Uptake of Water-soluble Gas-phase Oxidation Products Drives Organic Particulate Pollution in Beijing

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Abstract Despite the recent decrease in pollution events in Chinese urban areas, the World Health Organization air quality guideline values are still exceeded. Observations from monitoring networks show a stronger decrease of organic aerosol directly emitted to the atmosphere relative to secondary organic aerosol (SOA) generated from oxidation processes. Here, the uptake of water-soluble gas-phase oxidation products is reported as a major SOA contribution to particulate pollution in Beijing, triggered by the increase of aerosol liquid water. In pollution episodes, this pathway is enough to explain the increase in SOA mass, with formaldehyde, acetaldehyde, glycolaldehyde, formic acid, and acetic acid alone explaining 15%–25% of the SOA increase. Future mitigation strategies to reduce non-methane volatile organic compound emissions should be considered to reduce organic particulate pollution in China.

Plain Language Summary In the rapidly developing Chinese economy, air pollution from particulate matter (PM) is a major human health risk factor. We show that secondary organic aerosol (SOA) generated from oxidation processes represent 50%–80% of the organic PM in Beijing. We find that non-equilibrium dissolution of C1–C2 carbonyl compounds to particles is a major pathway of SOA formation during pollution events. These compounds are ubiquitous products in the chemical oxidation of hydrocarbons; thus, the reduction of a single volatile organic compound precursor would not reduce the organic PM, but rather a broad reduction of the organic reactivity is required.

1. Introduction

Air pollution exposure is ranked as the fifth-highest human health risk factor globally (Gakidou et al., 2017; Shiraïwa, Li, et al., 2017). Due to rapid economic and industrial developments, air pollution has become one of the largest environmental concerns in China (Chan & Yao, 2008). Although the number of winter pollution episodes have declined in Chinese megacities (Wang et al., 2019), the national and World Health Organization (WHO) air quality guideline values for particulate matter (PM) are still often exceeded (Chan & Yao, 2008; Sun et al., 2016). In the North China Plain, winter haze events are characterized by two stages: the transport stage, where air pollutants are transported under prevailing southerly winds, and a cumulative stage, characterized by a temperature inversion with low wind speed, high relative humidity (>50%) in the lower boundary layer and continuous growth of the mass loading of fine PM, i.e., with diameter smaller than 2.5 μm; PM2.5, (Cai et al., 2017; Chan & Yao, 2008; Wang et al., 2019; Zou et al., 2017).
Currently, in Beijing, the chemical composition of PM$_{2.5}$ is generally dominated by organic aerosol and nitrate, while sulfate has been substantially reduced through successful sulfur dioxide emission reduction regulations (Guo et al., 2014; Huang et al., 2014; Li et al., 2017). Secondary organic aerosol (SOA) originates from either the gas-phase oxidation of volatile organic compounds (VOCs) followed by gas-particle partitioning or particle-phase reactions that oxidize organic aerosol emissions. SOA dominates the organic aerosol mass during haze events (Sun et al., 2016), implying fast SOA chemical formation processes even during wintertime (Lu et al., 2019). In recent years, the model attempts to explain the observed SOA that have initially fallen short by more than 50%. The models were improved only by adding heterogeneous oxidation of particle-phase organic species and irreversible uptake of glyoxal and methylglyoxal (Chen, Zhang, et al., 2017; Han et al., 2016; Tsai et al., 2015; Xing et al., 2019). It is essential to understand which chemical pathways drive SOA formation to elucidate the factors governing the abundance and composition of organic aerosol.

