-Flight Aerosol Chemical Speciation Monitor
US EPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet-visible
VAPS	Volatility and polarity separator
WSOM	Water-soluble organic matter

Nomenclature

a_w	Water activity
C	Molar concentration
C_i^O	Molar concentration of compound in octanol-rich phase
C_i^W	Molar concentration of compound in aqueous phase
C^{salt}	Molar concentration of the salt solution
C_k	Curvature term
D_0	Spherical diameter of the dry particle
D	Spherical diameter of the wet particle
D_{OW}	Total octanol-water partition coefficient
$F(x)$	K_{OW} distribution function
f	Mole fraction
$G(x)$	Distribution function
I	Normalized signal intensity
$K(x)$	Kernel function
K_a	Dissociation constant
K_{IP}	Dissociation constant for the formation of an ion pair
K_s	Setschenow coefficient
K_{OA}	1-octanol–air partition coefficient
K_{OW}	1-octanol–water partition coefficient
m/z	Mass to charge ratio
M_w	Molecular weight of water
M	Mass fraction
n	Number of moles
O:C	Oxygen to carbon ratio
Q	Quality-of-fit parameter
Q_{exp}	Expected Q
$r^{(N-1)}$	Volume fraction of X_{N-1} solution
R	Ideal gas constant
R	Pearson correlation coefficient (Pearson's R)
S	Solubility
S_{salt}	Solubility of an organic solute in salt solution
S_{water}	Solubility of an organic solute in pure water
T	Temperature

V	Volume
V^X	Volume of solution X
V_s	Volume of solute
V_w	Volume of water
$V_r^{(N)}$	Volumetric ratio of 1-octanol and aqueous phases in the N^{th} extraction
X_N	Notation of a solution
A_0	Aqueous phase (original)
A_1A_0	Aqueous phase after first extraction
$A_2O_1A_0$	Aqueous phase after second extraction
O_1A_0	1-octanol phase after first extraction
$O_2O_1A_0$	1-octanol phase after second extraction
y	Measured data
α	Estimated mass fraction of compounds partitioned to aqueous phase
ε_s	Dissolved solute fraction
ε	Error
κ	Hygroscopicity parameter
ρ_w	Density of water
σ	Standard deviation
σ_s	Surface tension of the wet particle at the solution/air interface
γ	Activity coefficient

Chapter 1 Introduction

1.1. Atmospheric aerosol particles

Atmospheric aerosols are solid or liquid fine particles suspended in the air, with diameter ranging from nanometer to micrometer (10^{-9} – 10^{-4} m) (Seinfeld and Pandis, 2016). Aerosol particles can be generated from several types of natural and anthropogenic sources. Aerosol particles originated from sea salt, mineral dust, volcanic eruption, biomass burning, and fossil fuel combustion, are directly emitted to the atmosphere and are termed as primary aerosol particles (Seinfeld and Pandis, 2016). On the other hand, aerosol particles formed in the atmosphere after a series of gas-to-particle conversion are known as secondary aerosol particles (Hallquist et al., 2009). The resulting aerosol particles can be characterized into nuclei mode (0.005 to 0.1 μm), accumulation mode (0.1 to 2 μm) and coarse mode (2 to ~ 50 μm) (Whitby, 1978). Nuclei mode contains the highest number of particles, which mainly form from photochemical reactions. Particles in the accumulation-mode can be attributed to primary emissions, secondary formation from condensation of the gas phase species, and coagulation of smaller particles, while those in the coarse mode mainly come from mechanical processes such as erosion. Aerosol particles can be removed from the atmosphere by either dry or wet deposition processes, depending on the presence of water (Amodio et al., 2014).

Aerosol particles play an important role in the climate system by altering Earth's energy budget through aerosol direct and indirect effects. Aerosol direct effect accounts for the ability of aerosol particles to scatter and absorb solar radiation. Scattering of solar radiation increases the amount of light reflected by the planet, decreases the amount of solar radiation reaching the surface, and leads to degradation of visibility (Faxvog and Roessler, 1978). In contrast to greenhouse gases (e.g. CO_2 , CH_4 , and N_2O), aerosol particles can lead to both heating and cooling effects on Earth's energy balance, depending on size, chemical composition, and mixing state (Toll et al., 2019). The variability thus hinders the prediction of global temperature by general circulation models. Aerosol indirect effect describes the influence of cloud condensation nuclei (CCN) on cloud formation

process, which subsequently modifies cloud albedo and lifetime, changing the radiation budget and hydrologic cycle on Earth (Ramanathan et al., 2001; Rosenfeld et al., 2019).

In addition to climate effect, aerosol particles are correlated with severe health effects such as pulmonary and cardiovascular diseases (Dockery et al., 1993). Particle size was found to play an important role in efficiency and location of respiratory tract deposition. Large particles, including PM_{2.5} and PM₁₀ (particulate matter with diameter up to 2.5 and 10 μm), tend to deposit on the respiratory tract, leading to pulmonary diseases. Smaller particles such as PM₁ (particulate matter with diameter up to 1 μm) can penetrate the alveolar epithelial barrier and further affect cardiovascular function (Amatullah et al., 2012). Inflammatory effects of aerosol particles are associated with particle surface area as well as surface reactivity. Particles with greater surface area are known to be more toxic (Duffin et al., 2007).

The climatic and health effects of aerosol particles are determined by their concentration, size, structure, and chemical composition (Pöschl, 2005). These parameters are highly variable due to the complex physical and chemical reactions between compounds in a particle, between particles, and between a particle and the surrounding gas phase. The reactions include condensation, evaporation, nucleation, adsorption, absorption, and coagulation (Kulkarni et al., 2011). The interplay between aerosol particles and ambient water vapor is a pivotal interaction in determining the physicochemical property of aerosols and the influence of aerosol particles on climate and human health (Farmer et al., 2015). Water uptake by aerosol particles could also enhance the formation of secondary organic aerosol (Hennigan et al., 2008).

1.2. Theoretical background of water uptake

Aerosol water uptake is a dynamic process in the atmosphere. Whether the dissolution of compounds is dominated by thermodynamic process or kinetic changes depends on size, temperature, and state

of the particle (Bones et al., 2012; Price et al., 2015). For non-viscous sub-micron particles above 240K, water diffusion is fast (time scale: 0.01s), and the process of dissolution can be described thermodynamically (Price et al., 2015). Köhler theory (Köhler, 1936) takes into account the thermodynamic equilibrium of water vapor between ambient environment and an aerosol particle, which is governed by Raoult's solute effect and the Kelvin curvature effect. At a specific relative humidity (RH), Köhler equation can be expressed as

$$\frac{\text{RH}}{100\%} = a_w C_k, \quad [1-1]$$

where a_w is the water activity of aqueous solution in the particle phase, and C_k is the curvature term:

$$C_k = \exp\left(\frac{4M_w\sigma_s}{RT\rho_w D}\right). \quad [1-2]$$

The curvature term is determined by the molecular weight of water (M_w), the surface tension of the wet particle at the solution/air interface (σ_s), the ideal gas constant (R), temperature (T , in degree Kelvin), the density of water (ρ_w), and the spherical diameter of the wet particle (D).

The interplay between Raoult's effect and the Kelvin effect results in the Köhler curve. As shown in Figure 1.1, maximum of the particle vapor pressure on the Köhler curve is defined as critical supersaturation. When the ambient supersaturation is higher than the corresponding critical super-saturation, the particle can grow to pass the critical size to become cloud droplets. The value of critical supersaturation depends on size, surface tension, and chemical composition of the aerosol particle. For instance, chemical composition of the aqueous solution can regulate the water activity term. The water activity term can be defined by a single hygroscopicity parameter κ (Petters and Kreidenweis, 2008):

$$\frac{1}{a_w} = 1 + \kappa \frac{V_s}{V_w}, \quad [1-3]$$

where V_s and V_w refer to the volume of solute (i.e. dry particle) and water, respectively. Köhler theory can be presented by κ as:

$$\frac{RH}{100\%} = \frac{D^3 - D_0^3}{D^3 - D_0^3(1 - \kappa)} \exp\left(\frac{4M_w\sigma_s}{RT\rho_w D}\right), \quad [1-4]$$

where D_0 is the dry diameter of aerosol particle. Eq. (1-4) is the so-called κ -Köhler theory (Petters and Kreidenweis, 2007). Dissolved solute fraction ε_s is introduced in consideration of incomplete dissolution (Petters and Kreidenweis, 2008). In the case of fully solubilized species, ε_s is unity. For partially solubilized species, $0 < \varepsilon_s < 1$, and the value of ε can influence the κ value. The κ value is given by

$$\kappa = \sum_i \varepsilon_{si} \kappa_i H(x_i), \quad [1-5]$$

for

$$H(x_i) = \min\left[1, \left(\frac{D^3}{D_0^3} - 1\right) \frac{S_i}{\varepsilon_{si}}\right], \quad [1-6]$$

for a system with multiple solutes (i), where κ_i is the intrinsic κ for the solute, $H(x_i)$ is the dissolved fraction of the solute, and S_i is the solubility of the solute in water. Water uptake property of a particle can be simplified into four scenarios, including infinitely soluble, highly soluble, slightly soluble, and insoluble, depending on the value of S : (1) infinitely/highly soluble ($S > 10^{-1}$), (2) slightly soluble ($10^{-4} < S < 10^{-1}$), (3) insoluble ($S < 10^{-4}$) (Petters and Kreidenweis, 2007; Kuwata et al., 2013). Recently, solubility distribution of a solute is also suggested to be an important regulator when considering water uptake of aerosol particles (Riipinen et al., 2015).

Figure 1.1. Theoretical Köhler curve of an ammonium sulfate particle with an initial dry particle diameter of 100 nm. Particle wet diameter shown in the abscissa indicates the diameter of aerosol particles after taking up water.

1.3. Measurement of hygroscopic growth and CCN activity

Measurements of hygroscopic growth for bulk aerosol particles can be made with a humidified tandem differential mobility analyzer (HTDMA) (Duplissy et al., 2009). A dry particle at a certain size is selected by the first DMA and allowed to enter a controlled humid environment where water condensation happens. Subsequently, the size-number concentration of the wet particles is measured by a second DMA with CPC to determine the number and particle size of wet particles.

Quantification of particle hygroscopic growth can be done by calculation of the hygroscopic growth factor (HGF). HGF is defined as

$$\text{HGF} = \frac{D}{D_0}, \quad [1-7]$$

where D and D_0 are wet and dry diameter of an aerosol particle. Other setups such as a quartz crystal microbalance (Liu et al., 2018) and an optical tweezer (Cai and Zhao, 2018) can also be applied to measure the hygroscopic growth of aerosol particles.

CCN activity is defined as the capability of an aerosol particle to serve as a CCN.

Measurement of CCN activity can be done by a CCN counter (Roberts and Nenes, 2005). Particles are allowed to grow by condensation of water vapor at a certain supersaturation, which is generally controlled by the difference in heat and mass diffusion. The process of an aerosol particle to be activated as CCN is termed as CCN activation.

1.4. Aerosol-related problems with biomass burning in Southeast Asia

Aerosol particles and gases emitted during the Southeast Asian haze, particularly in 1997 and 2015, have severe impact on regional air quality and ecosystems (Page et al., 2002; Heil et al., 2007). The haze episodes not only cause adverse effects on human health but also affect the climate by reducing visibility and altering cloud formation processes (Kopplitz et al., 2016). Peatland fires in Southeast Asia are induced by development of peatland for agricultural use, serving as the main contributor to haze in the region (Ketterings et al., 1999). The situation has become worse by timber, oil palm and logging industries converting peatland into plantation areas in Indonesia for the past decades (Marlier et al., 2015). The resulting polluted air can be transported in the atmosphere to other countries including Thailand, the Philippines, Malaysia, and Singapore (Koe et al., 2001). Regional haze can be intensified by the increase of biomass burning potential and the decrease of aerosol scavenging during dry conditions such as El Niño events (Wooster et al., 2012; Field et al., 2016).

Particles emitted from Indonesian biomass burning are suggested to be inefficient CCN (Dusek et al., 2005) although they contain a large fraction of organic aerosols (See et al., 2007). A laboratory experiment conducted by Dusek et al. (2005) demonstrated the inefficiency of freshly

emitted peat smoke particles from Indonesian and German peat combustion to become CCN active, particularly for large particles. Chand et al. (2005) also found low hygroscopic growth for laboratory generated Indonesian and German peat aerosols, and it has been suggested that the high hygroscopic growth of Indonesian biomass burning reported by an ambient measurement was due to atmospheric aging processes (Gras et al., 1999). Iinuma et al. (2007) proposed a hypothesis that the lack of ability for particles emitted from Indonesian peat combustion to be CCN active may be due to their significant difference in chemical composition compared with other biomass burning particles. To bridge the gap between Southeast Asian haze and its influence on cloud formation process, information about the chemical composition of biomass combustion particles is necessary.

1.5. Motivation and organization of the thesis

Hygroscopic growth and CCN activation processes of aerosol particles can be significantly contributed by organic matter (OM) (Novakov and Penner, 1993). OM accounts for 20–90% of aerosol mass in the atmosphere (Jimenez et al., 2009). OM comprises myriad types of chemical species with various degrees of oxidation, volatility, and solubility, leading to difficulties in evaluation of its climate and health effects (Pöschl, 2005). To unfold the complexity of organic matter, several approaches have been developed. Gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/MS (LC/MS) are applied to measure individual organic species, whereas nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy provide information about functional groups (Hallquist et al., 2009). Aerosol mass spectrometer (AMS) and chemical ionization mass spectrometry (CIMS) were recently developed for molecular composition measurement (Jayne et al., 2000; Voisin et al., 2003). Some of the methods allow on-line measurement (i.e., in-situ-monitoring), while off-line analysis (e.g., sampling techniques such as filters, impactors, and denuders) is also applied to measure the chemical composition of aerosol

particles. Nevertheless, less than 10% of OM can be identified at the molecular level (Turpin et al., 2000).

OM can be described by simplified metrics to predict the hygroscopicity. These measurable surrogates, including the elemental oxygen to carbon ratio (O:C) (Aiken et al., 2008), the fraction of mass spectral fragment at mass-to-charge ratio 44 (m/z 44, CO_2^+ , f_{44}) (Ng et al., 2010), and the oxidation state of carbon (Kroll et al., 2011), may sometimes fail to predict the hygroscopicity of OM (Rickards et al., 2013). A number of studies suggest inconsistency between hygroscopic growth (κ_{HGF}) and CCN activity (κ_{CCN}) of aerosol particles ($\kappa_{\text{HGF}} < \kappa_{\text{CCN}}$) (Hodas et al., 2016; Rastak et al., 2017). The enhancement of CCN activity can be attributed to the non-ideality of mixing between water and solutes (Liu et al., 2018). Gradual dissolution of organic matter during hygroscopic growth can increase particle water uptake thereby enhance CCN activity (Riipinen et al., 2015). Recently, liquid–liquid phase separation (LLPS) has been proposed to be an important regulator for the enhancement of CCN activity (Renbaum-Wolff et al., 2016; Liu et al., 2018). LLPS in a particle leads to the formation of a highly-polar aqueous phase in the bulk and a less-polar organic-rich phase on the surface. With the increase of RH, sparingly soluble organic matter gradually dissolves in the aqueous phase. The increased amount of dissolved solutes in the aqueous phase results in an increase of water uptake. At high RH ($\text{RH} > 95\%$), formation of the organic-rich phase on the particle surface can reduce surface tension thus facilitating the activation of CCN (Renbaum-Wolff et al., 2016; Ruehl et al., 2016; Ovadnevaite et al., 2017). Determining the water uptake properties of the gradually dissolved sparingly soluble/less-polar compounds would provide a comprehensive understanding regarding the hygroscopicity of OM (Petters et al., 2009; Pajunoja et al., 2015).

In order to investigate and better predict the hygroscopicity of OM, in particular for the sparingly soluble compounds, several analytical techniques were developed to access physical and chemical properties of OM in a metric of polarity. One of the straightforward methods is multiple solvents extraction. Water and organic solvents with different polarities (e.g., hexane,

dichloromethane, ethyl acetate, acetone, and methanol) are often chosen for this purpose (Polidori et al., 2008; Mihara and Mochida, 2011). OM can be separated into several polarity classes by sequential extraction. Yet, solubility of most of the derived extractions tends to be low, which means that these fractions might not significantly contribute to water uptake. Another technique is solid-phase extraction. With an XAD-8 resin, WSOM can be isolated into hydrophobic and hydrophilic fractions (Sullivan and Weber, 2006), but the degrees of hydrophobic and hydrophilic are operationally defined. High-performance liquid chromatography (HPLC) (Mayol-Bracero et al., 2002) as well as the developed volatility and polarity separator (VAPS) (Martinez et al., 2016) are useful for characterizing OM into bins of polarity, yet quantification of polarity of the classified bins remains challenging. A more appropriate framework is needed to represent the complexity and hygroscopicity of OM.

The objective of this thesis was to investigate the polarity of water-soluble organic matter (WSOM) by theoretical and experimental approaches. A novel framework using 1-octanol–water partitioning was developed for representing OM with polarity distribution. Chapter 2 describes the theoretical background of the 1-octanol–water partitioning method. Chapter 3 further develops numerical methods to derive polarity distribution. In these chapters, the 1-octanol–water partitioning method was developed and verified by mosquito coil burning particles, which serve as a proxy of biomass burning particles (Li et al., 2012). In chapter 4, the 1-octanol–water partitioning method was applied to Indonesian biomass burning particles. Conclusions and future works are summarized in Chapter 5.

Chapter 2 1-octanol–water partitioning as a classifier of water soluble organic matter:

Implication for solubility distribution*

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2.1. Introduction

Solubility of aerosol particles plays an important role in affecting the hygroscopic growth and cloud condensation nuclei (CCN) activity (Farmer et al., 2015). Particles contain less soluble compounds uptake less water content during hygroscopic growth, requiring larger critical saturation value to activate than particles with more soluble compounds (Farmer et al., 2015). Aerosol particles contain inorganic and organic species. For inorganic compounds such as ammonium sulfate or ammonium nitrate, the water uptake property and contribution to CCN activity have been well-studied (Farmer et al., 2015). In comparison, measuring the water uptake property and CCN activation process of particles with organic compounds is more complicated since they contain numerous species with different physical and chemical properties and a wide range of water solubility (Saxena and Hildemann, 1996). However, the importance of organic compounds to cloud formation processes should not be ignored for their significant fraction among the submicron particulate matter (Zhang et al., 2007; Jimenez et al., 2009).

To further investigate the hygroscopicity of organic particles, several researches have been conducted to measure the relationship between chemical composition, hygroscopic growth, and CCN activity. Some studies merely separated chemical compounds into water-soluble (WSOM) and water-insoluble fractions (Decesari et al., 2000; Graham et al., 2002; Mayol-Bracero et al., 2002; Sun et al., 2011; Daellenbach et al., 2016) while other studies further divided the WSOM fraction into highly soluble, slightly soluble and less soluble compounds by methods including solid phase extraction techniques, high-performance liquid chromatography and multiple extraction by solvents with different polarity (Sullivan and Weber, 2006; Asa-Awuku et al., 2008; Mihara and Mochida, 2011). However, it was found by Riipinen et al. (2015) that the information from these studies is inadequate to reveal the cloud formation mechanism of organic compounds. The theoretical research suggested that only WSOM with water solubility higher than 10^2 g m^{-3} can contribute to CCN activity. In

addition, the water solubility distribution in this region plays a crucial role in affecting the solute term in Köhler theory.

To our knowledge, the theory provided by (Riipinen et al., 2015) has not been verified by laboratory experiments yet. Verification of theory is always necessary to justify the deviation from modelling and real world. In order to verify the theory, we consider classifying WSOM according to their solubility by utilizing the relationship between 1-octanol–water partition coefficient (K_{OW}) and water solubility (Yalkowsky and Valvani, 1980). Correlation between K_{OW} and water solubility has been well-established in pharmacology (Hansch et al., 1962), but it has not been well-studied in aerosol technology (Pun et al., 2006; Spranger et al., 2017). For this reason, we propose the theory of solubility classification with K_{OW} and test the theory by laboratory mosquito coil burning experiments.

2.2. Theory

The framework of applying 1-octanol–water partitioning to classify organic compounds in aerosol particles is developed in this chapter.

2.2.1. Applying the 1-octanol–water partition coefficient to aerosol particles

K_{OW} is defined for a compound i in neutral condition as

$$K_{OW_i} = \frac{C_i^o}{C_i^w} \quad [2-1]$$

where C_i^o and C_i^w are the molar concentrations of compound i in octanol-rich and water-rich phases, respectively (Sangster, 1989). Since the amount of solute added to the octanol–water mixture is generally small, activity coefficients of compound i in each phase can be treated as at infinite diluted solution:

$$K_{ow} = \frac{C^O \gamma_i^{W,\infty}}{C^W \gamma_i^{O,\infty}} \quad [2-2]$$

where C^W and C^O account for the total molar concentration, $\gamma_i^{W,\infty}$ and $\gamma_i^{O,\infty}$ are the infinite dilution activity coefficients in aqueous and 1-octanol phases, respectively.

For aerosol particles, the partitioning of organic compounds can be affected by (1) the amount of water content, which sometimes leads to variations in activity coefficient, (2) aerosol acidity, which can vary the equilibrium distribution of the dissociable species, and (3) organic-inorganic interactions, which can induce salting-in and salting-out effects. Details of the effects are described as follows.

2.2.1.1. Activity coefficient

Due to limited amount of water content, activity coefficients of the compounds in aerosol particles would differ from those in bulk aqueous environment. However, since the differences are less than 30% for the majority of compounds of interests (Schwarzenbach et al., 2005), which is several orders of magnitude less than the K_{OW} values to be classified in this study, the differences are assumed to be negligible.

2.2.1.2. Aerosol acidity

Dissociation of ionizable species in the aerosol particles can affect aerosol acidity and influence the partitioning of organics. As shown in Figure 2.1, considering an octanol–water biphasic system with monoprotic acid and salt,

Figure 2.1. Partitioning of monoprotic acid (HA) and buffering salt (X^+) between octanol and water phases. Adopted from Chen and Lin (2016).

