

Reviewer 2#

This article estimates the sensitivity of ozone formation using a random forest model with not only total VOCs concentrations but also observed concentrations and initial concentrations of VOC species. The result showed that the ozone prediction performance using initial concentrations of VOC species was better than that using total VOCs concentrations. Analytical reports using machine learning with total VOCs concentrations have been published recently. This article simply indicates the superiority of using overserved or initial concentrations of VOC species. From this aspect, the significance of this study is evident. The reviewer would recommend it for publication.

Reply: Thank you for your positive comments. We have carefully responded to all of your **point-by-point** comments and issues and have revised the manuscript accordingly. These revisions are described in detail below.

Q1: However, the reliability of analytical data and explanation of the initial concentration of VOC species are not sufficiently indicated in this article. And some expressions seem to be somewhat inadequate for well understanding. Slight revisions are required.

Reply: Thank you for your good suggestions. The reliability of analytical data will be replied in the following question. We have added more details about the initial concentration of VOC species. 1) We added the selection rules of tracers to calculate OH exposure and confirmed these rules based on our observation data. As shown in Figure R1 (Figure S9), the concentrations of xylene and ethylbenzene are well correlated, which indicates that they are simultaneously emitted. In addition, we compared the photochemical initial concentrations (PICs) calculated using xylene/ethylbenzene with that using toluene/benzene (Figure R2 or Figure S10). 2) We performed sensitivity tests about OH exposure calculation. The results showed that the uncertainty caused by the OH exposure (from -10% to +10%) ranged from 0.55 to 1.57 (Table R1 or Table S4). 3) we compared the chemical ages in this work with those reported in literatures. For example, the photochemical ages of isoprene were 0.01–6.21

h (1.26 ± 1.12 h). This value is comparable with previously reported photochemical ages (Shao et al., 2011; Gao et al., 2018). 4) The diurnal curves of measured and initial VOC concentrations were added in the revised SI (Figure R3 or Figure S12).

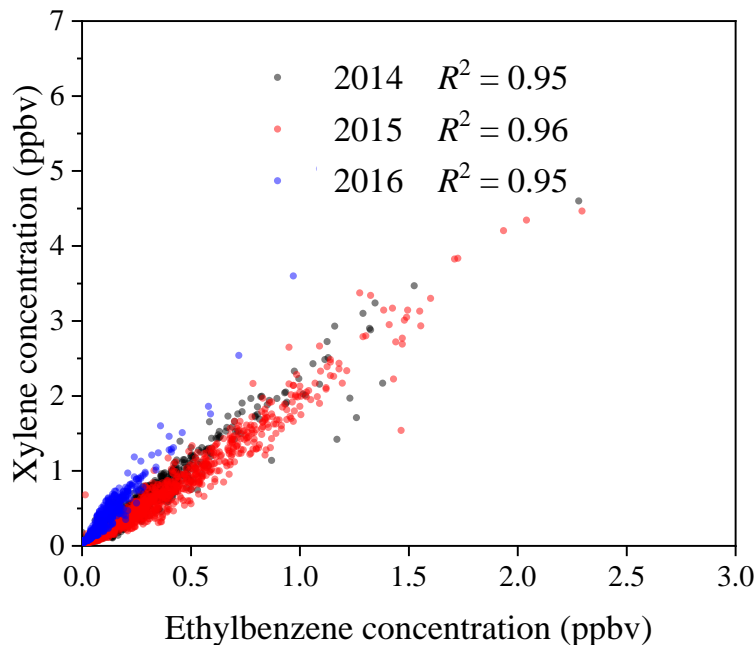


Figure R1. The relationship between xylene and ethylbenzene.