Major SOA formation pathways were investigated during haze events by deploying a super-site of trace-gas and aerosol instrumentation in Huairou, northeast of Beijing, from January 1 to 5 March 2016 in the field campaign BEST-ONE (Beijing winter fine particulate Study – Oxidation, Nucleation, and light Extinctions) (Tan et al., 2018) (Section S1). Measurements in this campaign have shown that gas-phase oxidation reactions of primary pollutants (nitrogen oxides, NO$_x$, and VOCs) with photochemically formed hydroxyl radicals (OH) can be surprisingly fast under low light levels during winter haze conditions (Lu et al., 2018; Tan et al., 2018). Wang et al. (2020) showed that gas-phase chemistry produces sufficient amounts of dinitrogen pentoxide and nitric acid that heterogeneously react to increase particulate nitrate. The process is facilitated by the liquid water content of the aerosol, which grows during haze events partly due to the nitrate enhancement in the particles. Here, we investigate whether the uptake of organic gas-phase oxidation products is also fast and sufficient to explain the growth of the organic particle fraction. We investigate the role of water-soluble gas-phase organic compounds, in particular photochemically formed small aldehydes and acids for SOA formation.

2. Results and Discussion

The observed gas- and particle-phase concentrations of organic and inorganic compounds during the campaign were variable depending to a large extent on the meteorological conditions. Air parcels arriving from Mongolia and Siberia resulted in periods with clean air (44 days of 58), while air parcels that had passed over the downtown Beijing region and were transported to the site at lower wind speeds resulted in haze events (14 days of 58). Figure 1 shows the gas- and particle-phase species that are directly emitted (herein ‘primary’), the gas- and particle-phase organic and inorganic components related to oxidation processes (herein ‘secondary’), and their average concentration enhancements during haze events relative to clean periods. Alkanes and alkenes measured by gas chromatography-mass spectrometry and gas-phase highly oxidized organic molecules (HOMs) measured by nitrate-chemical ionization mass spectrometry were considered primary and secondary, respectively (Sections S2–S5). Different fractions of gas- and particle-phase organics measured by a proton transfer reaction-time of flight-mass spectrometer or a high resolution-time of flight-aerosol mass spectrometer, respectively, were ascribed to primary and secondary through positive matrix factorization (PMF, Section S3–S4). PMF results showed that primary gas-phase mass was related to industry, solvent use and industrial volatile chemical products (McDonald et al., 2018), transportation, biomass burning, and coal combustion (Section S4) while primary particle-phase organic mass was dominated by traffic, biomass burning, and coal combustion (Section S3). Despite winter conditions, high oxidation product concentrations were observed in the gas-phase and SOA accounted for 50%–80% of the organic aerosol mass. SOA was either oxygenated organic aerosol or aqueous-oxygenated organic aerosol related predominantly to photo-oxidation and aqueous processes, respectively (Section S3). Relative humidity increased in every haze event, along with the measured aerosol liquid water (ALW) content (see Section S2.5) and particulate nitrate (Wang et al., 2020). Concentrations of emitted gas-phase pollutants during haze events were 5 times higher than during clean periods and emitted particle-phase pollutants were 2–3 times higher (Figure 1a). Enhancement of SOA, particulate nitrate, and ALW during haze events was greatest during the last haze event with 20, 40, and 18 times higher concentrations, respectively. Gas-phase species attributed to oxidation processes by the PMF data analysis or by their nature as HOMs were 10%–20% of the
total mass of measured VOCs during haze events and their mass concentration was enhanced by a factor of 5. Evidently, secondary oxidation products were a significant fraction of the gas- and particle-phase mass during pollution episodes.

