1 **Source analyses of ambient VOCs considering reactive losses: methods of**

2 **reducing loss effects, impacts of losses, and sources**

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Abstract

Chemical losses of ambient reactive volatile organic compounds (VOCs) is a long-term issue yet to be resolved in VOC source apportionments. These losses substantially reduce the concentrations of highly reactive species in the apportioned factor profiles and result in the underestimation of source contributions. This review assesses the common methods and existing issues in ways to reduce losses and loss impacts in source analyses and suggest research directions for improved VOC source apportionments. Positive Matrix Factorization (PMF) is now the main VOC source analysis method compared to other mathematical models. The issue in using any apportionment tool is the processing of the data to be analyzed to reduce the impacts of reactive losses. Estimating the initial concentrations of ambient VOCs based on photochemical age has become the primary approach to reduce reactive loss effects in PMF except for selecting low reactivity species or nighttime data into the analysis. Currently, the initial concentration method only considers daytime reactions with hydroxyl ($\cdot$OH) radicals. However, the $\cdot$OH rate constants vary with temperature and that has not been considered. Losses from reactions with O_3 and NO_3 radicals especially for alkene species remain to be included. Thus, the accuracy of the photochemical-age estimation is uncertain. Beyond developing accurate quantitative approaches for reactive losses, source analyses methods for the consumed VOCs and the accurate quantification of different source contributions to O_3 and secondary organic aerosols are important additional directions for future research.

Keywords: Reactive loss; Consumed VOCs; Source analyses; PMF; Initial concentrations

1 Introduction

43

44   Ambient VOCs are key precursors of ozone (O_3) and secondary organic aerosols (SOAs)

45 formation (Li et al., 2016; Li et al., 2018a; Wu and Xie, 2018). Accurate apportionment of their

46 sources can be important in developing effective prevention and control measures for atmospheric O_3

47 and secondary organic particulate matter pollution (Carrillo-Torres et al., 2017; Meng et al., 1997;

48 Wang et al., 2022a). Current research on source analyses of atmospheric VOCs has been primarily

49 conducted utilizing the species ratio method (Che et al., 2019; Zhang et al., 2021), the photochemical

50 age-based parameterization method (Huang et al., 2020; Zhu et al., 2021), and receptor models (e.g.,

51 positive matrix factorization (PMF) (Gu et al., 2020; Liu et al., 2016), chemical mass balance (CMB)

52 (Song et al., 2019), and principal component analysis/multiple linear regression (PCA/MLR) (Jia et

53 al., 2016; Sanchez et al., 2008), etc.) based on the measured concentration data. Receptor models,

54 especially PMF, are the most widely used source apportionment methods (Song et al., 2008; Vega et

55 al., 2022; Yang et al., 2022b). However, compared to particulate matter, ambient VOC species can

56 undergo rapid, complex chemical reactions with •OH radicals, NO_3 radicals, O_3, etc. (Atkinson and

57 Arey, 2003), resulting in substantial chemical losses during their transport from their sources to the

58 receptor site (Yang et al., 2022b; Yuan et al., 2012a). Therefore, the source apportioned results based

59 on the measured VOC data have difficulty to reflect the actual impacts of emission sources on air

60 quality (Wu et al., 2023b; Yang et al., 2022a).

61   To reduce the impact of reactive losses, many studies have selected low-reactivity VOC species

62 to conduct source analyses when using PMF source analyses (Guan et al., 2020; Yang et al., 2022a).

63 However, this method cannot fully solve the issues related to reactive losses and provide complete

64 source apportionments since some highly active marker species such as isoprene (Tan et al., 2020)

65 cannot be excluded from the PMF input species without a substantial loss of information (Liu et al.,

66 2023a). Therefore, recent studies estimated the initial concentrations of ambient VOCs (i.e., the VOC

67 concentrations in the fresh emissions before they can undergo chemical reactions) utilizing the

68 photochemical age-based parameterization method and then performed source analyses with PMF

69 (He et al., 2019; Zou et al., 2023). However, there could still be high uncertainties in the estimated

70 photochemical age of VOC species (Parrish et al., 2007; Yuan et al., 2012b).

71   There were studies that only used nighttime data for source analyses to reduce the loss impacts

72 (Kim et al., 2005), but the representativeness of the apportioned results was likely limited since there

73 could be daytime only sources that would not be observed at night (Buzcu and Fraser, 2006). Some

74 studies applied decay factors to correct the impact of reactive losses in using CMB for VOC source

75 analyses (Friedlander, 1981; Lin and Milford, 1994; Na and Pyo Kim, 2007). However, there were

76 relatively few studies and the effectiveness of this method still needs to be assessed. In 2023, Liu et

77 al. (2023a) systematically investigated the impact of VOCs photochemical losses on the PMF source

78 apportioned results, and found that photochemical losses reduced the concentrations of highly

79 reactive species in factor profiles resulting in the contributions of biogenic emissions and polymer

80 production-related industrial sources being substantially underestimated. However, there has been

81 little related research to assess the limitations of VOC apportionments.

82 With the substantial increase of O_3 concentrations in many locations worldwide in recent years

83 (Li et al., 2020; Zhang et al., 2018; Zhao et al., 2021), accurate source apportionment approaches of

84 the key precursor VOCs have been acquired increasing attention (Gu et al., 2022). Thus, a related

85 issue is the determination of the VOCs consumed in the formation of the observed O_3 and SOAs (Gu

86 et al., 2023). Although some studies have investigated the underestimated contributions of emission

87 sources by comparing the apportioned results based on the initial and measured data (He et al., 2019;

88 Wu et al., 2023a), there are few publications that conducted source analyses for the consumed VOCs

89 and apportioned the contributions of different sources to the formation of O_3 and SOA. In 2023, Gu

90 et al. (2023) attempted to develop a method for apportioning the emission sources of the consumed

91 VOCs, and Wang et al. (2022b) conducted a similar study. Currently, although some studies have

92 been conducted on these issues of VOC reactive losses and achieved some important results (Gu et

93 al., 2023; Watson et al., 2001; Wu et al., 2023b), there remain unresolved issues. To better promote

94 progress on the development of better VOCs source apportioned methods, the present work

95 systematically investigated the main methods and shortcomings of those methods that are currently

96 applied to resolve these issues by reviewing relevant papers, with the aim of identifying directions

97 for the future developments and improvement of VOCs source apportionment methods.

98

99 2 Materials and methods

100 Relevant papers were collected by searching Science Direct (Elsevier), the Web of Science, and

101 the China National Knowledge Infrastructure (CNKI) with keywords: volatile organic compounds

102 (VOCs), oxygenated VOCs (OVOCs), initial concentrations/mixing ratios, chemical/photochemical

103 losses, source apportionment/analysis, positive matrix factorization (PMF), chemical mass balance

104 (CMB), receptor model, and photochemical age-based parameterization method. The information

105 extracted from each publication included methods for reducing the impacts of photochemical losses,

106 the impacts of VOC photochemical losses on source analyses, the source apportioned methods and

107 the results for the consumed VOCs in the atmosphere. This study identified a total of 151 papers, of

108 which 62 were published in the past five years (i.e., 2019-2023), accounting for 41% of the total

109 publications.

