A Closure Study of Secondary Organic Aerosol Estimation at an Urban Site of Yangtze River Delta, China

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Abstract: Secondary organic aerosols (SOA) are crucial components of ambient particulate matters. However, their composition and formation mechanisms remain uncertain. To investigate the SOA formation and evaluate various SOA estimation approaches, a comprehensive measurement was conducted at an urban site, Changzhou, in Yangtze River Delta (YRD) region. 98 kinds of volatile organic compounds (VOCs) were measured by an online gas chromatography-mass spectrometer/flame ionization detector (GC-MS/FID). Non-refractory submicron particulate matters (NR-PM 1) were measured by an Aerodyne Aerosol Chemical Speciation Monitor (ACSM). Both bottom-up approaches, i.e., VOCs oxidation yield method, and top-down approaches, i.e., elemental carbon (EC) tracer method and ACSM, combined with positive matrix factorization (PMF) method, were utilized to estimate SOA. ACSM-PMF method estimated the highest SOA concentration, followed by EC tracer method. SOA from VOCs oxidation yield method accounted for 43.2 ± 41.9% of that from EC tracer method, suggesting the existence of missing SOA precursors, e.g., semivolatile organic compounds. The influencing factors of SOA formation were investigated and a good correlation of SOA with odd oxygen rather than aerosol liquid water content was found, suggesting the importance of photochemical formation of SOA.

Keywords: secondary organic aerosols; closure study; EC tracer method; yield method; PMF

1. Introduction

Atmospheric fine particulate matter (PM 2.5) has been long studied due to its close relationship with human health, air quality, and climate change [1–3]. Organic aerosol (OA) consists of primary organic aerosol (POA) and secondary organic aerosol (SOA). Compared with POA, SOA has a percentage of more than 50% in some environments [4,5]. However, the formation mechanisms, sources, and estimations of SOA remain largely uncertain [6–8]. Therefore, more study on SOA is necessary.

Various approaches were used to estimate SOA, including top-down method, e.g., the tracer-yield method [9], the nonprimary organic carbon method (the receptor model) [10,11], the water-soluble organic carbon (WSOC) method [12,13], the elemental carbon (EC) tracer method [3,14], and bottom-up method, e.g., volatile organic compounds (VOCs) oxidation yield method [15–17]. A few studies have explored the discrepancies between different estimation approaches [18,19], but there are still many uncertainties. Previous studies...
reported the discrepancies between the EC tracer method and the VOCs oxidation method and found that the explained share varies among different climatic and environmental conditions [16,17].

In recent years, the Yangtze River Delta (YRD) region develops rapidly due to fast urbanization and industrialization. This fast development leads to severe and complex air pollution, which is featured as secondary pollution [20]. SOA contributed up to ~70% of OA in the YRD region [21], so it is important to understand the SOA formation mechanism to control PM\textsubscript{2.5} in the YRD region. Changzhou is situated at the west of the YRD region. As the receptor region, the air quality of Changzhou was significantly influenced by the transport from the “Nanjing-Shanghai” riverside industrial belt, which emitted large amounts of VOCs. As a result, it is significant that we should comprehend the SOA formation in Changzhou to characterize the secondary aerosol formation in the YRD region.

In the present study, organic aerosols, non-refractory submicron particulate matter (NR-PM\textsubscript{1}), and ambient VOCs were measured from 2 November 2020 to 23 November 2020 simultaneously. Both bottom-up method, i.e., the VOCs oxidation method, and top-down method, i.e., EC tracer method, and Aerosol Chemical Speciation Monitor (ACSM)-Positive Matrix Factorization (PMF) method were utilized to estimate SOA. This work aims to: (1) provide basic information on particle concentrations and chemical compositions; (2) evaluate the closure of SOA formation through different approaches; (3) explore the impact factors for SOA characteristics in Changzhou.

2. Materials and Methods

2.1. Sampling Site

All the measurements were conducted at the Changzhou environmental monitoring center site (31.76°N, 119.96°E), which is an urban site situated in the northeast of Changzhou City, from 2 November to 23 November 2020. The sampling site was on the rooftop, ~20 m above the ground (see Figure S1 in Supplementary Materials). The Changzhou site is located in the downwind of the YRD region, which can be regarded as a regional receptor site. The air pollution at the Changzhou site reflects the regional pollution characteristics of the YRD region, which can also be affected by local emissions.

