Source Apportionment of VOCs and O3 Production Sensitivity at Coastal and Inland Sites of Southeast China

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ABSTRACT

Urbanization and industrialization levels have a significant impact on the pollution of O3 and its precursors. However, current studies of VOC sources and O3 formation sensitivity in the regions with different urbanization and industrialization levels remained limited. Therefore, offline and online VOC observations were conducted at coastal sites (CS) and inland sites (IS) of southeast China to analyze spatial-temporal characteristics, source apportionment of VOCs based on the positive matrix factorization (PMF) model, and their effects on O3 formation using the observation-based model (OBM). The results showed that the average concentrations of TVOCs at CS and IS were 49.1 ± 14.4 and 28.4 ± 9.6 ppb, respectively, with higher levels in autumn compared to those in spring and summer. Alkene species contributed the largest to the OH radical loss rate (LOH) and ozone formation potential (OFP). The contributions of vehicle exhaust and combustion sources, industrial sources, solvent usage, biogenic sources, and fuel evaporation at CS and IS were 42.2% and 34.5%, 22.4% and 18.2%, 12.7% and 4.5%, 11.7% and 19.4%, and 11.0% and 23.4%, respectively. Meanwhile, vehicle exhaust and combustion sources (31.8%), fuel evaporation (21.3%) were the major contributors to O3 formation in Ningde. The results of sensitivity analysis indicated that O3 formation at CS was mainly VOC control in spring and autumn, and controlled by both VOCs and NOx in summer, but the VOCs is the key factor for the O3 formation at IS, and the emission control of alkenes and aromatics was conductive to decrease O3 levels. The scenario analysis suggested that the 20% reduction of VOC concentrations and 3% reduction of NOx concentrations could realize the 5% reduction of O3 concentrations. This study might enhance the understanding of O3 and its precursors in southeast China with different urbanization levels, as well as the emission reduction strategies.

Keywords: Volatile organic compounds, Source apportionment, Ozone formation, Sensitivity analysis, Emission reduction

1 INTRODUCTION

Volatile organic compounds (VOCs) play a significant role in the formation of ozone (O3) and secondary organic aerosol (SOA) (Zhao et al., 2020; Song et al., 2021), which can enhance atmospheric oxidation capacity, and affect air quality and human health (Bari and Kindzierski, 2018;
In China, although the concentrations of PM$_{2.5}$ show a decreasing trend, the photochemical pollution of O$_3$ has attracted more and more attention. As the precursor of O$_3$, VOCs have a wide variety of sources and reactive activities, which brings great challenges to the control of O$_3$ formation. Therefore, it is vital to identify particular VOC sources and reduce VOC emissions to decrease O$_3$ formation.

Population densities, industrial structure, and local regulations for VOC emissions directly affect the concentrations and sources of VOCs (Li et al., 2019a). In developed urban areas, the average concentrations of TVOCs were relatively higher than those in suburban or remote areas, and vehicle exhausts, solvent usage, and industrial emissions were generally primary contributors of VOCs (Liu et al., 2017; Song et al., 2018; Liu et al., 2021). In addition, combustion sources might be a major source of VOCs in medium-sized urban regions due to frequent agricultural activities such as biomass burning (Qin et al., 2021). Additionally, different VOC groups have significant effects on O$_3$ formation, attributed to the difference of their chemical reactivity. Previous studies suggested that aromatics and alkenes contribute the largest to the ozone formation potential (OFP) (Song et al., 2018; Li et al., 2019b). Thus, aromatics and alkenes were considered as key VOC groups to control their emissions. However, controlling atmospheric O$_3$ formation is much more complex than what had been expected, due to the fact that O$_3$ formation is non-linearly related to VOCs and NO$_x$. Field observation and model results indicated that O$_3$ formation is generally more sensitive to VOCs in most developed urban regions, but more sensitive to NO$_x$ in rural regions (Li et al., 2018; Song et al., 2021; Meng et al., 2022).