The total octanol–water partition coefficient (D_{OW}) can be described as

$$D_{OW} = \frac{[HA]^O + [A^-]^O + [X^+A^-]^O}{[HA]^W + [A^-]^W + [X^+A^-]^W} \quad [2-5]$$

Since the dissociation constant (K_a) and the dissociation constant for the formation of an ion pair (K_{IP}) is defined as

$$K_a = \frac{[A^-]^W \cdot [H^+]^W}{[HA]^W}, \quad [2-6]$$

and

$$K_{IP} = \frac{[X^+A^-]^W}{[A^-]^W \cdot [X^+]^W}, \quad [2-7]$$

respectively, the partition coefficient can be presented as

$$D_{OW} = \frac{K_{OW,N} + K_{OW,I} K_a / [H^+]^W + K_{OW,IP} K_{IP} / [X^+]^W K_a / [H^+]^W}{1 + K_a / [H^+]^W + K_{IP} / [X^+]^W K_a / [H^+]^W} \quad [2-8].$$

Let

$$\sigma = \frac{K_a}{[H^+]^w + K_a} = \frac{1}{10^{-(pH-pK_a)} + 1} \quad [2-9]$$

and assume no dissociation,

$$D_{OW} = (1 - \sigma) K_{OW,N} \quad [2-10]$$

if free ions form,

$$D_{OW} = (1 - \sigma) K_{OW,N} + \sigma K_{OW,I} \quad [2-11]$$

if ion-pairs form,

$$D_{OW} = (1 - \sigma) K_{OW,N} + \sigma K_{OW,IP} \quad [2-12].$$

Modeling study suggested that the discrepancy from dissociation only appears in very basic environments ($pH > 9$) (Chen and Lin, 2016). Hence, for most of the atmospheric aerosol particles, pH effect on the 1-octanol–water partitioning can be ignored.

2.2.1.3. Organic-inorganic interactions

Organic-inorganic interactions in aerosol particles lead to non-ideal thermodynamic behavior (Zuend et al., 2008). Organic compounds are denoted as solvents/antisolvent when they increase/decrease the solubility of the inorganic salts. Higher tendency of the effects may lead to salting-in, salting-out, and phase separation (Marcolli et al., 2004; Marcolli and Krieger, 2006), altering the solubility and water uptake of the organic and inorganic compounds, and further changing the mixing state of aerosol particles (Marcolli et al., 2004; Marcolli and Krieger, 2006).

In the octanol–water system, the existence of inorganic salts increases ionic strength and thus influences the activity and solubility of organic solutes in the water-rich phase (Wang et al., 2014):

$$\log \frac{\gamma_{\text{salt}}}{\gamma_{\text{water}}} = \log \frac{S_{\text{water}}}{S_{\text{salt}}} = K_s C^{\text{salt}} \quad [2-13]$$

where γ_{salt} and γ_{water} are the activity coefficients of an organic solute in salt solutions and pure water, S_{water} and S_{salt} are the solubilities of an organic solute in pure water and salt solutions, K_s (M^{-1}) is the Setschenow coefficient, C^{salt} is the molar concentration of the salt solution (mol/L). Alternatively, equation [2-13] can be described by partition coefficient:

$$\log \frac{K_{\text{octanol/salt}}}{K_{\text{octanol/water}}} = K_s C^{\text{salt}} \quad [2-14]$$

where $K_{\text{octanol/salt}}$ is the partition coefficient of a solute between octanol-rich phase and salt water, $K_{\text{octanol/water}}$ is the partition coefficient of a solute between octanol-rich phase and pure water. K_s is an empirical number which depends on the involved organic solute as well as the type of salts. A positive value of K_s indicates a salting-out effect, which shifts the partitioning equilibrium to the 1-octanol phase, and vice versa.

2.2.2. $K_{\text{ow}}-S$ relationship

Correlations between K_{ow} and S have been obtained using experimental datasets for molar and mass concentrations (Kenaga and Goring, 1980; Chiou et al., 1982). Since the unit of mass concentration can better describe water uptake properties of aerosol particles, the $K_{\text{ow}}-S$ relationship on mass concentration is applied in this study. As shown in Table 2.1 and Figure 2.2 (Kenaga and Goring, 1980; Valvani et al., 1981; Coates et al., 1985; Isnard and Lambert, 1989), variabilities exist in the proposed empirical relationships between K_{ow} and S due to the nature of empirical correlations. For the application in atmospheric aerosol, the empirical correlation was tested for a series of water-soluble atmospheric relevant compounds (Table 2.2) (Yu et al., 1999; Graham et al., 2002). The values of K_{ow} and S were taken from experimental data if they are available (Yalkowsky and Dannenfelser, 1992; Hansch et al., 1995; Hartz et al., 2006; Yalkowsky et al., 2016). Otherwise, the values were derived from functional group contribution methods such as KOWWIN v 1.68 and

WSKOW v. 1.41, which are implemented in Estimations Programs Interface for Windows (EPI Suite) from the United States Environmental Protection Agency (US EPA) (Meylan et al., 1996). As shown in Figure 2.3, predicted values of K_{OW} and S agreed well with those derived from experiments. The K_{OW} - S relationship provided by Kenaga and Goring (1980) is applied in the study as it best correlates with atmospheric relevant species [$\Delta \log S = 0.39$ (mean squared error)].

Table 2.1. The relationships between K_{OW} and S proposed in literature. Unit conversion factors were applied to original equations so that S can be represented in g cm^{-3} .

Reference	Equation
Kenaga and Goring (1980)	$\log K_{OW} = -0.642 - 0.8 \log S$
Valvani et al. (1981)	$\log K_{OW} = -0.63 - 1.05 \log S$
Coates et al. (1985)	$\log K_{OW} = -1.79 - 0.94 \log S$
Isnard and Lambert (1989)	$\log K_{OW} = 0.3 - 0.72 \log S$

Figure 2.2. K_{ow} - S relationships of organic compounds. Empirical relationships for these quantities are also shown (Table 2.1).

Figure 2.3. Comparisons of experimental and estimated values of (a) K_{ow} and (b) S . The values of K_{ow} and S were estimated using KOWWIN v.1.68 and WSKOW v. 1.41, which are implemented in EPI suite <https://www.epa.gov/tsca-screening-tools/epi-suite-tm-estimation-program-interface>.

Table 2.2. List of atmospheric relevant compounds employed for validating the log (K_{ow}) - log (S) relationships. The list was developed based on chemicals identified by Yu et al. (1999) and Graham et al. (2002). The values of K_{ow} and S were estimated using KOWWIN v.1.68 and WSKOW v. 1.41, which are implemented in EPI suite (<https://www.epa.gov/tsca-screening-tools/epi-suite-tm-estimation-program-interface>).

Compound	Chemical formula	log (K_{ow})		log (S (g cm ⁻³))		Reference
		experiment	estimated	experiment	estimated	
Malonic acid	C ₃ H ₄ O ₄	-0.81 ^a	-1.25	-0.11748 ^b	0	Graham et al. (2002)
Succinic acid	C ₄ H ₆ O ₄	-0.59 ^a	-0.75	-1.07988 ^b	-0.09264	Graham et al. (2002)
Levogluconan	C ₆ H ₁₀ O ₅	N/A	-1.25	N/A	-0.10735	Graham et al. (2002)
Galactosan	C ₆ H ₁₀ O ₅	N/A	-1.25	N/A	-0.10735	Graham et al. (2002)
Glyceric acid	C ₃ H ₆ O ₄	N/A	-0.51	N/A	-0.12228	Graham et al. (2002)
Methylsuccinic acid	C ₅ H ₈ O ₄	N/A	-0.34	-0.24795 ^c	-0.36452	Graham et al. (2002)
Glutaric acid	C ₅ H ₈ O ₄	-0.29 ^a	-0.26	0.20412 ^b	-0.4022	Graham et al. (2002)
Adipic acid	C ₆ H ₁₀ O ₄	0.08 ^a	0.23	-1.51145 ^b	-0.78595	Graham et al. (2002)
3,4-Dihydroxybenzoic acid	C ₇ H ₆ O ₄	0.86 ^a	0.91	-1.73993 ^b	-1.2926	Graham et al. (2002)
hydroxy pinonic acid	C ₁₀ H ₁₆ O ₄	N/A	1.05	N/A	-1.35047	Yu et al. (1999)
norpinic acid	C ₈ H ₁₂ O ₄	N/A	0.84	N/A	-1.54348	Yu et al. (1999)
sabinic acid	C ₉ H ₁₄ O ₄	N/A	0.84	N/A	-1.54348	Yu et al. (1999)
2,2-dimethyl-3-formyl-cyclobutyl-methanoic acid	C ₈ H ₁₂ O ₃	N/A		N/A		
			1.17		-1.75449	Yu et al. (1999)
2-(2-isopropyl)-2-formyl-cyclopropyl-methanoic acid	C ₈ H ₁₂ O ₃	N/A		N/A		
			1.17		-1.75449	Yu et al. (1999)
2,2-dimethyl-3-formyl-cyclobutyl-methanoic acid	C ₈ H ₁₂ O ₃	N/A		N/A		
			1.17		-1.75449	Yu et al. (1999)
norpinonic acid	C ₉ H ₁₄ O ₃	N/A	1.1	-1.85387	-1.7602	Yu et al. (1999)
3-Hydroxybenzoic acid	C ₇ H ₆ O ₃	1.5 ^a	1.39	-2.13966 ^b	-1.77032	Graham et al. (2002)
Phthalic acid	C ₈ H ₆ O ₄	0.73 ^a	1.07	-2.15677 ^d	-1.81645	Graham et al. (2002)
4-Hydroxybenzoic acid	C ₇ H ₆ O ₃	1.58 ^a	1.38	-2.30103 ^b	-1.83863	Graham et al. (2002)
2,2-dimethyl-cyclobutane-1,3-dicarboxaldehyde	C ₈ H ₁₂ O ₂	N/A		N/A		
			0.92		-1.86423	Yu et al. (1999)
Syringaldehyde	C ₉ H ₁₀ O ₄	N/A	0.88	N/A	-2.02109	Graham et al. (2002)

pinic acid	C ₉ H ₁₄ O ₄	N/A	1.33	N/A	-2.031	Yu et al. (1999)
Vanillin	C ₈ H ₈ O ₃	1.21 ^a	1.05	-1.95861 ^b	-2.16273	Graham et al. (2002)
Syringic acid	C ₉ H ₁₀ O ₅	1.04 ^a	1.04	N/A	-2.23785	Graham et al. (2002)
Azelaic acid	C ₉ H ₁₆ O ₄	1.57 ^a	1.7	-2.61979 ^b	-2.24535	Graham et al. (2002)
pinonic acid	C ₁₀ H ₁₆ O ₃	N/A	1.6	-2.1549 ^c	-2.24734	Yu et al. (1999)
(2,2-dimethyl-3-acetyl)- cyclobutyl formate	C ₁₀ H ₁₆ O ₃	N/A				
			1.33	N/A	-2.41942	Yu et al. (1999)
Vanillic acid	C ₈ H ₈ O ₄	1.43 ^a	1.22	-2.82391 ^b	-2.42366	Graham et al. (2002)
nopinone	C ₉ H ₁₄ O ₁	N/A	2.59	N/A	-3.28233	Yu et al. (1999)

^a (Hansch et al., 1995)

^b (Yalkowsky and Dannenfelser, 1992)

^c Beilstein Database

^d (Yalkowsky and He, 2003)

^e (Hartz et al., 2006)

2.2.3. Notations for solutions extracted by 1-octanol–water partitioning

Notations of the 1-octanol and aqueous solutions produced after liquid–liquid extractions by 1-octanol and water are provided in this section (Figure 2.4). An aqueous solution which contains WSOM derived from offline (e.g., filter sampling) or online (e.g., Particle-into-liquid-sampler: PILS) technique is termed as A_0 (Weber et al., 2001). An aliquot of A_0 is added by 1-octanol to classify WSOM by 1-octanol–water partitioning. The 1-octanol and aqueous phases are termed as O_1A_0 and A_1A_0 , respectively. Subsequently, WSOM in O_1A_0 is further separated by adding water, while WSOM in A_1A_0 could be separated by adding 1-octanol. The separation can be repeated until the desired classification of WSOM is pursued. The notation of a solution following N extractions (X_N : X is A or O) is given as follows:

$$X_N = \left\{ \begin{array}{l} \text{aqueous phase:A} \\ \text{1-octanol phase:O} \end{array} \right\}_N \left\{ \begin{array}{l} \text{aqueous phase:A} \\ \text{1-octanol phase:O} \end{array} \right\}_{N-1} \dots \left\{ \begin{array}{l} \text{aqueous phase:A} \\ \text{1-octanol phase:O} \end{array} \right\}_1 A_0 \quad [2-15]$$

where N is a positive integer. This notation rule is employed throughout the study.

Figure 2.4. Notations for different solutions.

2.2.4. Single extraction from aqueous solution ($N = 1$)

Partitioning of compound i from the original WSOM solution (A_0) into 1-octanol (O_1A_0) or aqueous (A_1A_0) phases after single extraction depends on its K_{OW} . K_{OW_i} can be expressed as

$$K_{OW_i} = \frac{V^{A_1} n_i^{O_1A_0}}{V^{O_1} n_i^{A_1A_0}} \quad [2-16]$$

by representing molar concentration (C_i) using number of moles (n_i) and volume of each phase (V^{A_1} and V^{O_1}). Since the total number of moles in the aqueous phase ($n_i^{A_1A_0}$) and 1-octanol phase ($n_i^{O_1A_0}$) remains the same as the original WSOM solution:

$$n_i^{A_0} = n_i^{A_1A_0} + n_i^{O_1A_0} \quad [2-17]$$

the mole fraction (f) of compound i in aqueous ($f^{A_1A_0}$) and 1-octanol ($f^{O_1A_0}$) phases can be represented as

$$f_i^{A_1A_0} = \frac{n_i^{A_1A_0}}{n_i^{A_0}} = \frac{1}{K_{OW_i} V_r^{(1)} + 1} \quad [2-18]$$

and

$$f_i^{O_1A_0} = \frac{n_i^{O_1A_0}}{n_i^{A_0}} = \frac{K_{OW_i} V_r^{(1)}}{K_{OW_i} V_r^{(1)} + 1} \quad [2-19]$$

respectively, where V_r is the volumetric ratio of 1-octanol and aqueous phases:

$$V_r^{(1)} = \frac{V^{O_1}}{V^{A_1}} \quad [2-20]$$

Since both $f_i^{O_1A_0}$ and $f_i^{A_1A_0}$ are only dependent on K_{OW_i} and $V_r^{(1)}$, and chemical characteristics of compound i determines K_{OW_i} , $V_r^{(1)}$ is the only controllable variable which can regulate the classification of WSOM.

As discussed in Section 2.2.2, K_{OW} of atmospheric relevant compounds could be converted to S using the empirical relationship developed by Kenaga and Goring (1980). Equations 2-19 and 2-18 can be converted to provide $f_i^{A_1A_0}$ and $f_i^{O_1A_0}$ as a function of S_i (water solubility of compound i):

$$f_i^{A_1A_0} = \frac{1}{10^{-0.642-0.8 \log(S_i)} V_r^{(1)} + 1} \quad [2-21]$$

$$f_i^{O_1A_0} = \frac{10^{-0.642-0.8 \log(S_i)} V_r^{(1)}}{10^{-0.642-0.8 \log(S_i)} V_r^{(1)} + 1} \quad [2-22]$$

These equations quantitatively relate f_i and water solubility.

Examples of $f_i^{O_1A_0}$ and $f_i^{A_1A_0}$ plotted as functions of K_{OW} and S are shown in Figure 2.5. Three different values of $V_r^{(1)}$ (0.01, 0.1, and 1) are applied for the calculation. The distributions of $f_i^{O_1A_0}$ and $f_i^{A_1A_0}$ have sigmoidal shapes when plotted in logarithmic scales. Compounds with lower values of K_{OW} tend to partition to the aqueous phase, especially when the values of $V_r^{(1)}$ are smaller (Figure 2.5a). The trend can be applied to classify WSOM by its water solubility (Figure 2.5b). For the classification at $V_r^{(1)}$ equals to 1, the aqueous phase is enriched by WSOM with high solubility ($S > 10^{-1}$ [g cm⁻³]). On the other hand, less-soluble species ($S \sim 10^{-3}$ [g cm⁻³]) partition to the aqueous phase at a lower value of $V_r^{(1)}$ ($V_r^{(1)} = 0.01$). Due to the nature of single extraction, the estimated K_{OW} /solubility distribution functions are broad. The classified resolution would be improved by conducting multiple extractions, although it could be time and labor intensive.

Figure 2.5. (a) Fractions of organic materials partitioning to 1-octanol against K_{OW} . (b) Same as (a) but plotted against S .

2.2.5. Multiple extractions ($N \geq 2$)

The fractions of compound i in the 1-octanol and aqueous phases following the N^{th} extraction ($f_i^{X_N}$) are denoted by $f_i^{A_N X_{N-1}}$ and $f_i^{O_N X_{N-1}}$, respectively. In the case of multiple extractions, these values can be related with K_{OW_i} by the following equations:

$$f_i^{O_N X_{N-1}} = \frac{n_i^{O_N X_{N-1}}}{n_i^{A_0}} = \frac{n_i^{O_N X_{N-1}}}{n_i^{X_{N-1}}} \frac{n_i^{X_{N-1}}}{n_i^{A_0}} r^{(N-1)} = f_i^{X_{N-1}} r^{(N-1)} \frac{K_{OW-i} V_r^{(N)}}{K_{OW-i} V_r^{(N)} + 1} \quad [2-23]$$

$$f_i^{A_N X_{N-1}} = f_i^{X_{N-1}} r^{(N-1)} \frac{1}{K_{OW-i} V_r^{(N)} + 1} \quad [2-24]$$

In Equations 2-23 and 2-24, $r^{(N-1)}$ is volume fraction of X_{N-1} solution, which is used for the N^{th} extraction. The value of $r^{(N-1)}$ is equal to unity when the whole part of X_{N-1} is used for the N^{th} extraction, whereas it is less than one if only a fraction of X_{N-1} is employed for the N^{th} extraction. Expressing equations 2-23 and 2-24 as functions of solubility by using the relationship provided by Kenaga and Goring (1980) yields

$$f_i^{O_N X_{N-1}} = f_i^{X_{N-1}} r^{(N-1)} \frac{10^{-0.642-0.8 \log(S_i)} V_r^{(N)}}{10^{-0.642-0.8 \log(S_i)} V_r^{(N)} + 1} \quad [2-25]$$

$$f_i^{A_N X_{N-1}} = f_i^{X_{N-1}} r^{(N-1)} \frac{1}{10^{-0.642-0.8 \log(S_i)} V_r^{(N)} + 1} \quad [2-26]$$

Examples of $f_i^{A_N X_{N-1}}$ and $f_i^{O_N X_{N-1}}$ calculated with $\{V_r^{(1)}, V_r^{(2)}, V_r^{(3)}\} = \{1, 0.1, 0.01\}$ are shown in Figure 2.6. While the distribution of 1-octanol phases ($f_i^{O_1 A_0}$, $f_i^{O_2 O_1 A_0}$, and $f_i^{O_3 O_2 O_1 A_0}$) shown in Figure 2.6 are similar to those shown in Figure 2.5, the distributions of aqueous phases after multiple extractions (i.e., $f_i^{A_2 O_1 A_0}$ and $f_i^{A_3 O_2 O_1 A_0}$) are sharper than those shown in Figure 2.5. The sharp distributions of WSOM in the aqueous phase shown in Figure 2.6 indicate that conducting multiple extractions can significantly improve the resolution of the classification.

Figure 2.6. (a) Fractions of organic materials partitioning to 1-octanol and aqueous phases following multiple extractions, plotted against K_{OW} . (b) Same as (a) but plotted against S .

2.3. Experiment

The experimental setup for mosquito coil burning and subsequent filter sample collection is shown in Figure 2.7. The mosquito coil (Tennen Jochuugiku, Kicho-no-uzumaki, natural pyrethrum spiral, Kincho, Japan) was chosen because it does not contain any artificially synthesized compounds.

About 1.0 g of coil was burned at 350°C in a 100-L stainless steel chamber. Particle-free air was provided by an air compressor with high-efficiency particulate air (HEPA) filter attached. The resulting particles were collected by two sets of 47 mm Teflon filters (P0450, sigma-aldrich) and filter holders (BGI Inc.) at a flowrate of 5 L min⁻¹. Chemical composition of the particles were measured using a Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM, Aerodyne Inc.) (Fröhlich et al., 2013). The sampled filters were store in a freezer (−27°C) until analysis.

Figure 2.7. Experimental setup for mosquito coil burning experiment.

The collected filter samples were sonicated with 10 mL of purified water (Type I, 18.2 MΩ·cm) for 30 minutes to ensure the extraction of WSOM. The resulting solutions (i.e., A_0) were filtered by a 0.2 μm PTFE syringe filter (514-0070, VWR) to remove insoluble debris. An aliquot of A_0 was added by 1-octanol (Wako first grade, Wako) for liquid–liquid extraction. Glass syringes with metal needles were used to transfer the solutions. The liquid–liquid extraction was done in separation funnels with mixing ratio (V_r) of 0.01, 0.1 and 1, to evaluate the organic compounds with $-1 < \log K_{OW} < 4$, which are important for CCN activation (Riipinen et al., 2015). The separation funnel was shaken until emulsion could be observed. A clear difference of 1-octanol and aqueous

phases appeared after settling the liquids for at least 12 hours. The 1-octanol (O_1A_0) and aqueous (A_1A_0) solutions were then separated into glass vials for further analysis.

The resulting solutions (A_0 , A_1A_0 , and O_1A_0) were nebulized by glass nebulizers (V type, AS ONE) to generate aerosol particles. The aqueous phases (A_0 and A_1A_0) were nebulized without dilution, while the octanol phases were diluted with methanol (ACS grade, 99.8%, VWR) more than 10 times. Particle-free air was provided by a pump with a flowrate of 2.5 L min^{-1} controlled by a mass flow controller (MC-20 SLPM-D, Alicat Scientific, Inc.). A diffusion dryer (Model 42000, Brechtel Manufacturing, Inc.) with activated charcoal (granular 6–10mm, Wako) or silica gel (Chameleon 83000.360, VWR) was deployed to remove the solvents. Charcoal was used for the 1-octanol solutions, while silica gel was employed for aqueous solutions. Solvent blanks were also analyzed to represent possible contaminations from the experimental procedure (Figure 2.8). It is noted that the loss of organic compounds in the diffusion dryer was not quantified, as quantitative analysis is beyond the scope of this study.

Figure 2.8. Comparison of mass spectra of mosquito coil burning particles ($O_1A_0 (V_r^{(1)} = 0.1)$) and blank test (1-octanol diluted by methanol).

2.4. Results and discussion

2.4.1. Visual inspection of the 1-octanol and aqueous phases

O_1A_0 and A_1A_0 solutions of mosquito coil burning particles classified at $V_r^{(I)} = 1, 0.1$, and 0.01 are shown in Figure 2.9. In general, color of the octanol-phase is yellower than that of the aqueous phase. The highly soluble fraction, A_1A_0 ($V_r^{(I)}=1$), is almost colorless, whereas A_1A_0 ($V_r^{(I)}=0.01$) is slightly yellow. This result indicates that light-absorbing species tend to be less-polar. It should be noted that the solution volumes in individual vials are different due to the applied $V_r^{(I)}$. Application of UV–Visible spectroscopy would be necessary to quantify the exact amount of light-absorbing species in each fraction.

