

1 Reconstructed VOC emissions reveal hidden ozone precursors: 2 Overlooked roles of primary OVOCs and unmeasured species

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13 **Abstract.** Ambient volatile organic compounds (VOCs), including non-methane hydrocarbons (NMHCs) and oxygenated
14 VOCs (OVOCs), are critical precursors of tropospheric ozone (O₃). However, conventional estimates of the ozone formation
15 potential (OFP) derived from observed VOC concentrations may introduce substantial biases, as they neglect the
16 photochemical degradation of primary VOCs and the concurrent generation of secondary OVOCs during atmospheric
17 transport. This study quantified the sources of ambient OVOCs at a suburban site in Shanghai, China during summer 2020 to
18 reconstruct their initial emission concentrations. Together with the reconstructed initial concentrations of NMHCs, we
19 estimated the OFP of freshly emitted VOCs. In addition, the sources and the OFP of unmeasured VOCs were inferred by
20 concurrent measurements of missing OH reactivity. Our results demonstrate that photochemical reactions substantially
21 altered the composition and source characteristics of VOCs, leading to pronounced discrepancies in the OFP estimation
22 between observed and reconstructed initial concentrations. Specifically, the OFP contributions from reconstructed primary
23 emitted NMHCs (52.3%) were underestimated by 31.7% when derived from observed concentrations for this site, whereas
24 those from reconstructed primary emitted OVOCs (33.2%) were overestimated by 42.6%. Reconstructed VOC emissions
25 indicated that anthropogenic sources dominated total emissions (71.5%), whereas OVOCs constituted a substantial fraction
26 of total VOC emissions (40.8%). Unmeasured VOCs, primarily of biogenic origin, contributed an additional 12.6%.
27 Collectively, OVOCs and unmeasured species exhibited an OFP comparable to NMHCs, underscoring their critical role in
28 O₃ production and the necessity of incorporating these species into the design of comprehensive and effective O₃ control
29 strategies.

30 1 Introduction

31 As a critical group of precursors for ozone (O_3), atmospheric volatile organic compounds (VOCs), including non-methane
32 hydrocarbons (NMHCs) and oxygenated VOCs (OVOCs), have attracted considerable attention in air pollution mitigation
33 strategies (Atkinson and Arey, 2003; Atkinson and Carter, 1984; Mellouki et al., 2015). To identify key O_3 precursors, the
34 maximum incremental reactivity (MIR) method is widely applied to calculate the ozone formation potential (OFP) of VOCs
35 (Gu et al., 2021; Huang et al., 2020; Ou et al., 2015; Wang et al., 2023). By definition, the MIR coefficient quantifies the
36 mass of O_3 formed per unit mass of a freshly emitted VOC (i.e., before any photochemical processing) (Carter, 1994, 2010);
37 a physically consistent OFP must therefore be evaluated from the initial emission concentrations rather than from ambient
38 observations. However, most OFP studies are performed with observed VOC concentrations after atmospheric processing
39 (Cui et al., 2022; Huang et al., 2020; Hui et al., 2023; Shang et al., 2022), which may bias the identification of key O_3
40 precursors, as the degradation of NMHCs and the concurrent formation of secondary OVOCs during atmospheric transport
41 can significantly alter compositions and concentrations of VOCs. This bias has recently been demonstrated by reconstructing
42 emitted concentrations from ambient observations, which revealed that observation-based OFP underestimates reactive
43 NMHCs and overestimates OVOCs (Zheng and Xie, 2025).

44 While it is relatively straightforward to understand the photodegradation of NMHCs and trace back to their initial
45 concentrations, it is less common to notice that ambient OVOCs are not only directly emitted from anthropogenic and
46 biogenic sources, but also generated from photochemical oxidation of precursors (Huang et al., 2020; Ou et al., 2015).
47 Therefore, calculating OFP using observed OVOC concentrations could overestimate their true contributions unless the
48 secondary fraction is excluded. However, this overestimation bias in the OFP of OVOCs has been previously explored, but
49 not for a broad range of OVOCs detected by multiple state-of-the-art instruments. An accurate source apportionment of
50 primary and secondary OVOCs is thus essential for a reliable OFP estimation.

51 Commonly used VOC source appointment approaches, including principal component analysis, positive matrix factorization,
52 and chemical mass balance, generally rely on observed VOC concentrations as input without explicitly accounting for
53 photochemical loss of VOCs during atmospheric transport, and thus could introduce uncertainties in source apportionment
54 results. In contrast, the photochemical age-based parameterization method (PAPM) explicitly incorporates OH radical
55 oxidation and photolysis of OVOCs (De Gouw et al., 2005, 2018), enabling a more precise quantification of their sources.
56 While the PAPM has been widely applied to OVOC source apportionment in China (Huang et al., 2020; Li et al., 2024b), its
57 application remains limited to a few OVOCs, such as formaldehyde, acetaldehyde, and acetone. The source distributions of
58 other critical OVOCs are yet to be characterized (Li et al., 2024b).

59 In addition, a large number of VOCs remain undetected or unquantified by current analytical techniques, especially those
60 with multifunctional groups or complex molecular structures (Spinelle et al., 2017; Wang et al., 2024b). These unmeasured
61 VOCs can profoundly affect our understanding of VOC contributions to O_3 formation. For instance, Tan et al. (2019)
62 reported that unmeasured species accounted for up to 60% of O_3 production and contributed nearly 50% to the total OH

63 reactivity (R_{OH}) at a suburban site in Heshan, China. Other studies have shown that unmeasured VOCs resulted in up to a 46 %
64 overestimation in the response of O_3 to nitrogen oxides (Wang et al., 2024b), and a 30% underestimation in simulated net O_3
65 production rates (Zhou et al., 2024). Collectively, these findings underscore the critical importance of unmeasured VOCs in
66 accurately characterizing O_3 formation.

67 In this study, we applied the PAPM to quantify the contributions of anthropogenic and biogenic sources to 208 OVOCs
68 measured at a suburban site of Shanghai, China from 1 August to 15 September 2020 (Yang et al., 2022). In addition, the
69 sources of unmeasured VOCs were inferred using measurements of missing R_{OH} combined with a multiple linear regression
70 (MLR) approach. Based on the source apportionment results, the initial emission concentrations of OVOCs, NMHCs, and
71 unmeasured VOCs were reconstructed to evaluate their OFP at the emission site, and to identify the key O_3 precursors and
72 contributing sources.

73 2 Methods

74 2.1 Field campaign

75 A field campaign was carried out at the Dianshan Lake (DSL) Air Quality Monitoring Supersite (120.98°E, 31.09°N),
76 Shanghai, China (Fig. S1). The sampling site is ~15 m above ground, and surrounded by farmland, vegetation, several
77 villages, and Dianshan Lake. As a representative of the suburban environment, this site has been frequently selected as a
78 reference site for the study of air pollution in the Yangtze River Delta region (Feng et al., 2023; Wu et al., 2023; Yang et al.,
79 2022).