2.2. Sampling and Chemical Analysis

During the measurement, an online gas chromatography coupled with a mass spectrometer detector and a flame ionization detector (GC-MS/FID, Tianhong, China) was deployed to measure ambient VOCs, including 56 hydrocarbons (alkanes from C\textsubscript{2} to C\textsubscript{11}, acetylene, alkenes, and aromatics), 14 oxygenated VOCs (OVOCs), and 28 halogenated hydrocarbons. Details are described in previous works [22]. All SOA species measured in this study are shown in Table S1.

The mass concentrations of NR-PM\textsubscript{1} chemical composition were measured by an Aerosol Chemical Speciation Monitor (ACSM), with a time resolution of 15 min. The detailed operations of ACSM were described in previous work [23,24]. Briefly, the sampling flow rate, ionization efficiency (IE), and relative ionization efficiencies (RIE) were calibrated at the beginning and end of the campaign. The mass concentrations were analyzed with ACSM standard data analysis software (v 1.5.10.0). The composition-dependent collection efficiency (CE) used in this study was around 0.5, as recommended by Middlebrook, et al. [25].

Hourly organic carbon (OC) and EC mass concentrations were measured by an in situ semicontinuous OC/EC analyzer (Sunset Laboratory Inc., Tigard, OR, USA), which was equipped with a PM\textsubscript{2.5} cyclone. Improved ACE-Asia (NIOSH 5040) method for temperature protocol was used to collect ambient aerosol. The area of the quartz filter was 1.03 cm\textsuperscript{2}, and the flow rate was 8 L/min. Details of the measurement were described in other works [26,27]. The Pearson correlation coefficient between OA measured by ACSM and OC measured by the OC/EC analyzer is 0.87, with a p-value of 2.5 × 10\textsuperscript{-46}. 
Gaseous species (O$_3$, NO$_2$, SO$_2$, and CO) were measured by standard gas analyzers (Thermo Fischer Inc, Waltham, MA, USA). The PM$_{2.5}$ mass was recorded by β-ray device (Thermo Scientific, Colorado Springs, CO, USA). The water-soluble inorganic ions (SO$_4^{2-}$, Cl$^-$, NO$_3^-$, Mg$^{2+}$, Ca$^{2+}$, NH$_4^+$, K$^+$, and Na$^+$) were measured by a Monitor for AeRosols and GAses (MARGA). Details of the measurement were described in a previous study [28].

In this study, Aerosol liquid water contents (ALWC) were estimated from the ISORROPIA-II model, based on the water-soluble inorganic ions measured by MARGA [29]. The simulation model was forward mode and metastable state. The forward mode assumes that the total concentrations of precursors are solved for this model, thus it is a relatively closed system. Metastable state means that the aerosols were composed only of a supersaturated aqueous phase. In our study, the concentrations of Na$^+$, SO$_4^{2-}$, NH$_4^+$, NO$_3^-$, Cl$^-$, Ca$^{2+}$, K$^+$, Mg$^{2+}$, relative humidity, and temperature were used to calculate the concentration of ALWC.

2.3. Estimation of Secondary Organic Aerosols

2.3.1. Bottom-Up Method to Estimate SOA

Bottom-up method, i.e., VOCs oxidation yield method, was used to estimate SOA. In Equation (1), it is assumed that OH is the only oxidant for the loss of ambient VOCs [15,22]. Besides, if two VOC species are emitted by similar emission sources and have discrepant atmospheric reactivity, the measured ratio of these two VOC species could describe the atmospheric photochemical age ($\Delta$t), such as ethylbenzene to m, p-xylene (Equation (2)) [22,30].

$$VOC_{i,c} = VOC_{i,t} \times (\exp (k_i[OH] \Delta t) - 1)$$  (1)

where $VOC_{i,c}$ and $VOC_{i,t}$ are the consumption and measured concentration of VOC for species $i$, respectively. $k_i$ is the reaction rate constant of VOC with OH radicals. [OH] is the concentration of OH radicals, which is not necessary for calculating VOC considering that only the OH exposure (product of [OH] and $\Delta$t) is required in Equation (1).