Figure 2.9. A photo of A_1A_0 and O_1A_0 solutions separated at $V_r^{(I)} = 1, 0.1$, and 0.01 .

Light-absorbing species in biomass burning particles are known to be dominated by humic-like substances (HULIS), which can be separated by solid-phase extraction. The relationship between K_{OW} and the characteristics of organic compounds classified by XAD-8 is illustrated in Figure 2.10. In general, organic compounds with K_{OW} value smaller than unity ($\log K_{OW} < 0$) can penetrate the XAD-8 column. On the other hand, organic compounds with K_{OW} value higher than unity ($\log K_{OW} > 0$) mainly remain in the XAD-8 column. Since fulvic and humic acids from Suwannee River, which are surrogates of HULIS, do not penetrate XAD-8, we hypothesize that HULIS likely have K_{OW}

values higher than 1 ($\log K_{ow} < 0$). The separation of penetration experiment data for XAD-8 by K_{ow} demonstrates that the classification of WSOM by 1-octanol-water partitioning is comparable to traditional solid phase extraction. An advantage of 1-octanol–water partitioning is that the flexibility of the method allows designing ranges and thresholds of WSOM classification.

Figure 2.10. Comparison of penetration ratio of organic compounds through XAD-8 column measured by Sullivan and Weber (2006) with (a) experimentally determined K_{ow} , and with (b) estimated values of K_{ow} . All the data are summarized in Table 2.3.

Table 2.3. Comparison of *K_{ow}* and penetration ratio of organic compounds through XAD-8 column.

The penetration data is taken from (Sullivan and Weber, 2006). The values of *K_{ow}* and *S* were estimated using KOWWIN v.1.68 and WSKOW v.1.41, which are implemented in EPI suite

(<https://www.epa.gov/tsca-screening-tools/epi-suite-tm-estimation-program-interface>).

Compound	Chemical formula	log (<i>K</i> _{ow})		Penetration (%)
		experiment	estimated	
Monocarboxylic acids				
Formic acid	CH ₂ O ₂	-0.54 ^a	-0.46	114.5
Acetic acid	C ₂ H ₄ O ₂	-0.17 ^a	0.09	106.5
Butyric acid	C ₄ H ₈ O ₂	0.79 ^a	1.07	0
Caproic acid	C ₆ H ₁₂ O ₂	1.92 ^a	2.05	0
Dicarboxylic acids				
Oxalic acid	C ₂ H ₂ O ₄	N/A	-1.74	100.6
Malonic acid	C ₃ H ₄ O ₄	-0.81 ^a	-1.25	106.3
Succinic acid	C ₄ H ₆ O ₄	-0.59 ^a	-0.75	113
Maleic acid	C ₄ H ₄ O ₄	-0.48 ^b	0.05	100
Fumaric acid	C ₄ H ₄ O ₄	-0.48 ^b	0.05	0
Glutaric acid	C ₅ H ₈ O ₄	-0.29 ^a	-0.26	0
Adipic acid	C ₆ H ₁₀ O ₄	0.08 ^a	0.23	0
Pimelic acid	C ₇ H ₁₂ O ₄	0.61 ^a	0.72	0
Azelaic acid	C ₉ H ₁₆ O ₄	1.57 ^a	1.7	0
Carbonyls				
Glyoxal	C ₂ H ₂ O ₂	N/A	-1.66	100
Methyl glyoxal	C ₃ H ₄ O ₂	N/A	-1.5	100
Propanal	C ₃ H ₆ O	0.59 ^a	0.33	112
Butanal	C ₄ H ₈ O	0.88 ^a	0.82	0
Oxocarboxylic acid				
Glyoxylic acid	C ₂ H ₂ O ₃	N/A	-1.4	102
Amines				
Ethanolamine	C ₂ H ₇ NO	-1.31 ^a	-1.61	107.8
Polyols				
1,2-Ethanediol	C ₂ H ₆ O ₂	-1.36 ^a	-1.2	112.5
Saccharides				
Levoglucosan	C ₆ H ₁₀ O ₅	N/A	-1.25	102.5
Inositol	C ₆ H ₁₂ O ₆	N/A	-2.08	103
Sucrose	C ₁₂ H ₂₂ O ₁₁	-3.7 ^a	-4.27	100
Phenols				
Catechol	C ₆ H ₆ O ₂	0.88 ^a	1.03	0

Vanilin	C ₈ H ₈ O ₃	1.21 ^a	1.05	0
Syringaldehyde	C ₉ H ₁₀ O ₄	N/A	0.88	0
Salicyclic acid	C ₇ H ₆ O ₃	2.26 ^a	2.24	0
3-Hydroxybenzoic acid	C ₇ H ₆ O ₃	1.5 ^a	1.39	0
Aromatic acids				
Benzoic acid	C ₇ H ₆ O ₂	1.87 ^a	1.87	0
Phthalic acid	C ₈ H ₆ O ₄	0.73 ^a	1.07	0
Cyclid acids				
Pinic acid	C ₉ H ₁₄ O ₄	N/A	1.33	0
cis-Pinonic acid	C ₁₀ H ₁₆ O ₃	N/A	1.6	0

^a Hansch et al. (1995)

^b Sangster (1989)

2.4.2. ACSM mass spectra

ACSM mass spectra of (a) mosquito coil burning particles directly measured during the burning experiment (i.e., online measurement), and (b) WSOM (A_0) in the mosquito coil burning particles, are shown in Figure 2.11. Mass spectrum of the online measurement (Figure 2.11a) is dominated by hydrocarbon-like species, as demonstrated by the intense peaks at m/z 41, 43, and 55. Marker ions for levoglucosan-like species, which serve as an indicator of biomass burning particles, are also clearly identified (m/z 60 and 73) (Cubison et al., 2011). On the other hand, fractional contribution from m/z 44, which is a marker for degree of oxygenation (Ng et al., 2011), is minor, indicating that the mosquito coil burning particles are not highly oxygenated. Species fragmentized into ions in the range of $m/z > 100$ are termed as high molecular weight (HMW) species. While they are known to be significantly contributed by biomass burning, sources and formation mechanisms of HMW species are highly speculative. About 30% of the OM in mosquito coil burning particles resides in this range. The results are qualitatively consistent with those in a previous study for mosquito coil burning particles (Li et al., 2012). The slight differences (e.g., m/z 121, 137, and 167 are not distinct in our data) in the mass spectra, however, may be caused by the differences in burning condition and/or

types of mosquito coils. Mass spectrum of WSOM extracted from mosquito coil burning particles (Figure 2.11b), on the other hand, has a higher fraction of m/z 44. In addition, the contribution from hydrocarbon-like and HMW species is less than that in the online spectrum, implying that most of these species are insoluble in water.

Figure 2.11. Normalized mass spectra of organic materials quantified by the ToF-ACSM. (a) Online measurement and (b) WSOM.

Figure 2.12 shows the mass spectra of A_1A_0 and O_1A_0 with different values of $V_r^{(I)}$. In the mass spectra of A_1A_0 , the most significant signal is m/z 44, indicating that the OM in A_1A_0 is highly oxygenated. Signal at m/z 60 is also strong, implying that levoglucosan-like species are highly abundant in the A_1A_0 solutions. These signals (m/z 44 and 60) are less significant in O_1A_0 solutions, as compared with the A_1A_0 solutions with the same $V_r^{(I)}$. The O_1A_0 solutions are dominated by hydrocarbon and HMW species. Considering the theoretical curves of the separation, and the

relationship between K_{ow} and S , the results experimentally demonstrate that (1) highly-oxygenated and levoglucosan-like species are highly soluble in water, and (2) hydrocarbon-like and HMW species are less soluble. The findings can also be supported by comparing the mass spectra of $A_I A_0$ and $O_I A_0$ at different $V_r^{(I)}$ values. For instance, fractions of HMW species is higher at smaller value of $V_r^{(I)}$, while the signal intensities of m/z 44 decrease for lower values of $V_r^{(I)}$. The signal intensities of m/z 44 in the mass spectra of $O_I A_0$ solutions with $V_r^{(I)}$ at 0.1 and 0.01 are as small as those in the mass spectrum of “hydrocarbon-like organic aerosol (HOA)” fractions retrieved by the Positive Matrix Factorization (PMF) analysis of atmospheric organic aerosol particles (Ng et al., 2011), indicating that particles identified as HOA may still be water-soluble (while the solubility is low).

Figure 2.12. Mass spectra of WSOM measured by the ToF-ACSM following classification by 1-octanol–water partitioning (single extraction). (a) Aqueous phase ($A_I A_0$, $V_r^{(I)} = 1$), (b) 1-octanol

phase (O_1A_0 , $V_r^{(1)} = 1$), (c) aqueous phase (A_1A_0 , $V_r^{(1)} = 0.1$), (d) 1-octanol phase (O_1A_0 , $V_r^{(1)} = 0.1$), (e) aqueous phase (A_1A_0 , $V_r^{(1)} = 0.01$), and (f) 1-octanol phase (O_1A_0 , $V_r^{(1)} = 0.01$).

2.4.3. Fractions of WSOM partitioned to 1-octanol and aqueous phases

Mass fraction of organic compounds partitioned to aqueous and 1-octanol phases was estimated by combining mass spectra of A_0 , A_1A_0 , and O_1A_0 using the following metric

$$\min_{\alpha} \left[\sum_i \left(I_{A_0-i} - \left(\alpha I_{A_1A_0-i} + (1-\alpha) I_{O_1A_0-i} \right) \right)^2 \right] \quad [2-27]$$

where I_{X_n-i} is the normalized signal intensity of ion at $m/z = i$ in the X_n solution, and α and $(1-\alpha)$ are the estimated fraction of compounds partitioned to aqueous and 1-octanol phases, respectively.

Optimized α value was obtained by calculating the corresponding α value when the difference of the original and reconstructed mass spectra reaches its minimal value (Figure 2.13). The resulting α values were 0.45 ($V_r^{(1)} = 1$), 0.67 ($V_r^{(1)} = 0.1$), and 0.84 ($V_r^{(1)} = 0.01$), as shown in the bar chart in Figure 2.14. In general, the mass fraction of WSOM partitioned to aqueous and 1-octanol phases estimated by the least-square method agrees with the theoretical prediction: the fractions of WSOM partitioned to the 1-octanol phase increase with $V_r^{(1)}$. The obtained α values indicate the contribution of WSOM to CCN activity (Riipinen et al., 2015). For instance, from the classification at $V_r^{(1)} = 0.01$, it is known that the water solubility of 84% of the extracted WSOM could be higher than 10^{-4} (g cm^{-3}), and could possibly contribute to CCN activity. From the classification at $V_r^{(1)} = 1$, it is estimated that around 45% of WSOM is in the highly soluble range for CCN activity ($S > 10^{-1} \text{ g cm}^{-3}$). It is noted that particle size also need to be considered when considering CCN activity in the atmosphere (Dusek et al., 2006).

Figure 2.13. Optimization of α (fractional contribution of A_1A_0 to A_0) for reconstructing the WSOM (A_0) mass spectrum by a linear combination of mass spectra of organic materials partitioned to the 1-octanol (O_1A_0) and aqueous (A_1A_0) phases ($V_r^{(l)} = 0.1$).

Figure 2.14. Mass fractions of WSOM partitioned to 1-octanol and aqueous phases at $V_r^{(l)} = 0.01$, 0.1, and 1. The values were estimated from the reconstruction of ACSM mass spectra. Solid circles and the corresponding error bars indicate average value and standard deviation of the results derived from bootstrap analysis.

Uncertainty of the estimation can be attributed to the uncertainties in mass spectra measurement, which was evaluated by bootstrap analysis. Bootstrap analysis was conducted by randomly selected (1) 100 and (2) 150 peaks from the mass spectrum of A_0 , A_1A_0 , and O_1A_0 with $m/z \geq 29$. The selected peaks were then used for least-square analysis with an iteration of 100000. The results are shown in Table 2.4. It is noted that bootstrap analysis tends to provide higher value of α as compared with the optimized one. The deviations are lower for smaller value of V_r . The least-square analysis method was validated by reconstruction of mass spectra. As shown in Figure 2.15, differences in the resulting α value wouldn't significantly influence the reconstruction of mass spectra (standard deviation of the derived mass spectra was less than 10^{-3}).

Table 2.4. Comparison of the optimized α values and the results from bootstrap analysis.

	Optimized	Bootstrap: 100 peaks	Bootstrap: 150 peaks
$V_r^{(I)} = 1$	0.45	0.50 ± 0.05	0.49 ± 0.03
$V_r^{(I)} = 0.1$	0.67	0.69 ± 0.02	0.68 ± 0.01
$V_r^{(I)} = 0.01$	0.84	0.87 ± 0.02	0.86 ± 0.01

Figure 2.15. Reconstruction of the WSOM mass spectrum by a linear combination of mass spectra of organic materials partitioned to the 1-octanol and aqueous phases ($V_r^{(l)} = 0.1$). The solid line indicates the 1:1 relationship as reference.

2.5. Conclusions

Water solubility distribution of water-soluble organic matter (WSOM) was estimated by the relationship between 1-octanol–water partition coefficient (K_{OW}) and water solubility to understand their contribution to cloud condensation nuclei (CCN). A theory is provided to classify the water solubility of WSOM by its correlation to the volume ratio of 1-octanol and water (V_r). A laboratory mosquito coil burning experiment was conducted to verify the theory by a liquid–liquid extraction method. Chemical compositions of total WSOM, A_0 , A_1A_0 and O_1A_0 with different volume of 1-octanol and aqueous phase ($V_r = 1, 0.1, 0.01$) were obtained using a Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM). Highly oxygenated species with a significant peak at m/z 44 were detected for the mass spectra of aqueous phases (A_0 , A_1A_0) whereas 1-octanol phases (O_1A_0) were dominated by aliphatic species with peaks at m/z 41, 43, 55, 57 and large amounts of high molecular weight fragment ions ($m/z > 100$). Comparison between fractions of some key fragments among the mass spectra of A_1A_0 and O_1A_0 demonstrates the water solubility of WSOM in each extraction ($V_r = 1, 0.1, 0.01$). The fragments include m/z 43 for aliphatic species, m/z 44 for oxygenated species, m/z 60 and 73 for levoglucosan-like species, and $m/z > 100$ for aliphatic species with high molecular weight. Consistent with the theory, WSOM in A_1A_0 ($V_r = 1$) was found with the highest water solubility while that in O_1A_0 ($V_r = 0.01$) was the lowest. Furthermore, fractions of WSOM partition to 1-octanol and aqueous phases can be estimated by reconstruction of mass spectra. The results show 84%, 67% and 45% of the WSOM partitions to the aqueous phase for $V_r = 0.01, 0.1$ and 1, respectively, indicating the potential of these organic aerosols to contribution to CCN.

2.6. Supporting information

Table 2.S1. Database of the normalized mass spectra of mosquito coil sample (Figure 2.11–12).

m/z	Online	A_0	A_1A_0 ($V_r=1$)	A_1A_0 ($V_r=0.1$)	A_1A_0 ($V_r=0.01$)	O_1A_0 ($V_r=1$)	O_1A_0 ($V_r=0.1$)	O_1A_0 ($V_r=0.01$)
1	0	0	0	0	0	0	0	0
2	0	0	0	0	0	0	0	0
3	0	0	0	0	0	0	0	0
4	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0
6	0	0	0	0	0	0	0	0
7	0	0	0	0	0	0	0	0
8	0	0	0	0	0	0	0	0
9	0	0	0	0	0	0	0	0
10	0	0	0	0	0	0	0	0
11	0	0	0	0	0	0	0	0
12	0.000831	0.003151	0.003976	0.003635	0.003994	0.002122	0.001098	0.00069
13	0.000741	0.002009	0.00271	0.002513	0.002423	0.001431	0.000823	0.000498
14	0	0	0	0	0	0	0	0
15	0.007288	0.017293	0.019458	0.018794	0.017977	0.013712	0.008925	0.0066
16	0.000585	0.002179	0.003309	0.002945	0.002585	0.001465	0.000712	0.000406
17	0.003657	0.013616	0.02068	0.018405	0.016156	0.009159	0.004449	0.002536
18	0.014629	0.054463	0.082721	0.073621	0.064623	0.036636	0.017797	0.010145
19	1.74E-05	6.49E-05	9.85E-05	8.77E-05	7.70E-05	4.36E-05	2.12E-05	1.21E-05
20	2.93E-05	0.000109	0.000165	0.000147	0.000129	7.33E-05	3.56E-05	2.03E-05
21	0	0	0	0	0	0	0	0
22	0	0	0	0	0	0	0	0
23	0	0	0	0	0	0	0	0
24	0.00019	0.00057	0.000861	0.000835	0.000707	0.000346	0.000191	0.000124
25	0.000681	0.002117	0.003268	0.002936	0.002537	0.001208	0.000657	0.000375
26	0.004459	0.013156	0.019053	0.017242	0.015049	0.00754	0.004502	0.00274

27	0.02142	0.036051	0.043647	0.041246	0.037789	0.029803	0.023218	0.018717
28	0	0	0	0	0	0	0	0
29	0.028195	0.040248	0.053994	0.049444	0.044257	0.033188	0.026206	0.022086
30	0.00062	0.000885	0.001188	0.001088	0.000974	0.00073	0.000577	0.000486
31	0.00478	0.015262	0.022139	0.019014	0.01592	0.007005	0.005207	0.004415
32	0	0	0	0	0	0	0	0
33	0	0	0	0	0	0	0	0
34	0	0	0	0	0	0	0	0
35	0	0	0	0	0	0	0	0
36	0	0	0	0	0	0	0	0
37	0.00127	0.003124	0.004317	0.003965	0.003597	0.001939	0.00127	0.00079
38	0.002901	0.006486	0.008126	0.007748	0.00722	0.004409	0.003215	0.002277
39	0	0	0	0	0	0	0	0
40	0	0	0	0	0	0	0	0
41	0.049468	0.041378	0.043396	0.042135	0.041936	0.049879	0.044618	0.039812
42	0.015057	0.030362	0.039744	0.036394	0.032746	0.02057	0.016358	0.012299
43	0.058363	0.066904	0.070945	0.068319	0.066547	0.059199	0.06023	0.055535
44	0.014629	0.054463	0.082721	0.073621	0.064623	0.036636	0.017797	0.010145
45	0.005304	0.011981	0.015276	0.013801	0.012408	0.007893	0.005371	0.004276
46	0	0	0	0	0	0	0	0
47	0	0	0	0	0	0	0	0
48	0.000675	0.000821	0.000625	0.000752	0.000797	0.000871	0.000855	0.000788
49	0.000395	0.000826	0.001064	0.001067	0.001	0.000587	0.000398	0.000246
50	0.00317	0.004661	0.004797	0.004946	0.004977	0.004577	0.003859	0.003171
51	0.007091	0.009158	0.007522	0.008476	0.009027	0.010045	0.00986	0.009784
52	0.004407	0.007094	0.007272	0.007502	0.007564	0.006216	0.005813	0.005254
53	0.012211	0.014616	0.013367	0.014214	0.01468	0.01495	0.014514	0.014022
54	0.010361	0.010117	0.010987	0.011077	0.010452	0.008706	0.007697	0.006346
55	0.050519	0.02612	0.025985	0.025139	0.025201	0.03806	0.034891	0.032029
56	0.011066	0.010339	0.01191	0.011253	0.010591	0.013245	0.011378	0.009078
57	0.028685	0.016835	0.021034	0.018487	0.016869	0.02147	0.018421	0.014297

58	0.004325	0.007183	0.010039	0.008644	0.007632	0.003568	0.003206	0.002795
59	0.002339	0.002665	0.002809	0.002701	0.00263	0.003713	0.002744	0.002841
60	0.008274	0.009107	0.013108	0.011183	0.009452	0.004539	0.00316	0.002141
61	0.002161	0.002603	0.00342	0.003035	0.002661	0.001577	0.001291	0.001119
62	0.001349	0.001643	0.001251	0.001505	0.001594	0.001742	0.00171	0.001575
63	0.003772	0.00417	0.002684	0.003405	0.003923	0.005104	0.005395	0.005504
64	0.004263	0.004873	0.004077	0.004465	0.004822	0.005395	0.00523	0.005023
65	0.012232	0.00914	0.006319	0.007489	0.008592	0.012004	0.0123	0.012548
66	0.004479	0.005702	0.00526	0.00564	0.005735	0.005495	0.005321	0.005054
67	0.023963	0.0101	0.007898	0.008497	0.009453	0.014893	0.014787	0.014464
68	0.010604	0.010016	0.010671	0.010682	0.010332	0.008701	0.008349	0.007259
69	0.024103	0.012891	0.012597	0.012433	0.012423	0.017677	0.016973	0.015364
70	0.00911	0.010773	0.011675	0.011893	0.011045	0.010276	0.008826	0.00601
71	0.014247	0.014644	0.017927	0.016255	0.015059	0.011005	0.010476	0.008137
72	0.002084	0.003057	0.003442	0.003227	0.003078	0.002324	0.002286	0.001988
73	0.008051	0.007174	0.009701	0.008395	0.007301	0.00487	0.003616	0.003046
74	0.001972	0.002413	0.002476	0.002389	0.002336	0.002091	0.002036	0.001925
75	0.001554	0.001791	0.001403	0.001526	0.001671	0.001831	0.002027	0.002167
76	0.001809	0.003538	0.00396	0.003707	0.003606	0.002435	0.002687	0.002728
77	0.014024	0.011012	0.005415	0.007444	0.009649	0.016286	0.017967	0.020392
78	0.005356	0.005086	0.003357	0.003984	0.004667	0.006212	0.006602	0.006876
79	0.017372	0.009121	0.005117	0.006501	0.008158	0.013963	0.01474	0.015312
80	0.005291	0.005036	0.004158	0.004621	0.004939	0.004518	0.005267	0.00569
81	0.019668	0.00964	0.008043	0.008594	0.009179	0.011885	0.012195	0.012101
82	0.008066	0.006235	0.005965	0.006243	0.00617	0.006291	0.006496	0.00616
83	0.013021	0.00612	0.005735	0.005508	0.005803	0.009447	0.008977	0.008401
84	0.006386	0.005482	0.006163	0.005743	0.005424	0.005211	0.005239	0.004742
85	0.007424	0.004067	0.004301	0.004084	0.003946	0.005029	0.004675	0.004062
86	0.001893	0.002989	0.003015	0.003038	0.002942	0.002085	0.002319	0.00206
87	0.00226	0.002704	0.002987	0.002789	0.002603	0.00179	0.001877	0.001966
88	0.000946	0.001047	0.00097	0.000979	0.000997	0.000867	0.001067	0.001189

