Sources of methacrolein and methyl vinyl ketone and their contributions to methylglyoxal and formaldehyde at a receptor site in Pearl River Delta

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ABSTRACT

Methacrolein (MACR) and methyl vinyl ketone (MVK) are two major intermediate products from the photochemical oxidation of isoprene, the most important biogenic volatile organic compound. In addition, MACR and MVK have primary emissions. Investigating the sources and evolution of MACR and MVK could provide helpful information for the oxidative capacity of the atmosphere. In this study, hourly measurements of isoprene, MACR, and MVK were conducted at a receptor site in the Pearl River Delta region (PRD), i.e., the Heshan site (HS), from 22 October to 20 November, 2014. The average mixing ratios of isoprene, MACR, and MVK were 151 ± 17, 91 ± 6 and 79 ± 6 pptv, respectively. The daily variations and the ratios of MVK/MACR during daytime and nighttime suggested that other sources besides isoprene photooxidation influenced the MACR and MVK abundances at the HS. Positive matrix factorization was utilized to resolve the sources of MACR and MVK. Five sources were identified and quantified, including biogenic emissions, biomass burning, secondary formation, diesel, and gasoline vehicular emissions. Among them, secondary formation made the greatest contribution to observed MACR and MVK with average contributions of ~45% and ~70%, respectively. Through the yields of secondary products from the oxidation of MACR and MVK by the OH radical and the concentrations of MACR and MVK, it was found that methylglyoxal and formaldehyde were the main oxidation products of MACR and MVK at the HS site. Overall, this study evaluated the roles of primary emissions on ambient levels of MACR and MVK and advanced the understanding of photochemical oxidation of MACR and MVK in the PRD.

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Introduction

Volatile organic compounds (VOCs) as important air pollutants have a significant influence on tropospheric chemistry and have attracted more and more concerns (Guo et al., 2017).

Composed by hundreds of species with different photochemical reactivity, VOCs could be emitted from various anthropogenic and biogenic emissions. Biogenic VOCs (BVOCs) account for about 80% of the global annual emissions of VOCs, which have high reactivity and are important precursors of ozone
(O₃) and secondary organic aerosol (SOA) in different environments (Dreyfus et al., 2002; Makar et al., 1999). Therefore, investigating the roles of BVOCs in atmospheric photochemistry is important for air quality improvement on local, regional, and global perspectives.

Isoprene, with global emission budget of 500–750 Tg/year and a chemical lifetime (due to oxidation by OH radical) shorter than an hour, is the most important BVOC for the formation of O₃ and SOA formation at the boundary layer (Guenther, 2008; Atkinson et al., 2006; Guenther et al., 2006; Carter and Atkinson, 1996). In recent years, knowledge of the mechanisms for oxidation cycles of isoprene has advanced significantly based on a number of laboratory and simulation studies (Atkinson et al., 2006; Pinho et al., 2005; Jenkin and Clemitshaw, 2000; Chew et al., 1998). During daytime, isoprene experiences sequential oxidation initiated by the OH radical in NOₓ-rich environments to produce methyl vinyl ketone (MVK), methacrolein (MACR) and formaldehyde (HCHO) as oxidation products. Furthermore, oxidation of MACR and MVK by the OH radical in NOₓ-rich environments leads to the formation of glycolaldehyde, methylglyoxal and hydroxycetone (Spaulding et al., 2003), which could subsequently participate in O₃ and SOA formation.

The evolution of isoprene and its oxidation products in the atmosphere is different from that determined in the laboratory studies due to continuous emissions of isoprene, radical variations, and anthropogenic emissions of MACR and MVK in the atmosphere (Karl et al., 2009). Therefore, to advance the understanding of the behaviors of isoprene and its oxidation products in the real ambient air, many field studies have been conducted to investigate the evolution of isoprene and its contributions to O₃ formation in different environments (e.g., Jones et al., 2011; Park et al., 2011; Roberts et al., 2006; Spaulding et al., 2003). The most frequently used method for studying the contributions of secondary formation to the observed MACR and MVK concentrations is based on the ratios of isoprene and its oxidation products, i.e., [MACR]/[MVK], [MACR + MVK]/[isoprene], [MVK]/[isoprene] and [MACR]/[isoprene]. This method relies on differences in the photochemical reactivities of isoprene and its oxidation products in the atmosphere (Table 1). However, ratio methods are based on the assumption that no fresh emissions of isoprene, MACR and MVK are introduced into the atmosphere or, alternately, isoprene emissions are constant during the processes and physical processes do not influence the observed ratios of isoprene and its oxidation products during transport. Therefore, any other emissions of MACR and MVK (in addition to photochemical oxidation of isoprene) would cause the observed ratios of [MVK]/[isoprene] and [MACR]/[isoprene] to deviate from those calculated by the reaction yields of isoprene and OH (Grosjean et al., 2001).

