Molecular corridors and parameterizations of volatility in the chemical evolution of organic aerosols

Ying Li1,2, Ulrich Pöschl1, and Manabu Shiraiwa1
1Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz, Germany
2State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China

Correspondence to: Manabu Shiraiwa (m.shiraiwa@mpic.de)

Received: 23 September 2015 – Published in Atmos. Chem. Phys. Discuss.: 15 October 2015
Revised: 1 March 2016 – Accepted: 3 March 2016 – Published: 14 March 2016

Abstract. The formation and aging of organic aerosols (OA) proceed through multiple steps of chemical reaction and mass transport in the gas and particle phases, which is challenging for the interpretation of field measurements and laboratory experiments as well as accurate representation of OA evolution in atmospheric aerosol models. Based on data from over 30 000 compounds, we show that organic compounds with a wide variety of functional groups fall into molecular corridors, characterized by a tight inverse correlation between molar mass and volatility. We developed parameterizations to predict the saturation mass concentration of organic compounds containing oxygen, nitrogen, and sulfur from the elemental composition that can be measured by soft-ionization high-resolution mass spectrometry. Field measurement data from new particle formation events, biomass burning, cloud/fog processing, and indoor environments were mapped into molecular corridors to characterize the chemical nature of the observed OA components. We found that less-oxidized indoor OA are constrained to a corridor of low molar mass and high volatility, whereas highly oxygenated compounds in atmospheric water extend to high molar mass and low volatility. Among the nitrogen- and sulfur-containing compounds identified in atmospheric aerosols, amines tend to exhibit low molar mass and high volatility, whereas organonitrates and organosulfates follow high O:C corridors extending to high molar mass and low volatility. We suggest that the consideration of molar mass and molecular corridors can help to constrain volatility and particle-phase state in the modeling of OA particularly for nitrogen- and sulfur-containing compounds.

1 Introduction

Organic aerosols (OA) consist of a myriad of chemical species and account for a substantial mass fraction (20–90 %) of the total submicron particles in the troposphere (Jimenez et al., 2009; Nizkorodov et al., 2011). They influence regional and global climate by affecting radiative budget of the atmosphere and serving as nuclei for cloud droplets and ice crystals (Kanakidou et al., 2005). OA play a central role in air quality by causing haze formation in urban air (Huang et al., 2014; Fuzzi et al., 2015; Zhang et al., 2015) and inducing adverse health effects (Pöschl and Shiraiwa, 2015). OA are introduced into the atmosphere either by being directly emitted from fossil fuel combustion and biomass burning, or formed by multigenerational oxidation of gaseous precursors. Secondary organic aerosols (SOA) pose a wide range of volatility, hygroscopicity, and reactivity (Hallquist et al., 2009). SOA evolution is a complex process involving both chemical reaction and mass transport in the gas and particle phases (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012; Shiraiwa et al., 2013a), but most aerosol models do not resolve multiphase processes explicitly.

Several two-dimensional (2-D) frameworks have been proposed for efficient SOA representation in chemical transport models. These 2-D frameworks were built based mainly on OA properties including volatility or (effective) saturation mass concentration, number of carbon and oxygen atoms in a molecule, mean carbon oxidation state, and atomic O:C or H:C ratios (Donahue et al., 2006; Jimenez et al., 2009; Pankow and Barsanti, 2009; Heald et al., 2010; Donahue et al., 2011; Kroll et al., 2011; Cappa and Wilson, 2012; Zhang
and Seinfeld, 2013; Wania et al., 2014, 2015). The saturation vapor pressure or pure compound saturation mass concentration ($C_0$) is one of the key thermodynamic properties describing the equilibrium gas-particle partitioning of organic compounds (Pankow, 1994; Odum et al., 1996; Donahue et al., 2006; Krieger et al., 2012; Bilde et al., 2015). The effective saturation mass concentration (C*) includes the effect of non-ideal thermodynamic mixing with an activity coefficient ($\gamma$): 

$$C^* = \gamma C_0$$

(Donahue et al., 2011, 2014; Zuend and Seinfeld, 2012). The term volatility often refers to $C^*$ and can also be used for $C_0$ under the assumption of ideal thermodynamic mixing. The extent of importance of non-ideal mixing depends strongly on contents of hydrophobic and hydrophilic organic compounds, electrolytes, and water (Zuend and Seinfeld, 2012; Shiraiwa et al., 2013b).

The volatility basis set (VBS) approach uses volatility and O:C ratio that can be constrained by chamber experiments (Donahue et al., 2006, 2011, 2012). The total organic mass is classified into volatility bins and their distribution between gas and aerosol phases is calculated according to absorptive equilibrium partitioning, assuming that gas-phase formation of semivolatile organic compounds is a limiting step of SOA formation (Pankow, 1994). VBS has been extensively applied in chemical transport models, improving prediction of organic aerosol concentrations (Lane et al., 2008; Tsimpidi et al., 2010; Shrivastava et al., 2011; Ahmadov et al., 2012; Jathar et al., 2012; Murphy et al., 2012; Matsui et al., 2014; Morino et al., 2014; Tsimpidi et al., 2014).

Saturation mass concentration is a consequence of the molecular characteristics of molar mass, chemical composition, and structure. Even though molar mass is an explicit parameter in computing absorptive SOA partitioning (Pankow, 1994; Pankow and Barsanti, 2009), the current VBS method does not account for the dependence of volatility on molar mass, assuming that the products distributed in all volatility bins have the same value of molar mass, e.g., 150 g mol$^{-1}$ for anthropogenic SOA and 180 g mol$^{-1}$ for biogenic SOA (Murphy and Pandis, 2009; Hayes et al., 2015). Shiraiwa et al. (2014) have shown that SOA from a variety of biogenic and anthropogenic precursors can be represented well by molecular corridors with a tight inverse correlation between molar mass ($M$) and volatility of SOA oxidation products. The slope of these corridors corresponds to the increase in molar mass required to decrease volatility by 1 order of magnitude. Molecular corridors can help to constrain chemical and physical properties as well as reaction rates and pathways with characteristic kinetic regimes of reaction-, diffusion-, or accommodation-limited multiphase chemical kinetics involved in SOA evolution (Shiraiwa et al., 2014).