Current studies of atmospheric VOCs in China were mainly concentrated in developed regions, such as Beijing-Tianjin-Hebei (BTH), Yangtze River Delta (YRD), Pearl River Delta (PRD), and Chengdu-Chongqing regions (Yuan et al., 2013; Gong et al., 2017; Liu et al., 2017; Li et al., 2018; Zhao et al., 2020; Liu et al., 2021; Song et al., 2021). However, few studies were carried out in developing urban or county areas, with different levels of urbanization and industrialization. In these areas, biogenic VOCs and their interaction with anthropogenic VOCs and NO$_x$ emissions were undoubtedly essential in affecting O$_3$ formation. Ningde is a developing coastal city in the southeast of China (Fig. 1). With the relatively low PM$_{2.5}$ concentrations, O$_3$ pollution in Ningde has frequently occurred in recent years, and O$_3$ became primary pollutants in the evaluation system of ambient air quality from 2015 to 2020 (http://fjaqi.fjemc.org.cn/). Due to convenient traffic conditions, the coastal areas in Ningde have more developed industrial and economic levels than those in inland areas (Table S1). At the same time, population in coastal areas has been increasing in the past twenty years, due to the process of rapid urbanization and industrialization (Fig. S1). Given that different levels of urbanization and industrialization may bring different influence on O$_3$ and its precursors, it is necessary to study sources of VOCs and the sensitivity of O$_3$ formation in two types of areas with different levels of urbanization and industrialization to control O$_3$ concentrations in the ambient air.

In this study, VOCs, criteria air pollutants and metrological parameters were simultaneously measured in coastal and inland areas in Ningde, using the positive matrix factorization (PMF) and the observation-based model (OBM), to determine major sources of VOCs and their effects on O$_3$ formation. The study aims to (1) explore seasonal patterns of VOCs at coastal sites and inland sites, and (2) quantify the major sources of VOCs, and (3) identify key VOC species of O$_3$ formation and analyze the sensitivity of O$_3$ formation. This study will provide a helpful reference for the control measures to reduce O$_3$ concentrations in the ambient air in developing urban areas with different levels of urbanization and industrialization.

## 2 METHODS

### 2.1 Study Area

A total of eight offline sampling sites were selected, including Yizhong (Y2), Jiancezhan (JZC), Fu’an (FA), Fuding (FD), Xia pu (XP) as coastal sites (CS), and Gutian (GT), Pingnan (PN), Zhouning (ZNH) as inland sites (IS) (Fig. 1). They are all typical urban sites without direct pollutant emissions, and details about the study sites were summarized in supplementary material. Additionally, the online VOC observation was conducted in the Ningde Meteorological Bureau (119.54°E, 26.64°N) in coastal regions in Ningde, and the detailed description of the online analytical instrument of...
Fig. 1. Observations at coastal sites (CS, black dot) and inland sites (IS, red triangle) in Ningde in the southeast of China.

VOCs can be found in supplementary material. In this study, the online monitoring of VOCs was mainly used to analyze the relation of O₃ formation sensitivity and propose control strategies for both VOC and NOₓ emission in the area of Ningde.

2.2 Sampling and Observation

Offline VOC sampling was conducted simultaneously at eight sampling sites during May, August, and November in 2019, representative for spring, summer and autumn, respectively, and every month had 3–5 days for VOC sampling. Manual VOC samples were taken each day at, 6–7, 11–12, 13–14, 17–18, 20–21, 23–24, respectively. A total of 354 samples at CS and 103 samples at IS were collected with 3.2 L Summa canisters (model 3100A, Entech Instruments Inc., USA). To avoid interference from targeted VOCs, all canisters were flushed by ultra-pure N₂ at least three times before VOC sampling.