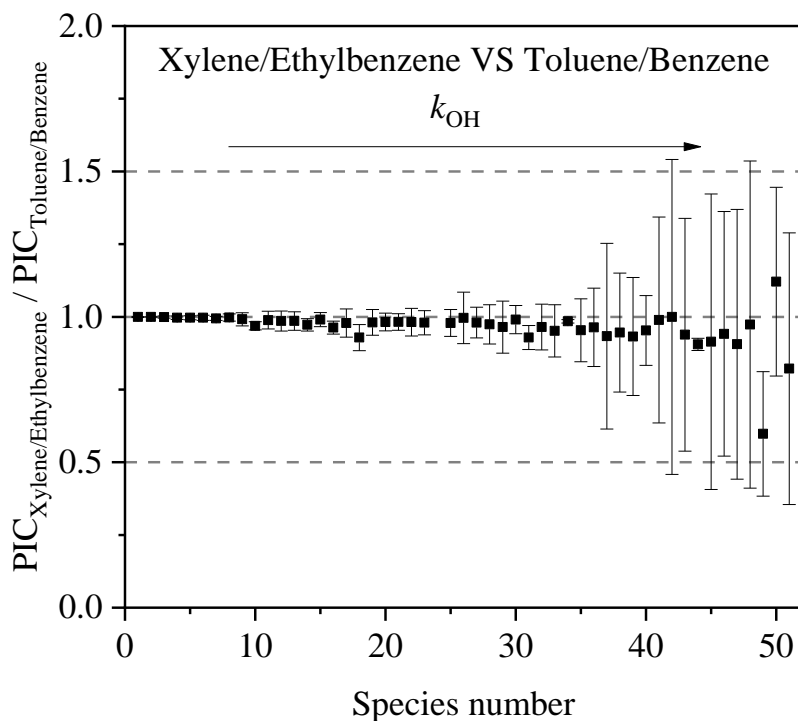


Figure R2. Comparison of the initial VOCs calculated using the ratio of xylene/ethylbenzene with that using the ratio of toluene/benzene in 2015. (Error bars are standard deviations.)

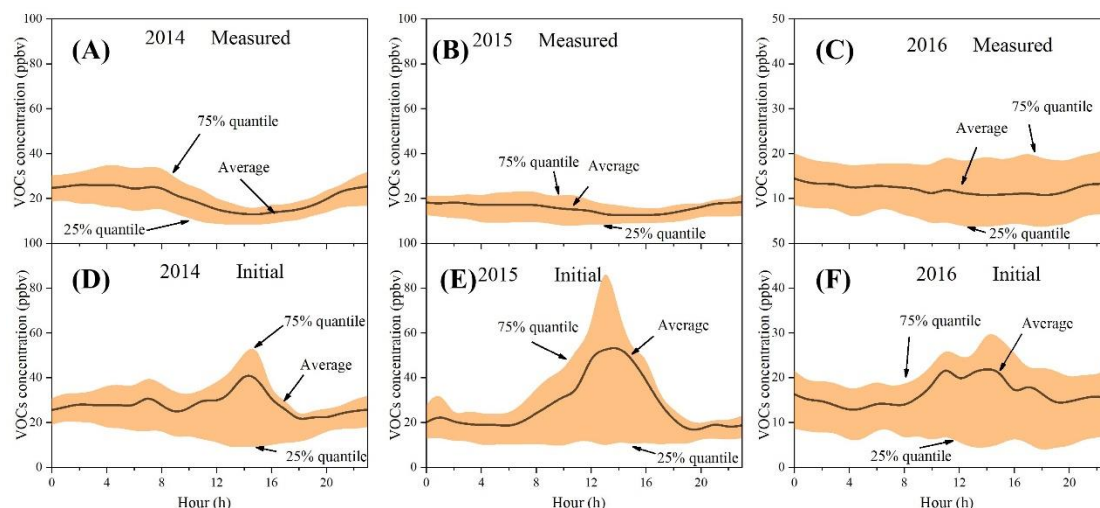


Figure R3. The daily variation of VOCs concentration. (A and D for 2014; B and E for 2015; C and F for 2016)