89	0.002646	0.003007	0.002195	0.002473	0.002757	0.002972	0.003632	0.004218
90	0.00144	0.00162	0.000923	0.00117	0.001454	0.001889	0.00236	0.002669
91	0.020704	0.012031	0.004941	0.007536	0.01059	0.021683	0.021742	0.023523
92	0.005141	0.003749	0.002134	0.002853	0.003524	0.00544	0.005573	0.005738
93	0.013294	0.007072	0.003589	0.004954	0.006378	0.010866	0.011587	0.01174
94	0.007055	0.006714	0.005544	0.006161	0.006585	0.006024	0.007022	0.007587
95	0.015373	0.00918	0.008188	0.008691	0.008905	0.008877	0.009603	0.009738
96	0.005108	0.004808	0.00467	0.004847	0.004866	0.004227	0.004524	0.004148
97	0.00817	0.00444	0.003985	0.004074	0.004196	0.006288	0.005876	0.005233
98	0.004218	0.003877	0.004263	0.004037	0.003847	0.003951	0.003736	0.003433
99	0.002289	0.002323	0.00218	0.002236	0.002218	0.002286	0.002417	0.002375
100	0.001244	0.001778	0.001857	0.001866	0.001718	0.001269	0.001331	0.0013
101	0.001553	0.001553	0.001382	0.001405	0.001444	0.001403	0.001675	0.001922
102	0.001962	0.001952	0.001357	0.00158	0.001751	0.001936	0.002387	0.002791
103	0.003416	0.003122	0.001818	0.002174	0.002682	0.003712	0.004509	0.005236
104	0.002796	0.002479	0.001636	0.001948	0.002277	0.003273	0.003772	0.003889
105	0.012956	0.005897	0.002512	0.003575	0.004976	0.009405	0.010972	0.012069
106	0.004499	0.003524	0.001973	0.00262	0.003267	0.004633	0.005313	0.005547
107	0.012146	0.007365	0.003755	0.005222	0.006781	0.012713	0.012634	0.013581
108	0.005121	0.00493	0.003554	0.004408	0.004752	0.005296	0.005921	0.006202
109	0.008508	0.006214	0.004744	0.005402	0.005906	0.006441	0.007259	0.007606
110	0.003739	0.003959	0.003457	0.003753	0.003805	0.003572	0.004065	0.003954
111	0.003908	0.003369	0.003013	0.003137	0.003276	0.003704	0.003955	0.003714
112	0.002049	0.002272	0.002362	0.002332	0.002269	0.002692	0.002232	0.002123
113	0.001688	0.001687	0.001226	0.00141	0.001596	0.001918	0.002206	0.002092
114	0.001248	0.001406	0.001087	0.001175	0.001278	0.001274	0.001656	0.00174
115	0.006764	0.004544	0.00212	0.002763	0.00365	0.005862	0.007606	0.009545
116	0.002737	0.002079	0.001087	0.001358	0.001722	0.002523	0.003335	0.003963
117	0.00633	0.003863	0.001863	0.002492	0.003259	0.00497	0.006448	0.007422
118	0.003173	0.002941	0.001973	0.002374	0.002726	0.003006	0.003861	0.00423
119	0.007983	0.004143	0.002019	0.002745	0.003592	0.00551	0.006958	0.007597

120	0.004076	0.003301	0.001957	0.002497	0.002987	0.003746	0.004806	0.005214
121	0.008778	0.00537	0.003021	0.004097	0.004901	0.006258	0.007895	0.008306
122	0.004017	0.0038	0.002473	0.0031	0.00352	0.003774	0.004855	0.005299
123	0.005603	0.004431	0.002924	0.00361	0.004062	0.004604	0.005985	0.007127
124	0.002165	0.002525	0.00178	0.00216	0.002369	0.002433	0.003046	0.003204
125	0.002248	0.002806	0.001949	0.002516	0.00275	0.003831	0.003317	0.003167
126	0.001806	0.001986	0.001746	0.001891	0.001894	0.001799	0.001924	0.001996
127	0.002831	0.002225	0.001138	0.001481	0.001835	0.00268	0.003546	0.004376
128	0.004781	0.003147	0.001384	0.001927	0.002544	0.00401	0.005277	0.006396
129	0.005085	0.002624	0.001123	0.001543	0.002202	0.003955	0.004882	0.005563
130	0.003019	0.00238	0.001194	0.001654	0.002082	0.00277	0.003787	0.004496
131	0.005859	0.003807	0.00171	0.002404	0.003202	0.004703	0.006547	0.007793
132	0.002937	0.002618	0.001513	0.001921	0.002335	0.002833	0.003869	0.004383
133	0.006089	0.003332	0.001716	0.00231	0.002899	0.004045	0.005477	0.006332
134	0.003343	0.002733	0.001493	0.001992	0.002476	0.003576	0.004308	0.004867
135	0.005646	0.003631	0.002048	0.002734	0.003282	0.004491	0.005415	0.006111
136	0.002699	0.00277	0.001596	0.002116	0.00256	0.003091	0.004008	0.004364
137	0.003525	0.00377	0.001789	0.002519	0.003097	0.004446	0.006238	0.00858
138	0.001809	0.002237	0.001384	0.001852	0.002056	0.002343	0.003057	0.003456
139	0.002062	0.00195	0.001087	0.001382	0.001642	0.002387	0.002915	0.003437
140	0.001366	0.001435	0.000804	0.001007	0.001267	0.001508	0.002137	0.002321
141	0.003677	0.002286	0.000949	0.001371	0.001884	0.003076	0.004138	0.005035
142	0.002505	0.001682	0.000778	0.00106	0.001425	0.002116	0.002876	0.003328
143	0.003562	0.002196	0.000955	0.001333	0.001838	0.002763	0.003859	0.00453
144	0.002572	0.00209	0.001064	0.001392	0.001757	0.002352	0.003461	0.004286
145	0.004961	0.003127	0.00142	0.002033	0.002679	0.003709	0.00539	0.00637
146	0.002396	0.002227	0.001159	0.001596	0.001975	0.002382	0.003508	0.004105
147	0.004551	0.003093	0.001461	0.00202	0.002659	0.00384	0.005369	0.006375
148	0.0022	0.002106	0.001058	0.001477	0.001842	0.002365	0.003466	0.004012
149	0	0	0	0	0	0	0	0
150	0.001925	0.002003	0.001069	0.00144	0.001742	0.002284	0.003204	0.003705

151	0.002356	0.002458	0.00111	0.001633	0.002039	0.003038	0.003948	0.00509
152	0.002893	0.00216	0.001025	0.00141	0.001803	0.00277	0.003676	0.004532
153	0.002595	0.002309	0.001048	0.001512	0.001976	0.003469	0.00387	0.004439
154	0.002135	0.002294	0.001089	0.001673	0.002014	0.002583	0.003269	0.00331
155	0.002535	0.001708	0.000758	0.001055	0.001389	0.002105	0.002914	0.00348
156	0.001937	0.001549	0.000727	0.000997	0.001299	0.001777	0.002579	0.003008
157	0.003033	0.002152	0.000816	0.001216	0.001739	0.00273	0.004062	0.004957
158	0.002052	0.001728	0.000862	0.001129	0.001464	0.001897	0.002894	0.003589
159	0.00346	0.002344	0.001019	0.001485	0.001975	0.00278	0.004242	0.005147
160	0.002026	0.001887	0.00087	0.001242	0.001599	0.002038	0.003184	0.003899
161	0.003252	0.002243	0.000891	0.001332	0.001774	0.002638	0.004226	0.005551
162	0.001769	0.001721	0.000762	0.001137	0.001433	0.002088	0.003168	0.003934
163	0.002212	0.001989	0.000975	0.00136	0.001709	0.002258	0.00329	0.003995
164	0.001585	0.001672	0.00087	0.001208	0.0015	0.001811	0.002652	0.003104
165	0.003253	0.001979	0.000873	0.001292	0.00163	0.002416	0.003311	0.004057
166	0.001757	0.001355	0.000684	0.000928	0.001165	0.001753	0.002318	0.002789
167	0.002449	0.002164	0.000853	0.001311	0.001783	0.003098	0.003904	0.004559
168	0.002035	0.001921	0.000753	0.00119	0.001606	0.00224	0.003439	0.00374
169	0.002164	0.001587	0.000644	0.000921	0.00126	0.002174	0.002987	0.003944
170	0.001485	0.001375	0.000632	0.000897	0.001114	0.001562	0.002431	0.003167
171	0.002177	0.001679	0.000837	0.001024	0.001376	0.002031	0.003132	0.003866
172	0.001467	0.001419	0.000693	0.000947	0.001216	0.001541	0.002429	0.003062
173	0.002221	0.001723	0.000717	0.001042	0.001407	0.002055	0.003258	0.004102
174	0.001471	0.001507	0.000608	0.000911	0.001214	0.001701	0.002856	0.003625
175	0.002423	0.001738	0.000624	0.00097	0.001379	0.002086	0.003445	0.004506
176	0.001586	0.001323	0.000562	0.000807	0.001048	0.001587	0.002615	0.003389
177	0.001599	0.001386	0.000562	0.00086	0.001136	0.001574	0.002474	0.003227
178	0.001918	0.001249	0.000528	0.000761	0.001029	0.001446	0.002243	0.002814
179	0.001687	0.001151	0.000529	0.000718	0.000934	0.001332	0.001932	0.002437
180	0.001379	0.001093	0.000511	0.000696	0.000903	0.001185	0.001783	0.002314
181	0.001908	0.001451	0.00058	0.000848	0.001139	0.001688	0.002546	0.003261

182	0	0	0	0	0	0	0	0
183	0	0	0	0	0	0	0	0
184	0	0	0	0	0	0	0	0
185	0.001846	0.001445	0.000655	0.000857	0.001128	0.00178	0.002954	0.003943
186	0	0	0	0	0	0	0	0
187	0.001938	0.001366	0.0005	0.000761	0.001055	0.001598	0.002701	0.003609
188	0.001297	0.001079	0.000429	0.000641	0.000848	0.001232	0.002086	0.00279
189	0.00331	0.001227	0.000484	0.000694	0.000951	0.001548	0.002575	0.003378
190	0.001621	0.001017	0.000389	0.000564	0.000782	0.001226	0.002068	0.002821
191	0.00174	0.001066	0.000467	0.000661	0.000864	0.001289	0.002006	0.002624
192	0.001261	0.001001	0.000425	0.000585	0.000793	0.001216	0.001942	0.002444
193	0.001272	0.000893	0.000404	0.000537	0.000702	0.000998	0.001512	0.001944
194	0.001187	0.000961	0.00039	0.000527	0.000713	0.000982	0.001611	0.002341
195	0.001427	0.000888	0.000379	0.000516	0.000705	0.001016	0.001653	0.002201
196	0.00118	0.000883	0.000368	0.000491	0.00068	0.000999	0.001676	0.002278
197	0.001421	0.000988	0.000372	0.000522	0.000698	0.0012	0.001941	0.002791
198	0.001175	0.000878	0.000355	0.000491	0.00067	0.000965	0.001614	0.002238
199	0.001376	0.000887	0.000374	0.000511	0.000678	0.001067	0.001693	0.002324
200	0.00117	0.000848	0.00034	0.000479	0.000652	0.000948	0.001594	0.00219
201	0.001344	0.000853	0.000373	0.000506	0.000662	0.001039	0.001623	0.002209
202	0.001164	0.000818	0.000324	0.000467	0.000635	0.000931	0.001574	0.002142
203	0.002105	0.000893	0.000342	0.000508	0.000706	0.001172	0.001898	0.00254
204	0.001303	0.000796	0.000312	0.000463	0.000644	0.000969	0.001679	0.00228
205	0.001337	0.000783	0.000323	0.000471	0.000636	0.000956	0.001534	0.002025
206	0.001008	0.000751	0.00029	0.000437	0.000573	0.000843	0.001411	0.001861
207	0.001189	0.000753	0.000417	0.000517	0.00061	0.000983	0.001363	0.001821
208	0.000996	0.000626	0.000281	0.000405	0.000522	0.000714	0.001128	0.001501
209	0.001065	0.000655	0.000284	0.000379	0.000504	0.000741	0.001182	0.00163
210	0.000984	0.000667	0.000275	0.000395	0.000523	0.000775	0.001291	0.001789
211	0.001188	0.000769	0.000255	0.000393	0.000542	0.000928	0.001602	0.002407
212	0.000693	0.000453	0.000195	0.00028	0.000366	0.000521	0.000847	0.001152

213	0.000789	0.000498	0.000189	0.00027	0.000366	0.000584	0.000974	0.001413
214	0.000495	0.000323	0.000139	0.0002	0.000261	0.000372	0.000605	0.000823
215	0.000563	0.000356	0.000135	0.000193	0.000261	0.000417	0.000696	0.001009
216	0.000297	0.000194	8.34E-05	0.00012	0.000157	0.000223	0.000363	0.000494
217	0	0	0	0	0	0	0	0

Chapter 3 Determining polarity distribution of atmospheric water-soluble organic matter by the 1-octanol–water extraction method

3.1. Introduction

Organic matter (OM) constitutes a significant fraction of submicron particulates in the atmosphere (Jimenez et al., 2009; Heald et al., 2011). OM absorbs water vapor, contributing to aerosol direct and indirect effects (Saxena and Hildemann, 1996; Scott et al., 2014). Aerosol direct effect, which is caused by scattering and absorption of the solar radiation by particles, is tightly linked to their hygroscopic properties at sub-saturated conditions (i.e., relative humidity (RH) < 100%) (Michel Flores et al., 2012). Aerosol indirect effect, which is the changes in physical properties of cloud induced by anthropogenically enhanced cloud condensation nuclei (CCN) active particles, is also related to water uptake characteristics (Ramanathan et al., 2001; Rosenfeld et al., 2019).

OM is a complex mixture of organic species, which have a wide range of polarity and water solubility (Psichoudaki and Pandis, 2013; Xu et al., 2017). For instance, water solubility (S) of OM in atmospheric aerosol particles varies 10 orders of magnitude ($10^{-10} \text{ g cm}^{-3} < S < 10^0 \text{ g cm}^{-3}$) (Psichoudaki and Pandis, 2013), suggesting that their hygroscopic and CCN properties are also highly variable (Suda et al., 2012). Experimental study of laboratory generated OM demonstrated that less water-soluble organic compounds ($S < 10^{-4} \text{ g cm}^{-3}$) do not contribute to CCN activity, while highly water-soluble species ($S > 10^{-1} \text{ g cm}^{-3}$) are highly CCN active (Kuwata et al., 2013). In addition, recent studies demonstrated that OM particles undergo phase separation upon hygroscopic growth due to coexistence of highly and less polar chemical species in a single particle (Renbaum-Wolff et al., 2016; Liu et al., 2018). Distributions of water solubility and polarity of OM will likely need to be represented as a distribution function in representing such phenomena. Such distributions will especially be important for water soluble fraction of OM (WSOM), as it dominates the contribution of OM on water uptake properties.

Polarity of WSOM in aerosol particles could be systematically represented using distribution of 1-octanol–water partition coefficients (K_{ow}). K_{ow} is defined by the following equation.

$$K_{ow} = \frac{C^o}{C^A} . \quad [3-1]$$

C^o and C^A denote molar concentrations of a chemical species in 1-octanol and aqueous phases, respectively. The values of K_{OW} are lower for more polar compounds. K_{OW} has widely been employed to represent partitioning phenomena in environment such as adsorption of organic compounds on soil (Fischer et al., 2018). K_{OW} is also known to correlate well with water solubility of OM, which is one of the most critical parameters in determining CCN activity (Psichoudaki and Pandis, 2013; Riipinen et al., 2015). In addition, K_{OW} can be used as a parameter to categorize hydrophilic and hydrophobic compounds in atmospheric OM (Pun et al., 2006). In our recent study, we experimentally demonstrated that atmospheric relevant WSOM can be classified based on K_{OW} in combination with the liquid–liquid extraction technique (Kuwata and Lee, 2017). Namely, mole fractions of chemical species in WSOM partitioning to 1-octanol (f^o) and aqueous (f^A) phases are regulated by both K_{OW} of the compound and volumetric ratio (V_r) of 1-octanol (V^o) and aqueous (V^A) phases in the case of single extraction process. As the value of V_r is fixed for each liquid–liquid extraction process, mole ratios of each chemical species in WSOM partitioning to 1-octanol and aqueous phases depends on their K_{OW} .

In the present study, we developed a numerical method to estimate the polarity distribution of WSOM by combining data inversion algorithms with the 1-octanol–water partitioning method (Kuwata and Lee, 2017). The method was evaluated by numerical experiments. Subsequently, the method was applied to OM generated by combustion of mosquito coil, which serves as a proxy of biomass burning.

3.2. Theory

Theoretical basis for the estimation of K_{OW} distribution function ($F(x)$) of WSOM, which is defined as a probability density function of polarity as determined by K_{OW} , is developed in this section. $F(x)$ is estimated by combining f^A, f^O , and mass fractions of WSOM partitioned to aqueous and 1-octanol phases (α). f^A, f^O , and α are dependent both on V_r and extraction steps (Kuwata and Lee, 2017). As both f^A and f^O have broad distribution with respect to K_{OW} for a certain value of V_r , a set of the Fredholm integral equation of the first kind needs to be numerical solved using a data inversion algorithm to retrieve $F(x)$ (Twomey, 1975; Kandlikar and Ramachandran, 1999). In general, the Fredholm integral equation is written in a following way:

$$y = \int K(x)G(x) dx + \varepsilon . \quad [3-2]$$

Quantity y stands for the measured data, $K(x)$ is the kernel function, $G(x)$ is the distribution function, and ε is the error term.

Based on the abovementioned concepts, the following equation can be developed to obtain relate α, f^a , and $F(x)$.

$$\alpha = \int f^A F(x) dx + \varepsilon . \quad [3-3]$$

Equation 3-3 can be discretized to facilitate numerical analysis.

$$\alpha = \sum_j f_j^A F_j + \varepsilon . \quad [3-4]$$

Measurements of α can be conducted for N conditions by varying V_r and number of steps for 1-octanol–water extraction (Kuwata and Lee, 2017). As a result, the following equation can be derived:

$$\begin{pmatrix} \alpha_1 \\ \alpha_2 \\ \vdots \\ \alpha_N \end{pmatrix} = \begin{pmatrix} f_{1-1}^A & f_{1-2}^A & \cdots & f_{1-j}^A \\ f_{2-1}^A & & & \vdots \\ \vdots & & & \vdots \\ f_{N-1}^A & \cdots & \cdots & f_{N-j}^A \end{pmatrix} \begin{pmatrix} F_1 \\ F_2 \\ \vdots \\ F_j \end{pmatrix} + \begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \vdots \\ \varepsilon_N \end{pmatrix}. \quad [3-5]$$

It has been widely recognized that an inversion analysis is required to obtain $\mathbf{F}$ from such a type of equation due to ε (Kandlikar and Ramachandran, 1999). In the following, an approach to obtain $\mathbf{F}$ using equation 3-5 is discussed.

3.2.1. 1-octanol–water partitioning function (f^A, f^O)

f^A and f^O are dependent on both V_r and extraction steps (Kuwata and Lee, 2017). Kuwata and Lee (2017) denoted original WSOM solution prior to 1-octanol–water extraction as A_0 . Aqueous and 1-octanol phases following single extraction process of A_0 are called as A_1A_0 and O_1A_0 , respectively. The corresponding functions of f^A and f^O are represented as $f^{A_1A_0}$ and $f^{O_1A_0}$. Second extraction could be conducted for O_1A_0 , allowing further classification of WSOM. The subsequent aqueous and 1-octanol solutions are defined as $A_2O_1A_0$ and $O_2O_1A_0$. Partitioning of WSOM in these solutions follows $f^{A_2O_1A_0}$ and $f^{O_2O_1A_0}$.

$f^{A_1A_0}$ and $f^{O_1A_0}$ are represented by the following equation (Kuwata and Lee, 2017):

$$f^{A_1A_0} = 1 - f^{O_1A_0} = \frac{1}{K_{OW}V_r^{(1)} + 1}. \quad [3-6]$$

$V_r^{(1)}$ is the value of V_r for the first extraction. Examples of $f^{A_1A_0}$ are shown in Figure 3.1. WSOM with lower values of K_{OW} tends to partition to aqueous phase, meaning that they are highly polar. In addition, mass fraction of WSOM partitioned to aqueous phase increases when the $V_r^{(1)}$ decreases.

$f^{A_2O_1A_0}$ and $f^{O_2O_1A_0}$ are represented in the following ways (Kuwata and Lee, 2017):

$$f^{A_2O_1A_0} = f^{O_1A_0} r^{O_1A_0} \frac{1}{K_{OW}V_r^{(2)} + 1}. \quad [3-7]$$

$$f^{O_2O_1A_0} = f^{O_1A_0} r^{O_1A_0} \frac{K_{OW} V_r^{(2)}}{K_{OW} V_r^{(2)} + 1}. \quad [3-8]$$

$r^{O_1A_0}$ denotes volume fraction of O_I , which was used for the second extraction process. $V_r^{(2)}$ is the value of V_r for the second extraction.

Figure 3.2 shows examples of $f^{A_2O_1A_0}$. Unlike $f^{A_1A_0}$, which has sigmoid-like distribution, $f^{A_2O_1A_0}$ has a Gaussian-like curve when it is plotted against $\log K_{OW}$. This result suggests that the second extraction process has potential to improve the inversion of $F(x)$ due to the less overlap in Kernel function (Kandlikar and Ramachandran, 1999).

Figure 3.1. Fraction of OM partitioned to aqueous phases after single extraction with (a) $V_r^{(1)} = 10$, (b) $V_r^{(1)} = 5$, (c) $V_r^{(1)} = 1$, (d) $V_r^{(1)} = 0.1$, and (e) $V_r^{(1)} = 0.01$.

Figure 3.2. Fraction of OM partitioned to aqueous phases after second extraction with $[V_r^{(1)}, V_r^{(2)}]$ values set as (a) [10, 5], (b) [5, 1], (c) [1, 0.1], and (d) [0.1, 0.01].