80 Table S1 summarizes the observed concentrations of VOCs. A gas chromatograph with mass spectrometry and flame
81 ionization detection (hereinafter referred to as GC-MS/FID; TH-PKU 300B, Wuhan Tianhong Instrument Co. Ltd., China)
82 was used to measure 56 Photochemical Assessment Monitoring Station (PAMS) compounds (including 29 alkanes, 10
83 alkenes, 16 aromatics, and acetylene) and 11 carbonyls (including 6 aldehydes and 5 ketones), a Kore proton transfer
84 reaction time-of-flight mass spectrometry (KORE PTR 3C, KORE Technologies, UK) was used to measure formaldehyde
85 and acetaldehyde, and a Vocus-2R PTR-TOF-MS (Vocus-PTR, ToFwerk AG and Aerodyne Research Inc., USA) was used
86 to measure 57 NMHCs and 195 OVOCs without definitive identity assignments. In total, 321 VOCs (including 56 PAMS,
87 13 carbonyls, 57 unspecified NMHCs, and 195 unspecified OVOCs) were quantified in this campaign. In addition to VOC
88 measurements, O_3 , NO_x , temperature, and relative humidity were continuously monitored during the campaign. Details of
89 the instruments and their operation have been described previously (Yang et al., 2022).

90 Additionally, R_{OH} was measured using a comparative reactivity method (CRM) (Sinha et al., 2008; Fuchs et al., 2017) and
91 calculated with measured inorganic and organic trace gas concentrations. In brief, pyrrole (C_4H_5N), used as a reference
92 substance, was passed through a glass reactor and monitored by Vocus-PTR. OH radicals were then introduced to react with
93 C_4H_5N , first in the presence of pure nitrogen gas and then in the presence of ambient air. Comparing the concentration of

94 C₄H₅N exiting the reactor with and without the ambient air allows determination of the measured OH reactivity (Sinha et al.,
95 2008).

96 2.2 Photochemical age-based parameterization method

97 The PAPM (De Gouw et al., 2005, 2018) assumes that the amount of each emitted OVOC is proportional to the amount of
98 an inert tracer (e.g., acetylene/C₂H₂), and that reactions with OH radicals and photolysis dominate the photochemical
99 removal of OVOCs. In this method, ambient OVOC concentrations can be attributed to anthropogenic primary emissions
100 (characterized by emission ratio ER_{OVOC}), anthropogenic secondary formation (characterized by emission ratio ER_{precursor}),
101 biogenic sources (characterized by emission ratio ER_{biogenic}), and regional background, as expressed in Eq. (1):

$$\begin{aligned}
 102 \quad [\text{OVOC}] = & \text{ER}_{\text{OVOC}} \times [\text{C}_2\text{H}_2] \times \exp[-(k_{\text{OVOC}}^* - k_{\text{C}_2\text{H}_2})[\text{OH}]\Delta t_a] \\
 103 \quad & + \text{ER}_{\text{precursor}} \times [\text{C}_2\text{H}_2] \times \frac{k_{\text{precursor}}}{k_{\text{OVOC}}^* - k_{\text{precursor}}} \times \frac{\exp(-k_{\text{precursor}}[\text{OH}]\Delta t_a) - \exp(-k_{\text{OVOC}}^*[\text{OH}]\Delta t_a)}{\exp(-k_{\text{C}_2\text{H}_2}[\text{OH}]\Delta t_a)} \\
 104 \quad & + \text{ER}_{\text{biogenic}} \times [\text{isoprene}]_{\text{source}} + [\text{background}] \quad (1)
 \end{aligned}$$

105 where ER_{OVOC} and ER_{precursor} are the emission ratios of OVOC and their precursors relative to C₂H₂; $k_{\text{C}_2\text{H}_2}$ and $k_{\text{precursor}}$ are the
106 OH rate coefficients of C₂H₂ and OVOC precursors, respectively; k_{OVOC}^* is the effective loss rate constant of OVOC
107 representing the combined loss due to OH radicals and photolysis, for which the daytime photolysis of 13 carbonyls was
108 considered in this study (Sect. S1 and Table S2); [C₂H₂] is the observed concentration of acetylene; ER_{biogenic} is the emission
109 ratio of OVOCs from biogenic emissions to isoprene ([Isoprene]_{source}, calculated using Eq.(2)), and [background] denotes the
110 background level. OH exposure of anthropogenic VOCs ([OH]Δt_a) is calculated from a species ratio method using the
111 observed ethylbenzene and m&p-xylene concentrations (Roberts et al., 1984).

112 Since OH radical reactions dominate VOC consumption during the daytime, only observations from 07:00 to 18:00 local
113 time were used for the PAPM fitting, ensuring that the underlying assumption of OH-driven oxidation (Eq. 1) is satisfied.
114 The source contributions of OVOCs were then determined by a least-squares fit, with the fitted emission ratios and
115 background levels summarized in Tables S3 and S4.

116 2.3 Estimation of initial VOCs

117 The photochemical loss of VOCs is dominated by reactions with OH radicals during the daytime, and other removal paths,
118 including deposition and reactions with nitrate radical (NO₃) or O₃, are regarded to be negligible. Thus, the initial
119 concentration of NMHCs emitted from sources can be estimated by Eq. (2):

$$120 \quad [\text{NMHC}_{i,j}]_{\text{source}} = [\text{NMHC}_{i,j}]_{\text{t}} \times \exp(k_i[\text{OH}]\Delta t_j) \quad (2)$$

121 where [NMHC_{i,j}]_{source} is the initial concentration of NMHC species *i* from the *j*th source; [NMHC_{i,j}]_t is the observed
122 concentration of NMHCs species *i* from the *j*th source (including anthropogenic and biogenic sources); k_i represents the first-

order rate coefficient for the reaction of species i with OH radicals (Sect. S4 and Table S5); $[\text{OH}]\Delta t_j$ is the OH exposure of VOCs from the j^{th} source, whose detailed descriptions are provided in Sects. S2 and S3. Unlike OVOCs, NMHCs are treated as directly emitted compounds with no secondary formation pathway. Among them, isoprene, monoterpenes ($\text{C}_{10}\text{H}_{16}$), and sesquiterpenes ($\text{C}_{15}\text{H}_{24}$) are classified as biogenic VOCs, whereas other measured NMHCs are categorized as anthropogenic VOCs.

Based on the source apportionment results (Sect. 3.1), the initial concentration of OVOCs can be estimated by Eq. (3).

$$[\text{OVOC}_{i,j}]_{\text{source}} = \text{ER}_{i,j} \times [\text{tracer}_j]_{\text{source}} \quad (3)$$

where $\text{ER}_{i,j}$ is the emission ratios of the OVOC species i relative to the initial tracer concentration from the j^{th} source ($[\text{tracer}_j]_{\text{source}}$, specifically $[\text{C}_2\text{H}_2]_{\text{source}}$ for anthropogenic and $[\text{isoprene}]_{\text{source}}$ for biogenic source).

2.4 Estimation of unmeasured VOCs

The difference between measured R_{OH} and calculated R_{OH} , termed as missing R_{OH} , is a parameter for assessing the reactivity of unmeasured or unrecognized compounds.

$$\text{Missing } R_{\text{OH}} = \text{Measured } R_{\text{OH}} - \sum_i k_i [\text{X}_i] \quad (4)$$

where $[\text{X}_i]$ represents the observed concentration of inorganic or VOC species i . To explore the potential sources of missing R_{OH} , we quantified the sources of missing R_{OH} by a MLR method introduced by Wang et al. (2024b).

$$\text{Missing } R_{\text{OH}} = a[\text{C}_2\text{H}_2] + b[\text{isoprene}]_{\text{source}} + c[\text{O}_x] + C_{\text{background}} \quad (5)$$

where $[\text{O}_x]$ is the observed concentrations of $\text{NO}_2 + \text{O}_3$. a , b , and c are regression coefficients representing the sensitivities of missing R_{OH} to the tracers of anthropogenic, biogenic and secondary sources, with fitted values of 0.39, 2.48 and $0.04 \text{ s}^{-1} \text{ ppb}^{-1}$, respectively. The intercept, $C_{\text{background}}$ (2.27 s^{-1}), represents the baseline missing R_{OH} that is independent of these three source categories.