110

111 **3 Results and discussion**

112 **3.1 Methods of reducing the impacts of reactive losses**

113 Ambient VOCs can be substantially oxidized by O_3, hydroxyl ($\cdot$OH), and nitrate (NO_3) radicals

114 (Atkinson and Arey, 2003; Bey et al., 2001; Finlayson-Pitts and Pitts, 1997), especially oxidation by

115 $\cdot$OH radicals primarily during the daytime (Wang et al., 2013). Therefore, reducing the impacts of

116 VOC reactive losses on source apportionment has long been an important but not easy issue to

117 resolve in VOC source apportionments (Liu et al., 2023a). Ambient VOCs primarily include alkanes,

118 alkenes, aromatic hydrocarbons, alkynes, OVOCs, and halogenated hydrocarbons, etc. Studies

119 suggested that the Photochemical Assessment Monitoring Stations (PAMS) VOCs (i.e., alkanes,

120 alkenes, aromatic hydrocarbons, and alkynes) accounted for ~58% of total VOCs (TVOCs), while

121 OVOCs and halogenated hydrocarbons contributed ~8.5%-63% and ~0.1%-14% to the TVOCs,

122 respectively (Table S1) (Li et al., 2016; Wu et al., 2023a; Zhu et al., 2021). The reported number of

123 measured species ranged from 13 to 116, including 0-32 alkanes, 2-16 alkenes, 1 alkyne (only

124 acetylene), 3-18 aromatic hydrocarbons, 4-21 OVOCs, and 28-35 halogenated hydrocarbons. There

125 were substantial differences in the identified emission sources for the different types of VOCs (Mo et

126 al., 2016). For example, PAMS VOCs mainly originate from primary anthropogenic sources (Chen et

127 al., 2010), while OVOCs can also be formed by oxidation of PAMS VOCs in addition to primary

128 source emissions (Chen et al., 2014; Seinfeld and Pandis, 1986). The contributions of secondary

129 formation to some OVOC species (e.g., acetaldehyde and propionaldehyde) can exceed 50% (de

Gouw et al., 2005). In addition to local emissions, the ambient concentrations of halogenated
hydrocarbons can also be affected by the long-distance transport (Mintz and McWhinney, 2008).
Therefore, utilizing only the same source analyses approach for multiple VOC species from different
sources might produce results with high uncertainties in the apportionments.

Source analyses methods for ambient VOCs mainly included PMF, CMB, and photochemical
age-based parameterization method (Table S2). PMF was the most commonly method used for
source analyses (Yang et al., 2022b). Approximately 61% of the reviewed publications focused on
source analyses of PAMS species using PMF, while OVOCs primarily used photochemical age-based
parameterization for source apportionment but with only relatively few studies (only 7 papers) (Table
S3). Additionally, the studies on data from simultaneous measurement of both PAMS and OVOC
species utilized two methods to conduct source analyses: one method was to simultaneously input
PAMS and some OVOC species into the receptor model (e.g., PMF) for source analyses and only
separated primary and secondary source contributions of ambient VOCs (Li et al., 2023; Liu et al.,
2023b; Tan et al., 2021) (Table S2). Another approach was to use the PMF and photochemical age-
based parameterization to obtain the source apportioned results for ambient PAMS and OVOCs,
respectively, and then combined the two apportioned results to obtain finally source resolution results
for the ambient VOCs (Zhu et al., 2021). However, the utilization of this method has been limited.

3.1.1 Methods for reducing reactive loss in PMF source analyses

3.1.1.1 Selecting low activity species or incorporating night only data into PMF

The methods of reducing effects of reactive losses for source apportionments utilizing different
models are shown in Fig. 1. At present, selecting the VOC species with lower reactivity to be input in
PMF for apportionment is the most commonly used approach (Chen et al., 2019; Tan et al., 2020;
Yang et al., 2022b). Many highly active alkene and aromatic hydrocarbon species were not included
in the PMF calculations (Gu et al., 2023; Liu et al., 2023a). For example, Liu et al. (2023a) excluded
highly active species such as 1-hexene, trans-2-butene, trans-2-pentene, cis-2-pentene, and cis-2-
butene. In addition, some studies have utilized nighttime only data for source analyses (Buzcu-
Guven and Fraser, 2008; Buzcu and Fraser, 2006; Kim et al., 2005; Xie and Berkowitz, 2006).
However, the volatile emission sources commonly contribute substantially to VOCs during the

159   daytime (Gu et al., 2023). For example, Buzcu and Fraser (2006) used nighttime and all-day data to

160   conduct VOC source apportionment in Houston, respectively. They found that the night only data did

161   not identify biogenic or gasoline sources due to minimal emissions at night. Thus, the contributions

162   of the nighttime emission sources substantially increased compared to the all-day results because of

163   the missing source types. Meanwhile, the all-day VOC source analysis conducted by Zhao et al.

164   (2004) in Houston during the same period also showed substantial differences from the results

165   reported by Buzcu and Fraser (2006) utilizing night-only data. An additional consideration is that

166   VOCs can react with NO_3 radicals at night causing reactive losses. Thus, this approach does not

167   eliminate the effects of all possible loss mechanisms.

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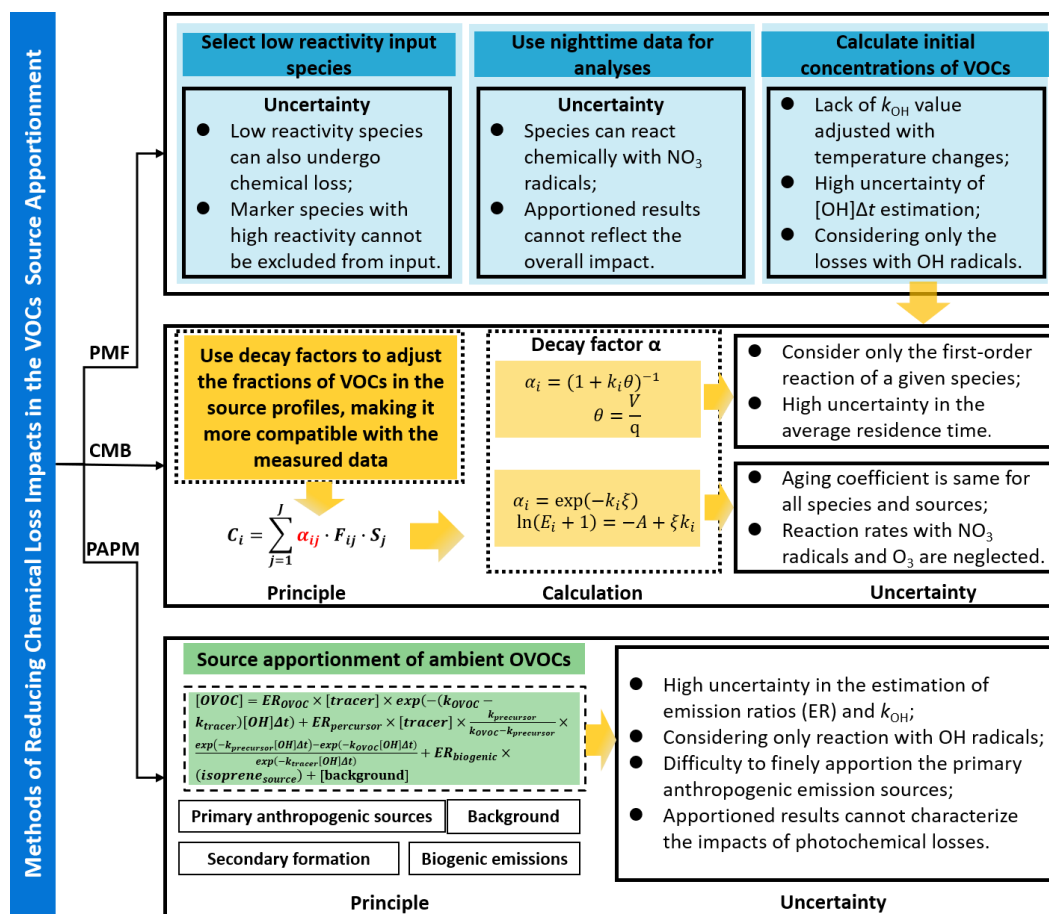

169

170   **Figure 1.** Methods for reducing the impacts of reactive losses for different source analyses models.

