Examining the major contributors and controlling factors of ozone production in a rural area of the Yangtze River Delta region during harvest season

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Abstract

Open biomass burning (OBB) has been reported to emit substantial amounts of non-methane hydrocarbons (NMHCs), and the mixing of OBB with urban plumes could exacerbate regional ozone \((O_3)\) pollution. In the present study, an observational field campaign was performed in a rural area at the edge of Yangtze River Delta region (YRDR) during harvest season when intensive open burning of wheat residues was observed. The \(O_3\) production rate at the site was calculated using a photochemical box model (Regional Atmospheric Chemical Mechanism, Version 2) constrained by real-time ambient measurements (e.g., \(O_3\), volatile organic compounds (VOCs), the sum of \(NO_2 + NO (NO_x)\), \(J\) values). During the period impacted by OBB, the \(O_3\) concentration frequently exceeded 100 ppbv. Analysis showed that the net \(O_3\) production was pronounced, in particular when the site was characterized by a prevailing southerly wind that also brought substantial amounts of \(NO_x\) emitted from urban areas. At these times, the maximum rate of \(O_3\) production was 20 ppbv h\(^{-1}\) with potential production rate of 102 ppbv on a daily basis. The \(O_3\) production at the site was typically VOC-sensitive in the morning because \(NO_x\) dominated the plumes. However, in the afternoon, conditions became \(NO_x\)-sensitive due to the rapid photochemical consumption of \(NO_x\) in the production of \(O_3\). A positive matrix factorization analysis indicated that solvent usage and OBB were the primary contributors to the mass fraction of ambient NMHCs observed at the study site, and were responsible for 35 and 23\% of the total \(O_3\) production, respectively. The preferential presence of \(NO_x\) in the morning inhibited net \(O_3\) production; meanwhile \(O_3\) built up in the afternoon due to a decrease in \(NO_x\) concentrations. These results indicated that a joint effort in the regulation of solvent (aromatics) usage and OBB, as well as \(NO_x\) from on-road vehicle exhaust may be effective in eliminating high-\(O_3\) pollution risk in the rural areas of the YRDR.
1 Introduction

Ozone (O$_3$) is a crucial component in the troposphere. It plays a key role in the atmosphere’s oxidation capacity, which strongly influences the lifetime of biogenic/anthropogenic compounds and their corresponding climate forcing effects (Sitch et al., 2007). High concentrations of tropospheric O$_3$ has been reported to have serious detrimental environmental and health effects (e.g., crop yield reduction, human respiratory disorders) (Cape, 2008). In principle, the net production of O$_3$ is evident due to the presence of peroxy radicals from the photochemical oxidation of non-methane hydrocarbons (NMHCs), which significantly disturbs the O$_3$–NO–NO$_2$ cycle, especially in urban areas where atmospheric loadings of NMHCs and the sum of NO$_2$ + NO (NO$_x$) are pronounced.

In China, the Yangtze River Delta region (YRDR) is one of the most important economic centers and is responsible for 11–12% of total emission of NMHCs and NO$_x$ in China (Zhang et al., 2009). These O$_3$ precursor emissions have increased by 71% (NMHCs) and 89% (NO$_x$) since 2000 (Kurokawa et al., 2013) due to rapid economic development in the region. Long-term observations have indicated that ground-level O$_3$ pollution in the YRDR has been increasing at a rate of +0.52 ppbv yr$^{-1}$ (Wang et al., 2009) and at a rate of 2.7% yr$^{-1}$ in terms of variability in the daily maximum from 1991 to 2006 (Xu et al., 2008). Extreme O$_3$ pollution (hourly averages reaching 286 ppbv) has been reported at a suburban site near the Beijing megacity due to an abundance of local O$_3$ precursors (Wang et al., 2006).

Although open biomass burning (OBB) occurs sporadically and intensively, its impact on ambient O$_3$ levels has been shown to be statistically evident. Onboard satellite observations have indicated that troposphere column O$_3$ concentrations are enhanced by 10–25% in near and downstream regions of fire (Ziemke et al., 2009). Such phenomena are supported by flight measurements (Takegawa et al., 2003) in which a clear positive correlation between O$_3$ and carbon monoxide (CO) measured in the OBB plume has been observed, implying that O$_3$ was photochemically produced from...
its precursors emitted from OBB. A recent study found that methyl vinyl ketone (MVK) and methylacrolein (MACR) (photooxidation products of isoprene), as well as isoprene, are also present at significant levels in some OBB plumes, indicating that isoprene played essential role in the O$_3$ formation processes (Hornbrook et al., 2011). In China, large amounts of crop residue are burned directly in the field in harvest seasons, and such activities have remained intensive in the YRDR despite being legally banned by the government. The mixing of the OBB plume with anthropogenic pollutants (rich in NMHCs and NO$_x$) emitted from urban areas may significantly boost O$_3$ formation.

Recent analysis of the impact of OBB on regional O$_3$ production have generally been based on model simulations by manipulating the emissions of O$_3$ precursors from OBB, and results have been heavily dependent on the appropriateness and accuracy of OBB information (e.g., emission strength, geographical location, duration) (Yamaji et al., 2010). Quantitive analysis of the contribution of OBB to in situ O$_3$ production using field observations is still limited. In response to this limitation, a field measurement was carried out in a rural area of the YRDR from the middle of May to the end of June. The O$_3$ production rate and sensitivity were investigated using the Regional Atmospheric Chemistry Mechanism (RACM) version 2, which was constrained by real-time measurements of O$_3$ precursors, meteorological conditions, and J values. Positive matrix factorization (PMF) was adopted in this study to identify the possible sources of NMHCs at the site. Besides diagnosis of the O$_3$ production mechanism, this study also aimed to provide recommendations to policy-makers for effectively reducing the risk of high-O$_3$ pollution in the rural area of the YRDR.