Unmeasured VOCs, such as long-chain alkanes, diterpenes, and OVOCs with more than four oxygen atoms, mainly originate from anthropogenic sources, biogenic sources, and secondary generation, respectively. These compounds exhibit high reactivity toward OH radicals and are therefore expected to be important sources of missing R_{OH} (Li et al., 2020; Wang et al., 2020; Wu et al., 2020). In addition to VOC species, other reactive gases such as hydrogen sulfide, HONO, and ammonia, etc., although not measured in this study, have been identified in previous studies as important contributors to total R_{OH} (Anglada and Solé, 2017; Pai et al., 2021; Wine et al., 1981). Moreover, heterogeneous OH uptake on atmospheric aerosol surfaces represents another non-negligible sink of OH radicals (Zhang et al., 2020), which may further contribute to missing R_{OH} . The background fraction of missing R_{OH} exhibited no correlation with $[\text{C}_2\text{H}_2]$, $[\text{isoprene}]_{\text{source}}$, or $[\text{O}_x]$, hinting that it could not be attributed to the three sources represented by these tracers. We therefore attributed the background fraction of missing R_{OH} to unmeasured inorganic reactive gases or unaccounted heterogeneous processes, and its OFP contribution was not considered in subsequent calculations. Missing R_{OH} associated with anthropogenic, biogenic, and secondary sources was attributed to unmeasured VOCs from the corresponding source. Given that unmeasured VOCs are likely a complex mixture of diverse

chemical species, we scaled the concentrations of the 191 measured species with available MIR values (Table S5) from the corresponding source to compensate for missing R_{OH} , as shown in Eq. (6):

$$[\text{unmeasured VOC}_{i,j}]_t = [\text{VOC}_{i,j}]_t \times \frac{\text{missing } R_{OH,j}}{R_{OH,j}} \quad (6)$$

where $[\text{unmeasured VOC}_{i,j}]_t$ denotes the ambient concentrations of unmeasured VOC_i originating from the j^{th} source, $[\text{VOC}_{i,j}]_t$ represents the concentrations of measured VOCs from the j^{th} source, missing $R_{OH,j}$ and $R_{OH,j}$ represent the OH reactivity of unmeasured and measured VOCs from the j^{th} source, respectively.

Based on the equivalent concentrations derived from Eq. (6), the initial concentrations of unmeasured VOCs, $[\text{unmeasured VOC}_{i,j}]_{\text{source}}$, were estimated following the same approach as that for measured species in Sect. 2.3. Note that unmeasured VOCs attributed to secondary formation were excluded from this calculation, as secondary OVOCs are produced during atmospheric transport rather than emitted at the source. Accordingly, the initial unmeasured anthropogenic and biogenic VOCs were determined using Eq. (7), with the same source-specific OH exposures and corresponding OH rate constants as those used for measured species.

$$[\text{unmeasured VOC}_{i,j}]_{\text{source}} = [\text{unmeasured VOC}_{i,j}]_t \times \exp(k_i[\text{OH}]\Delta t_j) \quad (7)$$

Eq. (7) follows the same formulation as Eq. (2), but is specifically applied to unmeasured VOCs using their inferred concentrations rather than directly measured values.

2.5 Ozone formation potential

The MIR method was applied to calculate the OFP of individual VOC species (OFP_i) to evaluate their respective contributions to O_3 generation.

$$\text{OFP}_i = [\text{VOC}_i] \times \text{MIR}_i \quad (8)$$

where $[\text{VOC}_i]$ is the concentration of a species i and MIR_i is the maximum incremental reactivity coefficient for an individual species i , as reported by Carter (2010). Note that MIR values are unavailable for many VOCs, particularly those detected by Vocus-PTR without structural information. To enable OFP estimation, MIR values for these species were assigned as follow: (1) If the molecular formula corresponds to a unique compound without isomers, the reported MIR value of that compound was directly assigned; (2) If the molecular formula matched multiple isomers, the minimum MIR value among multiple isomers was conservatively adopted; (3) Nevertheless, 130 OVOCs (Table S5), accounting for 7.8% of the total observed VOC concentration, still lacked MIR values. Including them without MIR values would require additional assumptions that would introduce unquantifiable uncertainties; therefore, to ensure the robustness of the results, these species were excluded from both the OFP calculations and the estimation of unmeasured VOCs. Thus, we estimated the OFP of unmeasured VOCs with the equivalent concentrations and corresponding MIR coefficients of the 191 measured species with available MIR values. The MIR coefficients used for the OFP estimation are summarized in Table S5.

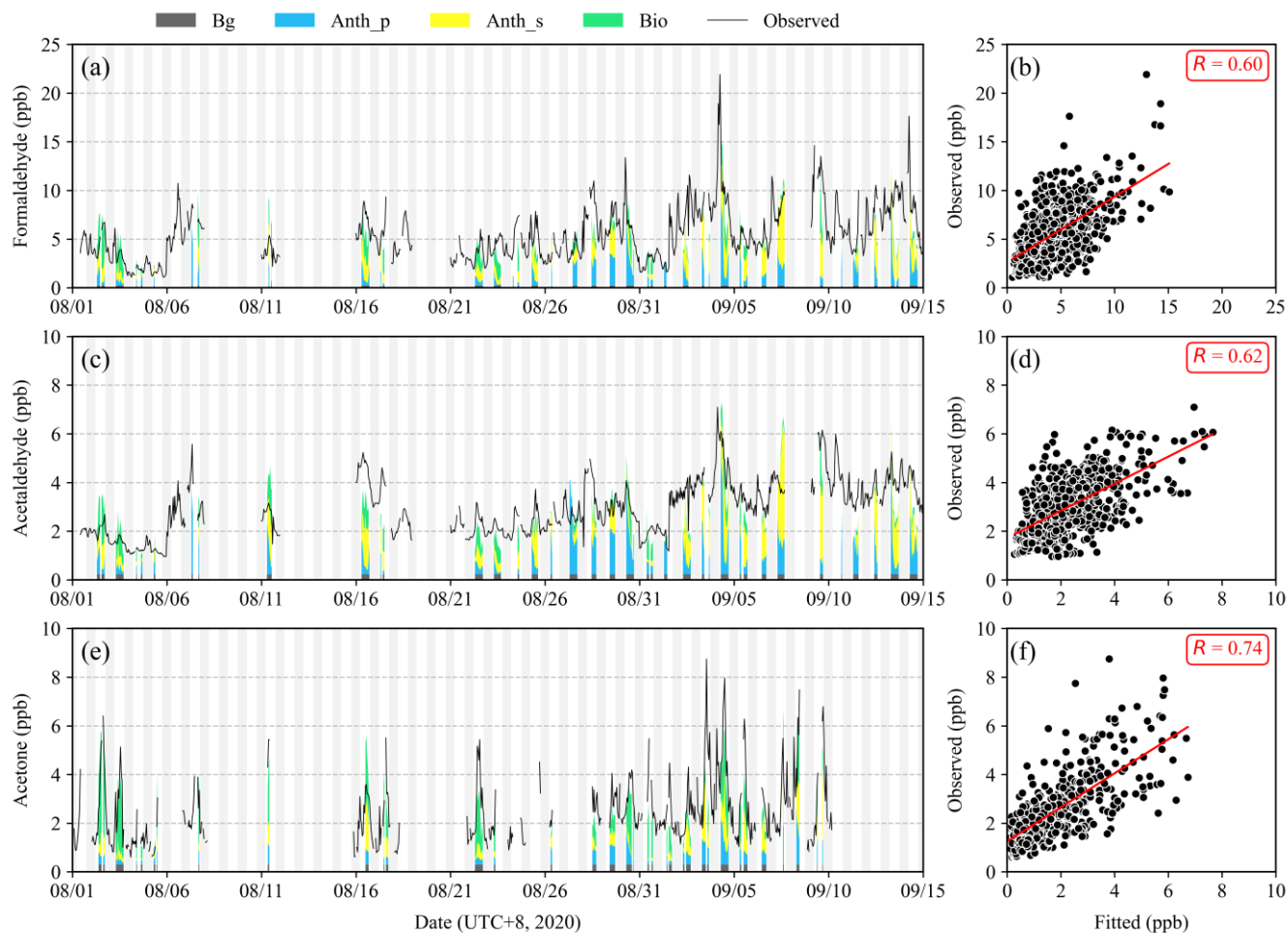
185 These assignment strategies and the inference of unmeasured VOCs inevitably introduce uncertainties into the OFP
186 calculations. A detailed discussion on the uncertainties associated with VOC measurements, k_i and MIR assignments, and
187 assumptions with unmeasured species is provided in Sect. S5, together with their impacts on the OFP estimation.
188 Additionally, it should be noted that MIR-based OFP represents a simplified reactivity metric under idealized conditions and
189 does not explicitly account for region-specific chemical regimes. The OFP values reported in this study should therefore be
190 interpreted as relative indicators of precursor reactivities, rather than direct representations of O_3 production under ambient
191 conditions.