In recent years a high-resolution mass spectrometry has been employed for measurements on atmospheric aerosols, providing definitive determination of molar mass and elemental composition (Tolocka et al., 2004; Reemtsma, 2009; Williams et al., 2010; Kampf et al., 2011; Nizkorodov et al., 2011; Laskin et al., 2012; Chan et al., 2013; Hamilton et al., 2013; Holzinger et al., 2013; Kourtchev et al., 2014). Soft ionization methods such as electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and direct analysis in real time (DART) ionization are commonly applied for detailed molecular characterization, offering minimal fragmentation of the analytes (Nozière et al., 2015, and references therein). Such measurements have revealed that nitrogen- and sulfur-containing organic compounds are commonly present with a substantial fraction of mass in atmospheric organic aerosols. A significant amount of N-heterocyclic alkaloid and nitroaromatic compounds were found in biomass-burning plumes (Laskin et al., 2009; Kitanovski et al., 2012). Organonitrates have been observed to account for a substantial fraction of SOA in field and laboratory studies (Farmer et al., 2010; Rollins et al., 2012; Fry et al., 2013; Boyd et al., 2015). Organosulfates have also been detected in ambient OA (Romero and Oehme, 2005; Jinuma et al., 2007; Surratt et al., 2007, 2008; Lukács et al., 2009; Ehn et al., 2010; Schmitt-Kopplin et al., 2010; Gómez-González et al., 2012; Lin et al., 2012; Stone et al., 2012; Kahnt et al., 2013; Kundu et al., 2013; Ma et al., 2014; O’Brien et al., 2014; Staudt et al., 2014; Tao et al., 2014). Reduced sulfur-containing compounds were observed in supercooled clouds (Zhao et al., 2013) and rainwater (Mead et al., 2015).

Although nitrogen- and sulfur-containing organic compounds are important components of atmospheric aerosols, their physical properties and chemical behaviors are still poorly understood (Nozière et al., 2015) and thus are untreated in air quality models so far. In this study, we apply the molecular corridor-based approach to analyze ambient and indoor observations of organic aerosols including nitrogen- and sulfur-containing organic compounds to provide insights on the physical and chemical processes driving OA evolution in the atmosphere.

2 Characterization of 31 066 organic compounds in molecular corridors

More than 30 000 organic compounds were analyzed to examine whether molecular corridors can constrain a variety of organic compounds. The used data set is the National Cancer Institute (NCI) open database (http://cactus.nci.nih.gov/download/nci/), which contains 31 066 organic compounds and corresponding SMILES codes. A list of the compounds was also provided in Wei et al. (2012). Saturation vapor pressure of each compound was estimated by the Estimation Programs Interface (EPI) Suite software (version 4.1) developed by the US Environmental Protection Agency (US EPA, 2015). The EPI Suite reports vapor pressure calculated in three separate methods, including the Antoine method (Lyman et al., 1990), the modified Grain method (Lyman, 1985), and the Mackay method (Lyman, 1985). In this study, the modified Grain estimate was used for solids and the average
of the Antoine and the modified Grain estimates was used for liquids and gases, following the suggestions of the EPI Suite. The vapor pressure was then converted to the saturation mass concentration \( C_0 \) in µg m\(^{-3}\) through the following relationship:

\[
C_0 = \frac{M10^6 \rho_0}{760 RT},
\]

where \( M \) is the molar mass (g mol\(^{-1}\)), \( \rho_0 \) is the saturation vapor pressure (mm Hg), \( R \) is the ideal gas constant (8.205 \times 10\(^{-5}\) atm K\(^{-1}\) mol\(^{-1}\) m\(^3\)), and \( T \) is the temperature (K).

We classified these organic compounds into six classes based on chemical composition: CH, CHO, CHN, CHON, CHOS, and CHONS, with the number of compounds of 328, 8420, 2968, 13628, 925, and 3367, respectively. These compounds cover a molar mass from 41 to 1779 g mol\(^{-1}\). In total we consider 22 structural sub-classes including N-containing compounds of amine (primary, secondary, tertiary, and quaternary), amide, azo, azide, amino acid, imine, nitroso, nitro, alkyl nitrite, nitrite, and organonitrate as well as S-containing compounds of organosulfate, sulfonate, sulfone, sulfoxide, sulfite, heterocyclic ring, thioate, and thiocarbamate.

Figure 1 shows that most of the organic compounds (small markers color-coded by atomic O : C ratio) fall into the molecular corridor with upper and lower boundaries represented by linear alkanes (C\(_n\)H\(_{2n+2}\), O : C = 0; purple dashed line) and sugar alcohols (C\(_n\)H\(_{2n+2}\)O\(_n\), O : C = 1; red dashed line), respectively. It indicates that the 2-D space of molar mass and saturation mass concentration can constrain most of the organics, including compounds containing heteroatoms of N and S. About 1000 compounds with branched structures lie above the linear alkane line among the CHO class (Fig. 1b), as volatilities of branched compounds are higher than those of compounds with linear structures. The surrogate compounds with the mean values of \( M \), \( C_0 \), and O : C ratio computed for each of the structural sub-classes are indicated by larger symbols with error bars indicating standard deviations. Figure 1c shows clearly that mean values of \( C_0 \) decrease as more hydrogen atoms of an ammonia structure are replaced by alkyl or aryl groups, forming the primary, secondary, tertiary and quaternary amine. Figure 1d–f show that the molar mass of CHON, CHOS, and CHONS can be up to 1000 g mol\(^{-1}\) and \( C_0 \) can be as low as 10\(^{-30}\) µg m\(^{-3}\). The compounds with high O : C ratios are organosulfate and sulfite (the mean O : C of ~ 1), followed by compounds in subclasses of sulfonate, sulfone, sulfoxide, organonitrate, nitro, alkyl nitrites, nitroso, or amino acid, which tend to occupy the space close to the sugar alcohol line.