2 Measurements

Field measurements of O$_3$, CO, NO$_x$, and NMHCs were carried out in a Science and Technology park in a rural area of the YRDR (32.25° N, 121.37° E; Rudong Town, Jiangsu Province, China) in June 2010. Local anthropogenic emissions in the Science and Technology park were very limited. The observation site was ∼ 180 km north of
the Shanghai megacity, surrounded by acres of agriculture fields with few inhabitants. The geographic information for the observation site is shown in Fig. 1. In this study, the mixing ratio of O$_3$ was measured using a commercial UV-absorption O$_3$ analyzer (model 49c, time resolution: 1 min; zero noise: 0.25 ppbv with 1 min average; Thermo Scientific Inc.). The ambient CO mixing ratio was measured using a gas filter non-dispersive infrared carbon monoxide gas analyzer (model 48c, zero noise: 0.04 ppm with 30 s average; Thermo Scientific Inc.). The zero point was periodically checked during the beginning 20 min of each hour using purified air produced by a heated Pt catalyst (model 96; Thermo Electron Co.). Span calibrations were performed on site with standard span gas (2.03 ppmv, produced by Nissan-Tanaka Corp., Japan). Mixing ratios of NO and NO$_2$ were detected using a commercial NO$_x$ analyzer (model 42CTL; Thermo Scientific Inc.). We used two converters in parallel that were switched from one to the other, a molybdenum converter for measurements of NO$_y$ and a photolytic converter for selective measurements of NO$_2$. The precision of the instrument is specified to be 0.4 ppbv with a zero noise of 0.2 ppbv with a 1 min average. The instruments were placed in a temperature-controlled container and ambient air mass was drawn into the room through a 2.5 m-long, 1/4 inch Teflon tube.

Fifteen NMHCs species were detected using an online gas chromatography-flame ionization detection (GC-FID) and gas chromatography-mass spectrometry (GC-MS) at a time resolution of ∼2 h. During measurement, ambient air was first directed to a pre-concentration unit (GAS-30; DKK-TOA Corp., Ltd., Japan) with a sampling time of 10 min. Valves and transfer lines were maintained at 80°C to minimize the loss of VOCs in samples, and the trapping tube was held at ∼−78°C using liquid carbon dioxide. Calibration of the GC/FID/MS was carried out using a gas standard of 1 ppm containing 58 VOC components (PAMS-J58; Sumitomo Seika Chemicals Corp., Ltd., Japan). Oxygenated volatile organics (e.g., MVK/MCAR, MEK/butanal, acetone/propanal) and acetonitrile were also concurrently measured using a commercially available proton transfer reaction mass spectrometer (PTR-MS; Ionico Analytik GmbH, Austria). A detailed explanation of NMHC measurements is given in literature (Kudo et al., 2014). The
spectral actinic flux was measured using a single monochromator/photodiode array instrument (Meteorologie Consult Inc., Germany) with a wavelength ranging from 274 to 698 nm. The uncertainty in the photolysis of ozone ($JO^1D$) for a similar instrument has been estimated to be 14%. Chemical composition and the size distribution of aerosol particles were also measured during the field campaign. Detailed descriptions of these methods can be found in the literature (Pan et al., 2012).

3 Methodologies

3.1 Observation-based simulation of $O_3$ production

The simulation of $O_3$ photochemistry was based on a photochemical box model, RACM, version 2, which was released recently (Goliff et al., 2013). Compared with its previous version (RACM version 1) (Stockwell et al., 1997), the new version has expanded aromatic chemistry with a greater number of species, and additional and separate reaction schemes for benzene, $m$-xylene, $p$-xylene, and $o$-xylene chemistry. This mechanism employs 363 reactions and 120 species. In the calculations, $O_3$, NO, NO$_2$, SO$_2$, CO, and $J$ values, as well as NMHC species, were processed into a dataset with a time resolution of 10 min. The missing data were linearly interpolated. Concentrations of all species at 00:00 LST were regarded as the initial condition, and the integration was conducted repeatedly with an integration step of 0.01 s for five times on each day. Results of the last 24 h were used as the output of simulations after the stabilization of unmeasured species. The mixing ratio of NO was assumed to be 0.01 ppbv when the observation was below the detection limit. $O_3$ photochemistry in the daytime (06:00–18:00 LST) was manifested on the basis of the constrained steady-state calculation, and the instantaneous net $O_X$ ($O_3 + NO_2$) production rate [$P(O_X)$] was also estimated since NO$_2$ is known to exist at high concentrations comparable to $O_3$ at the observation site. $O_X$ net formation rate [$P(O_X)$] was calculated by subtracting its loss [$D(O_X)$] from
gross formation rate, \( F(O_x) \). The formulae are given by

\[
F(O_x) = k_1[\text{HO}_2][\text{NO}] + \sum k_{2i}[\text{RO}_2][\text{NO}]\phi_i \tag{1}
\]

\[
D(O_x) = k_3[\text{O}^1(\text{D})][\text{H}_2\text{O}] + k_4[\text{OH}][\text{O}_3] + k_5[\text{HO}_2][\text{O}_3]
+ \sum k_{6i}[\text{O}_3][\text{olefin}]_i + \sum k_7[\text{OH}][\text{NO}_2] \tag{2}
\]

\[
P(O_x) = F(O_x) - D(O_x) \tag{3}
\]

where \( \text{RO}_2 \) and \( \phi \) represent organic peroxy radicals (e.g., \( \text{CH}_3\text{O}_2 \)) and the yield of \( \text{NO}_2 \) from the \( \text{RO}_2 + \text{NO} \) reactions, \([X]\) is the number density of species \( X \), and \( k_1 - k_7 \) are the reaction rate coefficients for the \([X][Y]\) reaction. The calculation of \( F(O_x) \), \( D(O_x) \), and \( P(O_x) \) depend on the final output of RACM simulations after the photochemical balance of peroxy radicals is achieved.