171 PMF represents positive matrix factorization, CMB represents chemical mass balance, and PAPM
172 represents photochemical age-based parameterization method.

173

3.1.1.2 Incorporating VOC initial concentration estimated by photochemical age-based
174
175 **parameterization method into PMF**

176   The photochemical age-based parameterization method is an approach to estimate the initial

177 concentrations of ambient VOCs (Shao et al., 2011; Wang et al., 2013; Yuan et al., 2012b). This

178 method assumes that the chemical loss of ambient VOCs mainly originates only from reactions of

179 the VOCs with •OH radicals (Parrish et al., 1992; Sun et al., 2016; Wang et al., 2013). The

180 photochemical ages (Δt) of VOC species are estimated, and then combined with the rate constants

181 for reaction for •OH radicals with the VOC species ($k_{\bullet OH}$) to calculate their initial concentrations and

182 quantified the VOC photochemical losses (Shao et al., 2011; Wang et al., 2013; Zhan et al., 2021).

183 The equation for the initial concentration calculation is shown in Eq. (1), where $k_{\bullet OH}$ and Δt are the

184 key parameters in this approach.

185     $[VOC]_t = [VOC]_0 \times \exp\left(-k_{\bullet OH} \times [\bullet OH]\Delta t\right)$ (1)

186 where $[VOC]_0$ and $[VOC]_t$ are the initial and measured concentrations of VOC at time t, $[\bullet OH]$

187 represents the concentration of •OH radical. However, many studies estimated $[\bullet OH]$ Δt because of

188 the lack of •OH radical concentration data and defined the product as the •OH exposure (Shao et al.,

189 2011; Wei et al., 2022; Yuan et al., 2012b).

190   The $k_{\bullet OH}$ of VOC species are substantially affected by atmospheric temperature (Atkinson and

191 Arey, 2003), which could be commonly measured in laboratory (or chamber) experiments or through

192 the use of detailed chemical computer models (Atkinson and Arey, 2003). According to the reviewed

193 papers regarding the estimation of photochemical age, it was found that approximately 46% of the

194 publications used the Atkinson and Arey's 2003 summary of $k_{\bullet OH}$ values at 298° K (Atkinson and

195 Arey, 2003), and approximately 9% used Carter's 2010 summary of $k_{\bullet OH}$ values at 300° K (Carter,

196 2010). The detailed $k_{\bullet OH}$ values for different VOC species summarized in these two publications are

197 provided in Table S4. However, other relevant studies cited $k_{\bullet OH}$ values from other papers by

198 Atkinson and/or Carter (Atkinson, 1991, 2007; Atkinson et al., 2006; Talukdar et al., 1994). The rate

199 constant for a bimolecular reaction between a hydroxyl radical and a VOC molecule has a roughly

200 exponential dependence on temperature in the Arrhenius equation (Liu et al., 2023a). Therefore,

201   these published papers only used $k_{\cdot OH}$ values at specific temperatures, which made it difficult to

202   characterize the actual reaction rates at the actual temperatures in the atmosphere. To address this

203   issue, Wang et al. (2022b) and Wang et al. (2023) utilized the Arrhenius expression to locally

204   optimize the $k_{\cdot OH}$ values of VOC species based on the actual temperature conditions to further

205   improve the accuracy of estimating the VOC initial data. In addition, some studies used the $k_{\cdot OH}$ of

206   m,p-xylene instead of values of more reactive species to reduce high-outliers when estimating the

207   initial concentration (Wang et al., 2013). However, the validity of this method was difficult to assess.

208   There are two main methods (as shown in Table S5) for estimating Δt, namely, the species ratio

209   method (Roberts et al., 1984; Shao et al., 2011; Wan et al., 2022) and the sequential reaction model

210   (Gong et al., 2018; Shao et al., 2011; Xie et al., 2008). The specific details are as follows:

211   **(1) Estimation of Δt based on the species ratio method**

212     $\Delta t = \frac{1}{(k_A - k_B) \times [OH]} \times \left[ln\left(\frac{[A]_0}{[B]_0}\right) - ln\left(\frac{[A]_t}{[B]_t}\right) \right]$ (2)

213   where k_A and k_B are the reaction rate constants with •OH radicals for species A and B of highly

214   homologous species with substantial differences in reaction activity, respectively, $\frac{[A]_0}{[B]_0}$ is the initial

215   concentration ratio of A to B in fresh emissions, $\frac{[A]_t}{[B]_t}$ is the measured concentration ratio of A to B at

216   time t. The determination of initial concentration ratio of A to B was extremely critical for estimating

217   the Δt. The Δt is used to then calculate the initial concentrations of the VOCs of interest using Eq. (1).

218   The initial concentrations can then be the input variables to PMF (Liu et al., 2023a).

219   This ratio method was first proposed by Roberts et al. (1984). The method has been

220   commonly applied to PAMS species emitted by anthropogenic sources. There have been differences

221   in the species used to calculate the initial ratio in different papers (Table S6). Generally aromatic

222   hydrocarbons (e.g., benzene, toluene, ethylbenzene, or m,p-xylene) were used as the selected species.

223   The substantial differences in activity and high homology are generally the main basis for selecting

224   species-ratio types (Lin et al., 2011; Shao et al., 2009; Zou et al., 2021; Zou et al., 2023). Most

225   publications used the initial ratios of ethylbenzene/m,p-xylene (E/X) or m,p-xylene/ethylbenzene

226   (X/E) to calculate Δt. These two species accounted for ~36.8% of the total reviewed publications in

227   this study (Table S6), respectively. Approximately 15.8% of the papers used toluene/benzene (T/B),

228   while m,p-xylene/benzene (X/B) and ethylbenzene/o-xylene (E/O) had limited use, accounting for

229   ~5.3% and ~10.5% of the reviewed publications.

230   The methods for obtaining the initial species ratio in the reviewed papers mainly included

231   referring to other similar studies (Wang et al., 2016), source emission inventory values (Wang et al.,

232   2013), and estimation based on the observed concentration data at the receptor sites at times when

233   low reactivity was expected (Fang et al., 2021; Han et al., 2019; Wu et al., 2023b). There were

234   several papers using the first two methods to obtain the initial species ratios (Table S6). The initial

235   species ratios obtained by these methods had difficulty to accurately characterize the comprehensive

236   impacts of multiple sources in the study area. Most studies were based on the observed data of low

237   photochemical reaction periods at night (~ 19:00 to 07:00 LT) to calculate the initial species ratios

238   (Table S6). This method assumes that VOC species emitted by different sources during the certain

239   periods of night would not undergo oxidative reaction, and the concentration ratio of two

240   homologous species had no the change during the transport process from source emissions to the

241   receptor sites (Liu et al., 2023a; Sun et al., 2016; Yuan et al., 2012b). Since there could be residual

242   reactions with nitrate radical and multiple sources of the indicator species, there remains uncertainty

243   in the results. For example, McKeen and Liu (1993) and McKeen et al. (1996) found that the species

244   ratios can be substantially influenced by the oxidative chemistry and atmospheric mixing.