OA can be classified as (1) volatile organic compounds (VOC; \( C_0 > 3 \times 10^6 \) µg m\(^{-3}\)), (2) intermediate volatility OC (IVOC; 300 < \( C_0 < 3 \times 10^6 \) µg m\(^{-3}\)), (3) semivolatile OC (SVOC; 0.3 < \( C_0 < 300 \) µg m\(^{-3}\)), (4) low-volatile OC (LVOC; 3 \times 10\(^{-4}\) < \( C_0 < 0.3 \) µg m\(^{-3}\)), and (5) extremely low-volatile OC (ELVOC; \( C_0 < 3 \times 10^{-4} \) µg m\(^{-3}\)) (Donahue et al., 2011; Murphy et al., 2014). Figure 2 shows the relationship between saturation mass concentration and molar mass derived from these 30 000 compounds. The molar mass of VOC is usually less than 160 g mol\(^{-1}\), 130–250 g mol\(^{-1}\) for IVOC, 180–330 g mol\(^{-1}\) for SVOC, 210–400 g mol\(^{-1}\) for LVOC, and larger than 260 g mol\(^{-1}\) for ELVOC. As the volatility decreases, the covered molar mass range becomes wider, indicating more compounds are encompassed with increasing complexity. Meanwhile, the volatility decreases as the average molar mass of every composition group increases. For example, the average molar mass of the CHO class in the VOC group is 117 g mol\(^{-1}\), which increases to 471 g mol\(^{-1}\) in the ELVOC group. The symbol sizes are scaled with relative abundance of compounds in each composition class. Many of the CH compounds (~ 69 %) are distributed in the VOC and IVOC groups. Of the CHO and CHN compounds, 70 % are populated in the IVOC and SVOC groups. More than 80 % of the CHON and CHOS compounds are located in the range covered from IVOC to LVOC, and about 10 % of them belong to the ELVOC group. Of the CHONS compounds, 90 % cover the range from SVOC to ELVOC. Given that the molar mass is observationally constrained, it is suitable to use the molar mass to constrain the volatility of organic compounds.

### 3 Parameterization of saturation mass concentration by elemental composition

Accurate prediction of volatility requires structural information of the organic compounds, which is often difficult to obtain from field measurements. We predict \( C_0 \) as a function of elemental composition that is often determined by soft-ionization high-resolution mass spectrometry. Donahue et al. (2011) have developed a parameterization to estimate \( C_0 \) as \( \log_{10} C_0 = f(n_C, n_O) \) for the CHO compounds. We broaden this formulation to \( \log_{10} C_0 = f(n_C, n_O, n_N, n_S) \) to be applicable to the N- and S-containing compounds:

\[
\log_{10} C_0 = \left( n_C^0 - n_C \right) b_C - n_O b_O - 2 \frac{n_O n_S}{n_O + n_S} b_{CO} - n_N b_N - n_S b_S,
\]

where \( n_C^0 \) is the reference carbon number; \( n_C, n_O, n_N, \) and \( n_S \) denote the numbers of carbon, oxygen, nitrogen, and sulfur atoms, respectively; \( b_C, b_O, b_N, \) and \( b_S \) denote the contribution of each atom to \( \log_{10} C_0 \), respectively, and \( b_{CO} \) is the carbon–oxygen nonideality (Donahue et al., 2011). Values of \( b \) coefficients were obtained by fitting with multi-linear least squares analysis to the 30 000 compounds for each class (CH, CHO, CHN, CHON, CHOS, and CHONS). The best-fit parameters obtained at 298 K in this analysis are presented in Table 1. The nonlinear terms of nitrogen–oxygen and sulfur–oxygen are not considered, as they impact the predicting results only slightly. Considering the number of hydrogen atoms in Eq. (2) could improve the prediction for compounds.
Figure 1. Molecular corridors of molar mass (M) vs. saturation mass concentration (C₀) for organic compounds in elemental composition classes of (a) CH, (b) CHO, (c) CHN, (d) CHON, (e) CHOS, and (f) CHONS. The data comprise 31,066 compounds from the NCI open database. The dotted lines represent linear alkanes CₙH₂ₙ₊₂ (purple with O : C = 0) and sugar alcohols CₙH₂ₙ₊₂Oₙ (red with O : C = 1). The small markers correspond to individual compounds identified in each structural sub-class (see Sect. 2), color-coded by atomic O : C ratio. The larger symbols indicate the surrogate compounds with the mean values of M, C₀, and O : C ratio computed for each of the structural sub-classes with error bars indicating standard deviations. Note that the data points above the linear alkane line in (b) represent molecules with branched structures.
in the CH class slightly, but they have little impact on the prediction for compounds in other composition classes. Detailed information including an estimated $b_\text{H}$ (the contribution of hydrogen atoms to log$_{10}C_0$) can be found in the Supplement. As the effect of inclusion of hydrogen is limited, further analysis was conducted using Eq. (2) for simplicity.

The temperature dependence of $C_0$ can be approximated by an Arrhenius-type equation resembling the Clausius–Clapeyron equation (Donahue et al., 2006; Cappa and Jimenez, 2010):

$$C_0(T) = C_0(T_{\text{ref}}) \left( \frac{T_{\text{ref}}}{T} \right) \exp \left[ \frac{-\Delta H_{\text{vap}}}{R} \left( \frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right],$$

(3)

where $T_{\text{ref}}$ is the temperature at a reference state (298 K in this study). The enthalpy of vaporization $\Delta H_{\text{vap}}$ (kJ mol$^{-1}$) could be estimated by $C_0$, as there is a nearly linear relationship between log$_{10}C_0$ (300 K) and $\Delta H_{\text{vap}}$ (Epstein et al., 2010).

The developed estimation method was compared with the EPI Suite for the 30 000 compounds as shown in Fig. 3 and Table S2. The agreement between the two methods was assessed by statistical measures of correlation coefficient ($R$), mean absolute gross error (MAGE), and mean bias (MB). As shown in Fig. 3, our new method performs well with $R$ above 0.8 and MAGE below 1.8 for all the composition classes. In the CHN class, our method performs well for primary, secondary, and tertiary amines, heterocyclic rings, imines, and nitriles (Table S2). Our method overestimates $C_0$ of the quaternary amine located in LVOC and ELVOC ranges. For the CHON class, relatively large errors are found for quaternary amine and amino acid. Note that there are relatively few data for organonitrate. When nitrate functionality appears in the amine, they are assigned to the amine class. Nitroso and alkyl nitrite are treated similarly. For structural classes in the CHOS and CHONS, our method works well with $R > 0.82$.