$$EB\text{ and } MP\text{ represent ethylbenzene and m, p-xylene, respectively. } k_{EB} \text{ and } k_{MP} \text{ are the reaction rate constants of ethylbenzene and m, p-xylene with OH radical, with value of } 7.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ and } 18.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \text{ respectively [31].}$$

\[
\frac{(k_{EB} - k_{MP})[OH]\Delta t}{ln(\frac{|EB|}{|MP|}_{t=0}) - ln(\frac{|EB|}{|MP|}_{t})}
\]

(2)

In this study, ethylbenzene and m/p-xylene presented a better correlation (0.97) than benzene and toluene (0.26), for which we used the measured concentration ratios of $EB$ to $MP$ to estimate the photochemical age (Figure S2). The estimation of photochemical age by $EB$/MP ratio method has been proved to be suitable in the YRD region in previous studies [16,17]. We used the lowest 5% value of the measured ratio of $EB$ to $MP$ to represent the $\langle [EB]/[MP] \rangle |_{t=0}$. As shown in Figure S3, the initial ratio of $EB$ to $MP$ is 0.41.

We estimated the photochemical consumption ($C_{i,t}$) of total VOCs by Equations (1) and (2), which depends on the measured concentration ($C_{i,t}$), reaction rate constant, and OH exposure for given VOCs. In Equation (3), the photochemical consumption of total VOCs was used to calculate the formation of SOA$_{VOC}$ considering that VOCs are significant precursors of SOA [11,16,32].

$$SOA_{VOC} = \sum_i VOC_{i,c} \times Y_i$$  (3)

where SOA$_{VOC}$ are the concentration of SOA measured from VOCs oxidation method; $VOC_{i,c}$ was mentioned above; $Y_i$ is the SOA yield of VOC$_i$, which is determined from chamber studies. The SOA yield are nearly zero for short-chain alkanes as well as short-chain alkenes, while being relatively higher for aromatics. Previous studies pointed out that the concentration of NO$_x$ generally appears an opposite trend with SOA yields for most
VOCs, especially hydrocarbons and aromatics [33]. In this work, SOA yields on high-NO\textsubscript{x} conditions were applied. The reaction rate constants and SOA yields for each VOC species in our previous work [17].

2.3.2. Top-Down Method to Estimate SOA

Two top-down methods were used to estimate SOA, i.e., EC tracer method, and ACSM-PMF method.

EC is widely used to estimate the concentration of primary organic carbon (POC), due to its chemical inertness [34], for which it assumes that both EC and POC are mostly emitted by combustion processes [14]. The most important hypothesizes of this method are that the ratio of primary OC to EC, i.e., (OC/EC\textsubscript{pri}) is assumed to be constant, and POC comes from the same combustion source with EC. SOC was estimated by Equations as follows:

\[
POC = (OC/EC)_{pri} \times EC + OC_{non} \tag{4}
\]

\[
SOC = OC - POC \tag{5}
\]

where the OC\textsubscript{non} is the regional background carbon, which is usually interpreted as the POC concentration that didn’t involve the combustion process [35].

The only undetermined variable in Equations (4) and (5) is (OC/EC)\textsubscript{pri}. In previous studies, many methods were used to determine the (OC/EC)\textsubscript{pri}, aimed to lower the influence of photochemical activity i.e., SOA formation. These estimations include: focusing on the periods with high levels of CO and NO\textsubscript{x} that co-emitted with POA and EC [36], using the data only in the early morning to ensure a low level of solar radiation intensity [37,38], using minimum R squared method to determine the ratio when the R\textsuperscript{2} between SOC and EC was the lowest [14,39].

In our study, the (OC/EC)\textsubscript{pri} ratio was determined by the slope of a regression line between OC and EC. Only the lowest 0–10% percentile concentration of EC was considered to be from primary emission and thus was used in the regression. As shown in Figure S4, the (OC/EC)\textsubscript{pri} was 2.65 in this observation. The correlation was high with R\textsuperscript{2} = 0.94.

ACSM data combined with receptor model e.g., PMF is often used to measure and apportion OA into POA from various sources and SOA. Positive matrix factorization 2.exe (PMF2.exe) algorithm [40] and the PMF Evaluation Toolkit version 2.08D [41] were performed on OA mass spectral matrix to determine the potential sources. PMF factors were evaluated following the procedures detailed in Zhang, et al. [42]). Two OA factors including one primary OA, i.e., a hydrocarbon-like OA (HOA), and one secondary OA, i.e., an oxygenated OA (OOA), were identified during the whole observation period. The OOA is the so-called SOA\textsubscript{ACSM} in this study. Details of the PMF approach for SOA estimation are described in other works [43].