3.2 PMF analysis

Positive Matrix Factorization (PMF, version 5.0) is an advanced receptor model that analytically decomposes an \( n \times m \) dimension matrix of observations into several factors (\( p \)), the species profile (\( f \)) of each source, and the amount of mass concentration (\( g \)) by solving a constrained and weighted least-squares optimization equation as follows:

\[
x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{4}
\]

where \( i \) and \( j \) represent the number of samples and chemical species that were measured, respectively, \( e_{ij} \) is the residual for each sample/species. The PMF solution minimizes the object function \( Q \) as follows:

\[
Q = \sum_{i=1}^{n} \sum_{j=1}^{m} [e_{ij}/u_{ij}]^2 \tag{5}
\]
Where $u_{ij}$ is the uncertainty for each samples/species, the detailed description the model is in the user guide (http://www.epa.gov/heasd/research/pmf.html). This approach integrates non-negativity constraints into the computation to make the results physically meaningful and explainable. To avoid arbitrariness, the $Q$ value was examined on the basis of theoretical calculations (Eq. 6) and the number of factor $p$, for which the PMF derived $Q$ value nearest to the $Q_{\text{theory}}$ value, was accepted as the numbers of NMHCs source:

$$Q_{\text{theory}} = m \times n - (m + n) \times p$$  \hspace{1cm} (6)

In the PMF run, 1-butene, trans-2-butene, cis-2-butene, and isoprene were categorized as “weak” based on low signal-to-noise ($S/N$) ratios and their relatively strong photochemical activity. Final source appointment was determined on the basis of NMHCs tracers (such as alkane, aromatics, and acetonitrile). Bootstrap runs with 100 random seed were tested. Scatterplots of different factors generally filled the G-space, and F-peak calculations also showed very similar results, implying that the PMF calculation was reliable for use in the following analysis.

### 3.3 Footprint analysis

An ensemble simulation of a 72 h back trajectory of air masses was performed using the Hybrid Single Particle Lagrangian Integrated Trajectory model (Hysplit; http://ready.arl.noaa.gov/HYSPLIT.php) by offsetting the meteorological data by a single meteorological grid point in the horizontal and 0.01 sigma units in the vertical. Input meteorological data were provided by the NCEP Global Data Assimilation System (GDAS) model with a grid resolution of 1° × 1°. To better review the impact of emissions on the surface layer, only the footprint region of the air mass in units of residence time was demonstrated in the following analysis. Here, the footprint region was determined as the grids in which the geographical height of the trajectory point was lower than the mixing height in the meteorological field. The footprint region was generally consistent with...
the spatial distribution of source–receptor relationships determined by the FLEXPART dispersive model (Pan et al., 2012).

4 Results

4.1 Overview of observations

Temporal variations in the \(O_3\), NMHC, \(NO_x\), \(NO_y\), and CO mixing ratios are shown in Fig. 2, and statistics on the NMHC species are listed in Table 1. During observation periods, five pollution episodes (10–12 June, 14–17 June, 18–20 June, 22 June, and 23 June) were clearly observed on the basis of \(NO_x\) variations, and on 4 days (15 June, 19 June, 22 June, and 23 June), the hourly averaged \(O_3\) mixing ratio had maxima greater than 100 ppbv (dash line as shown in the Fig. 2). The highest \(O_3\) concentration (147 ppbv) occurred on 15 June when the site was affected by the intensive open burning of crop residues in the surrounding agriculture area, and the daily averaged CO mixing ratio was found to be 1000 ppbv. During high pollution periods, the significant increase in \(O_3\) during the daytime at the site was mainly related to the \(O_3\) precursors transported from the megacity cluster to the south, illustrated by the obvious enhancements in \(NO_x\) (mean: 30 ppbv) and \(NO_y\) (mean: 60 ppbv) observed with the prevailing southerly wind. In particular, the ambient \(O_3\) mixing ratio decreased to almost zero due to titration reactions when the nitrogenous species were present in the early morning of pollution days. The ambient NMHC concentration was found to be 200 ppbC on average, and the maximum concentration of NMHCs (451 ppbC) occurred at 05:00 LST on 19 June when the \(NO_x\) mixing ratio was as high as 30 ppbv, and the maximum \(O_3\) level also exceeded 120 ppbv due to strongly photochemical processes in the daytime. NMHCs showed a similar variation to CO, implying that they likely originated from the same sources during the field campaign. Note that the field campaign was just within the period of Shanghai World Expo 2010 with increased traffic and visitors. The local governments of Shanghai and Jiangsu Province implemented strict emissions control
operations including odd-and-even license plate rules for cars on the road, confining the assembly line of spraying treatment in auto-repair and industry enterprises, and prohibiting, e.g., OBB activities. Atmospheric O$_3$ precursors might have been even higher than this observation if no relevant regulatory measures had been in effect.