Our method was also tested with a different set of organic compounds and a different estimation method. We used 704 SOA oxidation products of CHO compounds (Shiraiwa et al., 2014) with saturation vapor pressure estimated using the EVAPORATION model (Compernelle et al., 2011). As shown in Fig. 4a, our newly developed parameterization also agrees well with EVAPORATION predictions, showing better agreement than Donahue et al. (2011), as indicated by smaller values of MB and MAGE. Figure 4b shows the comparison between $C_0$ estimated by our parameterization and the experimental data. The experimental $C_0$ values of 1729 organic compounds with heteroatoms including N or S are taken from the PHYSPROP database that is part of the EPI Suite (http://www.srcinc.com/what-we-do/environmental/scientific-databases.html). Our method gives a good performance with $R$ of 0.84, MB of $-0.41$, and MAGE of 1.24.

As shown in Fig. 4b, the estimation error increases as the saturation mass concentration decreases. An accurate prediction of low vapor pressure is difficult due, in large part, to the limitation caused by measurement challenges. For example, the measured vapor pressure of dicarboxylic acid, a low-volatility compound commonly found in atmospheric aerosols, disagreed by up to 2 orders of magnitude between different measurement techniques (Krieger et al., 2012; Huisman et al., 2013; Bilde et al., 2015). The effects of functionalization, phase states (crystalline, amorphous, subcooled liquid), and molecular structure need to be considered in future experimental studies (Huisman et al., 2013; Bilde et al., 2015). The vapor pressure estimation methods could give very divergent predictions for the same compound (Clegg et al., 2008; O'Meara et al., 2014). Another difficulty in predicting low vapor pressure is that most estimation methods, including the EPI Suite, are constrained by databases heavily biased toward mono-functional compounds with saturation vapor pressures in the range of $\sim 10^3$–$10^5$ Pa (Barley and McFiggans, 2010; Krieger et al., 2012). The EPI Suite uses the PHYSPROP database as its training data set. When comparing with the PHYSPROP database, the estimation error of EPI Suite increases as the vapor pressure decreases,

### Table 1. Composition classes and the $n_0^0$ and $b$ values for saturation mass concentration parameterizations obtained by least-squares optimization using the NCI database.

<table>
<thead>
<tr>
<th>Classes</th>
<th>$n_0^0$</th>
<th>$b_C$</th>
<th>$b_O$</th>
<th>$b_{CO}$</th>
<th>$b_N$</th>
<th>$b_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>23.80</td>
<td>0.4861</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHO</td>
<td>22.66</td>
<td>0.4481</td>
<td>1.656</td>
<td>-0.7790</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CHN</td>
<td>24.59</td>
<td>0.4066</td>
<td></td>
<td></td>
<td>0.9619</td>
<td></td>
</tr>
<tr>
<td>CHON</td>
<td>24.13</td>
<td>0.3667</td>
<td>0.7732</td>
<td>-0.07790</td>
<td>1.114</td>
<td></td>
</tr>
<tr>
<td>CHOS</td>
<td>24.06</td>
<td>0.3637</td>
<td>1.327</td>
<td>-0.3988</td>
<td></td>
<td>0.7579</td>
</tr>
<tr>
<td>CHONS</td>
<td>28.30</td>
<td>0.3848</td>
<td>1.011</td>
<td>0.2921</td>
<td>1.053</td>
<td>1.316</td>
</tr>
</tbody>
</table>

Figure 2. Average molar mass ($M$), saturation mass concentration ($C_0$), and O:C ratio for organic compounds from the NCI database categorized by elemental composition (CH, CHO, CHN, CHON, CHOS, CHONS) and volatility (VOC, IVOC, SVOC, LVOC, ELVOC). The data points and error bars represent arithmetic mean values and standard deviations for each class of elemental composition. The symbol sizes are scaled by the number of compounds in each class. The center and borders of the colored boxes represent the mean and standard deviations of all compounds included in each volatility class.
especially when the vapor pressure decreases below $10^{-4}$ Pa.

Despite of some limitations as described above, the new estimation parameterization derived from a large data set in this study is sufficiently good to predict $C_0$ for various structural organic classes as shown by overall good correlation. In the next section, the saturation mass concentration of ambient OA (e.g., the compounds with elemental composition measured by high-resolution mass spectrometry techniques) is estimated using Eq. (2).

### 4 Application of molecular corridors to atmospheric aerosols

Applying the newly developed saturation mass concentration estimation method to laboratory experiments and field campaigns, the observed organic compounds were mapped into the molecular corridor with an alternative representation displaying $C_0$ as a function of molar mass, which appears more straightforward for direct comparisons to mass spectra (Shiraiwa et al., 2014). The used observation data set is summarized in Table 2. In total, 9053 organic compounds were collected from chamber experiments for new particle formation.
Table 2. Summary of the number of organic compounds in the composition classes (CH, CHO, CHN, CHON, CHOS, and CHONS) measured in 11 observation events.