192 **3 Results and discussion**

193 **3.1 Source apportionment of measured and unmeasured VOCs**

194 During the daytime (07:00–18:00 local time), the mean temperature and relative humidity were 28.7 °C and 75.8%,
195 respectively. Ambient O_3 concentrations ranged from 24.0 to 324.0 $\mu\text{g m}^{-3}$ (mean $\pm$ one standard deviation: $127.1 \pm 58.4 \mu\text{g}$
196 m^{-3}), and NO_x averaged 14.0 ± 6.3 ppbv, indicating conditions favorable for photochemical oxidation of VOCs. Consistent
197 with this chemical environment, the daytime measured total R_{OH} averaged $39.9 \pm 20.9 \text{ s}^{-1}$ (Yang et al., 2022), comparable to
198 values reported at other suburban Chinese sites with substantial biogenic and photochemical influence. For example, Yang et
199 al. (2017) reported total R_{OH} of $\sim 30\text{--}40 \text{ s}^{-1}$ at the suburban Heshan site in the Pearl River Delta during summer. During our
200 campaign, the OH exposure of anthropogenic VOCs, derived from the ethylbenzene/m&p-xylene ratio method (Roberts et
201 al., 1984), was estimated to be $3.2 \pm 3.2 \times 10^{10} \text{ molecules cm}^{-3} \text{ s}$, corresponding to a photochemical age of approximately 4.4
202 h, assuming a mean daytime OH concentration of $\sim 2.0 \times 10^6 \text{ molecules cm}^{-3}$. For biogenic VOCs, the OH exposure
203 estimated using a sequential reaction model (Stroud et al., 2001) was $7.9 \pm 5.1 \times 10^9 \text{ molecules cm}^{-3} \text{ s}$, equivalent to a
204 photochemical age of 1.1 h. Overall, the air masses sampled at DSL site on average underwent 1–4 h of integrated
205 photochemical processing prior to arrival; therefore, the observed OVOCs are expected to reflect contributions from both
206 primary emissions and substantial secondary production.

207 Using the parametric method incorporating photochemical age, we quantified contributions of anthropogenic primary
208 emissions, anthropogenic secondary formation, biogenic sources, and regional background during the daytime for 8
209 aldehydes, 5 ketones, and 195 unspecified OVOCs. The fitted results from Eq. (1), with the fitted parameters summarized in
210 Tables S3 and S4, show good agreement with observed concentrations ($R = 0.40\text{--}0.90$) and reconstruct the time series well,
211 as illustrated for formaldehyde, acetaldehyde, and acetone in Fig. 1.



212

213 **Figure 1.** Time series (a, c, e) and scatter plot (b, d, f) of the PAPM fitting result from Eq. (1) (using the emission ratios and
 214 background levels in Tables S3 and S4) versus the measured concentrations of formaldehyde, acetaldehyde, and acetone.
 215 Sources include anthropogenic primary emissions (Anth_p), anthropogenic secondary formation (Anth_s), biogenic sources
 216 (Bio), and background (Bg). Shaded areas in (a, c, e) represent nighttime, and missing data in (a, c, e) are due to the
 217 unavailability of tracer gases or OH exposure.

219 Ambient aldehydes, as shown in Fig. S2a, were predominantly of anthropogenic sources, with a large fraction of
 220 anthropogenic secondary formation (36.5%) and anthropogenic primary emissions (33.1%). Biogenic sources (24.7%) also
 221 played a notable role, whereas the regional background was minor (5.6%). Specifically, anthropogenic secondary formation
 222 was dominant for several major aldehydes, including formaldehyde (37.5%), acetaldehyde (36.0%), and propanal (34.6%).
 223 In contrast, biogenic sources were dominant for methacrolein (81.8%), pentanal (39.7%), hexanal (67.2%), butanal (52.1%),
 224 and acrolein (48.7%).

225 Ketones exhibited a higher regional background contribution (9.2%) compared to aldehydes (Fig. S2b). Biogenic sources
 226 represented the dominant source of ketones (47.1%), with particularly high contributions of methyl vinyl ketone (69.0%), 2-
 227 pentanone (64.3%), 2-butanone (50.7%), and acetone (45.3%). Anthropogenic secondary formation (24.9%) and
 228 anthropogenic primary emissions (18.9%) were also important contributors. Collectively, our results underscore a substantial
 229 contribution of photochemically derived carbonyls from anthropogenic VOC precursors during daytime at the DSL site.