3. Results

3.1. Overview of the Meteorology and Air Pollutants

The time series of the meteorological conditions, chemical compositions in PM\textsubscript{1}, measured VOCs, and gaseous pollutants are shown in Figure 1. During the measurement, atmospheric conditions were stagnant with a wind speed of 1.4 ± 0.6 m/s, and the wind was mainly from the south.

The concentrations of NO\textsubscript{x} and CO were 30 ± 18 ppbv and 0.68 ± 0.62 ppmv, respectively. The concentration of PM\textsubscript{2.5} was 35 ± 20 µg/m\textsuperscript{3}, varying from 2 µg/m\textsuperscript{3} to 122 µg/m\textsuperscript{3}. The concentration of PM\textsubscript{1} was 32 ± 17 µg/m\textsuperscript{3}, accounting for 91% of the total PM\textsubscript{2.5} mass, among which OA was the main contributor (46.1%), followed by nitrate (26.3%), sulfate (13.9%), ammonium (12.2%), and chloride (1.5%).
atmospheric conditions were stagnant with a wind speed of 1.4 ± 0.6 m/s, and the wind was mainly from the south.

Figure 1. Time series of (a) wind direction (WD) and wind speed (WS); (b) relate humidity (RH) and temperature; (c) PM$_{1}$ compositions; (d) O$_3$, NO$_x$, and CO; (e) measured VOCs.

The concentration of measured VOCs was on average 44.2 ± 22.7 ppbv and alkanes were predominant (35.5%), followed by OVOCs (23.4%), halogenated hydrocarbons (19.3%), aromatics (12.2%), alkenes (6.0%), alkynes (3.5%), and biogenic volatile organic compounds (BVOCs, 0.1%). The concentrations of measured VOCs are listed in Table S1.

The concentrations of measured VOCs, EC, and OC are exhibited in Table 1. The pollution level of this site is comparable to that of Beijing (BNU site). Because of its location in the “Nanjing-Shanghai” riverside industrial belt and downwind zone, the Changzhou site is a regional receptor site in the YRD region. The Changzhou site was found to have a higher concentration of VOCs while comparable concentration of carbonaceous aerosols in the YRD region, indicating that Changzhou was influenced distinctly by industrial transport.

Table 1. Comparisons of measured VOCs and carbonaceous aerosols with other sites in the YRD region.

<table>
<thead>
<tr>
<th>Site</th>
<th>Station Types</th>
<th>Date</th>
<th>OC ($\mu$g/m$^3$)</th>
<th>EC ($\mu$g/m$^3$)</th>
<th>VOCs (ppbv)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Changzhou</td>
<td>U YRD</td>
<td>2020.11</td>
<td>7.4</td>
<td>2.2</td>
<td>44.2</td>
<td>This Study</td>
</tr>
<tr>
<td>Pudong</td>
<td>U, YRD</td>
<td>2017.7</td>
<td>n.a.</td>
<td>n.a.</td>
<td>22.7</td>
<td>[44]</td>
</tr>
<tr>
<td>Jiangsu AES</td>
<td>U, YRD</td>
<td>2016</td>
<td>n.a.</td>
<td>n.a.</td>
<td>25.7</td>
<td>[45]</td>
</tr>
<tr>
<td>Shanghai AES</td>
<td>U, YRD</td>
<td>2013.8</td>
<td>11</td>
<td>1.9</td>
<td>60</td>
<td>[16]</td>
</tr>
<tr>
<td>Pudong</td>
<td>U, YRD</td>
<td>2019.12–2020.2</td>
<td>5.17</td>
<td>1.02</td>
<td>14.6</td>
<td>[46]</td>
</tr>
<tr>
<td>Fudan University</td>
<td>U, YRD</td>
<td>2013–2014</td>
<td>8.4</td>
<td>3.1</td>
<td>n.a.</td>
<td>[47]</td>
</tr>
<tr>
<td>Nanjing University</td>
<td>U, YRD</td>
<td>2013–2015</td>
<td>10</td>
<td>5.2</td>
<td>n.a.</td>
<td>[48]</td>
</tr>
<tr>
<td>Shanghai</td>
<td>U, YRD</td>
<td>2012–2014</td>
<td>10.7</td>
<td>2</td>
<td>n.a.</td>
<td>[49]</td>
</tr>
<tr>
<td>Taizhou</td>
<td>R, YRD</td>
<td>2018.5–6</td>
<td>7.5</td>
<td>1.4</td>
<td>16</td>
<td>[17]</td>
</tr>
<tr>
<td>Nanjing University</td>
<td>R, YRD</td>
<td>2018.6–8</td>
<td>n.a.</td>
<td>n.a.</td>
<td>33.9</td>
<td>[21]</td>
</tr>
<tr>
<td>Beijing Normal University</td>
<td>U, BTH</td>
<td>2016</td>
<td>n.a.</td>
<td>n.a.</td>
<td>44.0</td>
<td>[50]</td>
</tr>
</tbody>
</table>