<table>
<thead>
<tr>
<th>Observations</th>
<th>CH</th>
<th>CHO</th>
<th>CHN</th>
<th>CHON</th>
<th>CHOS</th>
<th>CHONS</th>
<th>Total</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experiments</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New particle formation</td>
<td>55</td>
<td>55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>55</td>
<td>Ehn et al. (2012)a,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Schobesberger et al. (2013)a</td>
</tr>
<tr>
<td>Field</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forest</td>
<td>1</td>
<td>37</td>
<td>23</td>
<td>4</td>
<td>1</td>
<td></td>
<td>66</td>
<td>Ehn et al. (2010, 2012)a</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>13</td>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>51</td>
<td>Laskin et al. (2009)b</td>
</tr>
<tr>
<td>Urban</td>
<td>212</td>
<td>37</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>249</td>
<td>Lin et al. (2012)b,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Stone et al. (2012)b,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ma et al. (2014)b,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O’Brien et al. (2014)b,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tao et al. (2014)b</td>
</tr>
<tr>
<td>Mt. Sonnblick</td>
<td>33</td>
<td>211</td>
<td>47</td>
<td>271</td>
<td>37</td>
<td>31</td>
<td>630</td>
<td>Holzinger et al. (2010)c</td>
</tr>
<tr>
<td>Fog</td>
<td>1425</td>
<td>711</td>
<td>218</td>
<td>83</td>
<td>544</td>
<td>3941</td>
<td>2437</td>
<td>Mazzoleni et al. (2010)b</td>
</tr>
<tr>
<td>Cloud</td>
<td>1055</td>
<td>1985</td>
<td>357</td>
<td>544</td>
<td>3941</td>
<td></td>
<td></td>
<td>Zhao et al. (2013)b</td>
</tr>
<tr>
<td>Rain in New Jersey</td>
<td>192</td>
<td>6</td>
<td>320</td>
<td>129</td>
<td>52</td>
<td>699</td>
<td>811</td>
<td>Altieri et al. (2009a, b)b</td>
</tr>
<tr>
<td>Rain in Bermuda</td>
<td>50</td>
<td>734</td>
<td></td>
<td></td>
<td>27</td>
<td></td>
<td></td>
<td>Altieri et al. (2012)b</td>
</tr>
<tr>
<td>Indoor</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>26</td>
<td>Wisthaler and Weschler (2010)c</td>
</tr>
<tr>
<td>Reactions of skin lipids</td>
<td>1</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Sleiman et al. (2010a, b)d</td>
</tr>
<tr>
<td>and O₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tobacco smoke</td>
<td>20</td>
<td>42</td>
<td>13</td>
<td>13</td>
<td></td>
<td></td>
<td>88</td>
<td></td>
</tr>
</tbody>
</table>

Applied analytical methods: a atmospheric pressure interface time-of-flight mass spectrometry (APi-TOF-MS); b electrospray ionization mass spectrometry (ESI-MS); c proton-transfer-reaction mass spectrometer (PTR-MS); d gas chromatography mass spectrometry (GC-MS).

4.1 CH and CHO compounds

Figure 5 shows the CH and CHO compounds measured in different atmospheric conditions plotted in molecular corridors. The small markers show individual observed compounds color-coded by atomic O:C ratio. The larger symbols with error bars represent mean values of molar mass, saturation mass concentration, and O:C ratio derived from every observation event. Figure 5a shows abundant organic compounds found in new particle formation (NPF) experiments performed at the Cosmics Leaving Outdoor Droplets (CLOUD) chamber at CERN (Schobesberger et al., 2013) and the Jülich Plant Atmosphere Chamber (Mentel et al., 2009; Ehn et al., 2012). The values of O:C ratio are all above 0.3 and some organic compounds are remarkably highly oxidized (O:C up to 1.4). The compounds cover the mass range of 184–558 g mol⁻¹ in the volatility range of IVOC–ELVOC, spreading in a large space of the molecular corridor. These oxidized organic compounds play an important role in formation and growth of OA particles in ambient conditions (Ehn et al., 2012; Riipinen et al., 2012; Kulmala et al., 2013; Schobesberger et al., 2013; Ehn et al., 2014; Riccobono et al., 2014; Wildt et al., 2014).

Figure 5b shows highly oxidized compounds observed at the boreal forest research station in Hyytiälä, Finland, during NPF events (Ehn et al., 2010, 2012). The average O:C ratio is as high as 1.1. The locations of organic compounds observed in the CLOUD experiments (Fig. 5a) and at Hyytiälä (Fig. 5b) in the molecular corridor are similar by occupying the space close to the sugar alcohol line (high O:C corridor; Shiraiwa et al., 2014), indicating that chemical properties of these organic compounds are similar and chamber experiments represent ambient observations well. Such low-volatility and highly oxygenated compounds may be gener-
Figure 5. Molecular corridors of saturation mass concentration ($C_0$) vs. molar mass ($M$) for CH and CHO compounds measured in (a) chamber experiments for new particle formation (Ehn et al., 2012; Schobesberger et al., 2013), (b) field campaigns conducted in the boreal forest of Hyytiälä (Ehn et al., 2010, 2012), (c) a field campaign conducted at Mt. Sonnblick (Holzinger et al., 2010), and measurements of (d) fog in the city of Fresno (Mazzoleni et al., 2010), (e) clouds at Mt. Werner (Zhao et al., 2013), (f) rain in New Jersey (Altieri et al., 2009a, b), (g) indoor aerosols from human skin lipids and ozone (Wisthaler and Weschler, 2010), and (h) tobacco smoke (Sleiman et al., 2010a, b). The small markers represent individual compounds identified in each data set color-coded by atomic O:C ratio. The size of the small markers in (d) and (e) is linearly scaled by relative intensity of MS signal. The larger symbols with error bars indicate surrogate compounds with the mean values of $M$, $C_0$, and O:C ratio computed for each data set.

Figure 5c shows organic compounds observed in the remote area at Mt. Sonnblick, Austria (Holzinger et al., 2010). The observed compounds were less oxidized and lie close to the alkane line. Aqueous-phase processing of organic compounds leads to formation of highly oxidized compounds in fog (Fig. 5d; Mazzoleni et al., 2010), cloud (Fig. 5e; Zhao et al., 2013), and rain (Fig. 5f; Altieri et al., 2009a, b, 2012), suggesting that atmospheric water is enriched in polar compounds compared to atmospheric particulate matter. Higher oxidized compounds tend to have lower molar mass than less-oxidized compounds, indicating that fragmentation is an important pathway in aqueous-phase oxidation (Sun et al., 2010; McNeill et al., 2012; Carlton and Turpin, 2013; Dau- mit et al., 2014; Ervens, 2015). In addition, aqueous processing can produce high molar mass and high O:C compounds through oligomerization (Altieri et al., 2008; Lim et al., 2010; Ervens et al., 2011), as seen in super-cooled cloud water collected at a remote site on Mt. Werner in the USA in Fig. 5e.