3.2.2. Derivation of partitioning fraction (α)

3.2.2.1. Derive α from mass spectra of A_0 , A_1A_0 , and O_1A_0

Value of α can be estimated by reconstructing the mass spectra of A_0 using those for A_1A_0 and O_1A_0 in the following way (Kuwata and Lee (2017)).

$$I_{A_0-i} = \alpha I_{A_1A_0-i} + (1-\alpha)I_{O_1A_0-i} + \varepsilon_i \quad [3-9]$$

where I_{X_n-i} is the normalized signal intensity of ions with $m/z = i$ in the X_n solution, and ε_i is the experimental error. $\sum_i \varepsilon_i^2$ can be minimized to optimize the value of α :

$$\min \left[\sum_i \varepsilon_i^2 \right] = \min_{\alpha} \left[\sum_i \left(I_{A_0-i} - \left(\alpha I_{A_1A_0-i} + (1-\alpha)I_{O_1A_0-i} \right) \right)^2 \right]. \quad [3-10]$$

It is noted that the measurement of O_1A_0 solution is sometimes challenging due to the interference from background signals. Particularly, the interference of residual 1-octanol is prominent when the concentration of O_1A_0 solution is low.

3.2.2.2. Derive α from A_0 , A_1A_0 measurement, and PMF analysis

Another algorithm is thus proposed to estimate α . The mass spectra of A_0 and A_1A_0 can be deconvoluted using statistical methods such as the positive matrix factorization (PMF) (Ulbrich et al., 2009; Zhang et al., 2011; Lee et al., 2019) Such deconvolution of mass spectra allows us to represent them using linear combination of a few factors:

$$I_{X_n-i} = \sum_k M_{X_n-P_k} I_{P_k-i} + \varepsilon_i, \quad [3-11]$$

where I_{X_n-i} is the normalized signal intensity of ions with $m/z = i$ in the X_n solution, $M_{X_n-P_k}$ is the mass fraction of the k^{th} factor (P_k , $k = 1, 2, \dots$) in solution X_n , I_{P_k-i} is the normalized ion intensity of

ion with $m/z = i$ in the mass spectra of P_k , and ε_k is the error term. Combining equation 3-9 and 3-11 and assuming that $I_{P_{k-i}}$ are independent give rise to:

$$M_{A_0-P_k} = \alpha M_{A_1A_0-P_k} + (1-\alpha)M_{O_1A_0-P_k} + \varepsilon_k. \quad [3-12]$$

Parameters $M_{A_0-P_k}$ and $M_{A_1A_0-P_k}$ are derived from factor analysis. Values of α and $M_{O_1A_0-P_k}$ can be optimized by numerically solving the following equation:

$$\min \left[\sum_k \varepsilon_k^2 \right] = \min_{\alpha, M_{O_1A_0-P_k}} \left[\sum_k \left(M_{A_0-P_k} - \left(\alpha M_{A_1A_0-P_k} + (1-\alpha)M_{O_1A_0-P_k} \right) \right)^2 \right], \quad [3-13]$$

where

$$\sum_k M_{O_1A_0-P_k} = 1. \quad [3-14]$$

3.2.3. Optimization of K_{ow} distribution (F)

$F(x)$ was obtained by numerically optimizing equation 3-5. The employed inversion algorithms include MATLAB nonnegative least-squares fitting *lsqnonneg* (NNLS), Twomey's method (Twomey, 1975), and smoothed-Twomey (STWOM) (Markowski, 1987). The output of NNLS was set as the initial guess of Twomey's method and STWOM.

3.3. Pseudo experiments

Data inversion algorithms were evaluated by pseudo experiments of artificially produced distributions. In total, three types of distributions were tested. The assumed range of K_{ow} was $-2 < \log K_{ow} < 2$. The corresponding values of α were calculated using equation 3-2, assuming that five values of V_r were employed for the first extractions ($V_r = 10, 5, 1, 0.1$, and 0.01). The corresponding values for the second extractions were $V_r = 5, 1, 0.1$, and 0.01 . Subsequently, an error of 10%, which was generated by *randn* implemented in MATLAB, were added to α . The value of 10% was

estimated by conducting bootstrap analysis using the mass spectra derived from mosquito coil burning particles (c.f. Chapter 2). In total, 10000 of different input parameters were generated, allowing us to evaluate the sensitivity of numerical analysis on measurement uncertainties.

Results of the evaluation are summarized in Figure 3.3. Figures 3.3a and b show the results of case 1 for first extraction only and for both first and second extractions, respectively. In the case of Figure 3.3a, the distribution was reproduced well by NNLS. On the other hand, Twomey's method and STWOM fail to estimate the fractions of compounds in the two bins with lowest K_{OW} values by 30–40%. Inclusion of the data from second extraction reduced the discrepancy of the original and estimated distributions.

Figure 3.3c and d show the results of case 2, where most of the compounds exist in the bins of $\log K_{OW} = -1$ and 1. Twomey's method was able to reproduce the shape of K_{OW} distribution within the error of 10%, even when only the data from first extraction was used as input (Figure 3.3c). On the other hand, NNLS and STWOM provide almost flat distributions instead of the original M-shape distribution. The disagreement probably caused by over smoothing. Again, addition of second extractions measurements reduced the uncertainty for estimation of the K_{OW} distribution, especially when NNLS and Twomey's method were employed (Figure 3.3d). STWOM, however, still tends to over smooth the results and thus fails to capture the oscillation of K_{OW} distribution. In the case of case 3 (Figures 3.3e and f), K_{OW} distribution was reproduced by NNLS, Twomey's method, and STWOM within the uncertainties of less than 2.8% even when only the data from first extraction was employed.

Figure 3.3. Pseudo experiments for the case of single extraction (column a, c, and e), and inclusive of second extractions (column b, d, and f). An error of 10% was added to α .

Larger errors (20% and 50%) were also applied to α to evaluate the effects of uncertainty in the initial guess. As shown in Figures 3.4, larger errors lead to larger standard deviations, yet general trend of the result can still be predicted. To summarize, NNLS and Twomey's method provide reasonable results, especially when second extraction data was added. STWOM may help reducing the uncertainty induced by initial guess, but the algorithm sometimes over-smooths the output.

Figure 3.4. Pseudo experiments for the case of single extraction (column a, c, and e), and inclusive of second extractions (column b, d, and f). Errors of 20% and 50% was applied to α .

3.4. Experiment

Data inversion algorithms were applied to particles derived from smoldering of mosquito coil (Tennen Jochuugiku, Kicho-nouzumaki, natural pyrethrum spiral, Kincho, Osaka, Japan), which often serve as a proxy of biomass burning particles (Li et al., 2012). Approximately 1 g of mosquito coil were combusted at 350°C in a 100-L stainless steel container (see Kuwata et al. (2017) for detailed experimental setup). The particles were collected on 47 mm (diameter) borosilicate glass fiber filter (Whatman Grade EPM 2000) at a flowrate of approximately 10 L min⁻¹. The filters were baked at 500°C for 16 hours prior to sampling. The collected filter samples were sonicated for 30

minutes with 10 mL of Type I water (TU-6-UV, VWR) to extract WSOM. The extraction was conducted for three times. The resulting aqueous solutions (A_0) were passed through 0.2 μm PTFE syringe filters (514-0070, VWR) for the removal of suspended materials.

The 1-octanol–water extraction was conducted using separation funnels (Kuwata and Lee, 2017). 1-octanol (99%, Alfa Aesar) was added to an aliquot of A_0 solution in a separation funnel. The volumes of 1-octanol and A_0 , which controls V_r , were measured by using glass syringes. The separation funnel was shaken and allowed to stand until the formation of two phases. The 1-octanol and aqueous phases (O_1A_0 and A_1A_0) were extracted separately and placed in glass vials. A portion of O_1A_0 solution ($r^{O_1A_0}$) were collected for second extractions.

WSOM in the resulting solutions (A_0 , A_1A_0 , $A_2O_1A_0$, O_1A_0 , and $O_2O_1A_0$) were nebulized using a glass nebulizer to measure generated particles by the Time-of-Flight Aerosol Chemical Speciation Monitor (ToF-ACSM). The aqueous solutions were nebulized directly, while the 1-octanol solutions were diluted by methanol (ACS grade, 99.8%, VWR International). Derived mass spectra were analyzed using Tofware (version 2.5.6) post-processing software.

3.5. Results and discussion

3.5.1. K_{ow} distribution of WSOM from mosquito coil burning particles

Figure 3.5a shows the estimated distributions of $F(x)$, those only employed the data from the first extraction. The error bar represents standard deviation (1σ) derived from NNLS analysis. All of the algorithms (NNLS, Twomey, and STWOM) provided very similar results for the region of $\log K_{ow} > 0$. However, relatively significant discrepancies were observed for highly polar ($\log K_{ow} < 0$) regime. The discrepancy significantly decreased when experimental data from the second extractions were employed (Figure 3.5b).

Figure 3.5. K_{OW} distribution of WSOM in smoldering of mosquito coil derived from measurements of (a) single extraction, and (b) inclusive of second extraction.

3.5.2. K_{OW} distribution derived from PMF factors

3.5.2.1. K_{OW} distribution of WSOM derived from PMF factors

PMF analysis was conducted for two cases. The first case employed the ACSM data from A_1A_0 and O_1A_0 solutions, and the second case used the mass spectra for A_1A_0 (only for solution with $V_r = 10$) and $A_2O_1A_0$ solutions. PMF analysis was performed using the PMF Evaluation Tool (v3.00B) (Ulbrich et al., 2009; Zhang et al., 2011). For case 1, the mass spectra were input in the sequence of A_1A_0 ($V_r=10$), A_1A_0 ($V_r=5$), A_1A_0 ($V_r=1$), A_1A_0 ($V_r=0.1$), A_1A_0 ($V_r=0.01$), O_1A_0 ($V_r=10$), O_1A_0 ($V_r=5$),

O_1A_0 ($V_r=1$), O_1A_0 ($V_r=0.1$), and O_1A_0 ($V_r=0.01$), to create a sequence of mass spectra with decreasing polarity. In scenario 2, mass spectra were input in the sequence of A_1A_0 ($V_r=10$), $A_2O_1A_0$ ($V_r^{(2)}=5$), $A_2O_1A_0$ ($V_r^{(2)}=1$), $A_2O_1A_0$ ($V_r^{(2)}=0.1$), $A_2O_1A_0$ ($V_r^{(2)}=0.01$). Both scenarios resulted in three factors. Factor 1 mainly contributes to solutions with negative log K_{ow} values, demonstrating the highly polar property. Contribution of Factor 2 is intense in the middle range of K_{ow} values. On the other hand, the contribution from Factor 3 is higher for larger log K_{ow} values, indicating its lower polarity (Figure 3.6).

Figure 3.6. Fractional contribution of PMF Factor 1, 2, and 3 to each solution.

Figure 3.7 shows the mass spectra of each factor. Peaks for highly oxidized species (e.g. m/z 60 and m/z 73, signature peaks for levoglucosan-like species) mainly contribute to Factor 1. Peaks for

nitrogen-containing species (e.g. m/z 77 and m/z 91) are more abundant in Factor 3. These results validate the idea that highly polar species are more oxygenated (Kondo et al., 2007). Substantial increase of fraction of peaks at $m/z > 100$ can be seen from Factor 1 to Factor 3. Distribution of these peaks demonstrates low polarity of high molecular weight (HMW) species. Mass spectra of Factor 1 and Factor 3 share similarities to those of OOA and HOA (oxygenated organic aerosol and hydrocarbon-like organic aerosol (Zhang et al., 2005)), respectively.

Figure 3.7. Mass spectra of the PMF factors derived from measurements of single extractions.

3.5.2.2. K_{OW} distribution of PMF factors

Relationships between K_{OW} distribution and chemical characteristics of WSOM derived from mosquito coil burning were further addressed by estimating K_{OW} distribution of the derived PMF factors. Based on equation 3-2, K_{OW} distribution of each factor can be described as follow:

$$M_{X_n - P_k} = \sum_j K_{X_n, j} F_{X_n - P_k - j} + \varepsilon_{X_n - P_k} \quad [3-15]$$

where $M_{X_n - P_k}$ is the mass fraction of the k^{th} PMF factor of solution X_n , $K_{X_n, j}$ and $F_{X_n - P_k - j}$ are the kernel function and distribution function, respectively, for the j^{th} bin of K_{OW} in solution X_n , and $\varepsilon_{X_n - P_k}$ is the residual. F_j , which is the K_{OW} distribution of PMF Factor k in the X_n solution, was estimated by MATLAB NNLS function *lsqnonneg*.

Results of the K_{OW} distribution of PMF factors are shown in Figure 3.8. Analysis of PMF results derived from single extraction (case 1) is shown in Figure 3.8a, and the analysis with the inclusive of second extraction (case 2) is shown in Figure 3.8b. Although trend of the estimated K_{OW} distributions broadly consist with each other, the resolution of the distribution can range about two orders of magnitude. K_{OW} distribution of PMF Factor 1, which accounts for 34–37% of WSOM, mainly resides in the region of $\log K_{\text{OW}} < 0$. The estimation from case 1 indicates that approximately 59% and 32% of Factor 1 distributes at $\log K_{\text{OW}} = -2$ and -1 , respectively, while case 2 estimated that about 87% of PMF Factor 1 is in the bin of $\log K_{\text{OW}} = -2$. PMF Factor 2 dominantly contributes to bins with $\log K_{\text{OW}} = 0$ and 1 . Estimations of mass fraction contributed by Factor 2 from PMF results derived from case 1 and 2 are about 0.32 and 0.17, respectively. A difference of 0.15 of mass fraction exists between estimations from the two cases. This may arise from propagated experimental errors, including (1) the nature of kernel functions, (2) the uncertainty of the PMF analysis, and (3) the uncertainty of the NNLS algorithm. Approximately 23–27% of WSOM was attributed to PMF Factor 3, which is the least-soluble fraction. PMF Factor 3 mainly exists in bins with $\log K_{\text{OW}} = 1$ and 2 . Estimation from case 1 indicates that about 95% of PMF Factor 3 is in the bin of $\log K_{\text{OW}} = 2$, while estimation from case 2 shows that about 33% of PMF Factor 3 resides in the bin of $\log K_{\text{OW}} = 1$, and only approximately 49% is attributed to the bin of $\log K_{\text{OW}} = 2$. It should also be noted that the estimation can result in 2–16% of errors, likely due to the uncertainty of the numerical analysis.

Figure 3.8. K_{OW} distribution of PMF factors derived from measurements of (a) single extraction, and (b) inclusive of secondary extraction.

Organic compounds with water solubility (S) $\geq 5 \times 10^{-2}$ (v/v) are classified as moderately soluble and thus are considered as highly polar and highly hygroscopic (Petters and Kreidenweis, 2008). Organic compounds in PMF Factor 1 categorized in this study ($\log K_{OW} < \sim 0$), which is similar to OOA, should be attributed to this category. OOA likely occupies the dominant portion of secondary organic aerosols (SOA), suggesting that SOA likely contributes to CCN activation (Kondo et al., 2007; Wang et al., 2019). Organic compounds in this category are supposed to dissolve completely at the point of activation, suggesting that their CCN activation is limited by molecular weight rather

than water solubility (Kuwata et al., 2013; Wang et al., 2019). In contrary, organic compounds with $S \leq 10^{-4}$ (v/v) are considered as effectively insoluble, limiting the water uptake properties of the bulk organics. These effectively insoluble organic compounds are included in PMF Factor 3 ($\log K_{OW} > 1$), which features similar properties to HOA.

Recently, water uptake of sparingly soluble organic compounds (10^{-4} (v/v) $< S < 5 \times 10^{-2}$ (v/v)) is of most interest because its influence on the interplay among solubility, LLPS, and surface tension during activation is still not well-explored (Ruehl et al., 2016; Ovadnevaite et al., 2017; Liu et al., 2018; Wang et al., 2019). With the increase of relative humidity, gradual dissolution of less-polar compounds can contribute to Raoult's solute effect by increasing the amount of dissolved solutes. Meanwhile, dissolution of solutes can reduce surface tension of the droplet. Particles may also undergo LLPS during the process of hygroscopic growth, leading to the enhancement of CCN activity (Renbaum-Wolff et al., 2016). Organic compounds associate with PMF Factor 2 ($\sim 0 < \log K_{OW} < \sim 1$) are categorized to this fraction. Atmospheric models often treat organic aerosols as completely water-soluble or completely water-insoluble when calculating CCN activity, leading to uncertainty when estimating the impact of aerosol indirect forcing (Liu and Wang, 2010). Results herein suggest the consideration of water uptake from sparingly soluble organic compounds for better estimating the contribution from organic compounds. Future studies about the influences of polarity distribution on surface tension, liquid–liquid phase separation, and water uptake properties of atmospheric aerosol particles would be needed to examine the role of polarity distribution.

3.6. Conclusions

Polarity distribution of water-soluble organic matter (WSOM) plays an important role in determining water uptake properties of aerosol particles. In this study, polarity distribution of WSOM was derived based on the 1-octanol–water partitioning method, which categorizes WSOM by a proxy of

polarity (i.e., 1-octanol–water partition coefficient, K_{OW}). Inverse modeling was performed to improve the categorization. The derivations of polarity distribution were verified and applied to particles generated by smoldering of mosquito coil. Factor analysis further provides highly soluble, medium-soluble, and less soluble factors. WSOM in the highly soluble factor mainly distributes in the range with $\log K_{OW}$ value less than zero. WSOM with medium solubility resides in the bin of $\log K_{OW} = 0$ and $\log K_{OW} = 1$. Less soluble components often have $\log K_{OW}$ values higher than 1. Deriving polarity distribution on the basis of $\log K_{OW}$ values enables quantitative assessment of water uptake properties of WSOM.

3.7. Supporting information

Table 3.S1. Database of the mass spectra derived from PMF analysis (Figure 3.7).

noNaNs_amus	Fac1	Fac2	Fac3
12	0.0065834	0.00421081	0.00128283
13	0.00411021	0.00277994	0.000894837
15	0.0287712	0.0174669	0.00853668
19	0.00013768	4.58E-05	7.10E-06
20	0.000231087	7.75E-05	1.19E-05
24	0.00135614	0.000729265	0.000139273
25	0.00520282	0.00243297	0.000402124
26	0.0286009	0.0153933	0.00278808
27	0.0593563	0.0451872	0.0207855
29	0.0891797	0.0425653	0.0175037
30	0.00199683	0.000915474	0.000391004
31	0.0341807	0.00737781	0.00235237
37	0.0080588	0.00346387	0.000960972
38	0.014292	0.00777978	0.0027889
41	0.0451442	0.0654626	0.046372
42	0.0494734	0.031878	0.0114843
43	0.0904826	0.0586806	0.0398097
45	0.0285847	0.00557514	0.00264394
48	0.00104753	0.0015527	0.00129469
49	0.00198823	0.00108266	0.000306276
50	0.00826661	0.00880607	0.00483929
51	0.0111121	0.0158393	0.0134178
52	0.00976325	0.0116315	0.00627095
53	0.0178289	0.0197266	0.0156975
54	0.0134463	0.0135589	0.00828853
55	0.0319855	0.038816	0.0385131
56	0.0135711	0.0227705	0.0068927
57	0.0265416	0.0198278	0.0076175
58	0.0123147	0.00268329	0.00051119
59	0.00352645	0.00191591	0.00163282
60	0.0242823	0.000142181	0.00020301
61	0.00616728	0.0010102	0.000540961
62	0.00209387	0.00311566	0.00257856
63	0.00392917	0.00819122	0.00850973
64	0.0062063	0.00850519	0.00702026
65	0.00806452	0.0149058	0.0167239
66	0.00838923	0.00740507	0.00557398
67	0.00769059	0.0135438	0.0217082
68	0.0145483	0.010448	0.0084177
69	0.0146191	0.0192683	0.0142716
70	0.0133992	0.0163154	0.00281568
71	0.0189671	0.0100059	0.00330578
72	0.00451785	0.00184602	0.00100338
73	0.0179418	0.000886537	0.000739226

74	0.0038758	0.00249224	0.00235015
75	0.00159629	0.00252904	0.00323453
76	0.00386479	0.00304674	0.00358743
77	0.00591553	0.0155019	0.0265331
78	0.00415023	0.00819653	0.00918882
79	0.00498711	0.0139755	0.019951
80	0.00695995	0.00478477	0.00508625
81	0.00782192	0.0119502	0.0153606
82	0.0070489	0.00721607	0.00602861
83	0.00559076	0.00870689	0.0071275
84	0.00868325	0.00631262	0.00306076
85	0.00599651	0.00451622	0.00196985
86	0.00403376	0.00246227	0.00150262
87	0.00446427	0.00155055	0.00196758
88	0.000895201	0.00105431	0.00152837
89	0.00200969	0.00415134	0.00598492
90	0.000806857	0.00207998	0.00308309
91	0.00399896	0.0190822	0.031019
92	0.00207843	0.00588696	0.00638909
93	0.00357561	0.00949739	0.0121886
94	0.00928514	0.00637273	0.00678249
95	0.00826032	0.00876591	0.00970003
96	0.00453334	0.00498147	0.00354977
97	0.00433518	0.00642544	0.00377617
98	0.00608872	0.00463159	0.00212211
99	0.00266249	0.00276818	0.00143643
100	0.00255634	0.00147197	0.000806227
101	0.00157094	0.00132882	0.0020323
102	0.00139189	0.00267142	0.00415201
103	0.00169033	0.00424757	0.00682833
104	0.00124387	0.00333691	0.00463383
105	0.00229643	0.0076444	0.0147213
106	0.00148564	0.00506407	0.00569711
107	0.00261446	0.0108968	0.0118722
108	0.00300681	0.00560513	0.00529758
109	0.00287855	0.00659312	0.00643061
110	0.00346344	0.00412087	0.00306468
111	0.00282555	0.0042019	0.00231332
112	0.00332956	0.00304899	0.00117799
113	0.00121593	0.00204112	0.00205285
114	0.00111817	0.0012112	0.00180782
115	0.00148172	0.00602074	0.0151948
116	0.000702372	0.00242329	0.00540241
117	0.000944307	0.00457631	0.0100906
118	0.00162482	0.00355443	0.00486009
119	0.00135287	0.00541408	0.00821926
120	0.00141471	0.0041243	0.0047982
121	0.00266809	0.00616695	0.00696487
122	0.0019437	0.00399581	0.0044181
123	0.00165043	0.00453622	0.00550005