245   Comparing one species versus another, both the model results and the observations were consistent

246   with an average rate of dilution roughly equivalent to n-butane oxidation (McKeen et al., 1996). This

247   result has negative implications for the use of hydrocarbon ratios as chemical reaction clocks

248   (McKeen et al., 1996). Parrish et al. (2007) also suggested that there were uncertainties in the

249   determination of Δt by the initial species ratios because of influence of fresh emissions along the

250   transport path that perturb the results. However, this approach can still provide a useful measure of

251   chemical processing in the atmosphere (Parrish et al., 2007).

252   There were differences in the estimation details of the initial species ratio in different reports

253   (Liu et al., 2023a; Shao et al., 2011; Yuan et al., 2012b). For example, Yuan et al. (2012b) utilized the

254   m,p-xylene and benzene data measured between 0:00 and 5:00 LT to conduct a linear fit. The

255   regression line was then extrapolated to the highest benzene concentration during this period so that

256   the initial ratio could be estimated from the m,p-xylene to benzene concentration ratios at this point.

257   Wu et al. (2023b) and Yang et al. (2022a) used time periods (00:00-04:00 LT and 20:00-05:00 LT,

258 respectively) with the lowest and the highest E/X and T/B ratios at night to calculate the average

259 values of corresponding E/X ratios less that various percentiles or the corresponding T/B values

260 above various percentiles, and then determined the initial ratio by the minimum average ratio (i.e.,

261 E/X) or the maximum average ratio (i.e., T/B) of the two species with the highest homology (i.e.,

262 highest correlation) below different percentiles. Wu et al. (2023a) reported that the maximum value

263 of X/E at 01:00-06:00 LT was considered as the initial species ratio. In addition, Liu et al. (2023a)

264 utilized the slope of the linear fit of the scatterplots of corresponding ethylbenzene and m,p-xylene

265 below the 10th percentile of E/X ratios during 00:00-05:00 LT to determine the initial ratio. Overall,

266 the E/X range in the reviewed papers was between 0.22 and 0.75, T/B was between 3.14 and 4.25,

267 X/E was between 0.39 and 2.47, E/O was between 1.30 and 1.32, and X/B was 2.2 (Table S6).

268 Zhang et al. (2020) attempted to confirm the feasibility and rationality of estimating Δt based on

269 T/B utilizing the regressions of benzene and toluene versus CO and Δt. Zou et al. (2023)

270 demonstrated the rationality of selecting the ratio of E and X to estimate the Δt through high

271 correlation of these two species having substantial activity differences. However, there were few

272 studies to systematically assess how to choose the most suitable species ratios and the calculated

273 method.

274 Multiple types of initial species ratios were used for estimating Δt of VOCs (Table S6), and the

275 results estimated by the different ratios could vary substantially. Shao et al. (2011) suggested that the

276 differences between the initial concentrations calculated using the ratios of three pairs of compound

277 ratios (i.e., T/B, X/E, and i-butene/propene (iB/P)) were generally within 50%, and the X/E and iB/P

278 results were in good agreement. Zou et al. (2021) examined the sensitivity of estimating initial

279 concentration based on E/X and E/O initial ratios. They found that the relative variation range of the

280 initial concentrations of PAMS species was between 0.41% and 68.06% for an initial E/O of 1.3

281 when compared with an initial E/X of 0.5.

282 Additionally, in the ratio method, the same Δt was calculated for different VOCs for each

283 sample, and the paired species for estimating the ratio were aromatic hydrocarbons (Table S6), which

284 are mainly emitted from anthropogenic emission sources such as solvent use and petrochemical

285 enterprises (Mo et al., 2015; Na et al., 2004; Yuan et al., 2010; Zhang et al., 2016). Therefore, the Δt

286 obtained based on these ratios may only reflect the chemical aging of VOC species emitted from

287 these specific sources. It is difficult to accurately characterize the Δt for these species from other

288 sources. In the future, different types of species ratios (not just aromatic hydrocarbons) need to be

289 selected based on VOC species from different sources. The Δt derived from different types of VOC

290 species should be calculated to improve traditional ratio methods.

291   An additional issue is that this method only considers the reactions between VOCs and •OH

292 radicals, while chemical reactions with O_3 during the day or NO_3 radicals at night were generally

293 excluded. Liu et al. (2023a) attempted to estimate the reactive losses between 19:00 and 23:00 LT,

294 but they considered the gradual loss of •OH radicals after sunset and did not consider the losses

295 caused by NO_3 radicals reactions that may be present at night since they are not photolyzed as occurs

296 in the daylight. Additionally, alkenes can directly react with O_3 in the atmosphere causing losses.

297 However, there are currently no reports on estimation methods for these reactive losses. In future

298 studies, the ratio of two alkene species with substantial differences in reaction rates with O_3 could be

299 used as the base ratio as in Eq. (2), and combined with measured O_3 reaction rate constants

300 (Atkinson and Arey, 2003) to estimate the chemical reaction time (Δt) of alkene species with O_3.

301 Then, chemical losses of alkene species in the reaction with O_3 could be estimated using Eqs. (1) and

302 (9) and the combined effects of O_3 and •OH could be estimated.

303

304 **(2) Estimation of Δt based on the sequential reaction model**

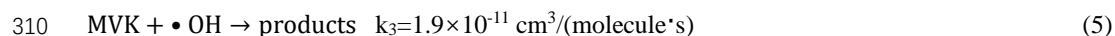
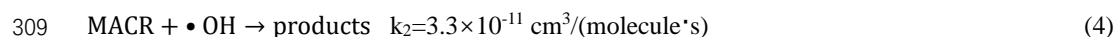
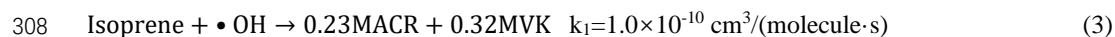
305   It has been found that using the ratio method to calculate the Δt of isoprene could result in

306 overestimation (Wu et al., 2023a; Yang et al., 2022b). An alternative is the sequential reaction

307 method. It is based on measurements of the reaction products of these reactions.

308  Isoprene $+$ • OH $\rightarrow$ 0.23MACR + 0.32MVK $k_1 = 1.0 \times 10^{-10}$ cm^3/(molecule·s)    (3)

309  MACR $+$ • OH $\rightarrow$ products $k_2 = 3.3 \times 10^{-11}$ cm^3/(molecule·s)        (4)

310  MVK $+$ • OH $\rightarrow$ products $k_3 = 1.9 \times 10^{-11}$ cm^3/(molecule·s)         (5)

311  $\frac{[MACR]_t}{[Isoprene]_t} = \frac{0.23k_1}{k_2 - k_1}(1 - e^{(k_1 - k_2)[•OH]\Delta t})$            (6)

312  $\frac{[MVK]_t}{[Isoprene]_t} = \frac{0.32k_1}{k_3 - k_1}(1 - e^{(k_1 - k_3)[•OH]\Delta t})$            (7)

313 where MVK is methyl vinyl ketone, MACR is methacrolein; k_1, k_2, and k_3 are the rate constants

314   reacting with •OH of isoprene, MACR, and MVK, respectively; $[MVK]_t$, $[MACR]_t$, and $[isoprene]_t$

315   are the measured ambient concentrations at time t.