4.2 Diurnal pattern

Figure 3 shows the average diurnal variations in O$_x$, CO, NO, NO$_x$, NO$_y$, NO$_z$, NO$_x$/NO$_y$, and NMHCs for days when the maximum hourly averaged O$_x$ concentration was greater than 100 ppbv (red dotted lines) and those days when it was less than 100 ppbv (blue dotted lines). The hourly averaged O$_x$ in high-O$_3$ pollution days showed a predominant single peak distribution with a daily increment of 94 ppbv (Fig. 3a), suggesting the significant depletion of O$_3$ at night and production of O$_3$ in the daytime due to the presence of substantial concentrations of O$_3$ precursors. In contrast, O$_x$ levels on the low-O$_3$ pollution days showed a moderate increase at noontime with a daily increment of 24 ppbv. Variation in NO (Fig. 3b) had a prominent peak at 07:00 LST, especially for the high-O$_3$ pollution days (maximum: 4.2 ppbv). For the low-O$_3$ pollution days, the hourly averaged NO normally had a weak peak (1.1 ppbv). As shown by the red line in Fig. 3c, diurnal variation in NO$_2$ at the site had a predominant peak (38.6 ppbv) between 00:00 and 08:00 LST, evidently different from the features (two peaks at 09:00 and 18:00 LST during rush hour) observed at the urban site of the Shanghai megacity. These results suggested that NO$_2$ at the site could be primarily attributable to transport from the urban area instead of in situ production. Diurnal variation in NO$_y$ (Fig. 3d) on high-O$_3$ pollution days showed a boarder peak (57 ppbv) than that of NO$_2$ due to the consecutive conversion from NO$_x$ to NOz (e.g., HNO$_3$, PANs) in the daytime. As expected, NO$_z$ also showed an obviously unimodal distribution (Fig. 3e) with a maximum value of 32.6 ppbv at 12:00 LST when O$_3$ photochemistry was proactive. We did not observe a clear increase in either NO$_y$ or NO$_z$ for the low-O$_3$ pollution days.
Diurnal variation in the NO$_x$/NO$_y$ ratio is illustrated in Fig. 3f. In general, a higher NO$_x$/NO$_y$ ratio indicates that pollution plumes have a shorter photochemical age. In the present study, we found that the plumes on high-O$_3$ pollution days were not photochemically aged (NO$_x$/NO$_y$ ratio > 0.5) when they were transported to the observation site in the morning, and they gradually became aged (NO$_x$/NO$_y$ = 0.2) due to strong photochemical processes in the daytime. For low-O$_3$ pollution days, the NO$_x$/NO$_y$ ratio did not vary significantly and had a mean of 0.34.

As shown in Fig. 3g, the total NMHC concentration (not including oxygenated VOCs) on the high-O$_3$ pollution days showed evident increases in the early morning (mean: 176.4 ppbC) and gradually decreased to 48.7 ppbC at night. On low-O$_3$ pollution days, the NMHC concentration was constantly low with a mean of 62.8 ppbC, implying limited contribution from the transport of urban emissions. Diurnal variations in $J$(NO$_2$) on the high-O$_3$ and low-O$_3$ pollution days during observation periods (Fig. 3h) showed nearly the same behavior, implying that the significant enhancement of O$_3$ production during the high-O$_3$ pollution period did not result from variations in solar radiation.

### 4.3 Identification of source regions

To identify the major source regions for O$_3$ precursors, the color-shaded polar graph for O$_3$, NO, NO$_2$, NMHCs, NO$_x$/NO$_y$ and NMHC/NO$_x$ is shown in Fig. 4. Figure 4a indicates that a weak southerly wind ($\sim$ 3 ms$^{-1}$) was mostly accompanied by the occurrence of high-O$_3$ pollution at the site, suggesting that in situ photochemistry was important in O$_3$ production; however, the high-O$_3$ concentration from the north and east was normally related with stronger winds (> 5 ms$^{-1}$), implying the potential contribution from direct transport. As expected, high NO$_x$ (Fig. 4b and c) and NHMCs (Fig. 4d) at the site were also related to prevailing southerly winds that brought substantial amounts of O$_3$ precursors from the megacity cluster (e.g., Shanghai). Figure 4e shows that polluted plumes from the west and south were normally fresh with an NO$_x$/NO$_y$ ratio larger than
0.5, especially during the high-O₃ pollution days when the NOₓ/NOy ratio was greater than 0.8.

The NMHC/NOₓ ratio partially reflected the characteristics of emissions sources and corresponding O₃ production potentials. The dependence of NMHC/NOₓ on wind direction is shown in Fig. 4f. We found that the polluted plumes from the north normally had high NMHC/NOₓ ratios with a mean of 41 ppbC ppb⁻¹. Nevertheless, typically low NMHC/NOₓ ratios (12 ppbC ppb⁻¹ on average) were observed in the present study for plumes transported from the metropolis to the south. Ran et al. (2009) reported an average NMHC/NOₓ ratio of 8 ppbC ppb⁻¹ for pollution in the downtown area of the Shanghai megacity, generally consistent with our observations. For a detailed discussion on the dependence of O₃ production on the NMHC/NOₓ ratio, see Sect. 5.3.