230 For unspecified OVOCs measured by Vocus-PTR, as shown in Fig. S2c, anthropogenic primary emissions accounted for the
 231 largest fraction (36.9%), followed by anthropogenic secondary formation (21.2%), biogenic sources (34.2%), and a low
 232 regional background level (7.7%). Specifically, $C_nH_{2n}O_2$ ($n=2-8$) were predominantly attributed to primary anthropogenic
 233 sources (34.7-84.4%). These compounds are likely alkanedioic acids, which have been previously linked to emissions from
 234 traffic and agricultural activities (Mattila et al., 2018). Similarly, compounds such as $C_6H_{14}O_2$, $C_9H_{10}O$, $C_2H_3NO_2$, C_3H_7NO ,
 235 C_5H_9NO , and $C_6H_5NO_3$ were also mainly associated with anthropogenic primary emissions (> 50%). These species are likely
 236 solvents and amides, with potential sources including industrial processes, volatile chemical products, and wildfire, as
 237 reported by previous studies (Salvador et al., 2024; Zhang et al., 2024). OVOCs with more than or equal to three oxygen
 238 atoms (e.g., $C_2H_4O_3$, $C_4H_4O_3$, $C_4H_2O_4$, $C_5H_6O_3$, $C_4H_4O_4$, and $C_5H_4O_4$) were likely formed via multi-generation oxidation
 239 reactions of anthropogenic VOCs, with over 60% attributed to anthropogenic secondary formation. Biogenic sources were
 240 dominant sources of $C_nH_{2n}O$ ($n=9-14$), $C_8H_8O_2$, $C_9H_6O_2$, $C_8H_6O_3$, $C_{10}H_{14}O_2$, and $C_{10}H_{20}O_2$, accounting for 45.0-74.2%.
 241 These species likely represent carbonyls, fatty acid derivatives, and phenylpropanoids, commonly identified as primary
 242 biogenic OVOCs (Ma et al., 2022a; Wang et al., 2024a). In addition, several compounds such as C_6H_8O , $C_6H_8O_3$, $C_8H_{10}O_3$,
 243 $C_8H_6O_4$, $C_9H_{14}O_2$, $C_9H_{10}O_3$, $C_9H_8O_4$, $C_{10}H_8O_3$, $C_{12}H_{18}O$, and $C_{13}H_{12}O_2$ also exhibited substantial contributions from biogenic
 244 sources, ranging from 44.8% to 77.7%. These OVOCs have been identified as dominant products of terpene oxidation in
 245 laboratory simulations, and frequently observed in forest environments (Calogirou et al., 1999; Li et al., 2020; Vermeuel et
 246 al., 2023).

247 Unlike OVOCs, 113 NMHCs, including 29 alkanes, 9 alkenes, 16 aromatics, 1 alkyne, 3 terpenes, and 55 unspecified ones,
 248 are considered directly emitted since there is no secondary formation for NMHCs. Among them, isoprene, $C_{10}H_{16}$, and
 249 $C_{15}H_{24}$ are classified as biogenic VOCs, whereas the other 110 NMHCs are categorized as anthropogenic VOCs. It should be
 250 noted, however, that terpenoids may also be emitted from anthropogenic activities, such as vehicular exhaust and the usage
 251 of volatile chemical products (Borbon et al., 2001; Gu et al., 2024; Xie et al., 2025). Moreover, certain benzenoid

252 compounds have been reported to be emitted from biogenic sources as well (Ma et al., 2022a; Misztal et al., 2015; Wang et
253 al., 2024a; Wohl et al., 2023). Nevertheless, the impact of these cross-sources was generally considered to be minor (Ma et
254 al., 2022a; Seltzer et al., 2021).

255 In addition to the detected VOCs, numerous other VOCs are present in the ambient air but were not measured during this
256 campaign. Those unmeasured VOCs led to a gap between the measured and calculated R_{OH} , i.e., missing R_{OH} . To explore the
257 potential sources of missing R_{OH} at the DSL site, we quantified its sources by applying an MLR method. The fitted and
258 calculated missing R_{OH} were in good agreement ($R = 0.63$, Fig. S3). The estimated missing R_{OH} is approximately 6.8 ± 4.4
259 s^{-1} during the daytime. Biogenic sources accounted for the largest fraction ($2.3 \pm 1.7 s^{-1}$, 34.3%), followed by background
260 ($2.1 s^{-1}$, 30.9%) and secondary sources ($2.1 \pm 1.3 s^{-1}$, 30.5%). In contrast, anthropogenic sources played a minor role in
261 missing R_{OH} ($0.3 \pm 0.2 s^{-1}$, 4.2%). These results are consistent with previous suggestions that missing R_{OH} was mainly from
262 biogenic sources or photochemical production processes (Di Carlo et al., 2004; Yang et al., 2017). To quantify the OFP of
263 unmeasured VOCs, the missing R_{OH} attributed to anthropogenic, biogenic, and secondary sources was converted into
264 equivalent concentrations of measured VOCs from corresponding sources using Eq. (6). The background fraction of missing
265 R_{OH} was not converted, as it was attributed to undetected reactive inorganic gases or unaccounted heterogeneous reactions
266 rather than unmeasured VOCs. Our results showed that unmeasured VOCs were dominated by secondary OVOCs (4.1 ± 2.6
267 ppbv, 43.8%) during daytime, followed by biogenic VOCs (3.7 ± 2.5 ppbv, 40.1%) and anthropogenic VOCs (1.5 ± 1.0 ppbv,
268 16.0%).

269 3.2 VOC evolution from initial emission to observation

270 Based on the above calculation, as shown in Fig. 2a, the daytime average concentration of total VOCs (TVOCs, including
271 measured and unmeasured VOC species) at the observation site was estimated to be 58.4 ± 24.2 ppbv. Among them,
272 measured species were 49.1 ± 21.3 ppbv. Measured OVOCs were the dominant group (52.4%), with unspecified OVOCs
273 comprising the largest fraction (26.4%), followed by aldehydes (17.2%) and ketones (8.8%). Measured NMHCs contributed
274 31.7% of TVOCs, with alkanes as the major fraction (17.7%), followed by unspecified NMHCs (4.0%), alkenes (3.2%),
275 aromatics (3.2%), terpenes (2.4%), and alkynes (1.3%). In addition, the daytime average concentration of unmeasured VOCs
276 at the observation site was estimated to be equivalent to 9.3 ± 5.2 ppbv of measured VOCs, which contributed approximately
277 15.9% of TVOCs.

278 Source apportionment reveals that anthropogenic primary sources were the largest contributors to TVOCs at the observation
279 site (48.9%), followed by biogenic sources (26.2%), anthropogenic secondary formation (21.1%), and regional background
280 (3.8%). This distribution reflects a substantial anthropogenic influence, consistent with nearby urban and traffic emissions at
281 the DSL site, although contributions from biogenic sources were also evident.

282 After deducting secondary formation contributions and accounting for photochemical aging, the initial concentration of
283 individual measured VOCs was estimated (Table S5). In addition, the initial concentration of unmeasured VOCs was
284 estimated using Eq. (7) based on the equivalent observed concentrations of measured VOCs. As shown in Fig. 2b, the

285 estimated daytime average initial concentration of TVOCs was 47.7 ± 22.6 ppbv. Among these, measured species were 41.7
286 ± 19.8 ppbv. In contrast to the distribution at the observation site, NMHCs (22.3 ± 18.4 ppbv, 46.6%) constituted the largest
287 fraction of the initial TVOCs, rather than OVOCs (19.5 ± 9.8 ppbv, 40.8%). Based on Eq. (7), the initial concentration of
288 unmeasured VOCs was estimated to be 6.0 ± 3.6 ppbv, accounting for 12.6% of initial TVOCs.

289 Anthropogenic and biogenic source emissions contributed 71.5% and 28.5% of initial TVOCs, respectively. A notable
290 feature of these emissions is the substantial presence of OVOCs in primary sources. Anthropogenic OVOCs alone
291 contributed 24.1% of the initial TVOCs, indicating that a considerable fraction of oxygenated compounds originated directly
292 from anthropogenic activities. Biogenic emissions also contained a large proportion of OVOCs, representing more than half
293 of the total biogenic VOCs. These findings are consistent with bottom-up emission inventories (Gu et al., 2021; Ou et al.,
294 2015; Salvador et al., 2024; Yan et al., 2024), as well as direct source measurements (Li et al., 2024a; Sekimoto et al., 2023;
295 Seltzer et al., 2021; Wang et al., 2024a), which have reported significant primary OVOC emissions from solvents, industrial
296 activities, volatile chemical products, and plant emissions. Concentrations of primarily emitted OVOCs were comparable to
297 those of NMHCs. However, previous studies mainly focused on NMHCs and neglected the role of primarily emitted OVOCs
298 (Ma et al., 2022b).