316   This sequential reaction method was first proposed by Bertman et al. (1995) and was commonly

317   used to estimate the Δt of isoprene emitted primarily from biogenic emissions (Gong et al., 2018;

318   Roberts et al., 2006; Wu et al., 2023a). Assuming the •OH-driven isoprene oxidation mechanism

319   (Eqs. (3)-(5)) from the laboratory chamber studies of Carter and Atkinson (1996), Stroud et al. (2001)

320   quantified the Δt of isoprene by the reaction relationship between isoprene and its oxidation products

321   (Eqs. (6)-(7)) (de Gouw et al., 2005; Wu et al., 2023a; Xie et al., 2008). The synchronous

322   measurement of MVK and MACR is critical to obtain Δt utilizing this method. Numerous studies

323   failed in estimating the isoprene Δt due to the lack of MVK and MACR (Gu et al., 2023; Liu et al.,

324   2023a; Wang et al., 2023). Although some studies have used the average of Δt obtained from both

325   MVK and MACR as the final Δt (Xie et al., 2008), there has been little assessment of which method

326   was more suitable.

327   Additionally, there were studies using the isotopic hydrocarbon clock method (Kornilova et al.,

328   2016; Rudolph and Czuba, 2000; Saito et al., 2009) to estimate the species Δt, that was calculated by

329   the decay of isotopes in the emissions to the ambient receptor site (Table S5). However, the studies

330   only calculated the Δt without estimating the species initial concentrations. Our study found that

331   approximately 76% of the publications that calculated the Δt used the species ratio method,

332   approximately 10% used both the ratio method and the sequential reaction model, while a few used

333   other methods (Table S5).

334

335   **3.1.2 Reducing the losses impacts in OVOC source analyses based on photochemical age**

336   Ambient OVOCs are an important fraction of VOCs, which primarily included aldehydes,

337   ketones, ethers, and alcohols (Mellouki et al., 2015) since OVOC photolysis is one of the main

338   sources of •OH radicals (Li et al., 2018b). The OVOCs can be directly emitted from biogenic and

339   anthropogenic sources (Huang et al., 2019; Huang et al., 2020; Tanimoto et al., 2014) and can also be

340   formed by oxidation with •OH radicals, O_3, and NO_3 radicals (Legreid et al., 2008; Sahu et al., 2016;

341   Tanimoto et al., 2014). OVOCs were commonly apportioned by the photochemical age-based

342   parameterization method as shown in Eq. (8).

343   $[OVOC] = ER_{OVOC} \times [tracer] \times \exp(-(k_{OVOC} - k_{tracer})[\bullet OH]\Delta t) + ER_{percursor} \times$

344   $[tracer] \times \frac{k_{precursor}}{k_{OVOC}-k_{precursor}} \times \frac{\exp(-k_{precursor}[\bullet OH]\Delta t)-\exp(-k_{OVOC}[\bullet OH]\Delta t)}{\exp(-k_{tracer}[\bullet OH]\Delta t)} + ER_{biogenic} \times$

345   $(isoprene_{source}) + [background]$ (8)

346   where [OVOC], [tracer], and [background] are the concentrations of measured ambient OVOCs, the

347   tracer (e.g., benzene, acetylene: C_2H_2, or carbon monoxide: CO, Table S7) from primary

348   anthropogenic sources, and background OVOC concentration, respectively; k_{OVOC}, k_{tracer}, and $k_{precursor}$

349   are the •OH rate constants of the OVOCs, tracer, and precursor, respectively, and k_{OVOC} and k_{tracer} are

350   commonly obtained from the related publications (Atkinson and Arey, 2003); ER_{OVOC} and $ER_{precursor}$

351   are the emission ratios of OVOCs and precursors relative to the tracer, respectively, $ER_{biogenic}$ is the

352   emission ratio of OVOCs to the isoprene concentration emitted from biogenic sources (i.e.,

353   $isoprene_{source}$), and ER_{OVOC}, $ER_{precursor}$, $ER_{biogenic}$, $k_{precusor}$, and [background] can be determined from a

354   linear least-squares fit that minimizes the difference between the measured [OVOC] and those

355   calculated from Eq. (8), ER values in the reviewed papers are listed in Table S8; [•OH]Δt represents

356   the exposure of •OH radicals, which can be estimated by Eq. (2); and $isoprene_{source}$ can be estimated

357   by Eqs. (6)-(7) and (1) based on the measured concentrations of ambient isoprene and its

358   photochemical products (i.e., MVK and MACR). The chemical removal of isoprene in the

359   atmosphere is so rapid that it is impossible to differentiate between primary and secondary OVOC

360   sources based on the measured data. Therefore, $isoprene_{source}$ represents both primary and secondary

361   biogenic sources (de Gouw et al., 2005).

362   However, this method remains highly uncertain because of the source complexities of OVOCs

363   (Mo et al., 2016; Schlundt et al., 2017). This method assumes that (1) anthropogenic emissions of

364   OVOCs and their precursors are proportional to the selected primary tracer, (2) the removal process

365   of OVOCs is dominated by reactions with •OH radicals, (3) biogenic sources of OVOCs are

366   proportional to the emission of isoprene, and (4) the photochemical age for a sampled air mass can

367   be determined (de Gouw et al., 2005).

368   This method estimates the source contributions of primary and secondary anthropogenic sources,

369   biogenic emissions, and background to different OVOC species, and then further obtained the

370   contributions of the four types of sources to the ambient OVOCs (de Gouw et al., 2005; Yuan et al.,

371 2012b; Zhu et al., 2021). This approach was difficult to finely apportion the contributions of primary

372 anthropogenic sources and to obtain the contributions of primary and secondary biogenic emissions.

373 Therefore, to obtain refined source apportioned results for OVOCs, many studies incorporated both

374 OVOC and PAMS species into the receptor model for source analyses (Guan et al., 2020; Yang et al.,

375 2019; Zhou et al., 2022).

376 This method defines the measured concentrations of OVOCs as the sum of the concentrations

377 after photochemical losses (i.e., losses caused by the formation of O_3 and SOAs via photochemical

378 reactions) of OVOCs directly emitted by anthropogenic sources (i.e., the first term in Eq. (8)), the

379 concentrations after photochemical losses of OVOCs formed by the conversion of precursors emitted

380 from anthropogenic sources (i.e., the second term in Eq. (8)), the concentration from biogenic

381 emissions (without considering losses because of small contributions of biogenic emissions) (i.e., the

382 third term in Eq. (8)), and the background concentration (i.e., the fourth term in Eq. (8)). Therefore,

383 although this approach considered the influences of photochemical losses in the calculation process,

384 the final results only reflected the contributions of four types of sources to the measured OVOCs and

385 could not characterize the impacts of photochemical losses. In addition, to compensate for the

386 photolytic losses in OVOCs in Eq. (8), which was not considered by de Gouw et al. (2005), Huang et

387 al. (2020) and Zhu et al. (2021) introduced a modification coefficient (m) before the k_{OVOC} to modify

388 it, assuming that the photolysis rate is proportional to the •OH reaction rate (de Gouw et al., 2005;

389 Wang et al., 2017). The m value depends on the relative rate of photolysis versus the •OH reaction

390 for an OVOC species. However, related studies remain limited at present.

391

392 **3.1.3 Methods for reducing loss effects in CMB source apportionments**

393 The chemical mass balance method uses known profiles measured at the source. Thus, any

394 reactions in transit will result in a change in that source's profile and difficulty in fitting the data at

395 the receptor site. Thus, corrections to the receptor site data are needed to make them comparable to

396 the measured source profiles. As early as the 1980s and 1990s, studies had been conducted to reduce

397 the impacts of different VOC species reactions on CMB estimation results, including minimization

398 of reaction effects by limiting source profiles to VOCs with similar reaction rates (Harley et al., 1992;

399 Lewis et al., 1993; Nelson and Quigley, 1983; Wadden et al., 1986) and VOC samples obtained

400 during winter (Aronian et al., 1989) or early in the morning (Scheff and Klevs, 1987). In 1983,

401 Nelson and Quigley (1983) estimated the reactions extent by the changes in the ratios of xylene to

402 ethylbenzene at the receptor and the release site and then obtained decay factors of other VOC

403 species. However, it was found that the concentrations adjusted by decay factors at the receptor site

404 had little impact on their estimated source contributions (Nelson and Quigley, 1983). Since the

405 emissions varied with time, especially during periods of intense photochemical reactions (Lin and

406 Milford, 1994), some studies tried to use decay factors to adjust the fractions of VOC species in the

407 source profiles at different times, making them more compatible with the data measured at the

408 receptor site (Lin and Milford, 1994; Na and Pyo Kim, 2007). However, this approach has not been

409 used other than in these two instances.