Offline VOC samples were analyzed based on a Model 7100 Pre-concentrator (Entech Instruments Inc., USA) combined with a gas chromatograph equipped with a mass spectrometer (GC/MS,
Shimadzu, Japan), according to our previous studies (Hu et al., 2018; Hong et al., 2019). Briefly, we used liquid-nitrogen glass beads cryogenic trap to condense VOC samples at −150°C. And the trapped VOCs were transferred through pure He into a further trap at −30°C with Tenax as absorbent. Then, the target VOCs were transferred to a third capillary cryo-focus trap by heating the secondary trap at −160°C. Finally, the preconcentrated VOCs were transferred into the GC/MS system. The GC oven temperature was programmed to be initially at −50°C holding for 7 min, then raised to 180°C at 4°C m⁻¹, finally, raised to 220°C at 15°C m⁻¹ holding for 3 min. The ionization technique was electron impacting (EI, 70 eV) with the ion source temperature of 230°C. The calibration curve should be recalibrated when its responses were in excess of ±15% of the original calibration curve. The correlation coefficients ($R^2$) of the standard curve varied from 0.990 to 1.000. Totally, 102 VOCs were detected, including 28 alkanes, 10 alkenes, 18 aromatics, 11 oxygenated VOCs (OVOCs), 34 halocarbons, and carbon disulfide.

In addition, the concentrations of criteria air pollutants (O₃, SO₂, CO, NO, NOₓ) and meteorological parameters including temperature (T), relative humidity (RH), and atmospheric pressure (P) were synchronously detected at each sampling site. NOx (NO/NO₂), CO, SO₂, and O₃ were measured using gas analysis instruments (Thermo Fisher Scientific 42i, 48i, 43i, and 49i, respectively, USA).

2.3 PMF Analysis

The PMF model is widely used to determine sources and contributions of VOCs. Its principle and instructions have been introduced in previous studies (Bon et al., 2011; Yuan et al., 2012; Abeleira et al., 2017). Details about the model were summarized in the supplementary material.

2.4 OBM Analysis

The OBM was used to explore the atmospheric oxidation processes and evaluate the sensitivity of O₃ production to its precursors by comparing their relative incremental reactivity (RIR) values, calculated by Eq. (1).

$$RIR = \frac{\Delta P(O_3)}{P(O_3)} \frac{P(O_3)}{\Delta X/X}$$

where, $\Delta P(O_3)/P(O_3)$ represents the change of the O₃ production rate; $\Delta X/X$ is the percentage of O₃ precursors reduction, adopted as 20%. Details of the OBM can be found in previous studies (Liu et al., 2022a, 2022b). In brief, the observed data including VOCs, air pollutants (i.e., CO, NO₂, NO, SO₂, O₃), and meteorological parameters (i.e., T, P, and RH) were input to constrain the model. In this study, the Empirical Kinetics Modeling Approach (EKMA) curve takes the average values of measured species other than NOₓ and VOCs as the constraints of the model. Given that the control of biogenic VOC emissions (BHC) are more difficult than the control of anthropogenic VOC (AHC) emissions, isoprene is set as a fixed value and no sensitivity experiment is performed on it. A total of 361 scenarios were performed, assuming that 19 emission scenarios were for NOₓ and AHC activity, to simulate O₃ production under the corresponding scenario to plot O₃ isopleth diagrams. In this study, $S(VOCs)$, $S(NO_x)$ and $S(O_3)$ is VOC, NOₓ, and O₃ concentrations, respectively.

3 RESULTS AND DISCUSSION

3.1 Characteristics of VOCs

3.1.1 Overview of characteristics

Average concentrations and percentages of VOCs during the sampling period are shown in Fig. 2. The average TVOC concentrations at CS and IS were 49.1 ± 14.4 and 28.4 ± 9.6 ppb, respectively. Compared to other urban regions, TVOC concentrations at IS were much lower than those in densely populated megacities, such as Beijing (64.9 ppb) (Gao et al., 2018), Shanghai (57.5 ppb) (Liu et al., 2019), Guangzhou (63.6 ppb) (Zou et al., 2015). However, TVOC concentrations at CS were close to those in the megacities, reflecting the rapid urbanization in coastal regions of southeast China resulting in more anthropogenic pollutant emissions. At CS, the concentrations
The average concentrations and percentages of different types of VOCs during the sampling period at CS and IS.