124	0.00127903	0.00271204	0.00250515
125	0.00111782	0.00467542	0.00180795
126	0.0014184	0.00281587	0.00167888
127	0.000728711	0.00278889	0.00543171
128	0.000633788	0.00437379	0.0103633
129	0.000519597	0.00344055	0.00852449
130	0.000709059	0.00269113	0.00535611
131	0.000831862	0.00421016	0.00952935
132	0.000776368	0.00270207	0.00467682
133	0.00104625	0.00374176	0.00624213
134	0.0010509	0.00321086	0.00421997
135	0.0011388	0.00432175	0.00507335
136	0.00117151	0.0028313	0.00388709
137	0.00100529	0.00337539	0.00739701
138	0.00146104	0.00216203	0.00270005
139	0.000605526	0.00268045	0.00411731
140	0.000497446	0.00135168	0.0025804
141	0.000396086	0.00309474	0.00814844
142	0.000301054	0.00217565	0.0047086
143	0.000346659	0.00254399	0.00583227
144	0.000561376	0.00177538	0.00471168
145	0.000600736	0.00286012	0.00697853
146	0.00054433	0.00198807	0.00397983
147	0.000654109	0.00339496	0.0059136
148	0.000594125	0.00207259	0.00339797
150	0.000536845	0.00204007	0.00342819
151	0.000414045	0.00246523	0.00529995
152	0.000300847	0.00332816	0.00631915
153	0.000374657	0.00356756	0.0050386
154	0.00034862	0.00326156	0.00356992
155	0.000234611	0.00218049	0.00462012
156	0.000288107	0.00174536	0.00360723
157	0.000302862	0.00181813	0.00551763
158	0.000348436	0.00121084	0.0036554
159	0.00034542	0.00172839	0.00502842
160	0.000332484	0.00142973	0.00349577
161	0.000373877	0.00177628	0.00481487
162	0.000393064	0.00139376	0.0032832
163	0.000397419	0.00213066	0.00369001
164	0.000475247	0.00177385	0.00276901
165	0.000174311	0.00278287	0.00644871
166	0.000209259	0.00168344	0.00302676
167	0.000135991	0.00278614	0.00546435
168	0.000265054	0.0012173	0.00459743
169	0.000155609	0.0014121	0.00475735
170	0.000304422	0.000929693	0.00312152
171	0.000188565	0.00118514	0.0039764
172	0.000231998	0.000820668	0.00274269
173	0.000232969	0.00109509	0.00366159
174	0.000198497	0.000947289	0.00301646

175	0.00026014	0.00113111	0.00360789
176	0.000190515	0.00111424	0.0031558
177	0.000155911	0.00121206	0.0027226
178	0.000157681	0.00134022	0.00325425
179	0.000137721	0.00117928	0.00279524
180	0.00017566	0.00107671	0.0023997
181	0.000134793	0.00104436	0.00353896
185	0.000144379	0.0005246	0.00356647
187	0.000185631	0.000628735	0.00303047
188	0.000134308	0.000596117	0.00214696
189	0.000193809	0.00087278	0.00300771
190	0.000151187	0.000592028	0.00221358
191	0.000177364	0.000859431	0.00221247
192	0.000143875	0.000646899	0.00207871
193	0.000116391	0.000665081	0.00162479
194	0.000131465	0.000408673	0.00220982
195	0.000107713	0.00041497	0.00194142
196	0.000129864	0.000334738	0.00188995
197	9.81E-05	0.000312803	0.00227069
198	0.000122055	0.00035587	0.0018742
199	0.000106158	0.000412669	0.00189647
200	0.000115673	0.000347177	0.00175162
201	0.000107554	0.000440759	0.001756
202	0.000108851	0.000339178	0.00162819
203	8.67E-05	0.000585852	0.00185362
204	0.00010879	0.000366714	0.00156256
205	0.000116362	0.000418183	0.00159078
206	8.38E-05	0.000280635	0.00132351
207	0.000109414	0.000482528	0.00123863
208	8.45E-05	0.000270811	0.00110508
209	8.67E-05	0.000211822	0.00111634
210	6.31E-05	0.000199489	0.00125174
211	7.01E-05	6.31E-05	0.00157569
212	5.30E-05	0.000166086	0.00082678
213	5.53E-05	9.63E-05	0.00094473
214	3.81E-05	0.000116404	0.00059285
215	3.99E-05	6.51E-05	0.000678505
216	2.30E-05	6.81E-05	0.000357704

Chapter 4 Polarity dependent chemical characteristics of water-soluble organic matter from Indonesian biomass burning revealed by the 1-octanol–water partitioning method*

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4.1. Introduction

Organic matter (OM) accounts for 20–90% of submicron aerosol particles in the atmosphere (Andreae and Crutzen, 1997; Zhang et al., 2007). OM can either be directly emitted from natural and anthropogenic sources such as biomass burning and fossil fuel combustion (primary OM) (Bond et al., 2004), or formed from oxidation of volatile organic compounds (secondary OM) (Kroll and Seinfeld, 2008; Hallquist et al., 2009). Both primary and secondary OM consist of water-soluble (water-soluble organic matter: WSOM) and water-insoluble fractions (Saxena and Hildemann, 1996; Sullivan et al., 2004). WSOM absorbs water vapor in the atmosphere, altering physicochemical properties of aerosol particles in addition to magnifying climatic impacts (Shulman et al., 1996; Facchini et al., 1999). For instance, processes of hygroscopic growth and cloud condensation nuclei (CCN) activation induced by WSOM influence radiative budget of the Earth (Novakov and Penner, 1993). The hygroscopic growth process also influences deposition of aerosol particles in human respiratory system (Broday and Georgopoulos, 2001; Löndahl et al., 2008; Vu et al., 2015).

WSOM is a mixture of numerous organic compounds, including acids, sugars, and humic-like substances (HULIS) (Saxena and Hildemann, 1996; Graber and Rudich, 2006). Both chemical and physical characteristics of these compounds are highly variable, necessitating the use of various characterization and separation methods. WSOM has been characterized with numerous spectroscopic techniques, such as nuclear magnetic resonance (NMR) spectroscopy, infrared spectroscopy, and mass spectrometry (Decesari et al., 2000; Graham et al., 2002; Polidori et al., 2008; Sun et al., 2011). These analytical techniques have frequently been combined with separation techniques, including solid phase extraction (SPE) and high-performance liquid chromatography (HPLC) (Duarte and Duarte, 2011). Combinations of these spectroscopic and separation techniques have revealed that water uptake properties of aerosol particles in different categories of WSOM are tightly linked to their chemical characteristics (Duarte et al., 2004; Mihara and Mochida, 2011; Chen

et al., 2016a). Since the degrees of polarity were not quantitatively defined for the fractions categorized by these methods, it is rather difficult to estimate the water uptake of WSOM.

Recently, distribution of WSOM between organic-rich and aqueous phases started to be regarded as one of the important factors in regulating hygroscopic growth and CCN activity (Psichoudaki and Pandis, 2013; Riipinen et al., 2015; Ruehl et al., 2016; Ovadnevaite et al., 2017). To quantitatively reveal dissolution and partitioning processes of WSOM in aerosol particles, we have recently developed the 1-octanol–water partitioning method (Kuwata and Lee, 2017). The merit of the 1-octanol–water partitioning method is that WSOM is categorized quantitatively using 1-octanol–water partition coefficient (K_{OW}), which is tightly linked to water solubility.

The method was employed to analyze WSOM from particles generated by smoldering of Indonesian biomass samples in laboratory (Chen et al., 2017). Indonesian biomass burning is known as one of the most significant wildfires in the world (van der Werf et al., 2010; Page et al., 2011). In 2015, the total carbon emission from Indonesian wildfire was estimated to be 380 Tg C (Field et al., 2016). Several field and laboratory studies showed that aerosol particles emitted from Indonesian fires mainly contain organic compounds (Iinuma et al., 2007; Fujii et al., 2015a; Fujii et al., 2015b; Black et al., 2016; Stockwell et al., 2016; Jayarathne et al., 2018). However, lack of knowledge in relationships between chemical characteristics and water uptake properties of the emitted organic compounds hinders the understanding about climatic effects of Indonesian wildfires in a global scale (Chen et al., 2017). Although majority of organic carbon in Indonesian peat burning emissions is water-insoluble, scope of this study was narrowed down to the water-soluble fraction (i.e., WSOM) due to its importance for water uptake (Chen et al., 2017).

The aim of this study is to qualitatively identify chemical and optical characteristics of WSOM in different polarity. Polarity dependent chemical and optical characteristic of WSOM in laboratory-generated Indonesian biomass burning particles was measured for the first time. The laboratory-generated particles can represent Indonesian biomass burning, as suggested by our previous study

(Budisulistiorini et al., 2017). WSOM in laboratory-generated Indonesian biomass burning particles was produced under smoldering condition. The generated particles were classified by the 1-octanol-water partitioning method. The classified WSOM was analyzed using the time-of-flight aerosol chemical speciation monitor (ToF-ACSM), UV–Visible (UV–Vis) spectrophotometer, and fluorescence spectrophotometer. Derived spectra were further investigated using the positive matrix factorization (PMF), parallel factor (PARAFAC), and least-square analysis methods to obtain chemical characteristics of WSOM in a metric of polarity. Data inversion method was also applied to determine the polarity distribution of WSOM from laboratory-generated Indonesian biomass burning particles.

4.2. Theory

A detailed theoretical background of the 1-octanol–water partitioning method is described in Kuwata and Lee (2017). The method is developed based on the 1-octanol–water partition coefficient (K_{OW}), which is defined by the molar concentration of compound (i) in 1-octanol (C_i^O) and aqueous (C_i^A) phases at equilibrium:

$$K_{OW_i} = \frac{C_i^O}{C_i^A}. \quad [4-1]$$

Partitioning of compound i from the original WSOM solution (A_0) into 1-octanol (O_1A_0) or aqueous (A_1A_0) phases depends on its K_{OW} . For instance, mole fraction of compound i partitioning to aqueous phase ($f_i^{A_1A_0}$) can be represented as

$$f_i^{A_1A_0} = \frac{n_i^{A_1A_0}}{n_i^{A_0}} = \frac{1}{K_{OW_i}V_r + 1}, \quad [4-2]$$

while the rest of compounds partition to 1-octanol phase ($f_i^{O_1A_0}$), where $f_i^{O_1A_0} = 1 - f_i^{A_1A_0}$. V_r is the volumetric ratio of 1-octanol and aqueous phases:

$$V_r = \frac{V^{O_1}}{V^{A_1}} . \quad [4-3]$$

As shown in Figure 4.1, adjusting the values of V_r enables the fractionation of WSOM into degrees of K_{ow} . The majority of compounds that partition to A_1A_0 with $V_r = 5$ and 10 are highly soluble ($S > 10^{-1} \text{ g cm}^{-3}$), suggesting that WSOM in this category is highly CCN active (Petters and Kreidenweis, 2008; Kuwata et al., 2013; Riipinen et al., 2015). On the other hand, most WSOM in O_1A_0 fraction with $V_r = 0.01$ does not contribute to water uptake due to the low water solubility ($S < 10^{-4} \text{ g cm}^{-3}$) (Petters and Kreidenweis, 2008; Kuwata et al., 2013; Riipinen et al., 2015). Other fractions of WSOM (A_1A_0 with $V_r = 0.01, 0.1$, and 1, and O_1A_0 with $V_r = 0.1, 1, 5$, and 10) cover the marginal solubility range ($10^{-4} \text{ g cm}^{-3} < S < 10^{-1} \text{ g cm}^{-3}$) where water uptake is regulated by conditions of particles, such as phase (You et al., 2014; Renbaum-Wolff et al., 2016).

Figure 4.1. Fraction of organic matter partitions to (a) aqueous and (b) 1-octanol phases, following liquid-liquid separation. Volume ratios (V_r) were set to 10, 5, 1, 0.1, and 0.01 to classify compounds in the critical range of CCN activation (i.e., $-2 < \log K_{OW} < 4$) (Riipinen et al., 2015). Water solubility (S) was estimated by the relationship between K_{OW} and water solubility ($\log K_{OW} = -0.642 - 0.8 \log S$) (Kenaga and Goring, 1980).

4.3. Methods

4.3.1. Particle collection

Biomass samples, including peat, leaves of fern (*Pteridium aquilinum* (L.) Kuhn. (Dennstaedtiaceae)), and leaves of acacia (*Acacia mangium* Willd. (Fabaceae)), were collected at Riau province in Indonesia. Fern is one of the native and dominant species in the region after forest fires (Yassir et al., 2010), while acacia is widely planted in Southeast Asia as a raw material of pulp (Otsamo et al., 1997). Approximately 1.0 g of each sample was burned in an airtight 100-L stainless steel chamber at 350°C (measured and controlled for the condition of the melting pot) to represent Indonesian peat fire, which is dominated by smoldering combustion. The smoldering condition was validated by visual inspection as well as the emission ratio of CH₄ and CO₂ (Kuwata et al., 2017). A schematic diagram of experimental setup is shown in Figure 4.S1. Biomass burning particles were collected at room temperature (about 25°C) using two sets of filter holders (BGI, Inc.) with Teflon filters (P0450, Sigma-Aldrich) at a flow rate of 5 L min⁻¹ for an hour. No dilution was made prior to the filter sampling. The filters were kept at -20°C until analysis. As reported in our previous study (Chen et al., 2017), approximately 13.58, 13.34, and 14.61 mg C of organic carbon can be collected for the burning of peat, fern, and acacia, while 1.63%, 3.42%, and 6.56% of the organic carbon was determined to be water-soluble.

4.3.2. WSOM extraction and separation by the 1-octanol-water extraction method

WSOM (A_0) was extracted by sonicating the filters three times for 30 minutes using 3 mL of Type I water (TU-6-UV, VWR). Subsequently, A_0 was filtered through 0.2 µm PTFE syringe filter (514-0070, VWR) to remove suspended materials. A_0 solutions derived from 6 filter samples (approximately 10.0 mg of particles on each filter) were combined and diluted with water to create a 150 mL solution. 1-octanol–water extractions were conducted using separation funnels. Volumetric ratios of 1-octanol and aqueous phases (V_r) were 0.01, 0.1, 1, 5, and 10 (Figure 4.1). Following

addition of 1-octanol (99%, Alfa Aesar) to A_0 , the separation funnels were vigorously shaken until emulsion formed. The funnels were placed in a fume hood for a minimum of 12 hours, allowing for clear separation of 1-octanol and aqueous phases. Partitioning of OM to the air was assumed to be negligible, as described in the supplementary document (S2). The resulting 1-octanol (O_1A_0) and aqueous (A_1A_0) phases were separately sampled and stored at 5°C until analysis.

4.3.3. UV–Vis and Fluorescence measurements

The extracted solutions (A_0 , A_1A_0 , and O_1A_0) and their corresponding blank samples (ultrapure water, blank A_1A_0 , and blank O_1A_0) were transferred to 2-mm quartz cuvettes for UV–Vis absorbance and excitation-emission matrix (EEM) fluorescence analysis.

UV–Visible absorbance spectra were measured by an UV–Visible Spectrophotometer (Evolution 300, ThermoFisher Scientific) at 2 nm bandwidth from 190 to 800 nm, with a resolution of 0.5 nm. Only absorbance spectra with wavelength ranging from 205 to 400 nm will be discussed in detail because of the interferences from solvents for the shorter wavelength range (< 205 nm) as well as limited absorbance for the longer wavelength region (> 400 nm). Absorbance intensities were normalized by the maximum absorbance after blank subtraction. Absorbance spectra were further analyzed by least-square and PMF method as described below (section 4.3.5).

Fluorescence was measured with a spectrofluorometer (Horiba Scientific FluoroMax-4, HORIBA Scientific). Excitation and emission wavelengths were ranged from 240 to 500 nm and from 300 to 600 nm, with increments of 5 and 2 nm, respectively. Blank subtraction, inner-filter effect correction, first order Rayleigh peak removal and Raman peak removal were processed by drEEM toolbox (version 0.2.0) in MATLAB as suggested by Murphy et al. (2013). Afterward, PARAFAC analysis was performed with non-negativity constraints. The 3-component PARAFAC model was selected and validated, as detailed in Section 4.7.2 (Murphy et al., 2013).

4.3.4. Particle regeneration and ToF-ACSM measurement

Aerosol particles were regenerated following the method of Kuwata and Lee (2017). A_1A_0 solutions were nebulized by a glass nebulizer without dilution, while O_1A_0 solutions were nebulized following dilution by methanol (ACS grade, 99.8%, VWR). The regenerated particles were introduced to a ToF-ACSM (Aerodyne Research) for chemical composition measurements. Each measurement lasts for approximately 30 minutes. Chemical composition of the regenerated particles was assumed to be homogeneous, as demonstrated by our previous study. Derived mass spectra were analyzed using Tofware (version 2.5.6) post-processing software. For O_1A_0 solutions, only those with $V_r < 1$ (i.e., $V_r = 0.1$ and 0.01) were discussed in detail, as the signals from residual of 1-octanol were significant for O_1A_0 solutions with $V_r = 10, 5$, and 1 . Measurement of blank filter extraction was also conducted, showing minimal interference ($0.7\text{--}1.4\%$) from Teflon filters.

4.3.5. PMF analysis

PMF analysis for ACSM data was conducted using PMF Evaluation Tool (v3.00B) (Ulbrich et al., 2009). Mass spectra derived from ToF-ACSM measurements were input in the sequence of A_0 , A_1A_0 ($V_r = 10$), A_1A_0 ($V_r = 5$), A_1A_0 ($V_r = 1$), A_1A_0 ($V_r = 0.1$), A_1A_0 ($V_r = 0.01$), O_1A_0 ($V_r = 0.1$), and O_1A_0 ($V_r = 0.01$) to form a matrix with decreasing polarity (except for A_0 , which was imported to estimate the fractional contribution from each factor in WSOM). O_1A_0 extractions with $V_r \geq 1$ were excluded from the analysis due to the interference of 1-octanol. Optimum solution was selected based on analysis of residual and uncertainty, as detailed in Section 4.7.3 (Ulbrich et al., 2009; Zhang et al., 2011).

Fractional contribution derived from ACSM-based PMF analysis was applied to constrain factor analysis for UV–Vis data (Moschos et al., 2018). Factor analysis of UV–Vis data was conducted using MATLAB non-negative least square function *lsqnonneg*. For comparison, UV–Vis

data were analyzed without constraints using PMF Evaluation Tool. Details about the PMF analysis can be found in the Section 4.7.4.

4.4. Results

Chemical and optical characteristics of organic species before and after liquid–liquid separation are described in this section. Discussions about inorganic ionic species were omitted in this study due to minimal amount of contribution ($< 2.8\%$).

4.4.1. Chemical characteristics

Figure 4.2a shows the mass spectrum of A_0 for peat burning particles (results for fern and acacia burning particles are similar, and are available in Figure 4.S2 and Figure 4.S3). The mass spectrum of A_0 is dominated by marker ions for highly oxygenated species (Ng et al., 2010) (fractional contribution of ions at m/z 44 (f_{44}) is 0.07) and levoglucosan-like species (Cubison et al., 2011) (m/z 60 and 73, $f_{60} = 0.03$, $f_{73} = 0.01$). A series of hydrocarbon ions (Ng et al., 2010) (C_nH_{2n+1} , e.g., m/z 41, 43, 55, 57...) is also present, in addition to the signature ions of aromatic compounds such as m/z 77 and 91 (McLafferty et al., 1993). The fraction of high molecular weight species (HMW, $m/z > 100$) is 0.16. The ions for HMW species include distinct peaks at m/z 115 and 121. A peak at m/z 115 was observed in several types of wood burning particles (Alfarra et al., 2007), and an ion signal at m/z 121 was observed during lignin-combustion (Li et al., 2012).

Figure 4.2b–d include the mass spectra of A_1A_0 and O_1A_0 . The mass spectra of A_1A_0 are dominated by a peak at m/z 44. The most polar portion (A_1A_0 solution with $V_r = 10$) has a f_{44} value of 0.14. The contribution of m/z 44 decreases to 0.08 for the least polar A_1A_0 solution ($V_r = 0.01$, Figure 4.2c). Peaks attributed to levoglucosan-like species (m/z 60 and 73) are also significant, contributing approximately 2.9% and 1.1%, respectively, to the mass spectra of A_1A_0 . On the other hand, mass spectrum of the least polar portion in WSOM (O_1A_0 , $V_r = 0.01$) is dominated by ions originating

from hydrocarbon chains. Signal intensity at m/z 44 is less than 0.02. Similarly, signal intensity of levoglucosan-like species is negligible.

Figure 4.2. Normalized ToF-ACSM mass spectra of organic matter in peat burning particles which partitioned to (a) A_0 , (b–c) $A_I A_0$, and (d) $O_I A_0$ solutions.

4.4.2. Optical characteristics

UV absorbance spectra of OM in A_0 , $A_I A_0$ ($V_r = 10$), $A_I A_0$ ($V_r = 0.01$), and $O_I A_0$ ($V_r = 0.01$) solutions are shown in Figure 4.3 for peat, fern, and acacia samples. Characteristics of absorbance spectra for peat, fern, and acacia samples are found to be similar for each fraction, indicating that polarity is more important in regulating the UV absorbance than types of biomass. Absorbance of OM in A_0 solutions decreases monotonically as the wavelength increases, which follows a trend similar to the absorbance spectra for WSOM in other types of combusted aerosol particles (Zhong and Jang, 2014; Li et al., 2018). Compounds that absorb UV in the wavelength range presented herein (205–400 nm) likely contain pi-conjugated products (Sun et al., 2007), which were reported to result from reactions

between ammonium and aldehydes and/or ketones in the aqueous phase of biomass burning aerosol (Budisulistiorini et al., 2017). Light absorption of OM can be modified by photochemical aging, while the effects depend on aging times and oxidation condition (Lee et al., 2014; Zhong and Jang, 2014). Enhancement in light absorption was suggested to be caused by chromophore formation, while sunlight bleaching likely decreases the light absorption of OM (Lee et al., 2014; Zhong and Jang, 2014).

As shown in Figure 4.3a, a distinct peak of absorbance at 250–280 nm, which is often attributed to aromatic compounds (Baduel et al., 2009; Zhong and Jang, 2014), is identified in the absorbance spectra of OM in A_0 solution, indicating the existence of aromatic compounds. The peak is more apparent in fern and acacia samples than in peat sample, probably due to decomposition of nitrogenous compounds during peat formation processes (O’Kelly and Pichan, 2013). As shown in Figures 4.3b–d, intensity of normalized absorbance in shorter wavelength (< 300 nm) regions increases as polarity decreases. Details about the categorization of absorbance spectra will be discussed in section 4.5.

Figure 4.3. Normalized UV–Vis absorbance spectra of organic matter in peat, fern, and acacia burning particles which partitioned to (a) A_0 , (b–c) $A_I A_0$, and (d) $O_I A_0$ solutions.

EEM plots of WSOM in A_0 , $A_I A_0$ ($V_r = 10$), $A_I A_0$ ($V_r = 0.01$), and $O_I A_0$ ($V_r = 0.01$) solutions for peat, fern, and acacia burning particles are shown in Figure 4.4. EEMs for all the measurements can be found in Figure 4.S4. The EEMs are shown for excitation wavelengths between 240 and 500 nm and emission wavelengths ranging from 300 to 560 nm. Five peaks are identified in the spectra: Peak P1 (Excitation/Emission, Ex/Em $\sim$ 250–270/320–340 nm), Peak P2 (270–290/310–340 nm), Peak M (280–340/340–400), Peak T1 (240–260/400–480), and Peak T2 (285–350/400–480).