The Pearl River Delta (PRD) region, one of the highly developed regions in China, experiences severe photochemical pollution characterized by a continuous increase in the O₃ abundance due to rapid urbanization and industrialization. To quantify the role of BVOCs such as isoprene, in photochemical O₃ formation, many efforts have been made in this region and include the development of emission inventories (Wang et al., 2011; Zheng et al., 2009), source identification (Cheung et al., 2014; Leung et al., 2010; Liu et al., 2009) and model simulation of potential contribution of isoprene to photochemical O₃ (Guo et al., 2012; Zheng et al., 2009). These studies have not only quantified the source attributions of some typical VOCs and oxygenated VOCs (OVOCs), but also highlighted the significance of BVOCs in photochemical O₃ formation. As important intermediate products of isoprene oxidation, the abundance and evolution of MACR and MVK could provide important insights into the relationships between isoprene and its secondary products. However, the contributions of primary emissions and secondary formation to MACR and MVK abundances as well as their subsequent photooxidation are still poorly understood in the PRD region which is characterized by diverse sources of MACR and MVK (Cheung et al., 2014; Liu et al., 2009). Therefore, in this study, we presented an intensive field measurement of isoprene, MACR and MVK at a receptor site (Heshan site, HS) in the PRD region. Additionally, the source contributions of MACR and MVK as well as their contributions to subsequently oxidation products were quantified. To the best of our knowledge, this is the first study on the source apportionments of MACR and MVK and the evaluation of their oxidized products in the PRD.

1. Materials and methods

1.1. Site description

The field measurement was conducted at Guangdong Atmospheric Supersite of China, Heshan (112.93°E, 22.73°N) (Fig. 1), Jiangmen City, Guangdong Province. The urban centers of Jiangmen City were ~30 km to the east of the study site, while the urban centers of Foshan and Guangzhou cities were ~50 and 80 km, respectively, to the northeast. The measurement was conducted from 22 October to 20 November 2014 since photochemical smog and air masses from the PRD were frequently observed during this season (Zhou et al., 2013; Zheng et al., 2010; Zhang et al., 2008). Detailed description of the sampling site and its surrounding environments has been provided in the previous study (Zhou et al., 2013).

1.2. Chemical analysis of VOCs

In this study, hourly VOC concentrations, including 58 non-methane hydrocarbons (NMHCs) and 19 OVOCs were determined and analyzed by an automated online GC-mass spectrometer (MS)/flame ionization detector (FID) system (Hewlett Packard 7890/5975). These target compounds were identified based on their retention times and mass spectra,

### Table 1 – Reaction rate constants for isoprene, MVK and MACR (cm³/molecule. sec⁻¹)

<table>
<thead>
<tr>
<th>Species</th>
<th>k_O3 ¹</th>
<th>k_OH ²</th>
<th>k_NO3</th>
<th>k_O ³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td>1.28 × 10⁻¹⁷</td>
<td>1.10 × 10⁻¹⁰</td>
<td>6.16 × 10⁻¹²</td>
<td>4.0 × 10⁻¹⁰</td>
</tr>
<tr>
<td>MVK</td>
<td>4.56 × 10⁻¹⁸</td>
<td>1.88 × 10⁻¹₁</td>
<td>&lt; 6.00 × 10⁻⁶</td>
<td>2.2 × 10⁻¹⁰</td>
</tr>
<tr>
<td>MAC</td>
<td>1.14 × 10⁻¹⁸</td>
<td>3.35 × 10⁻¹₁</td>
<td>3.30 × 10⁻¹⁵</td>
<td>2.4 × 10⁻¹⁰</td>
</tr>
</tbody>
</table>

¹ Carter and Atkinson, 1996
² Apel et al., 2002
³ Roberts et al., 2006

The reaction yields of isoprene and OH (Grosjean et al., 2001).
while their concentrations were quantified based on the calibration curves of standard and zero air samples. The configuration, quality control and assurance, and the analytical performance of the system have been provided in the previous study (Shao et al., 2009).