Of alkanes were the highest (21.6 ± 9.0 ppb) among all VOC groups, followed by OVOCs (11.3 ± 4.2 ppb), halocarbons (9.4 ± 3.4 ppb), aromatics (3.9 ± 2.3 ppb), and alkenes (2.4 ± 1.8 ppb). Similar pattern of VOC groups at IS was found, with the predominant species of alkanes (14.1 ± 5.9 ppb), followed by OVOCs (5.9 ± 2.3 ppb), halocarbons (4.7 ± 2.1 ppb), alkenes (1.9 ± 1.2 ppb), and aromatics (1.7 ± 1.2 ppb). Overall, the concentrations of different types of VOCs at CS were higher than those at IS, due to stronger anthropogenic emissions at CS. In coastal regions in Ningde, there are a busier traffic network and higher population density than those in inland regions, as well as the rapid development of port and industry (Table S1), causing more frequent anthropogenic activities in coastal regions. According the statistics of 2017 Ningde air pollutants emission inventory, the amounts of VOC emissions from industrial production at CS and IS were 20970.4 and 1374.4 ton per year, respectively (Fig. S2).

For VOC species, the concentrations of the top 10 VOC species at CS and IS accounted for 56.9% and 65.8% of TVOC concentrations, respectively (Table S4). Meanwhile, propane and acetone were the most abundant VOC species at CS and IS in Ningde, similar to those in other cities of Southeast China, such as Fuzhou city and Xiamen city (Hong et al., 2019), likely related to emissions from the transportation process. In addition, alkane species, including propane, iso-pentane, iso-butane, and n-butane, were the largest contributors of the top 10 VOC species at CS and IS. Also, n-butene, toluene, dichloromethane and chloromethane, were the most abundant species of alkenes, aromatics, and halocarbons at CS and IS, respectively.

### 3.1.2 Spatial and temporal variations

Table S5 shows spatial and temporal variations of VOC groups at JCZ, YZ, XP, FA and FD as CS, at GT, PN, and ZHN as IS. At CS, TVOC concentrations in autumn were the highest, followed by summer and spring; at IS, TVOC levels in autumn were also the highest, followed by spring and summer, due to the difference of the emission intensity of anthropogenic activities, meteorological factors during the sampling period (Li et al., 2019a), similar to Guangzhou (Zou et al., 2015). In addition, TVOC levels at XP among CS were the largest, followed by JCC, YZ; among IS, GT had the highest TVOC levels. Among VOC groups, alkanes were the most abundant groups
Table 1. Seasonal variations of major VOC species (ppb) at CS and IS.

<table>
<thead>
<tr>
<th>Site</th>
<th>Season</th>
<th>CS</th>
<th>IS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spring</td>
<td>Summer</td>
<td>Autumn</td>
</tr>
<tr>
<td>Propane</td>
<td>$5.32 \pm 4.27$</td>
<td>$11.65 \pm 3.92$</td>
<td>$12.99 \pm 6.73$</td>
</tr>
<tr>
<td>n-Butene</td>
<td>$0.42 \pm 0.47$</td>
<td>$0.89 \pm 0.06$</td>
<td>$2.34 \pm 1.65$</td>
</tr>
<tr>
<td>Chloromethane</td>
<td>$0.81 \pm 0.28$</td>
<td>$0.72 \pm 0.25$</td>
<td>$1.36 \pm 0.44$</td>
</tr>
<tr>
<td>Benzene</td>
<td>$0.19 \pm 0.09$</td>
<td>$0.15 \pm 0.05$</td>
<td>$0.18 \pm 0.10$</td>
</tr>
<tr>
<td>Toluene</td>
<td>$1.43 \pm 1.36$</td>
<td>$1.48 \pm 0.95$</td>
<td>$1.34 \pm 0.66$</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>$0.45 \pm 0.61$</td>
<td>$0.15 \pm 0.07$</td>
<td>$0.13 \pm 0.09$</td>
</tr>
<tr>
<td>m/p-Xylene</td>
<td>$0.30 \pm 0.40$</td>
<td>$0.21 \pm 0.14$</td>
<td>$0.15 \pm 0.11$</td>
</tr>
</tbody>
</table>

Because alkenes had the highest LOH, it is vital to identify key alkene species that contributed to higher photochemical reactivity of alkenes with the OH radical.