299 Comparison between initial and observed VOCs reveals a substantial compositional change during atmospheric transport.
300 The concentration of TVOCs at the observation site was 10.6 ppbv (22.3%) higher than the initial TVOCs. However, NMHC
301 concentrations were underestimated by 16.8%. Species with the largest discrepancies were alkenes and aromatics: the
302 average initial concentrations of alkenes and aromatics were 3.1 ± 1.7 ppbv and 2.5 ± 1.8 ppbv, respectively, significantly
303 exceeding their respective measured concentrations of 1.8 and 1.9 ppbv at the observation site. This discrepancy can be
304 primarily attributed to the high reactivity of these compounds and thus their rapid photochemical degradation during
305 atmospheric transport. OVOC concentrations, if inferred from observation, were overestimated by 57.1%. For instance,
306 unspecified OVOCs increased from 10.2 ± 5.1 ppbv at the real emission to 15.4 ± 12.2 ppbv at the observation site,
307 reflecting substantial secondary production during transport.

308 Photochemical aging also altered different sources' contributions to VOCs significantly. Anthropogenic and biogenic sources
309 emitted 71.5% and 28.5% of TVOCs, respectively. However, anthropogenic primary VOCs only accounted for 48.9% of
310 TVOCs when transported to the observation site. Photochemically degradable VOCs were converted into OVOCs, with
311 these secondary products accounting for 21.1% of TVOCs at the observation site, explaining the increase of OVOCs from
312 the real emission to ambient measurements.

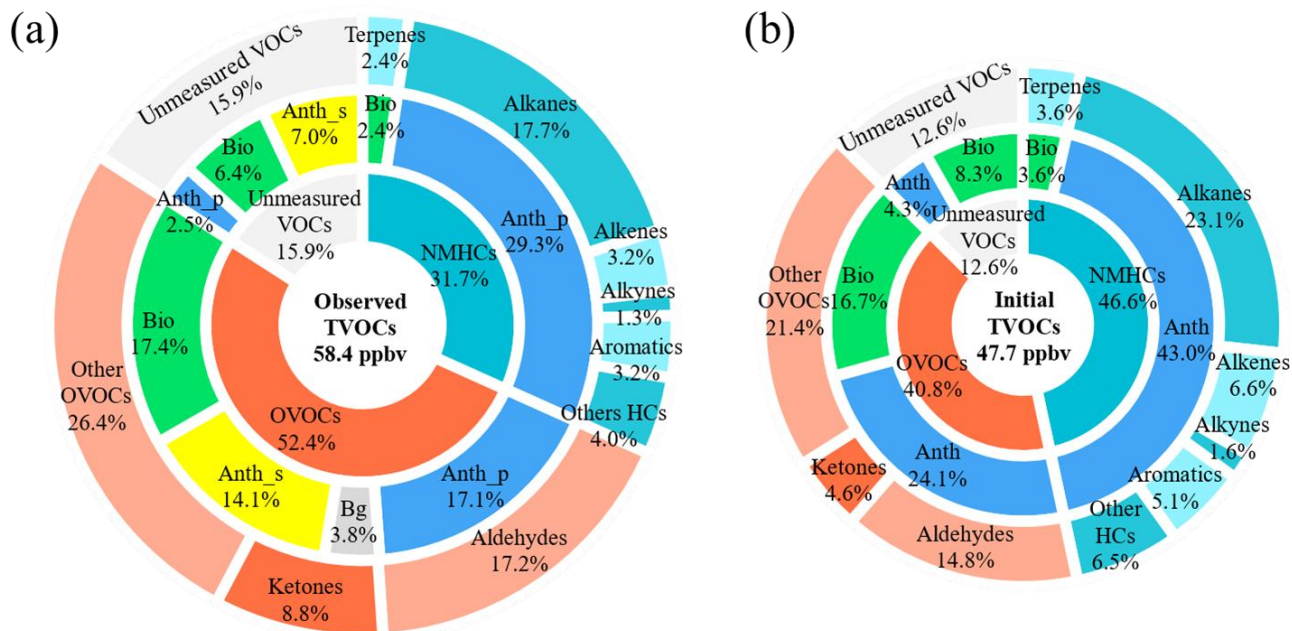


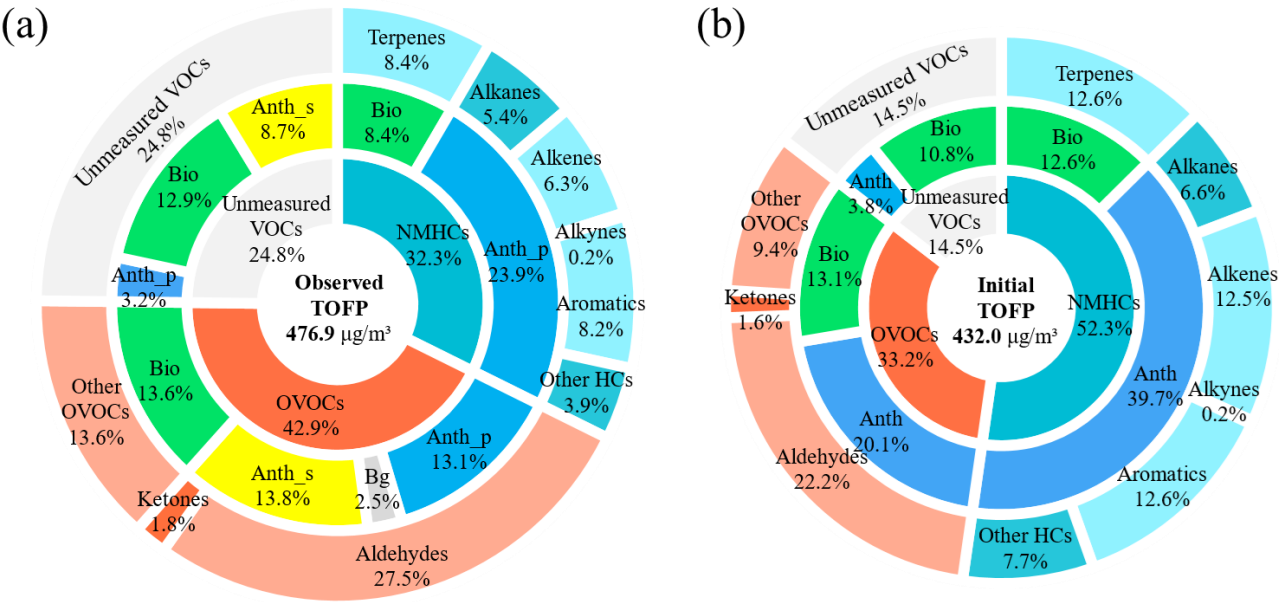
Figure 2. The contributions of different VOC groups and sources to (a) observed TVOCs at the observation site and (b) initial TVOCs at the emission site. The inner, middle, and outer rings represent the proportion of different VOC components, different sources, and different VOC groups to TVOCs, respectively. The size of the ring is proportional to TVOC concentrations.