1.3. Positive matrix factorization (PMF) model

The PMF (version 4.0) model was applied to the observed VOC data to explore the sources of MACR and MVK at the HS. Although, a total of 58 NMHCs were identified in the present study, not all were utilized in PMF due to the fundamental assumption of non-reactivity and/or mass conservation of the model (Zhang et al., 2012). Furthermore, the aim of this study was to investigate the source attributions of MACR and MVK based on the observed NMHC data rather than identifying the sources of the NMHCs (He et al., 2018). As such, species that are typical tracers of the sources were selected as the input for the PMF model (Chen et al., 2013). It should be noted that some studies (Ling et al., 2017; Yuan et al., 2012). Briefly, the model was tested with different numbers of factors and the most optimum source profiles and contributions were determined based on the correlations between the modeled and observed data as well as the comparisons of the modeled profiles with the results from emission-based measurements and other PMF model simulations (HKEPD, 2015; Wang et al., 2016). The third pattern was consistent with the findings of previous studies which indicated that the mixing ratios of isoprene, MACR and MVK were usually higher than those of MACR if photooxidation of isoprene were not important sources of MACR and MVK.

2. Results and discussion

2.1. Overall results of isoprene, MACR and MVK

The time series of isoprene, MACR and MVK concentrations as well as the meteorological parameters during the study period are shown in Fig. 2. The overall average mixing ratios of isoprene, MACR and MVK during the entire sampling period (30 days in total) were 151 ± 17, 91 ± 6 and 79 ± 6 pptv, with the median values of 60, 59 and 38 pptv, respectively. The levels of isoprene dropped to an average value of 75 ± 7 pptv due to the decrease in temperature from 02 November onwards (p < 0.05). In this study, daily variations of MACR and MVK at the HS presented three patterns: (1) comparable mixing ratios were observed for MACR and MVK for ~10% (three sampling days in total) of the total sampling days (p > 0.05) with average mixing ratios of isoprene, MACR and MVK being 52 ± 11, 37 ± 4 and 36 ± 6 pptv, respectively; (2) the mixing ratio of MACR was much higher than MVK on eighteen sampling days ([MACR] > [MVK], p < 0.05) with the average mixing ratios of isoprene, MACR and MVK being 147 ± 20, 85 ± 8, and 39 ± 3 pptv, respectively; and (3) higher mixing ratios were observed for MACR than MVK on nine sampling days ([MVK] > [MACR], p < 0.05) with average mixing ratios of isoprene, MACR and MVK being 193 ± 38, 106 ± 10, 153 ± 13 pptv, respectively. The second pattern was consistent with those observed at an urban site in Beijing during summer non-haze days and winter haze days (Rao et al., 2016). This indicates that biogenic emissions and photooxidation of isoprene were not important sources of MACR and MVK. Furthermore, the higher MACR and MVK levels in Beijing were related to variations in gasoline and diesel vehicle emissions as indicated by the principal component analysis (Rao et al., 2016). The third pattern was consistent with the findings of previous studies which indicated that the mixing ratios of MVK were usually higher than those of MACR if photooxidation of isoprene was the dominant source of MACR and MVK (Guo et al., 2012 and references therein). This could be attributed to the longer lifetime of MVK as well as the higher production rate of MVK from photooxidation of isoprene in contrast to MACR. Nevertheless, the large daily variations of MACR and MVK indicated the influence of other sources other in addition to photooxidation of isoprene at the HS.
2.2. Sources of MACR and MVK