n.a.: not available. AES: Academy of Environmental Science; YRD: Yangtze River Delta; BTH: Beijing-Tianjin-Hebei region; U: Urban site; R: Rural site.
3.2. Diurnal Variation of VOCs and Particle Chemical Composition

Diurnal variations of carbonaceous aerosols and NR-PM$_1$ are shown in Figure 2. The concentrations of EC and OC revealed the peak at dusk, varying on a large scale, which might be driven by the lower boundary layer and increment in emissions. Due to the high OH exposure in the noon, the OC/EC ratio showed a peak from 12:00 to 14:00, which might be explained by the formation of SOA. The peak of the OC/EC ratio is consistent with the peak of SOA$_{VOC}$ diurnal variation in Figure 3.

![Figure 2. The diurnal variation of (a) non-refractory submicron particulate matter (NR-PM$_1$); (b) the ratio of OC to EC; (c) OC; (d) EC. The pink area represents the 95% confidence interval.](image)

The diurnal variation of NR-PM$_1$ also presented a bimodal pattern. However, the composition of NR-PM$_1$ varied little in the morning while the OA component went up suddenly at dusk, which might be a piece of evidence that the high pollution was caused by POA and SOA in the morning and at dusk, respectively.

The diurnal variation of measured VOCs other than BVOCs, the ratio of [EB] to [MP], SOA estimated from ACSM data (SOA$_{ACSM}$), and SOA estimated by VOC oxidation (SOA$_{VOC}$) are shown in Figure 3.

The diurnal patterns of measured VOCs showed higher patterns from noon to evening, while the diurnal patterns of SOA$_{ACSM}$ showed a bimodal distribution. Vehicle emissions are the important source of VOCs emission in Changzhou according to source apportionment. Traffic emissions always showed higher peaks during the morning and evening rush hours. The peak of the bimodal distribution of SOA$_{ACSM}$ trailed behind the peak of vehicle emissions in the morning and evening, which may mean that VOCs oxidized into SOA after a time of photochemical reaction. The diurnal trend of vehicle emissions may be one of the reasons for the bimodal distribution of SOA$_{ACSM}$. The similar SOA diurnal patterns also occurred in other regions [51,52]. It should be noted that some major SOA precursors, e.g., styrene and isoprene, revealed distinct patterns. Industrial emissions are
regarded as the major source of styrene in the urban atmosphere [53], while industrial emissions and vehicle emissions are also significant sources of isoprene besides biogenic emissions [54–56]. The concentration of VOCs, which might be derived from industrial emissions in Changzhou, increased significantly at night due to the lower boundary layer and an increment in emissions. As a result, the formation of SOA reached its peak in the evening. Source apportionment using positive matrix factorization (PMF) was performed to further comprehend the sources of the predominant VOC species in Figure S5. In this study, 73 VOC species were utilized as inputs to the PMF model. Six source factors, including industrial, secondary formation, vehicle emissions, gasoline volatilization, biomass burning, and solvent volatilization, were identified by tracers in this observation. Details of this model were described in other works [57,58]. For styrene, the main contributor was from solvent usage sources (47%), followed by industrial (27%). For isoprene, the main contribution was industrial (29%), followed by secondary formation (28%), and vehicle emissions (20%). This indicated that industrial sources might be the crucial factor of primary VOC emissions.

Besides, though the relative diurnal trend of \( E/X \) varied significantly due to the variation of solar radiation, the absolute diurnal variation amount of \( E/X \) varied finitely (0.5 to 0.6 on average). The hydroxyl radical (OH) exposure in the observation varied finitely, so that the relative SOA formation potential at noon was not so high compared with other places. This might be another reason for the bimodal pattern of SOA formation.