3.3 Ozone formation potential and the key contributors

To identify key O_3 precursors, we further calculated the OFP of individual VOCs using the MIR method (Table S5). As shown in Fig. 3, the total OFP (TOFP) of TVOCs at the emission site was $432.0 \pm 319.2 \mu g m^{-3}$. Measured NMHCs contributed the largest fraction (52.3%), led by aromatics (12.6%), terpenes (12.6%), alkenes (12.5%), unspecified NMHCs (7.7%), alkanes (6.6%), and alkynes (0.2%). These results differed remarkably from those based on the observed concentrations, i.e., the OFP of measured NMHCs was smaller by 31.7% due to photochemical degradation. For instance, the OFP of initial alkenes was $54.1 \pm 29.6 \mu g m^{-3}$, but would be underestimated by 44.7% ($30.0 \pm 16.4 \mu g m^{-3}$) if photochemical losses were not considered.

OVOCs are often regarded as secondary oxidation products and overlooked as primary O_3 precursors. However, our results demonstrate that directly emitted OVOCs accounted for 33.2% of initial TOFP, primarily from aldehydes (22.2%) and unspecified OVOCs (9.4%), whereas ketones contributed only 1.6%. It should be noted that the actual contribution of OVOCs was likely larger, as many OVOCs (with a total initial concentration of 3.2 ppbv, accounting for 6.7% of the initial TVOCs) were excluded from the OFP calculation because their MIR coefficients were unavailable. These findings show that primary OVOCs have an O_3 formation impact comparable to or exceeding that of many NMHCs. On the other hand, when

332 estimated directly from the observed concentrations, the OFP of OVOCs, as inferred from Fig. 3, was overestimated by 42.6%
 333 (observed OVOCs: $204.6 \mu\text{g m}^{-3}$, i.e., $42.9\% \times 476.9 \mu\text{g m}^{-3}$; reconstructed primary emitted OVOCs: $143.4 \mu\text{g m}^{-3}$, i.e.,
 334 $33.2\% \times 432.0 \mu\text{g m}^{-3}$), which is a bias largely attributable to secondary production. This explains why, despite an
 335 underestimation of NMHCs' OFP, TOFP calculated from the observed TVOCs' concentrations, i.e., $476.9 \mu\text{g m}^{-3}$ (Fig. 3a),
 336 was still 10.4% higher than that ($432.0 \mu\text{g m}^{-3}$) derived from the reconstructed initial concentrations (Fig. 3b). These
 337 numbers highlight systematic biases introduced by photochemical aging and underscore the necessity of reconstructing
 338 initial VOC emissions for accurate OFP assessments.
 339 The contributions of unmeasured VOCs to TOFP were also considerable. The OFP of initial unmeasured VOCs was $62.8 \pm$
 340 $37.6 \mu\text{g m}^{-3}$, representing 14.5% of initial TOFP, mainly contributed by unmeasured biogenic VOCs ($46.5 \pm 30.2 \mu\text{g}$
 341 m^{-3} , 10.8%), followed by unmeasured anthropogenic VOCs ($16.3 \pm 12.0 \mu\text{g m}^{-3}$, 3.8%). Although their exact identities
 342 remain to be elucidated, unmeasured VOCs' substantial OFP demonstrates that they are a non-negligible fraction of the O_3
 343 precursors. Ignoring unmeasured VOCs would underestimate VOC's contributions to O_3 pollution.



344
 345 **Figure 3.** The contributions of different VOC groups and sources to TOFP (a) at the observation site and (b) at the emission
 346 site. The inner, middle, and outer rings represent the proportion of different VOC components, different sources, and
 347 different VOC groups to TOFP, respectively. The size of the ring is proportional to the total OFP.

348 In terms of individual VOCs at the emission site, formaldehyde was the largest single contributor to TOFP (13.4%),
 349 consistent with emission inventory findings in Beijing and Guangzhou, China (Huang et al., 2021; Wang et al., 2023).
 350 Isoprene ranked second (8.1%), which is emitted primarily from biogenic sources with a high photochemical reactivity.
 351 Acetaldehyde was the third contributor (6.9%), largely driven by its relatively high concentrations (2.3 ± 1.4 ppbv). Other

key VOCs with high OFP included propylene, m&p-xylene, monoterpenes, ethylene, toluene, n-hexane, and o-xylene, each accounting for more than 1.5% of TOFP (Fig. 4). The relative importance of these species differed notably from what is based on the observed concentrations (Fig. S4), particularly for propylene and n-hexane, which ranked the fourth and the tenth, respectively, based on their initial concentrations, but decreased to the seventh and the fifteenth when ranked by observed concentrations. This indicates that evaluations without considering initial concentrations could miss key O₃ precursors.

The top-ten reconstructed primary emitted VOCs collectively accounted for 55.3% of the initial TOFP, despite representing only 31.2% of initial TVOCs, highlighting that high OFPs did not necessarily correlate with high concentrations. For instance, C₂H₄O₂ (likely acetic acid), acetone, and ethane together comprised 12.1% of initial TVOCs but contributed only 1.2% to TOFP. Among the top ten contributors, eight species were primarily emitted from anthropogenic sources, reinforcing the dominant role of anthropogenic activities in O₃ formation in the suburban area of Shanghai.

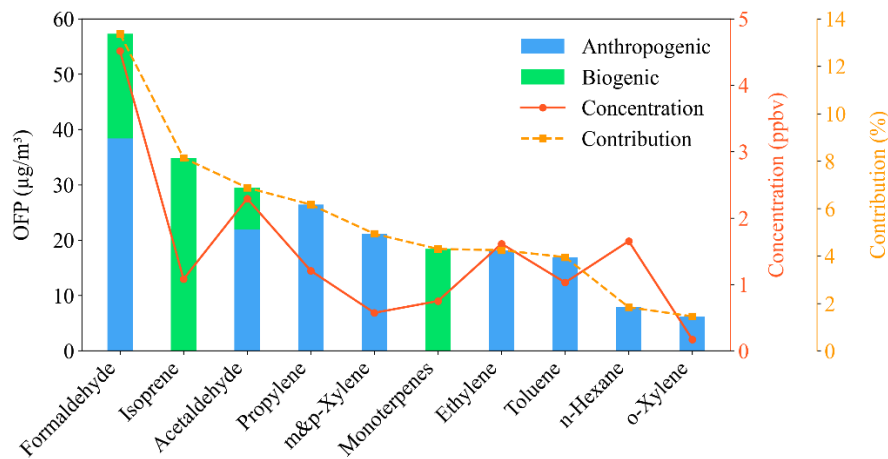


Figure 4. The reconstructed initial concentrations and contributions to the initial total OFP of the top-ten contributors during the daytime. Bar colors indicate source attribution (blue: anthropogenic sources; green: biogenic sources).

Anthropogenic emissions, including both measured and unmeasured species, have the potential to form about $274.4 \pm 128.6 \mu\text{g m}^{-3}$ of O₃, accounting for 63.5% of TOFP. Initial anthropogenic NMHCs were the dominant contributors (39.7%) to TOFP, followed by anthropogenic OVOCs (20.1%), whereas unmeasured anthropogenic VOCs also represented a non-negligible fraction (3.8%). Formaldehyde, propylene, and acetaldehyde were the top three contributors among anthropogenic VOCs, which cumulatively contributed 20.1% of TOFP, even though they accounted for only 12.4% of initial TVOC concentrations. Initial biogenic VOCs had the potential to form about $157.5 \pm 111.9 \mu\text{g m}^{-3}$ of O₃ (36.5% of TOFP), with biogenic OVOCs, terpenes, and unmeasured biogenic species contributing 13.1%, 12.6%, and 10.8% to TOFP, respectively. Isoprene, monoterpenes, and formaldehyde were the dominant biogenic contributors, with contributions of 8.1%, 4.3%, and 4.4%, respectively, mainly attributed to their abundant initial concentrations combined with their high MIRs.