Investigation of the ratio of MACR and MVK can provide instructive information on the importance of isoprene oxidation in determining the abundances of MACR and MVK. The MVK/MACR ratio based on the yields of MACR and MVK (0.23 and 0.32, respectively) from isoprene oxidation was estimated to be ~1.4 (pptv/pptv) (Carter and Atkinson, 1996). Additionally, this value ranged between 1 at night/early morning and 2 during daytime. The ambient MVK/MACR ratio usually increased with the time of the day due to longer lifetime of MVK than MACR (attributed to higher photochemical reactivity of MACR by OH) (Guo et al., 2012; Park et al., 2011; Fan and Zhang, 2004; Hakola et al., 2003; Apel et al., 2002; Stroud et al., 2001). Measurements conducted in rural areas where the sampling site was isolated from anthropogenic emissions and isoprene was presumed to be the dominant source indicated that the MVK/MACR ratio to be nearly 2.0 at midday. The ratios would decrease to approximately 1.0 at night/early morning due to the decrease in isoprene emissions, and O$_3$/NO$_x$ oxidation were the primary oxidation pathways for MACR and MVK. However, in areas directly influenced by primary anthropogenic emissions, the ratios of MACR and MVK presented different patterns (Guo et al., 2012; Park et al., 2011). Measurements conducted in rural areas where the sampling site was isolated from anthropogenic emissions and isoprene was presumed to be the dominant source indicated that the MVK/MACR ratio to be nearly 2.0 at midday. The ratios would decrease to approximately 1.0 at night/early morning due to the decrease in isoprene emissions, and O$_3$/NO$_x$ oxidation were the primary oxidation pathways for MACR and MVK. However, in areas directly influenced by primary anthropogenic emissions, the ratios of MACR and MVK presented different patterns (Guo et al., 2012; Park et al., 2011). Measurements conducted in rural areas where the sampling site was isolated from anthropogenic emissions and isoprene was presumed to be the dominant source indicated that the MVK/MACR ratio to be nearly 2.0 at midday. The ratios would decrease to approximately 1.0 at night/early morning due to the decrease in isoprene emissions, and O$_3$/NO$_x$ oxidation were the primary oxidation pathways for MACR and MVK. However, in areas directly influenced by primary anthropogenic emissions, the ratios of MACR and MVK presented different patterns (Guo et al., 2012; Park et al., 2011). Measurements conducted in rural areas where the sampling site was isolated from anthropogenic emissions and isoprene was presumed to be the dominant source indicated that the MVK/MACR ratio to be nearly 2.0 at midday. The ratios would decrease to approximately 1.0 at night/early morning due to the decrease in isoprene emissions, and O$_3$/NO$_x$ oxidation were the primary oxidation pathways for MACR and MVK. 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formation and solvent usage contributed significantly to MACR and MVK abundances. Furthermore, in addition to high correlations with MVK, propanal and acrolein, MACR correlated well with aromatics (e.g., C₆–C₈ aromatics, \( R^2 = 0.56–0.71 \)), and MTBE (methyl tert-butyl ether) (\( R^2 = 0.64 \)), typical species arising from gasoline vehicular emissions on “comparable” days, suggesting that gasoline vehicular emissions were another source affecting the abundances of MACR and MVK at the sampling site.

### 2.3. Source apportionments

The above-mentioned observed ratios of MACR and MVK as well as their correlations with other species (Section 2.2) suggest that other sources, apart from the oxidation of isoprene, contributed to the mixing ratios of MACR and MVK, thus resulting in variations of MACR and MVK at the HS. To quantitatively apportion the sources of MACR and MVK, the PMF model was applied to the dataset at the HS site. A five-factor simulation that best reproduced the observed concentrations was chosen based on the calculated statistical parameters and prior-knowledge about emission source profiles specific to the PRD region. The five factors included biogenic emissions, biomass burning, secondary formation, gasoline, and diesel vehicular emissions. Fig. 4 illustrates the explained variations of the individual apportioned sources as well as their corresponding profiles, i.e., the relative contribution of each source to the individual species at the HS.

The first factor is identified as biogenic emission, which is solely dominated by isoprene and accounts for ~83% of the measured concentration of isoprene at the HS site. About 26% of the MACR was attributed to this factor, whereas its contribution to MVK was negligible. Though these results are consistent with previous measurement studies, which reported that MACR was one of the most abundant OVOCs from biogenic emissions (Jardine et al., 2011; Carvalho et al., 2005), it should be noted that the OVOCs from biogenic emissions are dependent on the vegetation type and meteorological conditions (i.e., temperature and solar radiation). Therefore, further studies on the profiles of OVOCs primarily emitted from vegetation in the PRD region are needed.