Figure 2 shows the median distribution of non-methane carbon and oxygen mass apportioned to direct emissions and oxidation processes in the gas- and particle-phase for all haze events. Because the particle-phase measurements provide bulk information on the composition of all particle-phase components only (black carbon not included), cumulative gas-phase values were generated to evaluate the overall gas-particle distribution. The cumulative gas-phase carbon mass is calculated by summing HOMs (molecular weight range of 140–390 g mol\(^{-1}\)) and the mass concentrations of organic gas-phase C\(_12\) through C\(_1\) compounds (molecular weight range of 30–160 g mol\(^{-1}\)). The HOMs average chemical formula was determined to be C\(_{7}\)H\(_{10}\)O\(_{7}\)N, with an oxygen to carbon mass concentration ratio of 1.33 (Section S2.3). On average for all haze events, carbon mass in the gas-phase accounted for 89% of the total carbon mass (where total carbon mass is the sum of gas- and particle-phase carbon mass excluding CH\(_4\), CO, and CO\(_2\)), with a median carbon concentration of 90 µg C m\(^{-3}\) during haze events. Only 10 µg C m\(^{-3}\) (median value) of carbon mass was in the particle-phase. Gas-phase carbon mass related to primary emissions (hereby primary carbon)
was 18 times higher than particulate primary carbon mass. Gas-phase carbon mass related to secondary oxidation processes (hereby secondary carbon) was 11% of the total carbon mass and 1.6 times higher than the carbon mass associated with SOA. Detection of secondary carbon is a lower limit due to instrument limitations related to fragmentation and higher loss rates of oxygenated compounds during sampling (Section S6). Gas-phase HOMs comprised less than 1% of the total carbon mass, as expected due to their lower volatility favoring partitioning to the particle-phase (Bianchi et al., 2019). The majority (>90%) of the detected gas-phase oxidized organic mass was from molecules with fewer than six carbon atoms: mainly aldehydes (formaldehyde, acetaldehyde, and glycolaldehyde) and acids (formic acid and acetic acid) (Section S7). For the oxygen mass (Figures 2b), 9 µg O m⁻³ was observed in the gas-phase, 2.5 times higher than that found in the particle-phase (3.5 µg O m⁻³), with 95% of the gas-phase oxygen bound in C1–C5 compounds. The mass concentration ratio of the gas-phase cumulative oxygen to carbon (O:C) was high for HOMs (1.33) and decreased for lower carbon atom compounds (C5–C14). For C1–C4 compounds, O:C was 0.8, and exceeded the particle-phase O:C of 0.5. With the carbon and oxygen mass dominated by gas-phase C1–C2 aldehydes and acids, and the gas-phase O:C exceeding the particle-phase O:C, the SOA mass and particulate O:C can significantly increase in haze episodes when carbonyl compounds efficiently partition to the particle-phase at high ALW.

Changes of gas- and particle-phase primary and secondary pollutants during the last and most severe haze event (haze event 5) were investigated as a case study to address whether uptake of gas-phase secondary oxidation compounds could be a significant pathway to the SOA enhancements during haze events (Figure s13). During these five pollution days, increased pollutant concentrations and ALW were observed when air-parcels originated from the south, and decreased pollutant concentrations and ALW were observed when air-parcels originated from the north. During the period of increasing SOA and ALW and the decrease of gas-phase secondary concentrations after March 1, primary gas- and particle-phase concentrations were relatively constant. The simultaneous increase of ALW by 52 µg m⁻³, SOA by 14 µg m⁻³, and the decrease of secondary gas-phase concentrations by 20 µg m⁻³ indicate that changes in the gas-to-particle partitioning driven by the increase in particulate ALW could be quantitatively sufficient to explain the increase in organic aerosol mass. On the contrary, the relatively stable primary concentrations suggest that the conversion of primary particulate emissions to SOA was not a significant formation pathway for SOA during this period. Reduced formation rates of secondary gas-phase compounds due to increased pollution and decreased photochemical activity are excluded, as Lu et al. (2019) showed that photochemistry and turnover rates of OH-initiated reactions were high during this haze event (3–5 ppb h⁻¹). However, the increase of SOA and ALW started midday and continued during nighttime, in agreement with Sullivan et al. (2016), suggesting that the decrease of gas-phase secondary concentrations during this period could be due to both reduced photochemistry and enhanced water-uptake to the particles. With secondary gas-phase concentrations dominated by C1–C2 aldehydes and acids, these trends suggest that a substantial fraction of the SOA mass could be linked to the effective uptake of these molecules to the particles.