410 There are two methods to obtain the decay factors: one method was to considering an urban

411 airshed as a continuous stirred tank reactor and relating the decay factor for a given species to its

412 first-order reaction rate constant (Friedlander, 1981). The other method was to conduct estimation

413 based on the reaction rate constants of specific VOC species and "aging coefficients" (Junninen et al.,

414 2006; Lin and Milford, 1994). The details and limitations of the two methods are provided in Text S1.

415 However, this method of adjusting source profiles cannot truly address the issue of reactive losses

416 affecting the CMB apportioned results. Since the receptor measured data and adjusted source profiles

417 input to CMB were both data after reactive losses. With the progress of VOC source analyses studies

418 in recent years, this method has not been widely applied and further developed in CMB source

419 analyses. This change might be because CMB itself required input from VOC source profiles, but

420 there were relatively few locally measured VOC source profiles due to high costs and difficult to

421 obtain access to the source facilities (Yang et al., 2022b).

422 Alternatively, with the monitoring of highly time resolved VOCs data in recent years, it became

423 infeasible to use CMB to conduct source analyses, because CMB requires analysis of one sample

424 (one hour) at a time resulting in needing thousands of separate analyses (Yang et al., 2022b).

425 Additionally, the weights in the analyses are generally based only on the measurement uncertainties

426 of the measurement samples from specific sources at a few specific times. Thus, CMB does not

427 account for variability in the source profiles that is included in the uncertainty values used to weight

428 the data in PMF (Yang et al., 2022b). To reduce the impact of reactive losses, the initial concentration

429   data estimated by photochemical age-based parameterization method has been used as input into

430   CMB for source analyses (Shao et al., 2011). Additionally, the methods for reducing the impacts of

431   reactive losses in PMF and CMB primarily focused on the PAMS species, and few considerations for

432   OVOCs.

433

434   3.2 Effects of reactive losses on source analyses

435   According to the review of relevant publications, it has been found that most of the current

436   studies analyzed the impacts of VOC photochemical losses on the source contributions by comparing

437   the PMF apportioned results based on the measured and initial concentrations estimated by a

438   photochemical age-based parameterization method (Gao et al., 2018; Kong et al., 2023; Li et al.,

439   2023; Liu et al., 2023c; Zou et al., 2023). For example, Wang et al. (2013) found that the

440   contributions of biogenic and industrial emissions were underestimated by 30% and 10%,

441   respectively, due to photochemical losses. Liu et al. (2023a) suggested that biogenic emissions and

442   polymer production-related industrial sources in Tianjin were underestimated by 73% and 50%,

443   respectively. Wu et al. (2023a) also reported that the underestimation of the contribution of biogenic

444   emissions was substantially higher than other sources. In 2023, Liu et al. (2023a) systematically

445   investigated the impacts of photochemical losses of VOCs on the PMF apportioned factor profiles

446   and contributions by comparing the estimated results based on the initial and measured

447   concentrations, and found that the photochemical losses reduced the concentrations of these highly

448   reactive species in the apportioned factor profiles based on the measured data. Meanwhile, Gu et al.

449   (2023) also obtained similar results. However, due to the uncertainty of initial concentration

450   estimation, the reliability of these results needs further validation and evaluation. Thus, further

451   research is required.

452

453   3.3 Estimation methods of VOC reactive losses

454   There were two main methods for estimating the reactive losses of VOCs in the atmosphere.

455   The first was to estimate the initial concentrations of VOCs utilizing the photochemical age-based

456   parameterization method (Liu et al., 2023a; Wu et al., 2023b), and the differences between the initial

457   and the measured concentrations were considered to the photochemical losses of VOCs (Table S9)

458   (as shown in Eq. (9)) (Wang et al., 2023; Wu et al., 2023b). Due to the uncertainty in the initial

459   concentration estimation (as shown in section 3.1.1.2), there were also uncertainties in the estimated

460   photochemical losses.

461    $[VOC]_{C,t} = [VOC]_t \times (\exp(k_{VOC}[\bullet OH]\Delta t) - 1)$ (9)

462   where [VOC]$_{C,t}$ represents the photochemical loss of VOC at time t, $Kvoc$ represents the reaction rate

463   constants with •OH radicals of VOC, and [•OH]Δt represents the exposure of •OH radicals.

464   The second method applies to other VOC species without isoprene in which the losses could be

465   estimated utilizing isoprene conversion (Wiedinmyer et al., 2001). In this study, it was defined as the

466   isoprene loss reference method (Table S9). Its principle is to first use the photochemical-age

467   parameter method based on the sequential reaction model as shown in Eqs. (1) and (6)-(7), to

468   estimate the photochemical loss of isoprene (i.e., Δ isoprene), and then the photochemical losses of

469   other VOC species can be estimated by proportion relationship ($\frac{k_{VOC}}{k_{isoperene}} \times \frac{[VOC]_t}{[isoprene]_t}$) between Δ

470   isoprene and other species losses (Wiedinmyer et al., 2001; Xie et al., 2008) (as shown in Eq. (10)).

471   This method assumes that the relative source strengths of VOCs are constant in an immediate area

472   surrounding the site, that atmospheric transport and dispersion are non-limiting factors compared

473   with chemistry (Xie et al., 2008), and the photochemical losses of other VOC species can be

474   calculated by Eq. (10).

475    $[VOC]_{C,t} = \Delta isoprene \times \frac{k_{VOC}}{k_{isoperene}} \times \frac{[VOC]_t}{[isoprene]_t}$ (10)

476   where $k_{isoprene}$ represents the reaction rate constants with •OH radicals of isoprene, and [isoprene]$_t$

477   represents the measured concentration of isoprene at time t.

478   Because isoprene mainly originates from natural sources (Fu et al., 2008; Kuhn et al., 2004; Lu

479   et al., 2019), while many other VOC species are primarily emitted from anthropogenic sources (Li et

480   al., 2021; Seinfeld and Pandis, 1986; Wei et al., 2011). Therefore, the assumption of this method

481   itself has an obvious issue, which resulted in high uncertainties in the estimations. This defect

482   substantially limits its application, only 2 publications have utilized this method to quantify chemical

483   losses of VOCs in this study (Wiedinmyer et al., 2001; Xie et al., 2008), and most studies still used

484   the first method (Table S9).