4. Discussion

4.1. Closure Study on SOA Estimation from Different Approaches

4.1.1. Comparison of SOA Estimated from Different Approaches

The concentration of \( \text{SOA}_{\text{VOC}} \) estimated by VOC oxidation was \( 1.3 \pm 1.2 \, \mu g/m^3 \) on average during the whole period. In this work, 1.8 was used as the specific value...
of SOA to secondary organic carbon (SOC) [16,32,59]. The average SOC\textsubscript{VOC} was only 0.72 ± 0.66 µg/m\textsuperscript{3}, which was fairly lower than other YRD regions [16,17]. Styrene and isoprene contributed most to SOA, with contributions of 54.9% and 14.6%, respectively. However, their variations were contrary to those of the OH exposure (Figure S6). Generally, the SOA from anthropogenic VOCs oxidation, i.e., aromatics, was dominant, accounting for 73.6%. However, this percentage is lower than in other YRD regions [16,17].

The SOA concentration estimated by EC tracer method (SOA\textsubscript{tracer}) was 3.2 ± 2.1 µg/m\textsuperscript{3} on average during the whole period. The value of (OC/EC\textsubscript{pri}) in our study was comparable with some studies in YRD region cities [17,48], but a bit higher than some other studies [47]. The SOC concentration is lower than that calculated from other studies, and the SOC/OC ratio on average was only 28% ± 14%, while SOC accounted for approximately 50% of OC in other studies [17,60]. The concentration of SOA (SOA\textsubscript{ACSM}) and POA estimated from ACSM data was 12.1 ± 6.6 µg/m\textsuperscript{3} and 2.6 ± 2.7 µg/m\textsuperscript{3} on average. The ratio of SOA\textsubscript{ACSM} to OA was on average 83% ± 8%, which was comparable with other studies [5].

Here we compare the SOA concentration estimated from VOCs oxidation yield method (SOA\textsubscript{VOC}), EC tracer method (SOA\textsubscript{tracer}), and ACSM-PMF (SOA\textsubscript{ACSM}) (shown in Figure 4). The results showed that SOA\textsubscript{VOC} and SOA\textsubscript{ACSM}, SOA\textsubscript{tracer} and SOA\textsubscript{ACSM}, correlated significantly (p < 0.001). The SOA\textsubscript{VOC} also correlated with SOA\textsubscript{tracer}, but with lower correlation coefficient.

The low values of correlation coefficients mean that the linear correlations between the various methods are not obvious. Multiple reasons could cause this discrepancy. For instance, the compositions of PM\textsubscript{1} were measured by ACSM while the SOA\textsubscript{tracer} and SOA\textsubscript{VOC} were not size-resolved. The selection of yields for SOA\textsubscript{VOC} utilized in the yield method could also introduce uncertainties. However, the p-values of the Pearson correlation analysis were fairly low, which means that there is still a positive consistency but not a linear consistency of the SOA time series.

To explore the contributions of gas-phase VOCs oxidation to SOA, a closure study was conducted by comparing SOA\textsubscript{VOC} from bottom-up VOCs oxidation yield method with SOA estimated from top-down method. SOA\textsubscript{VOC} derived from VOCs oxidation could only explain 10.9% ± 8.6% of SOA\textsubscript{ACSM} and 43.2% ± 41.9% of SOA\textsubscript{tracer}. Missing precursors are the main reason for SOA\textsubscript{VOC} underestimation.

The ACSM-PMF method estimated the highest concentration of SOA. It is interesting to note that the SOA\textsubscript{ACSM} concentration was much higher than SOA\textsubscript{VOC} and SOA\textsubscript{tracer} at noon and in the early evening. This discrepancy may be due to the fact that part of the COA was apportioned to the SOA factor.

Underestimation of SOA was found in VOCs oxidation yield method. Previous studies found similar results, that the SOA\textsubscript{VOC} accounted for only 25–40% of top-down method SOA [17,32]. In this work, the diurnal pattern of SOA implied that SOA\textsubscript{VOC} differs most from SOA\textsubscript{ACSM} 1–2 h after the morning and evening peak-hour on vehicles. It may be a piece of evidence that SOA formation is highly related to the oxidation of IVOCs from urban cooking and vehicular sources.