The increase in ALW during haze events can trigger a particle-phase state transition from solid (or semi-solid) to liquid, thereby enhancing the uptake of water-soluble compounds such as aldehydes and acids. These small carbonyl compounds can contribute to the overall SOA mass and increase the O:C ratio not only by particle-uptake but also through heterogeneous reactions and oligomerization (Jang et al., 2002; Kroll et al., 2005). The presence of these carbonyl compounds in the organic aerosol fraction decreases aerosol viscosity and they become even more liquid (Shiraiwa et al., 2011). This can promote positive feedback, in which the dissolution of small carbonyl compounds in the particle-phase increases ALW, which in turn leads to the further dissolution of carbonyls. Wang et al. (2020) showed that a mutual promotion effect between ALW and nitrate formation led to severe nitrate particulate pollution during these haze episodes. Here, we assume a phase separation between organic and inorganic compounds since a liquid-liquid phase separation is very likely to occur when O:C < 0.5 (Song et al., 2012; You et al., 2012), a condition that is met during the entire campaign. The two feedback mechanisms are, therefore, assumed to be disentangled. To address the impact of the organic aerosol phase state transition on the dissolution of small aldehydes and acids, a glass-transition temperature was estimated. This temperature is defined as the gradual and reversible transition of a particle from a hard ‘glassy’ state into a viscous state (Shiraiwa, Li, et al., 2017) (Section S8).
Figure 2. Carbon and oxygen mass distribution in the gas- and particle-phase during haze episodes: (a) the cumulative median mass concentration of carbon atoms in the gas-phase (cumulative increase from left to right, boxed area circle markers) and particle-phase (square markers), and the pie chart of the overall contributions in both phases, and (b) the cumulative mass concentration of oxygen atoms from secondary oxidation processes (left) and the cumulative oxygen to cumulative carbon ratio (O:C) (right). Error bars show the 25th and 75th percentiles. The chemical structure of compounds with one and two carbon atoms, namely formaldehyde, acetaldehyde, glycolaldehyde, formic acid, and acetic acid are shown. These compounds are a major fraction of the carbon and oxygen mass concentration in the gas-phase.

Figure 3 shows the particle-phase-state transition from semi-solid to liquid compared to the ratio of the SOA to the secondary gas-phase mass, defined here as the partitioning ratio. Gas-phase secondary concentrations are the sum of oxygenated compounds with known chemical formulas, predominantly the above-mentioned carbonyl compounds, while the SOA mass is the bulk secondary organic mass with no structural information of the compounds composing the SOA. During haze events, the partitioning ratio increased when transitioning from the particle semi-solid to the liquid phase. For clean periods, the median of the partitioning ratio was 0.2; during haze events, the median increased to 0.6, with values up to 2.5, more than an order of magnitude higher than during clean periods. The longer the particles were in the liquid-phase-state, the higher the SOA mass: 12 µg m\(^{-3}\) in haze event 1, 8.2 µg m\(^{-3}\) in haze event 2, 11.2 µg m\(^{-3}\) in haze event 4, and 18.1 µg m\(^{-3}\) in haze event 5. ALW data were not available for haze event 3, and thus the particle-phase-state could not be determined. Haze event 2 had the lowest ALW concentrations and, therefore, incomplete aqueous-phase chemistry. During haze event 2, photochemical production of SOA could still
be an effective formation pathway, reflected by the higher fraction of oxygenated organic aerosol relative to aqueous-oxygenated organic aerosol as shown in Figure 1 (see Section S3). The simultaneous increase of the partitioning ratio and SOA mass indicate that SOA enhancements during haze events were linked to the dissolution of gas-phase oxidation products.

To examine whether the oxidation of primary organic aerosol is an additional significant source of SOA, the glass-transition temperature was compared to the ratio of secondary to primary organic aerosol mass (Section S9). During the transition to the liquid phase, the secondary to primary organic aerosol ratio remained constant for haze events 1–4; for the last and most severe haze event, a wide range of secondary to primary organic aerosol ratios was observed. However, there was no consistent trend, in contrast to the gas-particle partitioning ratio (Figure 3). This further supports the notion that SOA was predominantly formed via the photochemical oxidation of VOC emissions and subsequent condensation/dissolution rather than particle-phase oxidation of primary organic aerosol.