5 Discussions

5.1 O₃ production rate

The net photochemical production of O₃ [P(O₃)] during the field campaign was calculated on the basis of Eqs. (1)–(3). In general, the buildup of O₃ pollution at the site could be mostly explained by the instantaneous photochemical production rate assessed by the box model constrained by local observations of precursors. Figure 5 shows the diurnal variation in P(O₃) for high-O₃ pollution days and the entire observation period. For the high-O₃ pollution days, the maximum P(O₃) was 20.1 ppbv h⁻¹ at 11:00 LST. The 6 h (09:00–15:00 LST) average of P(O₃) was found to be 13.3 ppbv h⁻¹, which is similar to the 6 h averages found from observations over other urban areas (Philadelphia, PA: 11.3 ppbv h⁻¹; Houston, TX: 11.3 ppb h⁻¹) (Kleinman et al., 2002). The observation was higher than results at the top of Mt. Tai (1534 m) in Central East China (6.4 ppbv h⁻¹) where O₃ production has been found to be primarily NOₓ-limited (Kanaya et al., 2009). Daily integrated P(O₃) levels on high-O₃ and low-O₃ limited (Kanaya et al., 2009). Daily integrated P(O₃) levels on high-O₃ and low-O₃ limited (Kanaya et al., 2009).
(93 and 24 ppbv, respectively) in the daytime, implying that a buildup of O$_3$ at Rudong could be generally explained by in situ photochemical productions, without taking into account import of O$_3$ produced in other areas. One exception was 22 June when the $P$(O$_3$) (17 ppbv) accounted for only one-tenth of the observed O$_3$ production (151 ppbv) on a daily basis, suggesting that the direct transport of O$_3$ was more important for the enhancement of O$_3$ mixing ratio observed at the site. Footprint analysis implied that the contribution from the Shanghai megacity was significant.

5.2 Dependence of O$_3$ production sensitivity on the source region

The sensitivity of O$_3$ production to precursor concentrations was determined on the basis of model simulations by artificially multiplying the NO$_x$ concentration by factors of 0.5 and 2, while the NMHC concentration was kept unchanged, or by multiplying the NMHC concentration by factor of 0.5 and 2, while the NO$_x$ concentration remained unchanged. The sensitivity of the O$_3$ production rate on several O$_3$ pollution cases and their corresponding footprint regions was determined by a back trajectory model (Fig. 6). As shown in Fig. 4, the emission characteristics of O$_3$ precursors observed at the observation site differed for pollutants arising from different directions, resulting in specific O$_3$ production sensitivity. For the pollution that originated from the western inland area (Fig. 6a and b), O$_3$ production was very sensitive to the variation in VOCs, and a decrease in NO$_x$ led to an obvious increase in O$_3$ production, even in the afternoon when NO$_x$ had been significantly consumed, which suggested that O$_3$ production occurred in a typically VOC-controlled regime. However, when the air masses originated from the north/coastal region (Fig. 6d), O$_3$ production was primarily controlled by ambient NO$_x$ concentrations (Fig. 6c), as indicated by the extremely low NO$_x$ concentration (average: 0.93 ppbv) and relatively high NMHC concentration (42.5 ppbv) in the daytime.

Most notably, we observed an obvious alteration in O$_3$ production sensitivity for the pollution transported from the south region (Fig. 6e–h). O$_3$ production in the morning was much more sensitive to the NMHC concentration than to NO$_x$, and an increase in
NO\textsubscript{x} concentration resulted in a decrease in O\textsubscript{3} production (VOC-controlled regime); in the afternoon, the O\textsubscript{3} production became NO\textsubscript{x}-sensitive and a doubling of the NO\textsubscript{x} concentration led to a clear increase in O\textsubscript{3} production (NO\textsubscript{x}-controlling regime). This reflected significant variations in ambient NO\textsubscript{x} due to photochemical processes in the atmosphere, and the NO\textsubscript{x} mixing ratio decreased from 21.7 ppbv in the morning to 2.9 ppbv in the afternoon on 19 June and from 39.4 to 2.0 ppbv on 23 June. Footprint analysis (Fig. 6f and h) indicated that the air mass was mostly stagnant over polluted regions in the YRDR, implying that anthropogenic pollution (e.g., automotive vehicles) from urban areas was a determinant in the variation in O\textsubscript{3} production.

5.3 O\textsubscript{3} production isopleth diagram

To better evaluate the O\textsubscript{3} production sensitivity to NMHCs and NO\textsubscript{x} concentrations at the site, a series of model runs were carried out that artificially decreased and increased the NO\textsubscript{x} and NMHC concentration to cover wide areas to simulate real atmospheric conditions as described in Sect. 5.2. The mixing ratio of O\textsubscript{3}, NO\textsubscript{x}, and NMHCs, J values, and meteorological data observed at 10:00 LST on 19 June were used as constraints. The dependence of the O\textsubscript{3} production rate on NMHCs and NO\textsubscript{x} is shown in Fig. 7. The circles and squares in the plot represent the calculated O\textsubscript{3} production rate observed on high-O\textsubscript{3} pollution days (19 and 23 June), and the gray dashed lines indicate a variation in NO\textsubscript{x} during those days. The shift in the O\textsubscript{3} production regime on high-O\textsubscript{3} pollution days could be explained by the diagram. The model predicted that the ridge of the O\textsubscript{3} production rate was associated with an NMHC/NO\textsubscript{x} ratio of 10–20 ppbC/ ppbv\textsuperscript{−1}, similar to the prediction of urban photochemistry in central Tokyo (Kanaya et al., 2008). Relatively low NMHC/NO\textsubscript{x} ratios (∼5 ppbC/ ppbv\textsuperscript{−1}) were found in the mornings of high-O\textsubscript{3} pollution days owed to a substantial amount of NO\textsubscript{x}, which increased slightly up to 30–50 ppbC/ ppbv\textsuperscript{−1} due to rapid NO\textsubscript{x} photochemical loss. This tendency was generally consistent with the observation in Shanghai urban area (Ran et al., 2009).
In particular, O$_3$ production in the morning of 19 June approached the predicted “ridge” region due to the preferential presence of hydroperoxyl (HO$_2$) and peroxo radicals on the basis of model calculations, and the pathway forming NO$_2$ by peroxo radicals reacting with NO was predominant. Footprint analysis illustrated that the accumulation of NMHCs in air masses was associated with urban emissions north of the YRDR. The difference was that O$_3$ production in the morning of 23 June occurred in a typical NO$_x$-inhibition regime due to the extremely low NMHC/NO$_x$ ratio (1.1 ppbC/ppbv$^{-1}$). The footprint of air masses demonstrated a clear “U”-shape where the air masses were mostly transported from marine region and swept over the Shanghai megacity. As mentioned before, the field campaign was performed during the Shanghai Expo period. A reduction of NO$_x$ and NMHC emissions in the YRDR due to regulatory emission policies likely inhibited O$_3$ production; however it did not appear to change the primary conclusion of O$_3$ production sensitivity at this site, especially since the site was situated downwind of the polluted urban areas.