485

486   **3.4 Spatiotemporal variation of VOC reactive losses**

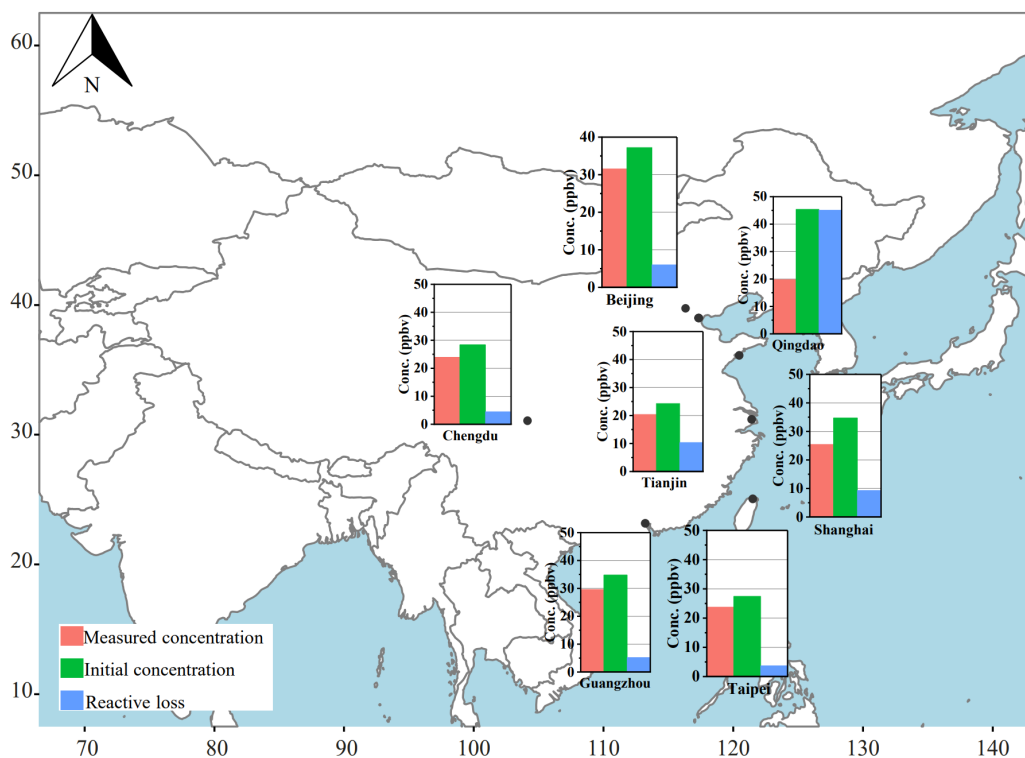
487   According to the papers reviewed in this study, we found that studies on the VOC

488   photochemical losses were mainly conducted in Chinese cities. The VOC losses in different cities are

489   provided in Figs. 2-3 and S1 and Table S10. Due to relatively limited number of studies, the

490   representativeness of the analyses of the spatiotemporal distributions of photochemical losses of

491   VOCs might also be limited. In addition, this study converted the unit of ppbC in some papers (Chen

492   et al., 2023) to ppbv for better comparative analyses.

493

494   **Figure 2.** The measured, initial, and reactive loss concentrations of ambient VOCs in Beijing (Gao et
495   al., 2018; Ma et al., 2022; Zhan et al., 2021), Tianjin (Liu et al., 2023a; Wang et al., 2023), Shanghai
496   (Wang et al., 2013), Chengdu (Kong et al., 2023), Guangzhou (Wang et al., 2023), Qingdao (Gu et al.,
497   2023), and Taipei (Chen et al., 2023). The data in Beijing was the average from three published
498   papers data. The horizontal axis represents longitude (ºE), and the vertical axis represents latitude
499   (ºN). The base map is from Natural Earth.

500

501   The photochemical loss of VOCs in Qingdao was the highest (45.1 ppbv), followed by Tianjin

502   (2.9-17.8 ppbv), Shanghai (9.00-9.60 ppbv), Taipei (0.76-8.29 ppbv), Beijing (3.40-7.72 ppbv),

503   Chengdu (2.30-6.60 ppbv), and Guangzhou (5.20 ppbv). The chemical loss rate (i.e., chemical

504   loss/initial concentration) in Qingdao (69.1%) was the highest, and the lowest was in Taipei (2.97%-

505 27.3%). Compared to other VOC groups, alkenes had the highest loss (Figs. 3 and S1), accounting

506 for 55.4%-93.3% of the total losses, followed by aromatic hydrocarbons (3.81%-38.7%), and alkanes

507 (2.33%-22.7%) (Table S11). There were substantial differences in VOC species with high losses in

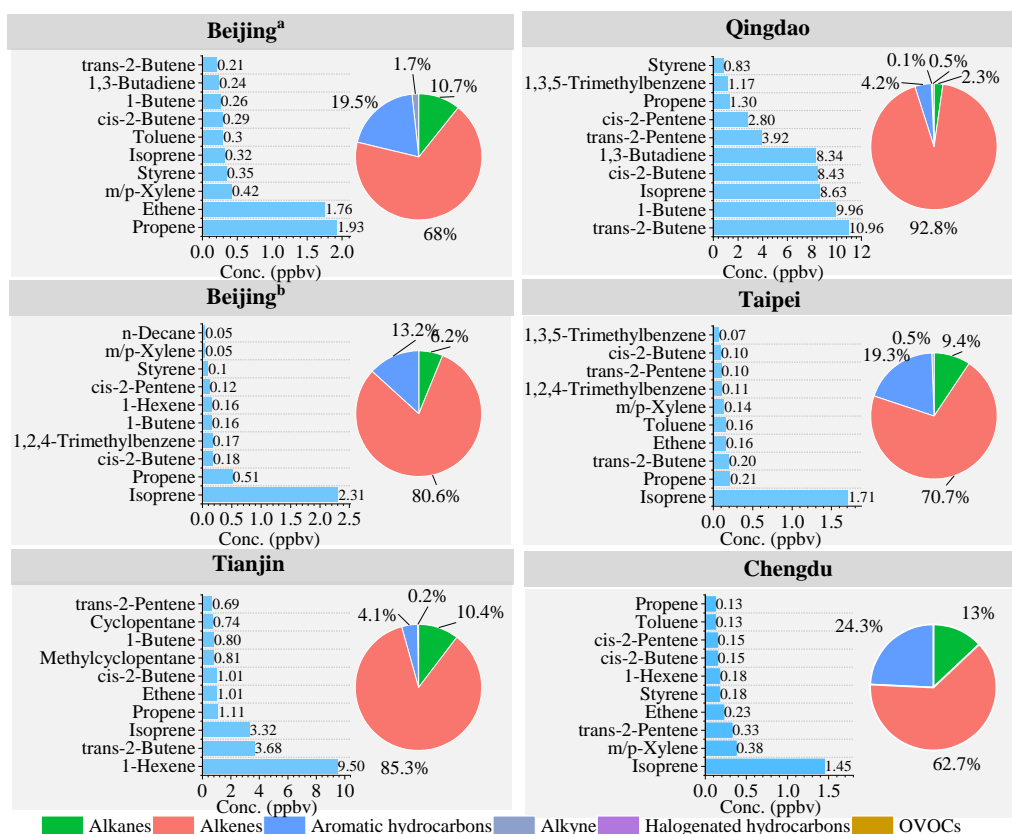
508 different cities (Fig. 3). The losses of ethene, propene, and isoprene in most cities were relatively

509 higher than those of other species (Fig. 3), likely closely related to their high reactivities (Table S4).

510 The reactive losses of 1-butene and trans-2-butene in Qingdao were 10.96 and 9.96 ppbv,

511 substantially higher than other species, while the loss of 1-hexene (9.50 ppbv) in Tianjin was

512 remarkably higher compared to other species. However, the losses of isoprene in Beijing, Chengdu,

513 and Taipei were the highest (Fig. 3).