Figure 4a shows the SOA fraction of organic aerosol versus the ALW for this study and other measurements during haze episodes in Beijing in the summer, winter, and autumn (Li et al., 2020; Xu et al., 2017), as well as in Hong Kong in the summer (Qin et al., 2016). For all studies daily averages during pollution episodes are reported except Li et al. (2020) where only daytime averages are included. Organics were 40%–50% of the PM mass followed by nitrate (14%–22%) and sulfate (20%–25%), in good agreement with this study (Figure S3). The exception is Hong Kong where sulfate contribution was higher (36%). The SOA fraction of organic aerosol increased with ALW for all studies, with a maximum of 80%. SOA dominated the organic aerosol mass from both megacities, while the primary organic aerosol mass fraction was less than 40% at median ALW concentrations higher than 4 µg m⁻³. The mutual increase of the SOA fraction of organic aerosol and the ALW for two Chinese megacities in all seasons extend the findings of this work and show that the dissolution of gas-phase oxidation products triggered by the increased ALW concentrations can be the dominant chemical pathway to SOA formation during haze events in China.

Figure 4b shows the correlation ($R^2 = 0.84$) of the median SOA to the median ALW mass for the different haze events in Beijing observed during winter 2016. Also, the modeled SOA mass is shown assuming that SOA is formed via dissolution following the equation:

$$\rho = H_{K} MW \cdot ALW / \rho_w \cdot C_g,$$

where $\rho$ is the modeled particle-phase mass, $K_H$ is the mean field-derived Henry's law constant, MW is the molecular weight of particulate organics (Section S10), ALW is the measured ALW content assuming organoic molecules can dissolve in the inorganic and organic fraction of the particle and then phase separate, $\rho_w$ is the water density, $C_g$ is the observed gas-phase secondary mass. $K_H$ was calculated by solving Equation 1 for $K_H$ using the observed $\rho$ during haze events. The derived pseudo-$K_H$ was $(2.4 \pm 1.2) \times 10^9$ M atm⁻¹, within the range of field derived effective Henry's law constants for glyoxal (range: $1.8 \times 10^9$ to $6.2 \times 10^9$ M atm⁻¹) and methylglyoxal (range: $1.4 \times 10^9$ to $2.2 \times 10^9$ M atm⁻¹) (Shen et al., 2018). Although glyoxal and methylglyoxal are not reported in this study, they are products of the oxidation of aromatic compounds that can contribute further to the SOA formation (Xing et al., 2019). The match of $K_H$ calculated from measured data in this campaign with the effective Henry's law constant of glyoxal and methylglyoxal suggest that these compounds will partition similarly to the secondary gas-phase species discussed in this study. Therefore, the variability of the gas-phase secondary mass can be used as a surrogate for all gas-phase secondary components that could dissolve to the particle-phase and contribute to SOA formation. By using a $K_H$ of $2.3 \times 10^9$ M atm⁻¹, the modeled SOA agrees with the median of the observed SOA mass within 25% for all haze episodes with the exception of haze event 2 characterized by incomplete aqueous-phase chemistry, where the model is a factor of 2 lower than measurements.

The reasonable prediction of the SOA mass based on the ALW and the concentration of secondary gas-phase compounds is further evidence that the uptake of water-soluble gas-phase oxidation products is the driving pathway for SOA formation. As highlighted above, the majority of the detected secondary gas-phase species were carbonyl compounds, namely formaldehyde, acetaldehyde, glycolaldehyde, formic acid, and acetic acid. Analogous to the above bulk analysis, Equation 1 was used to identify the contribution to SOA
for each of these compounds (Section S10) since particle-phase measurements were limited to the bulk mass concentration. The effective Henry’s law constant that was previously derived using direct partitioning measurements of acetaldehyde and formaldehyde in China (Shen et al., 2018), and the average effective Henry’s law constant for formic and acetic acids measured in the United States (Nah et al., 2018) were used to determine their contribution to SOA. Acetic acid and glycolaldehyde were detected at the same mass and therefore not quantitatively separated (Section S7). The effective Henry’s law constant of glycolaldehyde is currently unknown and is here considered to be the same as that for acetic acid.

Figure 4c shows the contribution of carbonyl compounds to SOA depending on the ALW mass. A correlation $R^2$ of 0.80 is found between modeled carbonyl SOA versus the ALW mass. The sum of the five carbonyl compounds explained up to 15%–25% of the total SOA mass when ALW was higher than 8 $\mu g m^{-3}$. During
clean periods, when the ALW mass was low, these compounds accounted for less than 5% of the SOA mass. Acetic acid/glycolaldehyde was the most abundant carbonyl compounds (50%), followed by formic acid (30%), formaldehyde (15%), and acetaldehyde (5%).