4.1.2. Influencing Factors of SOA Formation

The photochemical oxidation of VOCs is vital in SOA formation. Odd oxygen (O\textsubscript{x}, O\textsubscript{3} + NO\textsubscript{2}) has been widely used to represent the photochemical oxidation capacity [4]. Recent studies have found that the aqueous-phase reactions are also important pathways for SOA formation [61]. ALWC provides reaction interfaces and sites for liquid-phase reactions, for which the capability of aqueous-phase reactions could be represented by ALWC [9].

SOA was measured by three approaches, i.e., VOC oxidation, EC tracer method, and receptor model. Considering that there was distinct underestimation and overestimation from VOCs oxidation method and receptor model respectively, SOA\textsubscript{tracer} was applied as a function of O\textsubscript{x} and ALWC to investigate the impacts of photochemical oxidation reactions and aqueous-phase processing on SOA formation, as shown in Figure 5.
Figure 4. The correlation patterns of (a) \( \text{SOA}_{\text{VOC}} \) and \( \text{SOA}_{\text{ACSM}} \); (b) \( \text{SOA}_{\text{tracer}} \), \( \text{SOA}_{\text{ACSM}} \), and the frequency distribution histogram of each method.

\( \text{SOA}_{\text{tracer}} \) appeared an obvious same trend with \( O_x \) when \( O_x \) was less than 100 ppbv, indicating that photochemical oxidation reactions might contribute much to SOA formation. Figure 5a shows an obviously positive correlation between \( O_x \left( O_3 + NO_2 \right) \) and SOA with a \( p \)-value of \( 1.6 \times 10^{-208} \), indicating that \( O_3 \) was statistically correlated with SOA. This could be due to the high oxidation capacity of OH produced by \( O_3 \), which has an indirect effect on SOA, primarily through the generation of OH radicals, increasing the oxidation of POA.

During the observation, no significant same trend was found between \( \text{SOA}_{\text{tracer}} \) and ALWC in Figure 5b. The correlation coefficients between ALWC, \( \text{SOA}_{\text{ACSM}} \), \( \text{SOA}_{\text{tracer}} \), and \( \text{SOA}_{\text{VOC}} \) are 0.37, −0.30, and 0.04, respectively. Previous studies pointed out that a high concentration of ALWC would enhance the secondary formation \([62,63]\). This discrepancy might be caused by the negative correlation between \( O_x \) and ALWC and the relatively low concentration of ALWC compared to other regions. In our observation, the concentration of ALWC was mainly 0–30 \( \mu g/m^3 \). In other regions where the aqueous-phase processing dominates, the concentrations of ALWC were always from 200–500 \( \mu g/m^3 \) \([64,65]\). In Figure 5c, high \( \text{SOA}_{\text{tracer}} \) concentrations were observed in higher concentration levels of either ALWC or \( O_x \), indicating that both photochemical oxidation reactions and aqueous-phase processing would enhance the formation of SOA. However, high concentrations of \( \text{SOA}_{\text{tracer}} \) occurred more frequently with the high level of \( O_x \) than with the high level of ALWC. In general, photochemical processing was a more critical factor in SOA formation.
compared with aqueous-phase reactions in Changzhou, so the positive correlation could be observed only between \( O_x \) and SOA\(_{\text{tracer}}\).

**Figure 5.** The SOA\(_{\text{tracer}}\) as a function of (a) Odd oxygen (\( O_x \), bins of 20 ppbv) and (b) aerosol liquid water contents (ALWC, bins of 10 \( \mu \)g/m\(^3\)). Box: 25% and 75% percentile. Whisker: 10% and 90% percentile. (c) Scatterplot of ALWC and Odd oxygen.

\[ \text{(c) Scatterplot of ALWC and Odd oxygen.} \]

### 4.2. Uncertainty Analysis of Each Method

In our study, three approaches were used for SOA formation, and all of those methods presented various estimation biases, interfering with the closure of SOA formation. An uncertainty analysis of each method was performed accordingly.