Figure 5g shows the oxidation products from reactions of ozone and human skin lipids (Wisthaler and Weschler, 2010). The majority of products are VOC and IVOC with O:C $< 0.7$ and molar mass $< 200$ g mol$^{-1}$, mainly occupying the space close to the origin of the molecular corridor. Some products with higher molar mass ($> 300$ g mol$^{-1}$) are mainly first-generation products of ozonolysis of skin lipids, including hydroxyl geranyl acetone, polyunsaturated aldehydes, and fatty acids. These products can be further oxidized by ozone, generating fragmented secondary products with a relatively higher O:C ratio with carboxyl, carboxyl, or $\alpha$-hydroxy ketone groups (Wisthaler and Weschler, 2010).
Cigarette smoke is another pollutant frequently encountered in indoor air and residual secondhand tobacco smoke absorbed to indoor surfaces can react with atmospheric species such as ozone (Destaillets et al., 2006; Sleiman et al., 2010a) and nitrous acid (HONO) (Sleiman et al., 2010b) to form third-hand smoke hazards. As shown in Fig. 5h, most of the nicotine products have \( M < 300 \text{ g mol}^{-1} \) and \( \text{O: C} < 0.5 \) with \( \log_{10}C_0 > 0 \mu g \text{ m}^{-3} \). As oxidant levels in indoor air are relatively low compared to outdoor air (Weschler, 2011), indoor OA tend to be less oxidized and have lower molar mass.

### 4.2 Nitrogen- and sulfur-containing compounds

Figure 6 shows N-containing compounds plotted in the molecular corridor. Figure 6a shows 23 compounds observed at Hyytiälä, Finland, during NPF events (Ehn et al., 2010, 2012). They are mainly amines with a small molar mass range (69–169 g mol\(^{-1}\)) and intermediate volatility, covering the space close to the origin of the molecular corridor. Amines can stabilize sulfuric acid clusters efficiently and their role in nucleation may be significant (Loukonen et al., 2010; Smith et al., 2010; Wang et al., 2010; Erupe et al., 2011; Zhang et al., 2011; Kulmala et al., 2014).

N-containing organic compounds are important components of biomass-burning organic aerosols (Lobert et al., 1990; Simoneit, 2002). Figure 6b presents these compounds including amine, urea, alkyl amide, alkyl nitrile, amino acid, and N-heterocyclic alkaloid compounds (Laskin et al., 2009). These compounds spread separately in two parts in molecular corridors. Some compounds are assembled in the upper left space bounded by \( \log_{10}C_0 > 0 \mu g \text{ m}^{-3} \) and \( M < 300 \text{ g mol}^{-1} \). A part of these compounds may be a consequence of oxidative fragmentation or thermal decomposition. Compounds clustered in the lower right space are...
CHON compounds with molar mass higher than 300 g mol$^{-1}$ covering the range from LVOC to ELVOC. More than 200 N-containing compounds were identified at Mt. Sonnblick (Fig. 6c; Holzinger et al., 2010). Less-oxidized N-containing organic compounds could be formed through reactions transforming carbonyls into imines or reactions of NO with organic peroxy radicals (O'Brien et al., 2014). Highly oxidized organonitrates (O : C > 1) were suggested to be formed by nitrate radical chemistry (Holzinger et al., 2010). Many highly oxidized N-containing compounds with a range of O : C ratios from 1 to 2 were observed in fog (Fig. 6d; Mazzoleni et al., 2010), cloud (Fig. 6e; Zhao et al., 2013), rain in New Jersey (Fig. 6f; Altieri et al., 2009a, b), and Bermuda (Fig. 6g; Altieri et al., 2012). Aqueous-phase processing can form a variety of highly functionalized nitrated organic compounds including organonitrates, hydroxynitrates, carbonyl nitrates, and dinitrates (Zhao et al., 2013). Reduced nitrogen compounds were also identified in atmospheric water, mainly occupying the space close to the alkane line.

Figure 6h shows N-containing compounds found in the second-hand and third-hand tobacco smoke. Nitrosamines were found in third-hand smoke hazards when the residual nicotine reacts with HONO (Sleiman et al., 2010b). Similar to the trend of CHO compounds in the molecular corridors (Fig. 5h), N-containing compounds also mainly occupy the region close to the origin of the molecular corridor. Some high molar mass N-containing compounds (m/z 400–500) were also detected, but their elemental compositions and structures have not been identified (Sleiman et al., 2010a).

Figure 7 shows S-containing compounds plotted in the molecular corridor. Organosulfate and nitrooxy organosulfate were frequently identified in fine aerosols especially in urban areas including Shanghai (Ma et al., 2014; Tao et al., 2014) and Guangzhou (Lin et al., 2012), Taipei (Lin et al., 2012), Lahore (Stone et al., 2012), Bakersfield (O’Brien et al., 2014) and Los Angeles (Tao et al., 2014). (b) Mt. Sonnblick (Holzinger et al., 2010), (c) fog in Fresno (Mazzoleni et al., 2010), (d) cloud at Mt. Werner (Zhao et al., 2013), (e) rain in New Jersey (Altieri et al., 2009a, b), and (f) rain in Bermuda (Altieri et al., 2012). The small markers represent individual compounds color-coded by atomic O : C ratio. The size of the small markers in (c) and (d) is linearly scaled by relative intensity of MS signal. The larger symbols with error bars indicate the surrogate compounds with the mean values of $C_0$, $C_1$, and O : C ratio (relative abundance considered for c and d).
Figure 8. Molecular corridors of saturation mass concentration ($C_0$) vs. molar mass ($M$) for organosulfate, organonitrate, nitrooxy organosulfate, amine, and reduced sulfur compounds collected from outdoor observations (Table 2). The small markers represent individual compounds color-coded by O:C ratio. The larger symbols indicate surrogate compounds with the mean values of $M$, $C_0$, and O:C ratio.

Figure 9. Average molecular corridors for OA observed in indoor air, outdoor air, and atmospheric water. The markers show surrogate compounds with the mean values of molar mass ($M$), saturation mass concentration ($C_0$), and O:C ratio computed from every observation event (Figs. 5–7). The edge color of the symbols indicates the surrogate compound identified in indoor air (black), outdoor air (blue), and atmospheric water (red). The symbol size is scaled by the ratio of the number of compounds in each class (e.g., CH, CHO, CHON, CHONS) to the total number of compounds in each data set.

including functionalized (nitro and nitrooxy) organosulfates were formed in atmospheric water (Fig. 7c–f), which was located close to the sugar alcohol line in the range of LVOC and ELVOC. Compounds close to the alkane line are mostly reduced sulfur compounds, e.g., aromatic structures containing only one S and one O, which may be emitted from primary sources.