Peaks P1 and P2 are previously attributed to nitrogen containing species (e.g., protein-like species and aromatic amino acids) as well as non-nitrogen containing species (e.g., lignin and phenol-like components) in the EEM spectra for dissolved organic matter in river (Hernes et al., 2009), rain water (Yue et al., 2016), cloud water (Bianco et al., 2016), and atmospheric aerosols (Duarte et al., 2004; Chen et al., 2016b; Fan et al., 2016). One of the possible sources for the fluorescences at Peaks P1 and P2 in WSOM from biomass burning particles could be phenol-like components, as they can be directly emitted from lignin combustion (Hawthorne et al., 1989). Peaks P1 and P2 mainly exist in O_1A_0 solutions, indicating their less-polar characteristics.

Peaks M and T (including T1 and T2) are typically attributed to marine and terrestrial humic-like substances (hereafter marine-HULIS and terrestrial-HULIS), respectively (Coble et al., 1998; Yamashita and Jaffé, 2008; Lee et al., 2013). A caveat for the peak identification herein is the absence of marine and terrestrial sources for laboratory-generated biomass burning particles. Biomass burning is one of the important sources for atmospheric HULIS (Poulain et al., 2011). Chemical structure of HULIS is complex, containing polycyclic rings, hydrocarbon chains, hydroxyl, carboxyl and carbonyl groups (Graber and Rudich, 2006). The EEM peaks herein are denoted as marine- and terrestrial-HULIS due to their corresponding fluorescence characteristics. Similar peaks were also identified in secondary organic aerosols formed by photo-oxidation of benzene, toluene, p-xylene, and naphthalene (Aiona et al., 2018). Peaks M, T1, and T2 mainly exist in A_1A_0 solutions, indicating their high-polar characteristics.

Figure 4.4. Excitation–emission matrix of organic matter in peat (column a), fern (column b), and acacia (column c) burning particles which partitioned to A_0 (row 1), $A_I A_0$ (row 2-3), and $O_I A_0$ (row 4) solutions. The highest intensity was scaled to unity.

4.5. Discussion and atmospheric implications

The above-mentioned chemical and optical properties of WSOM were quantitatively categorized into three groups as a function of polarity.

Mass spectra of ToF-ACSM measurements were analyzed by PMF analysis. A three-factor solution was selected, as detailed in Section 4.7.3. Fractional contribution of each factor in WSOM of biomass burning particles is shown in Figure 4.5. Factor 1 dominantly contributes to highly polar fraction (84.4% for $A_I A_0$ ($V_r = 10$) of peat burning particles), while Factor 2 is in a marginal polarity range. Factor 3 is the least polar fraction (76.1% for $O_I A_0$ ($V_r = 0.01$) of peat burning particles). Similar trends were also observed for particles generated by combustion of fern and acacia (Figures 4.5b and 4.5c). It is noted that the residuals in the $A_I A_0$ ($V_r = 10$) and $O_I A_0$ ($V_r = 0.1$) solutions of peat

sample are 11.7% and 13.6%, respectively. The residuals are negligible (less than 5.1%) for fern and acacia burning particles (Figures 4.5b and 4.5c).

Figure 4.5. Fractional contribution of PMF Factor 1 (F1), Factor 2 (F2), Factor 3 (F3), and residuals (RES) to different extractions of (a) peat, (b) fern, and (c) acacia burning particles.

Mass spectra of the resulting factors for peat burning particles are illustrated in Figure 4.6. Factor 1 is highly oxygenated, as it is dominated by intense peaks at m/z 44, 60, and 73 (Figure 4.6a). The contribution of HMW species to the factor is less than 4.0%. Compared with Factor 1, intensities of signals at m/z 44, 60, and 73 are less significant for Factor 2, while the contribution of HMW species ($f_{\text{HMW}} = 0.20$) is higher. In the case of Factor 3, the mass spectrum is dominated by peaks of

hydrocarbons (e.g. m/z 41, 43, 55), aromatic compounds (e.g. m/z 77, 91), and HMW species.

Similar results are also observed for fern and acacia burning particles (Figures 4.S18 and 4.S19).

Figure 4.6. Mass spectra of (a) PMF Factor 1, (b) Factor 2, and (c) Factor 3 of peat burning particles.

Observational and experimental evidence suggests an empirical relationship between water uptake properties of OM and the value of f_{44} . For OM to uptake water, the value of f_{44} needs to be higher than 0.03–0.05 (Duplissy et al., 2011; Mei et al., 2013; Chen et al., 2017). Therefore, water uptake of the WSOM in the first group ($f_{44} = 0.06$ to 0.10 in PMF Factor 1) is likely much higher than the WSOM in the second group ($f_{44} = 0.03$ to 0.06 in PMF Factor 2). The WSOM in the third group would contribute to hygroscopic growth and CCN activity only marginally since the value of f_{44} in PMF Factor 3 is less than 0.02. The relationship between water uptake properties and the K_{OW} /solubility ranges can also be used to predict water uptake properties of the classified groups (Figure 4.1). Only a limited fraction of WSOM would be considered as highly-soluble in water ($S > 10^{-1} \text{ g cm}^{-3}$), while a significant fraction of WSOM may not be sufficiently soluble ($S < 10^{-4} \text{ g cm}^{-3}$) to contribute to water uptake in the atmosphere (Psichoudaki and Pandis, 2013; Riipinen et al., 2015). The less-soluble fraction of WSOM may even form an organic-rich phase in a particle. Concurrent

measurements of CCN activity and hygroscopicity of polarity segregated WSOM will be needed in the future to further validate these ideas experimentally.

Optical characteristics of WSOM derived from absorbance and EEM spectra were also categorized statistically. Absorbance spectra were categorized into three factors based on the fractional contribution estimated by PMF results of the ACSM data. Factor analysis for the absorbance spectra was also conducted without constraining fractional contribution, as described in Section 4.7.4. Similar characteristics were found in the resulting factors (Figure 4.S20). Discussion herein focuses on the factors derived with the constraints of fractional contribution for comparison with ACSM data.

Residuals of the factor analysis of absorbance spectra, as shown in Figure 4.S21–S23, were found to be less than 6.6% for fern and acacia samples, while the values for peat sample can be as high as 16.6%. As shown in Figure 4.7, consistent trends of absorbance among each factor exist in peat, fern, and acacia samples. UV absorbance of Factor 1 mainly exists at wavelength range of less than 220 nm, followed by a peak at 250 nm. Intensities of the normalized absorbance at region with wavelength larger than 285 nm are less than 20.0%. UV absorbance spectra of Factor 2 were distinguished prominently by absorbance from 250 to 320 nm, which can arise from aromatic compounds. Consistent result was found in Factor 2 in ACSM mass spectra, which shows characteristic peaks at m/z 121 and m/z 137 (Li et al., 2012). UV absorbance of Factor 3 decreases exponentially with increasing wavelength. A distinct absorbance at 250 nm was identified for fern sample, while the absorbance spectra of peat and acacia samples decayed monotonically. Absorbance intensity of Factor 3 remains the highest among the three factors in regions with wavelength shorter than 260 nm. As shown in Figure 4.S22–24 the comparison of the measured UV absorbance spectra and those derived from the PMF analysis, absorbance spectra of WSOM in A_1A_0 solutions with $V_r \geq 1$ are dominantly contributed by Factor 1, while those in O_1A_0 solutions mainly consist of contributions from Factor 2 and Factor 3.

Figure 4.7. Absorbance spectra of (a) Factor 1, (b) Factor 2, and (c) Factor 3 derived from factor analysis. Fractional contributions obtained from ACSM PMF analysis were set as model constraints.

Analysis of EEM data by PARAFAC model provided three components, as detailed in the Section 4.7.2 (Murphy et al., 2013). As shown in Figure 4.8, Components 1 and 2 are dominantly contributed by the peaks for terrestrial- and marine-HULIS, respectively. These two components mainly exist in A_1A_0 solutions, indicating their highly polar characteristics (Figure 4.8, b1–b2). For

peat and fern samples, fractional contribution of Component 1 in A_1A_0 solutions decreases from $V_r = 10$ to $V_r = 1$, and increases again from $V_r = 1$ to $V_r = 0.01$. An opposite trend was found for Component 2. The opposite trends of Component 1 and 2 for polarity may be due to the complex nature of chemical species those contribute to fluorescence at these peaks. The contribution of Component 2 was minimal for acacia sample. Component 3 mainly contains signals for aromatic compounds. Signal intensity of Component 3 is higher in O_1A_0 solutions, indicating a less-polar characteristic of aromatic compounds. Obviously, PMF analysis of the ACSM data and PARAFAC analysis of the EEM data provided different pictures about relative abundances of each factor/component. Differences in the measurement principles of the two types of data as well as the statistical analysis methods likely induced the discrepancy. Empirical relationships between EEM profiles and the hydrophobicity of OM were identified in previous studies (Chen et al., 2016b). The fluorophore of the hydrophobic composition mainly distributes in the shorter excitation/emission wavelength, and that of the hydrophilic composition tends to locate at regions with longer wavelengths. Further studies would be needed to unravel the physical meaning of the EEM profiles. Meanwhile, further measurement (e.g., using FTIR or NMR) will be needed to unravel the chemical species/functional groups that contribute to the absorbance/EEM spectra.

Figure 4.8. (a) Component 1 (Comp1, a1), Component 2 (Comp2, a2), and Component 3 (Comp3, a3) for EEM spectra provided by a 3-component PARAFAC model, and (b) their corresponding relative contributions to different extractions of peat, fern, and acacia burning particles.

To assess water uptake by organic particles, the contribution of HULIS on hygroscopic growth cannot be ignored. The abundance of HULIS in the atmosphere can range from 9 to 72% of the total water-soluble organic carbon (WSOC) (Zheng et al., 2013). However, the values of K_{ow} for atmospheric HULIS are known to be highly variable (e.g., $0.55 < \log K_{ow} < 1.9$) (Spranger et al., 2017), leading to significant differences in their hygroscopicity and CCN activity. For instance, the hygroscopic growth factor (HGF) of atmospheric HULIS at a relative humidity of 90% can range from 1.05 to 1.47, while the hygroscopicity parameter for CCN activation (κ_{CCN}) ranges between 0.05 and 0.34 (Gysel et al., 2004; Dinar et al., 2007; Ziese et al., 2008; Fors et al., 2010; Kristensen et al., 2012). As marine- and terrestrial-HULIS belong to different polarity groups in our samples, their roles on water uptake will need to be considered separately in the future.

The estimated K_{OW} distributions for peat, fern, and acacia burning particles are shown in Figure 4.9 a–c. The estimation employed the 1-octanol–water partitioning method developed in Chapter 3. For peat burning particles (Figure 4.9a), Twomey’s algorithm provided an extreme distribution showing that 83% of WSOM resides in the bin of $\log K_{OW} = -1$. Results from NNLS and STWOM algorithms suggest that more than half of the WSOM from peat burning particles is highly polar ($\log K_{OW} < 0$). The differences in the estimated K_{OW} distribution may be improved by performing second extraction, as suggested by numerical analysis and the case of mosquito coil burning particles (Chapter 3). Regarding the estimated K_{OW} distribution for fern and acacia burning particles, similar results were given by the three algorithms. As shown in Figure 4.9b and c, 68–84% of WSOM are attributed to the highly polar region ($\log K_{OW} < 0$). PMF analysis was also performed on the mass spectra of peat, fern, and acacia burning particles, as detailed in Section 4.3.5. K_{OW} distributions of the resulting PMF factors are shown in Figure 4.9d–f. Similar to the results of mosquito coil burning particles, the resulting three PMF factors can be attributed to the regions of $\log K_{OW} < 0$ (factor 1), $0 \leq \log K_{OW} \leq 1$ (factor 2), and $\log K_{OW} > 0$ (factor 3).

Figure 4.9. (a) K_{OW} distribution of WSOM in smoldering of Indonesian biomass, and (b) K_{OW} distribution of the resulting PMF factors. The error bar represents standard deviation (1σ) derived from the NNLS analysis.

Our parallel study (Chen et al., 2019) indicates that only WSOM attributed to Factor 1 can significantly contribute to water uptake at sub-saturated region, implying the importance in analyzing WSOM with $\log K_{ow} < 0$. PMF Factor 1 accounts for approximately 51%, 40%, and 43%, respectively, for WSOM from peat, fern and acacia burning particles. In the case of peat sample, about 82% of PMF Factor 1 appears in the bin of $\log K_{ow} = -1$, and another 18% resides in the bin of $\log K_{ow} = -2$ (Figure 4.9d). For fern and acacia samples, PMF Factor 1 appears only in the bin of $\log K_{ow} = -2$ (Figure 4.9e and f). The corresponding hygroscopicity parameter (κ) estimated from joint analysis of HTDMA–ACSM measurement is shown in Figure 4.10 (Chen et al., 2019). Values of the estimated κ are 0.20, 0.28, and 0.16, for PMF Factor 1 of peat, fern, and acacia burning particles. The κ value estimated for PMF Factor 2 and 3 of Indonesian biomass burning particles are negligibly small, suggesting that WSOM with $\log K_{ow} > 0$ only plays a minor role in water uptake. It should be noted that the derived K_{ow} distribution fails to explain the estimated κ value of PMF Factor 1, suggesting that water uptake of WSOM with $\log K_{ow} < 0$ may not be limited by polarity. The effect that κ is not a unique function of polarity was also found for secondary organic aerosol using the HPLC–CCN method (Suda et al., 2012). Statistical model further suggested that volatility, solubility, and surface activity of OM together control the hygroscopicity of aerosol particle (Harmon et al., 2013).

Further laboratory measurement on the water uptake properties of WSOM with varying RH would be useful for predicting liquid–liquid phase separation, partitioning of OM, and the change of surface tension during water uptake processes, while care must be taken when analyzing samples with significant amount of inorganic species (e.g. sulfate, nitrate, ammonium, ...). Future laboratory experiment and modeling studies are needed to identify the usefulness of parameterizing the thermodynamic properties of OM (e.g., hygroscopic parameter, κ) based on the measurement of K_{ow} /solubility distribution.

Figure 4.10. Estimated hygroscopicity parameter (κ) of each PMF factor for peat, fern, and acacia burning particles. Reproduced from Chen et al. (2019).

4.6. Conclusions

Polarity distribution of water-soluble organic matter (WSOM) is an important factor in determining the hygroscopic and cloud nucleation abilities of organic aerosol particles. A novel framework was applied to quantitatively classify WSOM based on the 1-octanol–water partition coefficient (K_{ow}), which often serves as a proxy of polarity. In this study, WSOM was generated in a laboratory biomass-burning experiment by smoldering of Indonesian peat and vegetation samples. The fractionated WSOM was analyzed using a UV–visible spectrophotometer, spectrofluorometer, and time-of flight aerosol chemical speciation monitor. Several deconvolution methods, including positive matrix factorization, parallel factor analysis, and least-squares analysis, were applied to the measured spectra, resulting in three classes of WSOM. The highly polar fraction of WSOM, which predominantly exists in the range of $\log K_{ow} < 0$, is highly oxygenated and exhibits similar optical properties as those of light-absorbing HULIS. WSOM in the least-polar fraction, which mainly distributes in $\log K_{ow} > 1$, mostly consists of hydrocarbon-like and high molecular weight species. In

between the most and least-polar fraction, WSOM in the marginally polar fraction likely contains aromatic compounds. The analyses have also suggested the existence of HULIS with different polarities. Comparison with previous studies indicates that only WSOM in the highly polar fraction ($\log K_{ow} < 0$) likely contributes to water uptake.

4.7. Supplementary information

Figure 4.S1. A schematic diagram of experimental setup for laboratory biomass burning.

Figure 4.S2. Normalized ToF-ACSM mass spectra of organic matter in fern burning particles which partitioned to A_0 (a), A_1A_0 (b–c), and O_1A_0 (d) solutions.

Figure 4.S3. Normalized ToF-ACSM mass spectra of organic matter in acacia burning particles which partitioned to A_0 (a), A_1A_0 (b–c), and O_1A_0 (d) solutions.

Figure 4.S4. Excitation–emission matrix fluorescence spectra for A_1A_0 with $V_r = 10, 5, 1, 0.1, 0.01$ (panels 1–5) and O_1A_0 with $V_r = 10, 5, 1, 0.1, 0.01$ (panels 6–10) for peat (column a), fern (column b), and acacia (column c) samples. The highest intensity is scaled to unity.

4.7.1. Estimating fractions of WSOM partitioning into air

The partitioning of WSOM to air was calculated using the 1-octanol–air partition coefficient (K_{OA}).

K_{OA} is defined as

$$K_{OA} = \frac{C_O}{C_A} = \frac{n_O V_A}{n_A V_O}, \quad [4-S1]$$

where subscript O and A stand for 1-octanol and air, respectively. C is the molar concentration, n is the number of moles, and V is the volume of solvent. Fraction of WSOM partitioning to air would be

$$\frac{n_A}{n_O} = \frac{1}{K_{OA}} \frac{V_A}{V_O}. \quad [4-S2]$$

Maximum value of V_A/V_O is assumed to be 100. Fraction of WSOM partitioning to air would be less than 1%, since most of WSOM has K_{OA} value which is higher than 10^4 (L_O/L_A) (Meylan and Howard, 2005).

4.7.2. PARAFAC Analysis

PARAFAC analysis for the EEM data was conducted using the drEEM toolbox (version 0.2.0) developed for MATLAB. EEM data of all the extractions (including A_0 , A_1A_0 , and O_1A_0 for peat, fern, and acacia samples) were collected for PARAFAC analysis (N=198). A 3-component model was chosen from for 2- to 5-component model by visual inspection and residual analysis (Figures 4.S5–S7). The 3-component model results in reasonable and explainable fluorescent components. In addition, insignificant decrease of residuals could be found from 3- to 4-component model. The 3-component model was also validated by split half analysis ($S_4C_3T_2$).

Figure 4.S5. Results of 2- to 5-component PARAFAC solutions. The highest intensity is scaled to unity.

Figure 4.S6. Spectral loadings for 2- to 5-component PARAFAC model.

Figure 4.S7. (a) EEM spectra of A_0 solution derived from peat sample. (b) Reconstructed EEM spectra from 3- and 4-component PARAFAC model. (c) Residuals for each model. The highest intensity is scaled to unity.

4.7.3. PMF Analyses

PMF analyses were performed using the PMF Evaluation Tool (v3.00B) in Igor (Ulbrich et al., 2009). Here, we show the evaluation of the PMF results following Ulbrich et al. (2009) and Zhang et al. (2011). The input matrix was a combination of measurement of A_0 , A_1A_0 ($V_r = 10$), A_1A_0 ($V_r = 5$), A_1A_0 ($V_r = 1$), A_1A_0 ($V_r = 0.1$), A_1A_0 ($V_r = 0.01$), O_1A_0 ($V_r = 0.1$), and O_1A_0 ($V_r = 0.01$) solutions. Each solution was measured for ~30 minutes, resulting in a dataset that included ~60 set of mass spectra.

First, a three-factor solution was chosen because (1) decrease of the PMF Q/Q_{exp} value (Q : quality-of-fit parameter, Q_{exp} : expected Q) is relatively small with additional factors (Figure 4.S8), (2) no significant structure remains in the residual signal, and (3) it simplifies the polarity of aerosol particles with physical meaning. Although output from four-factor solutions shows smaller residuals (Figure 4.S9) [e.g., for A_1A_0 ($V_r = 10$) solution from peat sample, residual decreases from 11.8% to 7.2%] and smaller Q/Q_{exp} value (7.63 and 4.40 for three- and four-factor solution of peat sample), since the four-factor solution provides similar mass spectra and hinders the explanation of resulting PMF factor (Figure 4.S10), the three-factor solution was employed.

The rotational ambiguity of the solutions was further explored by fPeak values ranging from -1 to 1 , with a delta of 0.2 (Figure 4.S11). Overall, the results can be grouped into: (1) fPeak < 0 , (2) fPeak $= 0$, and (3) fPeak > 0 . Time series of (1) fPeak $= -1$, (2) fPeak $= 0$, and (3) fPeak $= 1$ are shown in Figure 4.S12–S14. The rotational ambiguity influences the mass fraction to $\pm 20\%$ from fPeak $= 0$, while the residuals are almost the same. Hence, we selected fPeak $= 0$ for all of the samples. The uncertainty in the solutions were estimated by bootstrapping analyses (iterations = 1000), as shown in Figures 4.S15–S17.

Figure 4.S8. Q/Q_{exp} value as a function of number of factor.

Figure 4.S9. Fractional contribution of PMF Factor 1 (F1), Factor 2 (F2), Factor 3 (F3), Factor 4 (F4), and residuals (RES) to different extractions of peat burning particles.

Figure 4.S10. Fractional contribution of PMF Factor 1 (F1), Factor 2 (F2), Factor 3 (F3), Factor 4 (F4), and residuals (RES) to different extractions of peat burning particles.

Figure 4.S11. Mass fraction of each factor versus the constraint parameter (fPeak) a in three-factor solution.

Figure 4.S12. Time series of the three-factor solutions for selected fPeak values (peat sample).

Figure 4.S13. Time series of the three-factor solutions for selected fPeak values (fern sample).

Figure 4.S14. Time series of the three-factor solutions for selected fPeak values (acacia sample).

Figure 4.S15. Results from bootstrapping analysis of peat sample. Error bars with 1- σ are shown in the resulting mass spectra (upper panel) and time series (lower panel).

Figure 4.S16. Results from bootstrapping analysis of fern sample. Error bars with 1- σ are shown in the resulting mass spectra (upper panel) and time series (lower panel).

Figure 4.S17. Results from bootstrapping analysis of acacia sample. Error bars with $1-\sigma$ are shown in the resulting mass spectra (upper panel) and time series (lower panel).

Figure 4.S18. Mass spectra for the three factors derived from PMF analysis of fern burning particles.

Figure 4.S19. Mass spectra for the three factors derived from PMF analysis of acacia burning particles.

4.7.4. PMF analysis for UV–Vis data

Factor analysis of UV absorbance spectra with the constraints of fractional contribution was done by MATLAB non-negative least-square method (NNLS, *lsqnonneg*), as describe in the main text. UV absorbance spectra were analyzed without the constraints of fractional contribution using PMF Evaluation Tool (v3.00B) (Ulbrich et al., 2009). UV absorbance spectra were input in the sequence of A_0 , $A_I A_0$ ($V_r = 10$), $A_I A_0$ ($V_r = 5$), $A_I A_0$ ($V_r = 1$), $A_I A_0$ ($V_r = 0.1$), $A_I A_0$ ($V_r = 0.01$), $O_I A_0$ ($V_r = 10$), $O_I A_0$ ($V_r = 5$), $O_I A_0$ ($V_r = 1$), $O_I A_0$ ($V_r = 0.1$), and $O_I A_0$ ($V_r = 0.01$). A measurement error of 1% was assumed and set as error matrix. Absorbance spectra of peat, fern, and acacia were analyzed separately. Comparison of the factors derived with and without the constraints of fractional contribution is shown in Figure 4.S20. Characteristics of the absorbance spectra derived from both methods agree with each other.