3.2 Photochemical Reactive Activity of VOCs

The concentrations, LOH, and OFP of different VOC groups are presented in Fig. 3, and the LOH, and OFP of the top 10 VOC species are summarized in Table S6. Totally, the LOH showed an obvious seasonal pattern at CS and IS, with the maximum value in autumn, the minimum value in spring, likely due to higher concentrations of related VOC species in autumn. Besides, the LOH at CS were higher than that at IS during the spring, summer, autumn sampling period, indicating more active photochemical activities at CS with higher levels of VOCs. Among the LOH of VOC groups at CS and IS, the LOH of alkenes was the largest, followed by alkanes, aromatics, and OVOCs. The levels of alkenes were the highest, but the LOH of alkenes was lower than that of alkanes. Although the levels of alkenes were very low, the LOH of alkenes was the highest among all VOC groups, attributed to higher photochemical reactivity of alkenes with the OH radical. Because alkenes had the highest LOH, it is vital to identify key alkene species that contributed to the most abundant to the LOH. Among the top 10 VOC species, n-butene, isoprene, and propene accounted for 32.6% of the LOH; n-butene, propene, isoprene, cis-2-butene, and trans-2-butene at IS accounted for 49.4%. Meanwhile, isoprene in summer contributed the largest to the LOH at CS and IS, and isoprene at IS may be more important for the LOH in spring and autumn. Overall, the role of C2-C4 alkene species in atmospheric chemistry should not be ignored.
Fig. 3. The concentrations, \( L_{OH} \), and OFP of different VOC groups at CS and IS in Ningde.

The \( L_{OH} \) can only evaluate the photochemical reactivity of different VOC species, and the OFP can determine the contributions of different VOC species to \( \text{O}_3 \) formation. The largest OFP at CS and IS was in autumn, followed by summer and spring. Similar to the \( L_{OH} \), alkenes, alkanes, and aromatics were the major contributors to the OFP, and the OFP of alkenes was more than twice as high as the OFP of alkanes, aromatics, OVOCs, and halocarbons. The average OFP at CS (30.3 ppb) was higher than that at IS (21.1 ppb), suggesting that the photochemical \( \text{O}_3 \) pollution at CS may be more serious. The top 5 VOC species of the OFP at CS were n-butene, propene, toluene, propane, and isoprene, accounting for 56.6%; the top 5 VOC species of the OFP at IS were propene, n-butene, isoprene, propane, and i-pentane, accounting for 58.1%. It should be mentioned that the importance of isoprene to the OFP at IS should be valued.

3.3 Source Apportionment of VOCs

3.3.1 Diagnostic ratios

Ratios of certain VOC species, such as i-pentane/n-pentane, o-xylene/m/p-xylene, and cis-2-butene/trans-2-butene, are used to preliminarily identify the sources of anthropogenic VOC emissions. In this study, the correlation coefficient values between i-pentane and n-pentane (0.81 and 0.93), o-xylene and m/p-xylene (0.97 and 0.98), cis-2-butene and trans-2-butene (0.98 and 0.98) were observed during the sampling period (Fig. S3). The ratios of i-pentane/n-pentane can be used to identify combustion and vehicle exhaust sources, i.e., 0.56–0.8 for combustion sources and 2.93 for vehicle emissions (Liu et al., 2008; Yan et al., 2017). Besides, the ratios of o-xylene/m/p-xylene (0.35), cis-2-butene/trans-2-butene (1.14) were corresponded to traffic emissions (Liu et al., 2008; Yuan et al., 2010). In this study, the ratios of i-pentane/n-pentane at CS and IS were 2.64 and 3.44, respectively (Fig. S3(a)). The ratios of o-xylene/m/p-xylene, cis-2-butene/trans-2-butene at CS were 0.55 and 1.29, and were 0.84 and 1.34 at IS, respectively (Figs. S3(b) and S3(c)), indicating that vehicle exhausts may play an important role for VOC emissions at CS and IS.