Figure 8 summarizes the molecular corridor for amine, organonitrate, organosulfate, nitrooxy organosulfate, and reduced sulfur compounds. The small markers are compounds identified in the studies included in Figs. 6 and 7. Among these species, nitroxy organosulfates have the highest O:C ratio (> 0.9) and the lowest volatility falling into the ELVOC group with molar mass up to 400 g mol$^{-1}$. Organosulfates and organonitrates have an O:C ratio generally higher than 0.7, covering the range of IVOC to ELVOC with a broad molar mass range (100–600 g mol$^{-1}$) to occupy the high O:C corridor. Note that there exists a homologous series of organosulfates with molar mass between 400 and 600 g mol$^{-1}$ and log$_{10}(C_0) < -10$, which appear to have lower dlog$C_0$/d$M$ values. These compounds, e.g., C$_{17}$H$_{18}$O$_{16}$S$_1$, C$_{18}$H$_{20}$O$_{16}$S$_1$, and C$_{19}$H$_{22}$O$_{16}$S$_1$, were found in the cloud water and their formation may be due to esterification of hydroxyl groups with sulfuric acid or acid-catalyzed reactions of epoxides (Zhao et al., 2013). Reduced sulfur compounds have low O:C ratio (< 0.4) and are located close to the alkane line. Amine and N-heterocyclic alkaloid compounds found during new particle formation and biomass burning have the lowest O:C ratio and molar mass...
and the highest volatility (in VOC and IVOC groups), following the low O:C corridor.

5 Summary and conclusions

From the analysis of measured OA located into the molecular corridor, we can conclude that the molecular corridor characterized by molar mass, saturation mass concentration, and O:C ratio has successfully grasped the properties of organic compounds from different sources and formed in various atmospheric conditions. Figure 9 shows the trend of observed organic compounds with surrogate compounds with the mean values of molar mass, saturation mass concentration, and O:C ratio derived from every observation event. The symbol size is scaled with the ratio of the number of compound in each class (e.g., CH, CHO, CHON, CHONS) to the total number of compounds in each observation.

OA in indoor environments have relatively lower molar mass and higher volatility, mainly occupying the space close to the origin of the molecular corridor. Outdoor OA are constrained to a corridor in the range of IVOC–LVOC with a molar mass of up to ~400 g mol$^{-1}$. Atmospheric water of fog, cloud, and rain droplets often contain many highly oxygenated, high molar mass, and low-volatility compounds, extending to a wide space with higher molar mass and lower volatility. Molecular corridors are a useful framework for analysis and interpretation of measurements by a high-resolution mass spectrometer to visualize distribution of organic compounds providing insights into the evolution of OA properties.

Explicit consideration of molar mass in an OA model would also be useful in inferring particle-phase state (liquid vs. semisolids vs. amorphous solid), as the molar mass correlates with the glass transition temperature of organic compounds (Koop et al., 2011). In the future, we have been shown to affect various gas-particle interactions including heterogeneous and multiphase chemistry, SOA formation and evolution as well as activation to cloud droplets and ice crystals (Pöschl and Shiraiwa, 2015, and references therein). Molecular corridors may serve as a basis for better treatment of SOA properties and interpretation of model outputs in detailed SOA models (e.g., Shiraiwa et al., 2012; Cappa et al., 2013; Roldin et al., 2014; Zaveri et al., 2014) as well as for compact representation of OA formation and evolution in regional and global models of climate and air quality.

Acknowledgements. Ying Li was supported by the Lindau Fellowship (project no. GZ 1116), granted by the Sino-German Science Center. This work was supported by the Max Planck Society and the National Natural Science Foundation of China (grant no. 41405121). The authors gratefully acknowledge Lynn Mazzoleni (Michigan Technological University), Alexander Laskin (Pacific Northwest National Laboratory), Rupert Holzinger (Utrecht University), Neil Donahue (Carnegie Mellon University), Thomas Mentel (Research Center Jülich), Frank Wania (University of Toronto Scarborough), Yiyi Wei (Texas Tech University), Thomas Berkemeier (Max Planck Institute for Chemistry), Pascale Lakey (Max Planck Institute for Chemistry), and John Seinfeld (Caltech) for stimulating discussions. We thank Ulrich Krieger (ETH Zurich) and two anonymous referees for useful comments.

The article processing charges for this open-access publication were covered by the Max Planck Society.