Evidently, SOA formation during haze events in Chinese megacities depends on the oxidation of pollutants (NO\textsubscript{x}, VOCs) in the gas-phase and the subsequent uptake into aqueous aerosol particles. Wang et al. (2020) showed that increases in oxidized nitrogen compounds and ALW led to an increase in particulate nitrate pollution. Here, the same feedback mechanism between oxygenated VOCs (aldehydes, organic acids) and ALW is shown for SOA formation in haze episodes. Although a liquid-liquid phase separation of the inorganic and organic fraction of a particle is very likely to occur at O:C < 0.5 (Song et al., 2012; You et al., 2012), a condition met in this campaign, higher O:C values have been reported during haze episodes in Beijing (Xu et al., 2017). Since the ‘organic’ ALW accounted for 20% and the remaining 80% was associated with the inorganic aerosol fraction (Section S8), the dissolution of organic molecules to inorganic liquid particles and latter organic-inorganic phase-separation cannot be excluded. The two feedback mechanisms could, therefore, influence one another with the growth of the organic particle fraction affected by the emissions and oxidation of NO\textsubscript{x} in the gas-phase, which after conversion into particulate NO\textsubscript{3}\textsuperscript{−} lead to an increase of the ALW.

To summarize, during haze events increased concentration of nitrate, SOA, and ALW is evident. Anticorrelations between the gas-phase secondary mass and SOA coincide with a particle-phase-state transition from semi-solid to liquid particles and promote efficient gas-to-particle partitioning. Due to the lack of a detailed particle-phase chemical specification we use a simple thermodynamic model to predict SOA using the observed gas-phase secondary mass. Small aldehydes and acids are a large fraction of the gas-phase secondary mass and can explain up to 20% of the SOA mass in haze episodes. The remaining SOA mass could be related to the uptake of glyoxal, methylglyoxal, other aldehydes, e.g., propionaldehyde (Shen et al., 2018), as well as compounds with high carbon number that will follow the absorptive partitioning pathway to the organic-phase (Jathar et al., 2016). Future studies performing detailed chemical speciation of organic aerosol will provide further insights into the heterogeneous processes to SOA formation. Although PM\textsubscript{2.5} emissions have been successfully reduced recently in China, concentrations of non-methane VOCs have not declined (Li et al., 2019; Zheng et al., 2018). Measures to reduce anthropogenic VOC emissions will be essential to reduce SOA formation during haze events. Because formaldehyde and acetaldehyde are carcinogenic and genotoxic, it should be noted that these compounds alone could increase the exposure to toxicity from inhalation (IARC, 2012; Pang & Lewis, 2011; Park et al., 2018). The dissolution of smaller acids will further affect the acidity of the particles that have been linked to adverse respiratory effects (Miao et al., 2019;
Pozzer et al., 2017; Thurston et al., 1994; Weber et al., 2016). Due to the enhanced uptake of such carbonyl compounds in conditions where ALW is high, the toxicity of SOA might be significantly higher than previously assumed. Furthermore, the reported small aldehydes are products in the chemical oxidation of almost any atmospheric hydrocarbon. Thus, the reduction of a single, specific precursor VOC would not reduce the organic haze fraction more than any other, but rather a broad reduction of the organic reactivity is required. This is in support of recent findings of unexpected haze episodes in China during the COVID-19 outbreak despite the absence of motor vehicle traffic and the suspension of manufacturing (Le et al., 2020). With the dominant fraction (~70%) of VOC primary emissions related to the industry, solvent use linked to industrial volatile chemical products (McDonald et al., 2018), and transportation (Figure 1 and Section S4) this work emphasizes the necessity of regulating industrial and transportation VOC emissions to effectively reduce organic particulate pollution in Beijing and other Asian megacities.

Conflict of Interests

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

https://doi.org/10.26165/JUELICH-DATA/BQOLQF.
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