Figure 4.S20. Comparison of the UV absorbance factors derived with and without the constraints of fractional contribution. Derivation of factor with constraints is denoted as NNLS, while the one without constraints is indicated as PMF.

Figure 4.S21. UV absorbance spectra of peat sample derived from measurement and reconstruction of NNLS factors.

Figure 4.S22. UV absorbance spectra of fern sample derived from measurement and reconstruction of NNLS factors.

Figure 4.S23. UV absorbance spectra of acacia sample derived from measurement and reconstruction of NNLS factors.

Figure 4.S24. Comparison of UV absorbance spectra from measurement and factor analysis of peat sample.

Figure 4.S25. Comparison of UV absorbance spectra from measurement and factor analysis of fern sample.

Figure 4.S26. Comparison of UV absorbance spectra from measurement and factor analysis of acacia sample.

Table 4.S1. Database of the normalized mass spectra from peat sample measurement (Figure 4.2).

noNaNs_amus	A_0	A_1A_0 ($V_r=10$)	A_1A_0 ($V_r=0.01$)	O_1A_0 ($V_r=0.01$)
12	0.005279	0.007475	0.005937	0.00295
13	0.003296	0.003789	0.003593	0.001713
15	0.024288	0.022461	0.025757	0.015419
16	0.002762	0.005565	0.003203	0.001226
17	0.017264	0.034778	0.020022	0.007664
18	0.069054	0.139113	0.080086	0.030656
19	8.22E-05	0.000166	9.54E-05	3.65E-05
20	0.000138	0.000278	0.00016	6.13E-05
24	0.001056	0.001176	0.001173	0.000349
25	0.0038	0.004373	0.004501	0.001217
26	0.019133	0.021729	0.022036	0.007018
27	0.036708	0.038662	0.038568	0.027959
29	0.066487	0.091016	0.074894	0.031404
30	0.001463	0.002002	0.001648	0.000691
31	0.019883	0.021074	0.021451	0.006819
37	0.00589	0.0056	0.006352	0.002453
38	0.010497	0.009095	0.01132	0.005352
41	0.029441	0.023395	0.02701	0.051632
42	0.026367	0.027955	0.02809	0.016747
43	0.044083	0.03979	0.043523	0.050062
44	0.069054	0.139113	0.080086	0.030656
45	0.012594	0.023313	0.013425	0.005152
48	0.001825	0.001047	0.001784	0.001649
49	0.001815	0.002224	0.002082	0.000726
50	0.010023	0.009327	0.010548	0.006738
51	0.014005	0.010213	0.013437	0.013344
52	0.00965	0.008353	0.010258	0.006342
53	0.016638	0.012258	0.016358	0.01554
54	0.008533	0.007563	0.008936	0.006199
55	0.02748	0.024136	0.026927	0.040427
56	0.01163	0.012636	0.012457	0.011535
57	0.019444	0.019323	0.020788	0.01702
58	0.004219	0.004908	0.004562	0.002145
59	0.00244	0.002073	0.00231	0.002188
60	0.025971	0.028795	0.02982	0.001537
61	0.004213	0.00369	0.004655	0.001173
62	0.003649	0.002095	0.003569	0.003297
63	0.007657	0.003796	0.007128	0.008779
64	0.007949	0.006719	0.008155	0.006677
65	0.011572	0.007179	0.010715	0.014105
66	0.006883	0.005021	0.007051	0.0052
67	0.008011	0.004737	0.006916	0.014874
68	0.00959	0.008542	0.010185	0.006625

69	0.014567	0.01011	0.013381	0.02035
70	0.007394	0.006361	0.007685	0.007362
71	0.007145	0.006456	0.007323	0.008522
72	0.002649	0.002917	0.002846	0.001249
73	0.010572	0.011036	0.011781	0.002208
74	0.003645	0.002779	0.003576	0.002675
75	0.002408	0.001134	0.002016	0.003144
76	0.00285	0.001473	0.002404	0.003622
77	0.010286	0.005317	0.008283	0.018953
78	0.005875	0.00411	0.005762	0.006616
79	0.009139	0.004145	0.007993	0.014865
80	0.003712	0.002771	0.003807	0.003287
81	0.007143	0.00438	0.006325	0.011796
82	0.004428	0.003234	0.004342	0.004749
83	0.003812	0.002615	0.003487	0.008436
84	0.003962	0.003069	0.003978	0.003867
85	0.003911	0.003346	0.003866	0.004069
86	0.002172	0.002805	0.002257	0.001599
87	0.001904	0.001257	0.001724	0.002064
88	0.000985	0.000536	0.000838	0.001253
89	0.00333	0.001503	0.002652	0.004763
90	0.001647	0.000693	0.001308	0.001921
91	0.00879	0.003278	0.006504	0.020034
92	0.003338	0.001699	0.002882	0.00489
93	0.006087	0.001847	0.00523	0.010488
94	0.00495	0.003695	0.005076	0.004383
95	0.006275	0.004022	0.005735	0.008717
96	0.003887	0.002959	0.004008	0.003024
97	0.004746	0.003232	0.005021	0.005954
98	0.002727	0.002097	0.00269	0.002832
99	0.001846	0.001694	0.001872	0.001827
100	0.000868	0.000544	0.000827	0.0009
101	0.00158	0.001022	0.001456	0.001671
102	0.002343	0.001185	0.001959	0.002975
103	0.002638	0.000957	0.002012	0.004651
104	0.001915	0.000986	0.001581	0.002904
105	0.004591	0.002134	0.003219	0.011101
106	0.001978	0.000868	0.001581	0.00334
107	0.004019	0.001487	0.002971	0.008261
108	0.002611	0.001054	0.002231	0.004101
109	0.003968	0.001493	0.003353	0.005814
110	0.00243	0.001511	0.002283	0.002553
111	0.00175	0.000857	0.00153	0.0029
112	0.001493	0.001125	0.001403	0.001797
113	0.001618	0.000728	0.001371	0.001846
114	0.000998	0.000424	0.000779	0.001176

115	0.004926	0.001432	0.003396	0.011106
116	0.001813	0.000632	0.001348	0.003528
117	0.002574	0.000764	0.001854	0.005878
118	0.001856	0.000643	0.001461	0.002831
119	0.002977	0.000853	0.002144	0.006908
120	0.002204	0.000763	0.00186	0.003175
121	0.006805	0.001455	0.006524	0.009465
122	0.002403	0.001146	0.002117	0.003297
123	0.002848	0.000845	0.002266	0.005237
124	0.00137	0.000626	0.001151	0.001984
125	0.001694	0.00068	0.001644	0.002435
126	0.001414	0.000651	0.001221	0.001763
127	0.002721	0.000585	0.002098	0.004222
128	0.003125	0.000742	0.002016	0.00773
129	0.002425	0.00064	0.001619	0.006189
130	0.00133	0.000406	0.000969	0.002752
131	0.002643	0.000522	0.001752	0.006501
132	0.001362	0.000377	0.00106	0.002562
133	0.002139	0.000506	0.001494	0.00487
134	0.001533	0.000459	0.001191	0.002596
135	0.002096	0.000771	0.001604	0.004382
136	0.001511	0.000754	0.001247	0.002443
137	0.003114	0.000617	0.002512	0.00437
138	0.003181	0.00058	0.003217	0.003318
139	0.001997	0.000455	0.001466	0.003518
140	0.000997	0.000278	0.000784	0.001423
141	0.001991	0.000488	0.00128	0.005291
142	0.001243	0.000328	0.000794	0.003142
143	0.001462	0.000309	0.000919	0.003852
144	0.001274	0.000388	0.000906	0.002523
145	0.001937	0.000413	0.0013	0.005205
146	0.001142	0.000247	0.000796	0.002189
147	0.001888	0.00038	0.001301	0.004716
148	0.001162	0.000374	0.000909	0.001994
150	0.001259	0.000311	0.000951	0.002061
151	0.002507	0.00046	0.001858	0.004708
152	0.002049	0.000501	0.001361	0.004287
153	0.002524	0.000719	0.002263	0.004933
154	0.001339	0.000277	0.001011	0.002121
155	0.00153	0.000281	0.001031	0.003248
156	0.000787	0.00016	0.000521	0.00175
157	0.001269	0.000224	0.000779	0.00339
158	0.00085	0.000179	0.000561	0.001904
159	0.00128	0.000235	0.000792	0.003684
160	0.000871	0.000169	0.000591	0.001913
161	0.001354	0.000255	0.000875	0.003426

162	0.00101	0.000236	0.000757	0.001764
163	0.001375	0.000249	0.000973	0.002896
164	0.000929	0.000199	0.000674	0.001633
165	0.001807	0.000305	0.001164	0.004277
166	0.000895	0.000172	0.000603	0.001803
167	0.001549	0.000215	0.001237	0.002691
168	0.001593	0.000488	0.001595	0.002831
169	0.001021	0.00017	0.000648	0.00247
170	0.000658	0.000127	0.000442	0.001556
171	0.000911	0.000158	0.000524	0.002528
172	0.000619	0.000102	0.000393	0.00143
173	0.000979	0.000148	0.000555	0.00254
174	0.000709	0.00013	0.000433	0.001511
175	0.000983	0.000158	0.000638	0.002598
176	0.000859	0.000175	0.00055	0.001799
177	0.000945	0.000162	0.000607	0.0023
178	0.000954	0.000174	0.000601	0.002028
179	0.001015	0.000142	0.000624	0.002455
180	0.000637	9.08E-05	0.000447	0.00122
181	0.001366	0.000156	0.001034	0.00316
185	0.000689	9.57E-05	0.000431	0.00203
187	0.000807	0.000108	0.000433	0.002281
188	0.000575	8.69E-05	0.000338	0.001267
189	0.00092	0.000112	0.000524	0.002347
190	0.000571	8.83E-05	0.000354	0.0013
191	0.000799	0.000102	0.000467	0.002089
192	0.000602	8.46E-05	0.000358	0.00136
193	0.000548	6.05E-05	0.00034	0.00136
194	0.000607	8.27E-05	0.000395	0.001451
195	0.000476	6.83E-05	0.000279	0.001175
196	0.000448	6.57E-05	0.000301	0.001106
197	0.000482	6.44E-05	0.00025	0.001408
198	0.000468	6.45E-05	0.000305	0.001133
199	0.000463	6.99E-05	0.000255	0.001244
200	0.000428	5.79E-05	0.000276	0.001036
201	0.000452	7.23E-05	0.000249	0.001213
202	0.000388	5.14E-05	0.000248	0.00094
203	0.000588	7.46E-05	0.000307	0.001599
204	0.000353	4.31E-05	0.000235	0.000823
205	0.000476	5.20E-05	0.00025	0.001245
206	0.000305	4.02E-05	0.000174	0.000766
207	0.000375	0.000104	0.000215	0.001023
208	0.000296	3.75E-05	0.000172	0.000639
209	0.000254	3.60E-05	0.00013	0.00072
210	0.000229	3.12E-05	0.000133	0.000578
211	0.000289	2.57E-05	0.000115	0.000841

212	0.000184	2.40E-05	0.000107	0.000426
213	0.00019	2.16E-05	8.58E-05	0.000546
214	0.000131	1.72E-05	7.64E-05	0.000304
215	0.000136	1.54E-05	6.13E-05	0.00039
216	7.89E-05	1.03E-05	4.58E-05	0.000183

Table 4.S2. Database of the mass spectra derived from PMF analysis (peat sample, Figure 4.6).

noNaNs_amus	Fac1	Fac2	Fac3
12	0.007287	0.003296	0.002603
13	0.00426	0.002546	0.001327
15	0.026776	0.026745	0.011426
16	0.004346	0.001893	0.000922
17	0.026439	0.012048	0.005675
18	0.104579	0.048628	0.022475
19	0.00014	5.09E-05	2.95E-05
20	0.000232	8.73E-05	4.89E-05
24	0.001506	0.000624	0.000193
25	0.005585	0.002463	0.00065
26	0.027229	0.014082	0.004093
27	0.043534	0.037021	0.025325
29	0.094984	0.053024	0.022835
30	0.002124	0.001149	0.000508
31	0.028688	0.009366	0.005019
37	0.006992	0.006008	0.001189
38	0.01122	0.013413	0.002698
41	0.024201	0.01837	0.062566
42	0.032573	0.025266	0.013665
43	0.043688	0.042294	0.053748
44	0.104579	0.048628	0.022475
45	0.018642	0.006854	0.00412
48	0.001207	0.003116	0.001218
49	0.002405	0.001777	0.000351
50	0.010368	0.012548	0.004904
51	0.011464	0.018319	0.011899
52	0.010268	0.010948	0.004698
53	0.014345	0.021847	0.013517
54	0.008627	0.011799	0.004574
55	0.026583	0.018454	0.047427
56	0.014502	0.008897	0.012325
57	0.023089	0.019882	0.015986
58	0.005439	0.005661	0.001089
59	0.002488	0.001595	0.002287
60	0.043471	0.000214	5.55E-05

61	0.005481	0.002626	0.000534
62	0.002408	0.006291	0.002415
63	0.004105	0.013547	0.007481
64	0.007517	0.010091	0.005622
65	0.007863	0.016723	0.013651
66	0.006019	0.010178	0.003655
67	0.004788	0.007473	0.017602
68	0.010024	0.013747	0.004547
69	0.011248	0.016302	0.022194
70	0.007144	0.01064	0.006622
71	0.007493	0.006737	0.009072
72	0.003322	0.003342	0.000595
73	0.015796	0.00314	0.001314
74	0.003452	0.003816	0.002228
75	0.001189	0.003569	0.003064
76	0.00157	0.003398	0.003619
77	0.004497	0.011305	0.021926
78	0.00465	0.007671	0.006311
79	0.004221	0.014547	0.015549
80	0.003096	0.006233	0.002506
81	0.00458	0.008036	0.01335
82	0.003473	0.007414	0.00422
83	0.00268	0.00179	0.010485
84	0.003416	0.006658	0.003231
85	0.00376	0.004673	0.003966
86	0.002368	0.002663	0.001306
87	0.00138	0.002047	0.002012
88	0.000552	0.001221	0.001248
89	0.001601	0.004241	0.00487
90	0.000764	0.002124	0.001823
91	0.00267	0.007691	0.024646
92	0.001557	0.005329	0.005024
93	0.001676	0.011582	0.010881
94	0.00413	0.008297	0.003343
95	0.004353	0.008602	0.009106
96	0.003446	0.006744	0.002009
97	0.003734	0.00804	0.005495
98	0.00227	0.004508	0.002495
99	0.001649	0.00287	0.001611
100	0.000603	0.001434	0.000761
101	0.001228	0.001624	0.0016
102	0.00137	0.002605	0.00298
103	0.000934	0.003219	0.005054
104	0.001033	0.002105	0.003156
105	0.001466	0.002846	0.014187
106	0.000795	0.002686	0.003707

107	0.00126	0.004419	0.009908
108	0.001053	0.004248	0.004176
109	0.001432	0.007558	0.005741
110	0.001687	0.004275	0.002167
111	0.000809	0.002654	0.003114
112	0.001116	0.002319	0.001764
113	0.000736	0.003422	0.00155
114	0.000467	0.001159	0.001144
115	0.001191	0.004486	0.013011
116	0.00058	0.001927	0.004007
117	0.000609	0.002699	0.007064
118	0.00065	0.002672	0.002891
119	0.00072	0.003311	0.008314
120	0.000754	0.003847	0.003047
121	0.001236	0.017843	0.007593
122	0.000922	0.004114	0.003171
123	0.000736	0.004803	0.005748
124	0.000609	0.00217	0.002037
125	0.000666	0.003891	0.002158
126	0.000761	0.002004	0.001669
127	0.000578	0.004903	0.003944
128	0.000578	0.00249	0.009236
129	0.000481	0.001831	0.00755
130	0.000299	0.001456	0.003193
131	0.000381	0.002585	0.007641
132	0.0003	0.001709	0.002822
133	0.000371	0.002613	0.00573
134	0.000433	0.002174	0.002787
135	0.000541	0.002556	0.005287
136	0.000676	0.001732	0.00268
137	0.000567	0.006559	0.003791
138	0.000537	0.009568	0.00169
139	0.000379	0.00325	0.003708
140	0.000317	0.001515	0.001363
141	0.000341	0.001347	0.006637
142	0.000261	0.000791	0.003844
143	0.000204	0.001052	0.004749
144	0.000387	0.001233	0.002843
145	0.000261	0.001617	0.006245
146	0.000218	0.001363	0.002422
147	0.000269	0.001984	0.005585
148	0.000364	0.001488	0.002125
150	0.000289	0.001827	0.002107
151	0.000351	0.004105	0.005
152	0.000355	0.002139	0.00507
153	0.000599	0.005157	0.005124

154	0.000253	0.0023	0.002051
155	0.000211	0.002032	0.003645
156	0.000115	0.000876	0.002021
157	0.000157	0.000723	0.004151
158	0.000133	0.000736	0.002249
159	0.000135	0.000637	0.004611
160	0.000122	0.000863	0.002166
161	0.000148	0.00122	0.004145
162	0.000217	0.001352	0.001863
163	0.000176	0.001948	0.003218
164	0.00017	0.001277	0.001704
165	0.000167	0.001858	0.005103
166	0.000127	0.001075	0.002063
167	0.000115	0.003118	0.002622
168	0.000397	0.00398	0.002664
169	0.000104	0.001162	0.002928
170	9.07E-05	0.000677	0.001811
171	8.03E-05	0.000451	0.003162
172	5.94E-05	0.000569	0.001655
173	7.90E-05	0.000574	0.003121
174	0.000102	0.000585	0.001747
175	9.23E-05	0.000782	0.00308
176	0.00013	0.000888	0.002071
177	7.95E-05	0.000901	0.002792
178	0.000108	0.001064	0.002349
179	6.84E-05	0.001088	0.002869
180	5.22E-05	0.000947	0.001274
181	1.68E-05	0.002352	0.003609
185	2.04E-05	0.000417	0.002491
187	4.85E-05	0.000308	0.002773
188	4.81E-05	0.000447	0.001465
189	4.44E-05	0.000749	0.002856
190	5.76E-05	0.000512	0.001528
191	4.12E-05	0.000586	0.002578
192	3.54E-05	0.000603	0.001603
193	1.61E-05	0.000546	0.001664
194	4.44E-05	0.000522	0.001643
195	2.91E-05	0.000383	0.001433
196	2.41E-05	0.000527	0.001325
197	1.61E-05	7.68E-10	0.001901
198	3.26E-05	0.00048	0.001308
199	3.36E-05	0.000255	0.001583
200	2.95E-05	0.000441	0.001195
201	3.80E-05	0.000251	0.001556
202	2.55E-05	0.000399	0.001082
203	1.89E-05	0.000248	0.002067

204	1.58E-05	0.000386	0.000944
205	1.65E-05	0.000322	0.001531
206	1.27E-05	0.000236	0.000917
207	6.23E-05	0.000183	0.001365
208	9.80E-10	0.000406	0.000775
209	9.91E-06	0.000112	0.000931
210	3.01E-07	1.81E-05	0.000817
211	4.40E-11	1.62E-10	0.001095
212	1.74E-06	0.000177	0.000544
213	6.73E-06	3.13E-05	0.000713
214	2.16E-07	0.000128	0.000389
215	4.49E-06	2.32E-05	0.000509
216	2.22E-10	7.36E-05	0.000234

Chapter 5 Conclusions and future work

The objective of this thesis was to investigate the polarity of water-soluble organic matter (WSOM) by theoretical and experimental approaches. A novel framework to segregate WSOM by the 1-octanol–water partition coefficient (K_{OW}), which correlates well with polarity, was developed in Chapter 2. To the best of our knowledge, this is the first method to represent the polarity of WSOM using measurable representations (i.e., K_{OW}), which provides another aspect to simplify the complexity of WSOM. The framework was further developed to determine the polarity distribution of WSOM through numerical algorithms (Chapter 3). In Chapter 4, the 1-octanol–water partitioning framework was applied to analyze chemical and optical characteristics of burning emissions from three types of Indonesian biomass (peat soil, fern, and acacia leaves). The results experimentally demonstrated that hydrocarbon-like and high molecular weight species are in the least polar fraction, while highly oxygenated species are highly polar ($\log K_{OW} < 0$). Comparison with previous studies indicates that only WSOM in the highly polar fraction ($\log K_{OW} < 0$) likely contributes to water uptake.

Recent laboratory studies suggested that the observed inconsistency of water uptake at sub- and super-saturated region is caused by liquid–liquid phase separation (LLPS) in a single particle during RH cycling (Renbaum-Wolff et al., 2016; Liu et al., 2018). The hypothesis can be investigated by application of the 1-octanol–water partitioning method, which allows direct measurement of water uptake properties for the aqueous and organic-rich phases. Further analysis on chemical composition of the two phases will help to indicate if formation of LLPS can be explained by the average organic oxygen-to-carbon ratio (O:C) of the aerosol particle.

Polarity distribution of the compounds in the aerosol particle can influence gas-particle partitioning of volatile organic compounds, which leads to secondary organic aerosol (SOA) formation. Several modeling studies were developed to characterize the gas-particle partitioning of complex mixtures (Pankow and Barsanti, 2009; Heald et al., 2010; Wania et al., 2015). Recently, in

analogy to the 1-octanol–water partitioning method, the 1-octanol–air partitioning method has been developed (Lei et al., 2019). Additional laboratory experiments which couple the 1-octanol–air partitioning method and the 1-octanol–water partitioning method would be useful in verifying the modeling studies on the kinetics, mechanisms, and yields of SOA formation.

One of the difficulties in applying the 1-octanol–water partitioning method is that it is limited by concentration of WSOM. Concentration of WSOM needs to be high enough to counter with the non-negligible influence from 1-octanol. This effect hinders the understanding of less-polar WSOM as well as the estimation of α value. Although evaporating the solvent can concentrate the WSOM solution, the evaporation of less-volatile species may render uncertainties in the estimation of K_{OW} distribution. Simplifying the experimental process to classify WSOM by polarity would be helpful in estimating its water uptake properties. For instance, using K_{OW} value to standardize/calibrate the solid-phase extraction method and/or the HPLC program would provide polarity distribution without the interferences of 1-octanol. Translating the standardized OM separation method into the scale of K_{OW} (e.g., correlate retention time and K_{OW} values) would allow accessing water uptake properties of the OM in the existing database.

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