Edited by: A. Kiendler-Scharr

References


Y. Li et al.: Molecular corridors and parameterizations of volatility

Atmos. Chem. Phys., 16, 3327–3344, 2016 www.atmos-chem-phys.net/16/3327/2016/


Murphy, B. N., Donahue, N. M., Robinson, A. L., and Pandis, S. N.: A naming convention for atmospheric organic aerosol, At-
mos. Chem. Phys., 14, 5825–5839, doi:10.5194/acp-14-5825-
Murphy, B. N. and Pandis, S. N.: Simulating the formation of
semivolatile primary and secondary organic aerosol in a regional
4728, 2009.
Nizkorodov, S. A., Laskin, J., and Laskin, A.: Molecular chemistry
of organic aerosols through the application of high resolution
mass spectrometry, Phys. Chem. Chem. Phys., 13, 3612–3629,
2011.
Nozière, B., Kalberer, M., Claeys, M., Allan, J., D’Anna, B.,
Dececari, S., Finessi, E., Glasius, M., Grgić, I., Hamilton, J.
F., Hoffmann, T., Inuma, Y., Jaoui, M., Kahnt, A., Kampf, C.
J., Kourtchev, I., Maenhaut, W., Marsden, N., Saarikoski, S.,
Schnelle-Kreis, J., Suratt, J. D., Szidat, S., Szmiępski, R., and
Wisthaler, A.: The molecular identification of organic com-
pounds in the atmosphere: state of the art and challenges, Chem.
O’Brien, R. E., Laskin, A., Laskin, J., Rubitschun, C. L., Suratt, J.
D., and Goldstein, A. H.: Molecular characterization of S- and
N-containing organic constituents in ambient aerosols by neg-
ative ion mode high-resolution Nanospray Desorption Electro-
spray Ionization Mass spectrometry: CalNex 2010 field study, J.
Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagman,
C. C., and Seinfeld, J. H.: Gas/particle partitioning and secondary
organic aerosol yields, Environ. Sci. Technol., 30, 2580–2585,
1996.
O’Meara, S., Booth, A. M., Barley, M. H., Topping, D., and McFigg-
gans, G.: An assessment of vapour pressure estimation methods,
Pankow, J. F.: An absorption-model of the gas aerosol partitioning
involved in the formation of secondary organic aerosol, Atmos.
Pankow, J. F. and Barsanti, K. C.: The carbon number-polarity grid:
A means to manage the complexity of the mix of organic com-
pounds when modeling atmospheric organic particulate matter,
Pöschl, U. and Shiraiwa, M.: Multiphase chemistry at the
atmosphere-biosphere interface influencing climate and public
Reemtsma, T.: Determination of molecular formulas of natural or-
ganic matter molecules by (ultra-) high-resolution Mass spec-
trometry: status and needs, J. Chromatogr. A, 1216, 3687–3701,
2009.
Riccobono, F., Schoebesberger, S., Scott, C. E., Dommen, J., Ortega,
I. K., Rondo, L., Almeida, J., Amorim, A., Bianchi, F., Breiten-
lechner, M., David, A., Dourad, A., Dunne, E. M., Duplissy,
J., Ehrhart, S., Flagman, R. C., Franchin, A., Hansen, A., Janninen,
H., Kajos, M., Keskinen, H., Kupc, A., Kyrken, A., Kvaschin,
A. N., Laaksonen, A., Lehtipalo, K., Mahmutov, V., Mathot, S.,
Nielsen, T., Onnela, A., Petaja, T., Praplan, A. P., Santos, F.
D., Schallhart, S., Seinfeld, J. H., Sipilä, M., Spracklen, D. V.,
Stozhkov, Y., Stratmann, F., Tome, A., Tsagkogeorgas, G., Vaat-
tovaara, P., Vissanenn, Y., Vrtala, A., Wagner, P. E., Wein gart-
er, E., Wex, H., Wimmel, D., Carslaw, K. S., Curtius, J., Dona-
heur, N. M., Kirbky, J., Kulmala, M., Worsnop, D. R., and Bal-
tensperger, U.: Oxidation products of biogenic emissions con-
tribute to nucleation of atmospheric particles, Science, 344, 717–
721, 2014.
Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petaja, T., Worsnop, D. R.,
Kulmala, M., and Donahue, N. M.: The contribution of organics
to atmospheric nanoparticle growth, Nat. Geosci., 5, 453–458,
2012.
Roldin, P., Eriksson, A. C., Nordin, E. Z., Hermansson, E., Mo-
gensen, D., Rusanen, A., Boy, M., Swietlicki, E., Svennings-
son, B., Zelenyuk, A., and Pagels, J.: Modelling non-equilibrium
secondary organic aerosol formation and evaporation with the
aerosol dynamics, gas- and particle-phase chemistry kinetic mul-
tilayer model ADCHAM, Atmos. Chem. Phys., 14, 7953–7993,
doi:10.5194/acp-14-7953-2014, 2014.
Rollins, A. W., Browne, E. C., Min, K.-E., Pusede, S. E.,
Wooldridge, P. J., Gentner, D. R., Goldstein, A. H., Liu, S., Day,
D. A., Russell, L. M., and Cohen, R. C.: Evidence for NOx con-
rol over nighttime SOA formation, Science, 337, 1210–1212,
2012.
Romero, F. and Oehme, M.: Organosulfates – A new component
of humic-like substances in atmospheric aerosols?, J. Atmos.
Schmitt-Kopplin, P., Gelenčerš, A., Dabek-Zlotorzynska, E., Kiss,
G., Norbert, H., Harir, M., Hong, Y., and Gebefügi, I.: Analysis
of the unresolved organic fraction in atmospheric aerosols with
Ultrahigh-Resolution Mass Spectrometry and Nuclear Magnetic
Resonance Spectroscopy: organosulfates as photochemical smog
Schobesberger, S., Junninne, H., Bianchi, F., Lonn, G., Ehm, M.,
Lehtipalo, K., Dommen, J., Ehrhart, S., Ortega, I. K., Franchin,
A., Nieminen, T., Riccobono, F., Hutterli, M., Duplissy, J.,
Almeida, J., Amorim, A., Breitenlechner, M., Downard, A. J.,
Dunne, E. M., Flagman, R. C., Kajos, M., Keskinen, H., Kirkby,
J., Kupc, A., Kurten, A., Kurten, T., Laaksonen, A., Mathot, S.,
Onnela, A., Praplan, A. P., Rondo, L., Santos, F. D., Schallhart,
S., Schnitzhofer, R., Sipila, M., Tome, A., Tsagkogeorgas, G.,
Veikamaki, H., Wimmer, D., Baltensperger, U., Carslaw, K. S.,
Curtius, J., Hansel, A., Petaja, T., Kulmala, M., Donahue, N. M.,
and Worsnop, D. R.: Molecular understanding of atmospheric
particle formation from sulfuric acid and large oxidized organic
Shiraiwa, M., Pfrang, C., Koop, T., and Pöschl, U.: Kinetic mul-
tilayer model of gas-particle interactions in aerosols and clouds
(KM-GAP): linking condensation, evaporation and chemical re-
actions of organic compounds, oxidants and water, Atmos. Chem.
Shiraiwa, M., Yee, L. D., Schilling, K. A., Loza, C. L., Craven, J.
dynamics reveal particle-phase chemistry in organic aerosol
Shiraiwa, M., Zuend, A., Bertram, A. K., and Seinfeld, J. H.: Gas-
particle partitioning of atmospheric aerosols: interplay of physi-
cal state, non-ideal mixing and morphology, Phys. Chem. Chem.
Shiraiwa, M., Berkeemeier, T., Schilling-Fahnestock, K. A., Se-
infeld, J. H., and Pöschl, U.: Molecular corridors and kineti-
c regimes in the multiphase chemical evolution of sec-
ondary organic aerosol, Atmos. Chem. Phys., 14, 8323–8341,
doi:10.5194/acp-14-8323-2014, 2014.


et al.: Molecular corridors and parameterizations of volatility