Table R1. k_{OH} , Method Detection Limit (MDL) and sensitivity test on estimation of $[OH] \times t$ of different VOC species

number	species name	k_{OH}^*	MDL ^{**}	Ratio to the initial VOC ^{***}					
				2014		2015		2016	
				-10% [OH] $\times t$	+10% [OH] $\times t$	-10% [OH] $\times t$	+10% [OH] $\times t$	-10% [OH] $\times t$	+10% [OH] $\times t$
1	Ethane	0.254	0.050	1.00	1.00	1.00	1.00	1.00	1.00
2	Acetylene	0.756	0.022	1.00	1.00	1.00	1.00	1.00	1.00
3	Propane	1.11	0.013	1.00	1.00	1.00	1.00	1.00	1.00
4	Benzene	1.22	0.011	1.00	1.00	1.00	1.00	1.00	1.00
5	iso-Butane	2.14	0.010	1.00	1.00	1.00	1.00	1.00	1.00
6	2,2-Dimethylbutane	2.27	0.005	1.00	1.00	1.00	1.00	1.00	1.00
7	n-Butane	2.38	0.011	1.00	1.00	1.00	1.00	1.00	1.00
8	2,2,4-Trimethylpentane	3.38	0.008	1.00	1.00	1.00	1.00	1.00	1.00
9	iso-Pentane	3.6	0.008	1.00	1.00	1.00	1.00	1.00	1.00
10	Cyclopentane	5.02	0.005	1.00	1.00	1.00	1.00	1.00	1.00
11	n-hexane	5.25	0.011	0.99	1.01	0.99	1.01	0.99	1.01
12	Toluene	5.58	0.009	1.00	1.00	0.99	1.01	1.00	1.00
13	2,3-Dimethylbutane	5.79	0.004	1.00	1.00	1.00	1.00	0.99	1.01

14	n-Propyl benzene	5.8	0.008	1.00	1.00	1.00	1.00	0.99	1.01
15	iso-Propyl benzene	6.3	0.007	1.01	1.01	0.99	1.01	0.97	1.03
16	2,3,4-trimethylpentane	6.6	0.008	0.99	1.01	0.99	1.01	1.00	1.00
17	n-heptane	6.81	0.009	0.99	1.01	0.99	1.01	0.99	1.01
18	ethylbenzene	7	0.009	0.99	1.01	0.99	1.01	0.99	1.01
19	cyclohexane	7.02	0.011	1.00	1.00	0.99	1.01	0.99	1.01
20	2,3-Dimethylpentane	7.15	0.009	1.00	1.00	1.00	1.00	1.00	1.00
21	3-Methylhexane	7.17	0.009	1.00	1.00	0.99	1.01	1.00	1.00
22	ethene	8.15	0.021	0.99	1.01	0.99	1.01	0.99	1.01
23	n-octane	8.16	0.008	0.99	1.01	1.00	1.00	1.00	1.00
24	2-Methylheptane	8.31	0.008	1.00	1.00	0.99	1.01	0.99	1.01
25	3-Methylheptane	8.59	0.008	1.00	1.00	1.00	1.01	0.99	1.01
26	methylcyclohexane	9.64	0.005	0.99	1.01	0.99	1.01	0.99	1.01
27	n-nonane	9.75	0.006	0.99	1.01	0.99	1.01	0.98	1.02
28	n-decane	11	0.007	0.99	1.01	0.99	1.01	0.99	1.01
29	p-ethyl toluene	11.8	0.007	0.99	1.01	0.98	1.02	0.98	1.02
30	p-diethyl benzene	-	0.008	1.00	1.00	0.99	1.01	0.97	1.03
31	o-ethyl toluene	11.9	0.007	0.99	1.01	0.99	1.01	1.00	1.00
32	o-xylene	13.6	0.007	0.99	1.01	0.98	1.02	1.00	1.00
33	m-ethyl toluene	18.6	0.010	0.99	1.01	0.99	1.01	0.97	1.03
34	m-diethyl benzene	-	0.009	0.99	1.01	0.99	1.01	0.98	1.02
35	m/p-Xylene	23.1/1 4.2	0.008	0.99	1.01	0.98	1.02	0.98	1.03
36	propene	26	0.015	0.96	1.04	0.95	1.05	0.96	1.05
37	1-Butene	31.1	0.010	0.97	1.04	0.90	1.12	0.92	1.10
38	1-Pentene	31.4	0.009	0.98	1.02	0.93	1.09	0.93	1.08
39	1,2,4-trimethyl benzene	32.5	0.008	1.00	1.01	0.95	1.05	0.91	1.10
40	1,2,3-trimethyl benzene	32.7	0.009	0.96	1.04	0.96	1.04	0.97	1.03
41	a-pinene	51.8	0.010	0.97	1.04	0.96	1.05	0.75	1.35
42	cis-2-Butene	55.8	0.019	0.87	1.16	0.86	1.17	0.77	1.32
43	1,3,5-Trimethylbenzene	56.7	0.007	0.93	1.08	0.90	1.13	0.73	1.37
44	styrene	58	0.010	0.91	1.11	0.90	1.13	0.98	1.02
45	2-methyl-1-pentene	63	0.002	0.81	1.25	0.70	1.49	0.81	1.28
46	trans-2-Butene	63.2	0.014	0.84	1.22	0.82	1.25	0.76	1.35
47	cis-2-Pentene	65	0.006	0.86	1.19	0.74	1.42	0.83	1.24
48	1,3-Butadiene	65.9	0.024	0.88	1.16	0.82	1.26	0.87	1.18