3.3.2 PMF analysis

According to the PMF model analysis, five VOC sources were identified, including solvent usage, industrial sources, vehicle exhaust and combustion sources, fuel evaporation, and biogenic sources (Fig. S4). Fig. 4 shows the percentages of different sources to VOC concentrations (inner pie chart), the OFP (outer pie chart) in Ningde, and their contributions of VOC sources at CS and IS, indicating that vehicle exhaust and combustion sources (40.9%) were the largest VOC sources, followed by industrial sources (21.7%), fuel evaporation (13.1%), biogenic sources (13.0%), and solvent usage (11.3%). The contributions of different VOC sources to the OFP were as follows: vehicle exhaust and combustion sources (31.8%) contributed the most abundant, followed by fuel evaporation (21.3%), industrial sources (20.0%), solvent usage (15.8%), and biogenic sources (11.3%). Therefore, vehicle exhaust and combustion sources were the major VOC sources and had the largest OFP, similar to Zhengzhou (Li et al., 2017). In addition, the contributions of vehicle exhaust and combustion sources, industrial sources, solvent usage, biogenic sources, and fuel
evaporation were 42.2%, 22.4%, 12.7%, 11.0% at CS, and 34.5%, 18.2%, 4.5%, 19.4%, and 23.4% at IS, respectively. Compared to those at IS, the contributions of vehicle exhaust and combustion sources, industrial sources, and solvent usage at CS were obviously larger. However, the contributions of fuel evaporation and biogenic sources were more predominant at IS. It should be noted that the quantity of solvent usage at CS was over two times higher than that at IS, likely attributed to the influence of road asphalt pavement and household appliances coatings. The percentage of fuel evaporation at IS was larger than that at CS, due to the lack of control measures, such as fuel recovery in oil station. Owing to the high forest coverage rate, the percentage of biogenic sources at IS was almost two times higher than that at CS. Overall, vehicle exhaust and combustion sources, industrial sources, and fuel evaporation were the most abundant VOC sources contributing to O₃ production. In coastal regions in Ningde, the government needs to strengthen the management of road mobile sources and ship transportation emissions, whereas in inland regions in Ningde, biomass burning activities should be strictly enforced to be prevented, and the fuel leakage in oil stations should be inhibited.

3.4 Sensitivity Analysis of O₃ Production and Policy Implications

3.4.1 Ratio of VOCs and NOₓ

The VOCs/NOₓ value is usually used to determine whether O₃ production in a region is controlled by VOCs or NOₓ. When the VOCs/NOₓ value is lower than 8, the VOCs is the key factor for the O₃ formation in the region; the region will be controlled by NOₓ if the value is higher than 8. In this study, the average VOCs/NOₓ value at CS was 6.3 ± 3.8, with a seasonal order of summer (9.5 ± 3.6) > spring (4.8 ± 3.1) > autumn (4.4 ± 2.1). Besides, the average VOCs/NOₓ value at IS was 6.5 ± 3.3, with a seasonal order of summer (6.9 ± 4.2) > autumn (6.8 ± 3.2) > spring (5.9 ± 2.1) (Fig. S5). Therefore, O₃ formation at CS was more sensitive to VOCs in spring and autumn, but it was controlled by VOCs and NOₓ in summer; for IS, O₃ formation was mainly controlled by VOCs in spring, summer, autumn.
Fig. 5. The RIR values of O3 precursors in different seasons at the urban site in coastal regions of Ningde.

Because the coastal regions faced the problem of O3 and its precursors pollution, the following contents focused on analyzing controlling factors of O3 formation based on the OBM in coastal regions. The online observation of VOCs was only conducted in the Meteorological Bureau in coastal regions of Ningde city, thus, we analyzed the O3 formation sensitivity and emission reduction strategies at the urban site.