5.4 Contribution of O$_3$ production from different sources

5.4.1 Allocation of anthropogenic NMHC sources

Source appointment of NMHCs observed during the field campaign was performed on the basis of PMF calculation, and six anthropogenic sources were mathematically resolved. Factor 1 explained most of the aromatic mass fraction with 79% for toluene, 88% for ethyl-benzene, 79% for $m,p$-xylene, and 75% for $o$-xylene. Alkane and alkene accounted for only a minor percentage of the total mass, suggesting that this factor was primarily associated with solvent use sources. Mass ratios of $m,p$-xylene/$o$-xylene (1.4) were found to be similar to the values reported for painting factories (2.0) and the solvent-based industry (2.2) around the Shanghai megacity (Cai et al., 2010).

Factor 2 was regarded as OBB sources due to the predominant contribution of furan and acetonitrile to this factor with mass fractions of 70 and 39%, respectively. We found that OBB could explain 74.4% of total isoprene and 55.4% of the MVK + MACR (oxi-
dation production of isoprene) at the study site. This result was slightly higher than the value in the emissions inventory, which indicated that 54.3% of isoprene in the YRDR originated from biomass burning (Huang et al., 2011). We found that the furan/isoprene mass ratio in OBB was 16.2, much higher than the value (3.5) reported in the emissions inventory (Akagi et al., 2011) and higher than the value (2.6) observed in laboratory experiments (Christian et al., 2003). The higher ratio in the present study was probably due to the photo-oxidation of isoprene in the summer season, and the furan/isoprene ratio would be approximately equal to that of previous studies if MVK/MACR were taken into consideration. Note that the isoprene from biogenic sources was negligible compared to the contribution from OBB and anthropogenic emissions during these specific observation episodes (Sect. 5.4.3).

Factor 3 explained the majority of C₅ alkane mass representing 69% of i-pentane and 70% of n-pentane. i-pentane is a typical tracer for gasoline evaporation, and we therefore assigned this factor to fuel evaporation sources. Factor 4 accounted for 54 and 78% of the total mass of i-butane and n-butane, respectively, the latter of which is reportedly released from the use of liquid petroleum gas (LPG) and natural gas (NG), which are the major fuels consumed for household cooking in the YRDR. We then attributed this factor to domestic sources related with LPG usage. Factor 5 was assigned to vehicular-exhaust sources due to a predominance of NO₂ (77%), which was reported to be the characteristic product of the internal combustion of fossil fuel. Quantities of aromatics and alkane species in this factor were small. Factor 6 was attributed to the oil industry (such as petroleum refining) due to a significant contribution of propane (one of the major by-products of raw oil processing) and benzene (a petrol additive), accounting for 84 and 55%, respectively.

5.4.2 Diurnal variation in the factorial contribution to O₃ production

The sensitivity of each source to O₃ production at the study site is quantified in this section. First, the NMHC and NOₓ concentrations of one selected source were artificially increased/decreased by 10% while the concentration of NMHCs and NOₓ for
other sources remained unchanged. In such a situation, the total variation in NMHC and NO\textsubscript{x} concentrations was normally within 5%, guaranteeing that the RACM2 calculation could still be well constrained. The variation in O\textsubscript{3} production rates that resulted from chemical reactions was deemed as the relative contribution of the source to O\textsubscript{3} formation. Average diurnal variation in the relative sensitivity of six sources to in situ photochemical O\textsubscript{3} formation is shown in Fig. 8. The contribution of different sources to O\textsubscript{3} production demonstrated distinct variation patterns. Solvent usage was responsible for major contributions (52%) of O\textsubscript{3} production in the morning and minor contributions (18%) in the afternoon. The second most important contributor was OBB with a maximum contribution of 27% at 12:00 LST and 23% on a daily basis. These results imply that the regulation of OBB in the rural area of the YRDR is definitely effective in reducing the potential risk of high-O\textsubscript{3} pollution, although these effects may differ from region to region. Industrial sectors contributed 31% of the total O\textsubscript{3} formation in the afternoon. In particular, the increase in vehicle exhaust-related sources tended to depress the formation of O\textsubscript{3} in the morning because the air mass was rich in fresh NO\textsubscript{x} (typical VOCs-sensitive regime); however, in the afternoon, vehicle exhaust can boost the production of O\textsubscript{3} due to NO\textsubscript{x}-sensitive atmospheric state (as discussed in Sect. 5.3). The vehicle exhaust-related source was responsible for 16% of the O\textsubscript{3} production in the afternoon. In general, the total sensitivity of each source could explain most of the variability in O\textsubscript{3} production rates at the site (Fig. 5).