Factor 2 was distinguished by high percentages of methyl chloride (CH₃Cl), ethane, and benzene, as well as certain amounts of other combustion tracers (e.g., ethyne and C₃–C₄ alkanes). Furthermore, this factor made the highest contribution to ACN, a typical tracer for biomass burning plumes in the PRD region (Yuan et al., 2010). Therefore, this factor was assigned as biomass burning. Previous studies have demonstrated that MACR and MVK (MACR + MVK or MACR and MVK individually) were the major OVOC components in the emission profiles of biomass burning in China and other areas (Inomata et al., 2014; Wang et al., 2014; Kudo et al., 2013; Yuan et al., 2010; Ralf, 2007). Furthermore, a previous study based on data measured by the proton transfer reaction-mass spectrometer (PTR-MS) and fire hotspots from MODIS reported that biomass burning occasionally influenced the levels of VOCs in Jiangmen (Yuan et al., 2010). The contribution of biomass burning to MACR and MVK were 2% and 5%, respectively, which is consistent with the higher emission rate of MVK than MACR as indicated by the biomass burning emission-based measurement study in the US (Gillman et al., 2015).

The third factor was dominated by MACR, MVK, and PAN. The dominant contribution of PAN, a secondary product, in the profile suggested that this source was related to secondary formation. Additionally, its contribution to MACR and MVK was high at 45% and 70%, respectively.

Factor 4 was rich in ethene, propene, and 1-butene, as well as certain amounts of ethyne and aromatics, consistent with the profiles of diesel vehicular exhaust in the PRD region (HKEPD, 2015; Liu et al., 2008). Therefore, this source was identified as diesel vehicular emissions. The contribution of this source to MACR and MVK was approximately 11% and 2%, respectively. The presence of high levels of butanes, pentanes, methyl pentane and aromatics in Factor 5 as well as comparisons with source profiles of gasoline vehicular exhaust obtained from emission-based measurements (HKEPD, 2015; Liu et al., 2008) suggested that this source was related to gasoline vehicular emissions. Additionally, it contributed nearly 17% and 24% of MACR and MVK, respectively, at the HS. The tunnel and vehicular exhaust emissions measurements as well as the comparisons between the emission inventory and the observed data have indicated that MACR and MVK could be emitted...
from mobile sources including gasoline and diesel vehicles (Zheng and Sha, 2018; Ralf, 2007; Andrew et al., 2001; Biesenthal and Shepson, 1997).

As suggested by previous studies (Chen et al., 2013; Yuan et al., 2010), relationships between contributions of individual factors to NMHCs (factor fractions) and their photochemical reactivities could be utilized to evaluate the PMF model performance with regard to distinguishing between fresh emissions and factors associated with photochemically aged emissions (i.e., secondary formation). Fig. 5 presents the distributions of MACR, MVK and NMHCs in the individual sources as determined by the PMF model. In the PMF model results, species indicated in a specific profile were considered to be emitted from the same source. Isoprene was excluded from anthropogenic factors as it was the sole tracer for biogenic emissions. If a factor was associated with fresh emissions, the species, including MACR, MVK, and NMHCs, in that factor would be consumed together during the transport from emissions to the receptor site, thus resulting in a pattern that the distributions of MACR and MVK were similar to or lower than the NMHCs in that factor because the photochemical reactivities of MACR and MVK are within the ranges of NMHCs in PMF (Chen et al., 2013). However, the distributions of MACR and MVK would be higher than those of the NMHCs in factors related to photochemically aged emissions due to photochemical formation (Chen et al., 2013). As indicated in Fig. 5, the distributions of MACR and MVK were similar to or lower than those of the NMHCs for all factors except secondary formation. Therefore, the results suggest that the higher distributions of MACR and MVK with regard to Factor 3 indicated its association with photochemical formation while the remaining factors were related to fresh emissions.

Chen et al. (2013) studied the correlations between the contribution of each factor to each species (factor fractions) and the photochemical reactivities of NMHCs. A positive correlation indicated that the PMF-resolved factor originated from a specific NMHC source while the opposite trend (negative correlation) was observed for photochemically aged factors. In this study, positive correlations were determined for contributions and photochemical reactivities of NMHCs in sources of vehicular and biogenic emissions (Pearson correlation coefficients of 0.01, 0.24 and 0.85 correspond to gasoline vehicular emissions, diesel vehicular emissions, and biogenic emissions, respectively), while a weak negative correlation was observed for secondary formation (Pearson correlation coefficient of −0.04). The weak correlation suggested uncertainties in the distinction of fresh and photochemically aged factors by the PMF model (Chen et al., 2013). It should be noted that a negative correlation was observed with regard to biomass burning, thus suggesting that species characterizing biomass burning may have experienced photochemical processing. This is reasonable since species that contributed significantly by this source were mainly the species with relatively low photochemical reactivities. As photochemical aging proceeds, species with relatively high photochemical reactivities decay faster than those with low photochemical reactivities, resulting in higher concentrations of low reactivity species in relatively aged air masses. Nevertheless, the results of this study indicated that the PMF model could reasonably resolve the contributions of fresh emissions and secondary formation to MACR and MVK abundances (Chen et al., 2013).