3.4.2 RIR analysis

The O3 formation process was simulated, and RIR values of O3 precursors were calculated during the sampling period. The RIR values of CO, NOx, biogenic VOCs (BHC), anthropogenic VOCs (AHC) are displayed in Fig. 5. The RIR values of VOCs and NOx were positive and negative, respectively, in spring and autumn, indicating that O3 formation is more sensitive to VOCs. However, the positive RIR values of VOCs and NOx indicates that O3 formation is controlled by both VOCs and NOx in summer. AHC had the largest RIR values, followed by NOx, BHC, CO, especially in spring and autumn, implying that AHC had the largest effects on O3 formation. Hence, the control of AHC was more important to decrease O3 pollution. Among AHC, the RIR values of alkenes were the largest, followed by aromatics, alkanes, especially in spring and autumn. Therefore, the reduction of alkene and aromatic emissions was helpful to decrease O3 concentrations in spring and autumn, while abating NOx levels means the aggravation of O3 pollution. In summer, the reduction of both VOC and NOx emissions would suppress the formation of O3.

3.4.3 Emission reduction policies

The OBM was also used to make the scenario analysis with reduction by 0-100 % at intervals of 10% for the reduction of anthropogenic VOCs (ΔS(VOCs)/S(VOCs)) and NOx (ΔS(NOx)/S(NOx)) for control policies of O3 pollution. The EKMA results showed that O3 formation was more sensitive to VOCs in spring and autumn, and controlled by VOCs and NOx in summer (Fig. S6), consistent with the results of the VOCs/NOx value and RIR analysis. In addition, the maximum value of MDA8h O3 during the observation period was 91.5 ppbv, exceeding the national air quality standard of 81.5 ppbv by 12%, hence, 5%, 10%, and 15% reductions targets of O3 levels were considered to discuss the reduction proportions of VOCs and NOx (Fig. 6). As VOC control in spring, the appropriate way to achieve the 5% O3 reduction target was as follow: S(VOCs) is reduced by 20%, and S(NOx) is reduced by 3%. It is reasonable to reduce 30% of S(VOCs) and 3% of S(NOx) to achieve a 10% O3 control target. In order to realize the 15% O3 control goal, the reduction of S(VOCs) and S(NOx) is 50% and 10%, respectively. The reduction schemes in autumn were similar to those in spring. In summer, the 5% of O3 control target can be realized by the 2% reduction of S(NOx) and 10% reduction of S(VOCs) and achieving a 15% O3 control target needed to reduce 4% S(NOx) and 30% S(VOCs). To reach a 15% reduction of O3 levels control target, more strict emission reduction measures should be taken. Simultaneously, it is vital to adjust the schemes on the VOCs and NOx emission reduction in time when O3 formation sensitivity changes.
4 CONCLUSIONS

In this study, spatial and temporal characteristics of VOCs at coastal and inland sites with different levels of urbanization were investigated, and sources apportionment of VOCs and the sensitivity of O₃ formation were evaluated using the positive matrix factorization (PMF) and the observation-based model (OBM). The average TVOC concentrations at CS (49.1 ± 14.4 ppb) was obviously higher than those at IS (28.4 ± 9.6 ppb), indicating stronger anthropogenic activities emissions at CS. Alkenes played an important role in the LOH and OFP, and C2–C4 alkene species contributed the most abundant. The major contributors of VOC sources at CS were vehicle exhaust and combustion sources (42.2%), industrial sources (22.4%), solvent usage (12.7%), while the contributions of fuel evaporation (23.4%) and biogenic source (19.4%) were relatively larger at IS. O₃ formation at CS was controlled by VOCs in spring and autumn, and mainly VOC and NOₓ control in summer, but was controlled by VOCs at IS in spring, summer, and autumn, and the control of alkenes and aromatics emissions could reduce O₃ concentrations. The OBM simulated results showed that 20% reduction of S(VOCs) and 3% reduction of S(NOₓ) could realize the 5% reduction of S(O₃). It is vital to adjust the schemes on the VOCs and NOₓ emission reduction if the changing of O₃ formation sensitivity happens.

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SUPPLEMENTARY MATERIAL

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REFERENCES