514

515 **Figure 3.** The photochemical losses and percentages of the main VOCs in Beijing (a: cited from
516 publication (Gao et al., 2018) and b: cited from publication (Zhan et al., 2021)), Qingdao (Gu et al.,
517 2023), Taipei (Chen et al., 2023), Tianjin (Liu et al., 2023a), and Chengdu (Kong et al., 2023).

518

519   In addition, the VOC reactive losses in spring and summer were substantially higher than those

520   in autumn and winter. Atmospheric oxidation and meteorological factors can have impacts on the

521   VOC losses. The trend of the reactive losses of VOCs was often consistent with the changes in the

522   concentrations of O_x (O_3+NO_2) in the atmosphere (Wang et al., 2013). In addition, studies also found

523   that both solar radiation and temperature can have a substantial impact on the chemical reactions of

524   VOCs (Yadav et al., 2016). However, compared to the solar radiation, temperature directly affects

525   the reaction rates of VOC species (Atkinson and Arey, 2003). Liu et al. (2023a) suggested that the

526   reactive losses of ambient VOCs were highly correlated with temperature; when the temperature was

527   above 25 ℃, the losses of VOCs increased most substantially.

528

529   **3.5 Source analyses of VOC reactive losses in the atmosphere**

530   At present, source apportionments utilizing the measured and initial VOC concentrations do not

531   consider the complementary issues of O_3 and SOA formation (Gu et al., 2023; Wang et al., 2022b).

532   The chemical losses of VOCs by reaction (i.e., reactive VOCs forming SOA and O_3) were real

533   contributors to these pollutants (Ma et al., 2022; Wang et al., 2013). Thus, it is important to apportion

534   the reactive losses of VOCs to provide the input needed to identify the responsible source types and

535   thereby allow effective control of O_3 and secondary aerosol pollution. In 2023, Gu et al. (2023)

536   developed a source analyses method for consumed VOCs (i.e., the reactive losses of VOCs) in the

537   atmosphere and conducted an applied study. This method was that the measured and initial data were

538   first used to conduct source analyses by PMF, and then the difference in the contributions of the

539   same factors from the paired analyses were considered to be the source contribution of consumed

540   VOCs in the atmosphere. The ozone formation potential (OFP) and SOA formation potential

541   (SOAFP) of the consumed VOCs from the different sources were estimated. To reduce the impacts of

542   atmospheric dispersion on the apportioned results, dispersion-normalized PMF (DN-PMF) was

543   applied for source analyses in this method, and its principle is provided by Dai et al. (2020) and Gu

544   et al. (2022). The method flowchart is shown in Fig. 4. Similar studies were reported by Wang et al.

545   (2022b) and Wang et al. (2023). However, the current method for apportioning the sources of

546   consumed VOCs in the atmosphere is still imperfect. The shortcomings included: the uncertainty in

547   estimating the initial concentrations of VOCs (see section 3.1.1.2); the issue of factor identification,

548   even if identified as the same type of factor, there were substantial differences in their factor profiles

549   (Liu et al., 2023a); and the current studies focused on the PAMS species, and apportionments of

550   OVOC losses have not yet been conducted. There were numerous technical issues, for example, there

551   is still a lack of rational methods for estimating the OVOC initial concentrations.

552   The source analyses of the consumed VOCs conducted by Gu et al. (2023) in Qingdao found

553   that biogenic emissions (56.3%), vehicle emissions (17.2%), and gasoline evaporation (9.37%) were

554   the main sources of the consumed VOCs. However, the apportioned results from Wang et al. (2023)

555   in Tianjin and Guangzhou suggested that biogenic emissions (43% and 35%, respectively), solvent

556   usage (14% and 18%, respectively), and industrial sources (14% and 22%, respectively) were the

557   major contributors of the consumed VOCs. Therefore, biogenic emissions may be an important

558   source of reactive losses of VOCs. However, due to the limited research currently available, the

559   representativeness of the results is still insufficient at present.

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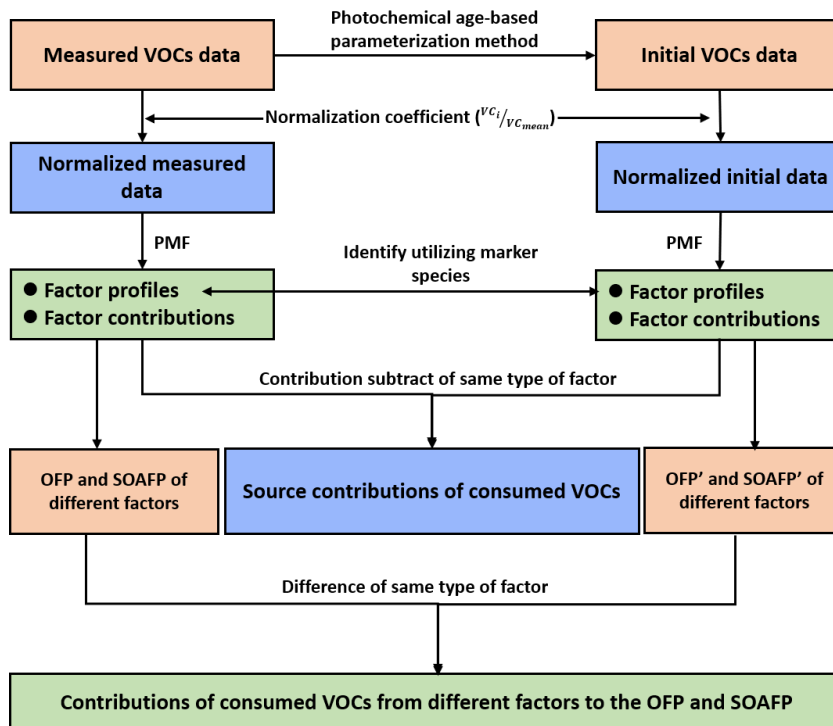
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562   **Figure 4.** The method flowchart of source analyses for consumed VOCs in the atmosphere.

563

4 Conclusions

This study systematically reviewed the major methods of reducing the impacts of reactive loss and the existing critical issues in the current VOC source analyses research. The purpose was to clarify the future research directions needed to improve the accuracy of VOC source apportionments, and provided a potential supporting role in completely solving the issue of VOC chemical conversion. PMF is currently the most useful tool in treating highly time-resolved data compared to other receptor models. Estimating the initial concentrations of ambient VOCs based on photochemical age is the primary approach to reduce reactive loss effects in PMF. However, due to the shortcomings existing in the photochemical-age estimation method, such as only considering the photochemical reactions with $\cdot OH$ radicals during the day and not considering the reactions with O_3 (especially for alkene species) and NO_3 radicals, difficulty in dynamically adjusting the required $\cdot OH$-radical reaction rate constants with temperature changes, high uncertainty in the estimation of photochemical age, and difficulty in quantifying the initial concentrations of OVOCs, etc., resulting in substantial uncertainty in the PMF apportioned results based on the initial concentration data. Furthermore, both the measured and initial VOCs data do not match the ambient O_3 or SOAs measured synchronously, the VOCs consumed by reactions are real contributors to these pollutants. Source analyses of the consumed VOCs can effectively guide the prevention and control of O_3 and SOAs pollution in the atmosphere. Therefore, in addition to the research into more accurate quantitative approaches for ambient VOC reactive losses, the source analyses of consumed VOCs and the accurate quantification of their separate contributions to O_3 and SOAs should also be important directions for future research.

Author contributions

BSL: Writing–original draft, Writing–review & editing. YG: Data curation, Writing–original draft. YTW: Data curation. QLD and SJS: Investigation and Supervision. YCF: Supervision. PKH: Supervision–review & editing.

Competing interests

The author declares that they have no competing interests.

593

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