The underestimation of SOA\(_{\text{VOC}}\) is mainly caused by the missing precursors. Only the measured VOCs, not all precursors, were used to estimate SOA due to the restriction on measurements and estimation methods. Intermediate volatility organic compounds (IVOCs), especially polycyclic aromatic hydrocarbons (PAHs), have been confirmed to be potentially large sources of urban SOA [66]. Previous studies revealed that semi-volatile organic compounds (SVOCs) oxidation could also account for a high percentage of SOA formation [67]. For instance, a study added two SVOCs, i.e., naphthalene and methylnaphthalene, and explained 10.2% more of the SOA formation [17]. Another reason for the uncertainty of SOA estimation is that the yields for VOCs to SOA which we assume are constant, are, in fact, changing. Recent studies also found that yields could be reduced by the mixture of VOCs [68,69]. The intermediate products reacting with each other to generate high volatility products may be one of the reasons. Another reason for the underestimation of SOA\(_{\text{VOC}}\) is that the aqueous-phase reactions were proved to be a significant process for SOA formation [63,70], which is not included in the VOCs oxidation yield method.
Besides, the process of VOCs oxidation with other oxidants is also not included in the yield approach.

The EC tracer method is restricted by the assumption that POC is nonvolatile and nonreactive, which has been proved improperly [67]. From the bimodal pattern of SOA diurnal variation and the low SOC/OC ratio from the EC tracer method, we predicted that there was a considerable amount of primary emissions with photochemical reactivity andsemi-/intermediate volatility during the whole observation. It might be the main reason for the underestimation of SOA_{tracer}. Besides, the estimation of SOA_{tracer} highly depends on the primary OC/EC ratio. The estimated SOA varied by about ±6% when the (OC/EC)_{pri} changed from 2.65 ± 0.1. Previous studies have found that biomass burning produces particulate matter with high OC/EC ratios [71]. This could result in an underestimation of (OC/EC)_{pri} and, as a result, an overestimation of SOC. However, in our study, biomass burning contributed 6% of the VOCs according to source apportionment from the PMF method. Due to the insignificant contribution of biomass burning, the influence of primary biomass burning on SOA estimation is inappreciable.

The concentration of SOA_{ACSM} was higher than SOA_{VOC} and SOA_{tracer}, the same as it is in other research [72,73]. Polidori found that POA represented 60–70% of the OA in Pittsburgh from June 2001 to November 2001, while Zhang estimated that only 33% of the OA was HOA in the same city in September 2002. The overestimation of SOA may be caused by the substitution of HOA for POA. POA included not only HOA but also cooking OA (COA), biomass burning OA (BBOA), and coal combustion OA (COCOA) [5]. The missing sources for POA calculation, especially COA, increased the estimation of SOA.

5. Conclusions

In this study, we presented a field measurement to estimate the formation of SOA through different approaches by using the state-of-the-art online instruments at Changzhou during November 2020. A bimodal pattern of SOA diurnal variation was observed during the period. From the perspective of VOCs oxidation, the major VOC precursors of SOA, i.e., styrene and isoprene, revealed distinct diurnal bimodal patterns compared with OH exposure. Emissions from vehicles and industries might be the main reason for the bimodal pattern of the diurnal variation of SOA. SOA estimated from VOCs oxidation yield method accounted for about only 10.7% of the SOA apportioned from the PMF receptor model and 40.2% of the SOA estimated from EC tracer method. This illustrated that there might be an underestimation of VOCs oxidation yield method. The underestimation of the VOCs oxidation yield method might be caused by the missing precursors, e.g., S/IVOCs. The inappropriate assumption that POC is nonvolatile and nonreactive might lead to the underestimation of the EC tracer method. Besides, the overestimation of the receptor model might come from the fact that part of COA was apportioned to SOA. A good correlation was found between SOA and O_3, suggesting the importance of photochemical processing in SOA formation. On the contrary, no clear relationship was found between SOA and ALWC. Further studies should be conducted to explore the impact of aqueous phase reactions on SOA formation.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/atmos13101679/s1. Figure S1: Location of observation sites in Changzhou from 2 November 2020 to 30 November 2020; Figure S2: Scatterplot of (a) toluene and benzene and (b) ethylbenzene and m/p-xylene; Figure S3: The distribution of measured ethylbenzene to m/p-xylene ratios during the observation; Figure S4: The regression line between OC and EC of the dataset with the lowest 0–10% percentile OC/EC ratios; Figure S5: Source profiles of measured VOCs in the observation; Figure S6: The diurnal variation of (a) styrene and (b) isoprene. The pink area represents the 95% confidence interval; Figure S7: The time series of SOA estimated by different approaches; Table S1: Summary of the concentrations of VOCs during the observation (Unit: ppbv).

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