### 5.4.3 Biogenic isoprene

In the present study, mean mass concentrations of isoprene and MVK/MACR (photooxidation products of isoprene) at the site were 0.16 ± 0.15 ppbv and 0.83 ± 0.55 ppb, respectively, with a mean MVK + MACR to isoprene ratio ([MVK + MACR]/isoprene) of 5.2. Biogenic sources (normally predominant at noon) were not mathematically resolved by the PMF calculation. Most of the isoprene was attributed to OBB sources and the rest was assigned to sources related to transport. First, the [MVK + MACR]/isoprene ratio was normally less than 0.4 in the biogenic sources-dominant...
environment (Montzka et al., 1993). Yuan et al. (2012) reported that the [MVK + MACR]/isoprene ratio was 0.3 for biogenic sources on the basis of PMF analysis. In the present study, the [MVK + MACR]/isoprene ratio was the highest, ranging from 3 to 25, suggesting that the impact of biogenic sources was not significant. Second, oxygenated VOCs (including MVK and MACR) might also be preferentially present in the OBB plumes, and the [MVK + MACR]/isoprene ratio was reported as ranging from 1.8 to 4.2 in the emissions inventory (Akagi et al., 2011). The relatively higher [MVK + MACR]/isoprene mass ratio in the present study implied that the isoprene might undergo further oxidization after being emitted. The upper limit of the [MVK + MACR]/isoprene ratio was ∼30 in this study. Third, observation site was located adjacent to a large area of wheat field, it is known that wheat plants emit little amount of isoprene (Kesselmeier and Staudt, 1999), the diurnal variation in isoprene at the site did not show a pronounced enhancement at noontime (10:00–15:00 LST), and the 6 h averaged isoprene concentration was 0.19 ± 0.16 ppbv. Given the above, we deemed that biogenic sources had limited impact on in situ O₃ production and was therefore neglected in the above discussion.

5.4.4 Impact of aerosols on O₃ production

The presence of particles reportedly can result in a significant heterogeneous loss of HO₂ (Taketani et al., 2008), which plays a key role in peroxy radical equilibrium and O₃ formation in the troposphere. The study at the mountain site in Central East China indicated that ambient HO₂ concentrations, and corresponding net O₃ production rates, declined significantly, due to the inclusion of a heterogeneous loss in HO₂ (Kanaya et al., 2009). In the present study, the effect of a heterogeneous loss of HO₂ on the O₃ production rate was investigated. The loss rate of HO₂ was calculated using the Fuchs–Sutugin equation (refers to the paper, Kanaya et al., 2009). The gas-phase diffusion coefficient of HO₂ was assumed to be 0.247 cm² s⁻¹. The dependence of the uptake coefficient of HO₂ on relative humidity (ranging from 0.2 to 0.35) was considered on the basis of laboratory studies (Taketani et al., 2008). The number size distribution of par-
particles (size bins: 0.3–0.5, 0.5–0.7, 0.7–1.0, 1.0–2.0, 2.0–5.0 µm) during the campaign were measured using a portable particle counter (model KR-12A; RION Inc.). As a result, the estimated loss rate of HO₂ ranged from $7 \times 10^{-3}$ to 0.05 s⁻¹. The incorporation effect of HO₂ loss into the RACM2 model calculation resulted in the O₃ production rate being reduced by 13% on average; however, it was still large enough to explain the buildup of O₃ at the site. Note that emissions of PM₂.₅ and ambient concentrations in the East China region have been increasing for the past decades due to rapid economic growth. Huang et al. (2011) reported that primary anthropogenic emissions of PM₂.₅ and PM₁₀ in the YRDR were 1510.8 Ggyr⁻¹ and 3115.7 Ggyr⁻¹, respectively, corresponding to 11 and 17% of the total emissions in China. O₃ production was inferred to have been depressed due to the presence of a substantial number of aerosol particles (heterogeneous loss of HO₂) in the atmosphere, and tropospheric O₃ concentrations were assumed to definitely increase provided that particle emissions are significantly reduced while NOₓ and NMHCs emission remain unchanged. Furthermore, a reduction in fine particle concentrations in atmosphere will also decrease the aerosol optical depth, resulting in an increase in the actinic flux and photolysis rates in the lower troposphere. A study by (Gerasopoulos et al., 2013) found a 40% reduction in $J O_1^D$ at a high solar zenith angle during high aerosol loading periods (AOD = 0.5–0.7), implying that the enhancement of O₃ production will more drastic if the effects of both a reduction of heterogeneous loss and an increase in $J$ values were considered. Moreover, the variability in meteorological conditions should also impact O₃ production. For example, an increase in relative humidity could lead to a more rapid heterogeneous loss of HO₂ on the wet surface of particles (Taketani et al., 2008). To summarize, including the impact of aerosols is extremely important in reviewing and predicting O₃ pollution in East Asia under the scenario of global warming.
6 Conclusion and implications

This study synthesized field observations in a rural area of the YRDR during harvest season. A photochemical box model (RACM version 2) was used to investigate the O$_3$ production rate, controlling regime and its possible contributors. These results demonstrated that O$_3$ pollution was serious, especially when the site was subject to the OBB plumes and urban pollutions transported from megacities (e.g., Shanghai). The hourly mixing ratios of O$_3$ and NMHCs on high-O$_3$ pollution days (hourly averaged O$_3$ mixing ratio > 100 ppbv) were 138 ppbv and 451 ppbC, respectively, almost the highest values reported in this region among previous studies. On high-O$_3$ pollution days, the diurnal variation in O$_3$ production rates had a maximum value of 20.1 ppbv h$^{-1}$ and a daily-accumulated O$_3$ production rate of 102 ppbv, suggesting that in situ photochemical production could explain most of the O$_3$ buildup at the site. When pollution came from the Shanghai megacity with southerly winds, O$_3$ production sensitivity at the site was NMHC-controlled in the morning, but changed to NO$_x$-controlled in the afternoon due to a significant depletion of NO$_x$. PMF analysis indicated that six anthropogenic sources (solvent usage, OBB, fuel evaporation, liquid petroleum usage, vehicle exhaust, and the oil industry) contributed to the NMHC species observed at the site. Among these sources, solvent usage and OBB were the two most important contributors to high-O$_3$ concentrations, accounting for 35 and 23 %, respectively, of the O$_3$ production on a daily basis, followed by the oil industry (21 %). Vehicular exhaust sources were mostly responsible for the net production of O$_3$ in the afternoon, which was NO$_x$-sensitive. Biomimic isoprene emissions were found to be less important to the O$_3$ production at the site during our study period. Our results imply that the regulation of solvent usage and OBB in the YRDR are optimal measures to reduce the risk of high-O$_3$ pollution events. Meanwhile a reduction in NO$_x$ emission from on-road transport seemed also to be effective in mitigating O$_3$ production in the daytime.