Our results are qualitatively consistent with, yet quantitatively and conceptually distinct from, those of Zheng and Xie (2025), who compared reconstructed primary emitted versus ambient VOC concentrations at three sites in the Sichuan Basin. Both studies found that NMHCs, particularly alkenes and aromatics, were underestimated in OFP estimation when using observed rather than primary emitted concentrations, while OVOCs' OFP were overestimated. A quantitative comparison of the observed and reconstructed initial OFP estimates between the two studies is summarized in Table 1. Specifically, Zheng and Xie (2025) found that OVOCs' OFP in Chengdu decreased from ~75.0 to ~50.0 $\mu\text{g m}^{-3}$ when emitted rather than ambient concentrations were used (~50.0% overestimation), consistent with the 42.6% overestimation identified here; conversely, the OFP of reactive NMHCs increased, mirroring the 31.7% underestimation for NMHCs at the DSL site. For individual species, isoprene, acetaldehyde, propylene, m&p-xylene, ethylene, toluene, and o-xylene were consistently identified as key O_3 precursors, reinforcing their priority status in O_3 control strategies. Notably, a key distinction is that our study covers a far broader range of VOC species, encompassing 321 measured VOC species (113 NMHCs and 208 OVOCs), together with R_{OH} inferred unmeasured species, compared to the 99 species (86 NMHCs and 13 OVOCs) analyzed by Zheng and Xie (2025). This broader coverage enables us to attribute 33.2% and 14.5% of initial TOFP to primary emitted OVOCs and unmeasured species. The two studies are thus complementary rather than hierarchical: Zheng and Xie (2025) additionally resolved nighttime NO_3/O_3 -driven alkene loss, whereas our reconstruction focuses on the daytime OH-dominated window to characterize a broader range of oxygenated and unmeasured species.

Table 1. Comparison of observed and reconstructed initial OFP ($\mu\text{g m}^{-3}$) and associated biases between this study (suburban, Shanghai) and Zheng and Xie (2025) (suburban, Chengdu).

This study				Zheng and Xie (2025)			
VOC group	Observed OFP	Initial OFP	bias	VOC group	Observed OFP ^a	Initial OFP ^a	bias ^a
113 NMHCs	154.0	225.7	-31.7%	86 NMHCs	~160.0	~250.0	~-36.0%
208 OVOCs	204.6	143.4	+42.6%	13 OVOCs	~75.0	~50.0	~+50.0%
Unmeasured species	118.3	62.8	+88.4%	Unmeasured species	-	-	-
Total OFP	476.9	432.0	+10.4%	Total OFP	~235.0	~300.0	~-21.7%

^a Values estimated from Fig. 3 in Zheng and Xie (2025); exact numbers may differ slightly from those extracted here.

'-': Not quantified.

4 Atmospheric implications

An accurate OFP estimation of VOCs is essential for designing effective O_3 pollution control strategies, particularly across the VOC-limited regimes of the Yangtze River Delta (Ren et al., 2022). However, ambient VOC measurements inherently represent photochemically processed mixtures rather than true emissions, complicating the identification of key O_3 contributors. This study demonstrates that photochemical aging substantially reshapes both the chemical composition and

source characteristics of VOCs, systematically leading to underestimation of NMHCs and overestimation of OVOCs when relying solely on observed concentrations. Therefore, a reconstruction of initial emissions is necessary to correctly diagnose O₃ precursors.

By reconstructing initial VOC emissions from ambient observations, we provide observationally constrained evidence that primary OVOCs constitute a large fraction of total VOC emissions (40.8%) during our campaign, and that both anthropogenic and biogenic activities directly emit reactive oxygenated species with OFP comparable to NMHCs. These reconstructed emissions help to reconcile previously reported discrepancies between ambient VOC observations and emission inventories. Previous inventories and direct source measurements in urban and suburban environments indicate that anthropogenic sources contribute roughly 70% of the total VOC burden, with OVOCs comprising approximately 20–65% of total VOC emissions (Gu et al., 2021; Ma et al., 2022a; Ou et al., 2015; Yan et al., 2024). Our reconstructed initial concentrations closely reproduce this source-level composition (OVOCs: 40.8%; anthropogenic origin: 71.5%). By contrast, ambient observations show a markedly reduced anthropogenic primary fraction (48.9%), alongside a substantially elevated OVOC proportion (52.4%), reflecting photochemical aging and secondary OVOC formation during atmospheric transport, which obscure the original VOC emission profile. Moreover, the substantial contribution of unmeasured VOCs (14.5% of the initial TOFP, despite only comprising 12.6% of the initial TVOC concentrations) underscores the limitations of current monitoring networks, particularly for biogenic and oxygenated species; expanding measurement capabilities is therefore critical for capturing the true O₃ formation capacity of the atmosphere. It should be emphasized, however, that the OFP reported in this study represents a relative reactivity metric rather than an estimate of actual O₃ production under ambient conditions. Quantifying the contribution of primary OVOCs and unmeasured species to ambient O₃ levels at the DSL site will require future work integrating detailed chemical mechanism modeling.

Current emission control strategies remain narrowly focused on a limited set of NMHCs (e.g., PAMS species) (Gao et al., 2025). However, our results show that the 56 PAMS compounds account for only ~40% (173.0 µg m⁻³) of the initial TOFP, implying that exclusive reliance on PAMS monitoring would leave ~60% of the total initial OFP unaddressed. The unaccounted fraction is composed of primary OVOCs (33.2%), reactivity-inferred unmeasured VOCs (14.5%), and non-PAMS NMHCs detected by Vocus-PTR (12.2%). These findings underscore the necessity of integrating these species into emission inventories, routine monitoring networks, and regional chemical transport models to improve the accuracy of O₃ predictions. On the other hand, given that these findings are based on observations from a single suburban site in Shanghai during summer, the spatial and seasonal representativeness of these results is inherently limited. While the quantitative contributions may vary across seasons and regions, the bias identified here is driven by photochemical aging and is expected to be generally applicable. Future investigations across diverse geographical regions and seasons are therefore warranted to evaluate the broader applicability of these conclusions. Consequently, by clarifying the OFP of a broader range of VOCs at the emission stage, this work provides an integrated observational–diagnostic framework that bridges ambient measurements with source emissions, offering a more robust tool for identifying key O₃ precursors and informing the design of future process-based modeling studies.

434 **Data availability**

435 The measured and reconstructed concentrations of VOCs detected by Vocus PTR-ToF-MS are available at
436 <https://doi.org/10.5281/zenodo.20606085> (Yin, 2026). The measured and calculated OH reactivity are available at
437 <https://doi.org/10.6084/m9.figshare.19361159> (Yang et al., 2022). The concentrations of PAMS compounds and carbonyls
438 measured by GC-MS/FID and Kore PTR are part of a routine monitoring network and are not publicly available due to data
439 privacy regulations; these data can be made available only with permission of the Shanghai Environmental Monitoring
440 Center.

441 **Supplement**

442 The supplement related to this article is available online.

443 **Author contributions**

444 SY, conceptualization, methodology, investigation, formal analysis, data curation, visualization, writing—original draft, and
445 editing; GY, QF, and JH, conducted the field measurement; CL, YF, and RY, editing; LW, conceptualization, methodology,
446 funding acquisition, project administration, supervision, and editing.

447 **Competing interests**

448 The contact author has declared that none of the authors has any competing interests.

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