Therefore, in this study, the source attributions of MACR and MVK at the HS were quantified by the PMF model.
Additionally, the model performance was evaluated using relationships between the contributions of individual factors to each species and the photochemical reactivities of NMHCs. However, it should be noted that uncertainties for source apportionments of MACR and MVK existed since PMF is a receptor model with the fundamental assumption of non-reactivity and/or mass conservation of selected species during the transport from emissions to the receptor site. Additionally, MACR and MVK with relatively short photochemical lifetimes (~10 and ~14 hr for MACR and MVK, respectively) were the intermediate products of isoprene oxidation. Therefore, further studies focusing on detailed and accurately measured profiles of MACR and MVK emissions, formation and removal of MACR and MVK through photochemical oxidation, and the investigation of potential source origins are still needed to provide more accurate quantitative information on source apportionments of MACR and MVK at the HS.

2.4. Contributions of different sources of MACR and MVK to methyglyoxal and formaldehyde formation

In the atmosphere, MACR and MVK could be degraded by photolysis and oxidized by O_3, NO_3, and OH radicals. Among these, the reaction with OH radical was the dominant removal pathway of MACR and MVK under the sufficient NO_3 environment (Fuchs et al., 2018). Methyglyoxal, glyoxal, and formaldehyde are the major secondary products from the photooxidation of MACR and MVK (Fuchs et al., 2018; Pinho et al., 2005). These secondary products are important precursors of SOA. In this study, the average mixing ratio of NO_3 at the HS was 46 ± 1 ppbv, thus indicating a NO_3-rich environment.

Fig. 5 – Relationships between factor contributions of each NMHCs, MACR, and MVK and their $k_{OH}$ values (a) Biogenic emissions; (b) biomass burning; (c) secondary formation; (d) diesel vehicular emissions; (e) gasoline vehicular emissions. Each blue circle represents one NMHC while MACR and MVK are represented by purple triangles and green squares respectively. $r_s$ represents the Pearson correlation coefficient.
the photooxidation of MACR and MVK.

In this study, MACR and MVK were measured continuously from 22 October to 20 November 2014, at a receptor site (i.e., the HS site) in the PRD region. Three different patterns of daily variations of mixing ratios of MACR and MVK were determined at the HS (i.e., the mixing ratios of MACR were higher/lower/comparable to those of the MVK) with overall average values of 91 ± 6 and 79 ± 6 pptv, respectively. The investigation of the ratios and correlations of MACR and MVK indicated that the ratios of MVK and MACR were mostly lower than those calculated from the reaction yields of isoprene oxidation by OH, suggesting that sources (with varied contributions) other than photooxidation of isoprene influenced the ambient levels of MACR and MVK at the HS. This was further confirmed by the linear regression analysis between MACR, MVK, and other species measured in this study. The PMF model was applied to the observed data to determine source apportionments of MACR and MVK. Five sources, including biogenic emissions, biomass burning, secondary formation, diesel, and gasoline vehicular emissions, were determined and the secondary formation was found to be the largest contributor to the abundances of MACR and MVK. In addition, biogenic emissions and diesel vehicular emissions contributed more significantly to MACR than MVK at the HS. Finally, the mixing ratios of products, i.e., formaldehyde and methylglyoxal, obtained from further oxidation of MACR and MVK by the OH radical were calculated. The results indicated that the photooxidation of MACR and MVK contributed 7 and 52 pptv, respectively, of ambient formaldehyde and 42 and 15 pptv, respectively, of methylglyoxal. Overall, this study advanced the understanding of source attributions of MACR and MVK and provided a preliminary evaluation of the oxidation products resulting from the photochemical evolution of MACR and MVK in the PRD region.

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REFERENCES