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References


Major contributors and controlling factors of O\textsubscript{3} production in a rural Yangtze River Delta area

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Table 1. Statistics on the mixing ratios of NMVOC species, NO$_2$, and black carbon (BC) during the field campaign.

<table>
<thead>
<tr>
<th>Species</th>
<th>Average</th>
<th>SD</th>
<th>Median</th>
<th>10th percentile</th>
<th>90th percentile</th>
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<tbody>
<tr>
<td>Propane</td>
<td>1.23</td>
<td>2.23</td>
<td>0.54</td>
<td>0.14</td>
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<tr>
<td>Propylene</td>
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<td>1.49</td>
<td>0.24</td>
<td>0.08</td>
<td>1.39</td>
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<tr>
<td>i-Butane</td>
<td>0.85</td>
<td>1.11</td>
<td>0.39</td>
<td>0.12</td>
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<tr>
<td>n-Butane</td>
<td>1.31</td>
<td>1.62</td>
<td>0.72</td>
<td>0.11</td>
<td>3.57</td>
</tr>
<tr>
<td>t-2-Butene</td>
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<td>0.20</td>
<td>0.06</td>
<td>0.03</td>
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<tr>
<td>1-Butene</td>
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<td>0.42</td>
<td>0.06</td>
<td>0.02</td>
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<tr>
<td>c-2-Butene</td>
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<td>0.08</td>
<td>0.04</td>
<td>0.01</td>
<td>0.12</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>0.82</td>
<td>0.71</td>
<td>0.60</td>
<td>0.25</td>
<td>1.62</td>
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<tr>
<td>n-Pentane</td>
<td>0.37</td>
<td>0.31</td>
<td>0.27</td>
<td>0.11</td>
<td>0.74</td>
</tr>
<tr>
<td>Isoprene</td>
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<td>0.13</td>
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<tr>
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<td>0.89</td>
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<td>5.14</td>
<td>1.77</td>
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<td>Ethyl-benzene</td>
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<td>m,p-Xylene</td>
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<td>o-Xylene</td>
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<td>2.01</td>
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<tr>
<td>Furan</td>
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<td>0.81</td>
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<tr>
<td>Acetonitrile</td>
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<td>Acetaldehyde</td>
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<td>Acetone/Propanal</td>
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<td>8.27</td>
</tr>
<tr>
<td>Acetic acid</td>
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<td>2.26</td>
<td>2.11</td>
<td>1.03</td>
<td>6.58</td>
</tr>
<tr>
<td>MVK/MACR</td>
<td>0.83</td>
<td>0.51</td>
<td>0.74</td>
<td>0.27</td>
<td>1.63</td>
</tr>
<tr>
<td>MEK/Butanal</td>
<td>1.09</td>
<td>1.08</td>
<td>0.70</td>
<td>0.30</td>
<td>2.62</td>
</tr>
<tr>
<td>BC</td>
<td>2.20</td>
<td>1.93</td>
<td>1.43</td>
<td>0.50</td>
<td>5.51</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>7.79</td>
<td>11.90</td>
<td>2.50</td>
<td>0.29</td>
<td>27.59</td>
</tr>
</tbody>
</table>
**Figure 1.** Geographic location of the observation site and the spatial distribution of monthly mean NO\textsubscript{x} column density (unit: \(\times 10^6\) molecule cm\(^{-2}\), the data was from OMI observation, DOMINO version 2.0, http://www.temis.nl/airpollution/no2.html) during the field campaign period and the surrounding environment at the site.
Figure 2. Time series of O$_3$, CO, NMHCs, NO, NO$_2$, and NO$_y$ during the field campaign.
Figure 3. Diurnal variation in O$_3$, NO, NO$_2$, NO$_y$, NO$_x$/NO$_y$, NO$_z$, NMHCs, and J(NO$_2$) during the field campaign. The blue and red colors represent the averaged diurnal patterns for the high-O$_3$ pollution (hourly O$_3$ mixing ratio > 100 ppbv even only once in a day) and low-O$_3$ pollution (hourly O$_3$ mixing ratio < 100 ppbv) days, respectively. The gray line in (c) indicates the NO$_2$ concentration in the downtown area of the Shanghai megacity.
Figure 4. Dependence of the mixing ratios of O$_3$, NO, NO$_2$, NMHCs, NO$_x$/NO$_y$, and NMHCs/NO$_x$ on wind direction and speed.
**Figure 5.** Diurnal variation in the net $O_3$ production rate for high-$O_3$ and low-$O_3$ pollution days.
Figure 6. O₃ production sensitivity of the air masses with different footprint regions. The left panel shows the variation in O₃ production by artificial alteration of NOₓ and VOCs; the right panel shows the footprint region for each case.
Figure 7. \(O_3\) production isopleth plot derived from RACM sensitivity simulations at the observation site. The gray dashed lines indicate the direction of variation for the ambient NO\(_x\) concentration. The dot lines represent the trend of variation of NMHCs and NO\(_x\).
Figure 8. Diurnal variation in the sensitivity of each source to in situ O$_3$ production.