49	trans-2-Pentene	67	0.009	0.88	1.16	0.63	1.63	0.75	1.38
50	β -pinene	73.5	0.010	0.90	1.12	0.81	1.26	0.92	1.10
51	isoprene	99.6	0.009	0.73	1.40	0.67	1.50	0.55	1.57

* Unit: $10^{-12} \text{ cm}^3 \text{ mole}^{-1} \text{ s}^{-1}$. k_{OH} values were under conditions of 300K. (Carter 2010)

** Unit: ppb. The relative standard derivations (RSDs) were within 10% for the target compounds in all six replicates.

*** All species were selected for sensitivity tests of initial VOCs to $[\text{OH}] \times t$. The reaction rates of these species with OH covered the range of 51 VOCs and were characterized by low, medium and high k_{OH} levels. The sensitivity test results showed that the uncertainty in the estimation of initial VOCs caused by the $[\text{OH}] \times t$ estimation uncertainty ranged from 0.55 to 1.57.

In Text S2, we have added more details about initial VOC concentration calculations and data reliability.

“Text S2. Calculation of initial VOCs concentrations

Photochemical initial concentration (PIC) proposed by Shao et al. (2011), which is calculated based on the photochemical-age approach and has been applied to evaluate the effect of photochemical processing on measured VOC levels. Equation S1 essentially describes the integrated OH exposure (Shao et al., 2011).

$$\int c_{\text{OH}} dt = \frac{1}{k_{\text{A,OH}} - k_{\text{B,OH}}} \left[\ln\left(\frac{\text{VOC}_\text{A}}{\text{VOC}_\text{B, initial}}\right) - \ln\left(\frac{\text{VOC}_\text{A}}{\text{VOC}_\text{B}}\right) \right] \quad (\text{S1})$$

The initial concentration of species i can be calculated using Equation S2.

$$\text{VOC}_{i, \text{initial}} = \frac{\text{VOC}_i}{\exp(-k_{i,\text{OH}}) \exp(\int c_{\text{OH}} dt)} \quad (\text{S2})$$

Substituting equation 1 into equation 2, then we can get equation S3.

$$\text{VOC}_{i, \text{initial}} = \frac{\text{VOC}_i}{\exp(-k_{i, \text{OH}}) \exp\left(\frac{1}{k_{\text{A,OH}} - k_{\text{B,OH}}} \left[\ln\left(\frac{\text{VOC}_\text{A}}{\text{VOC}_\text{B, initial}}\right) - \ln\left(\frac{\text{VOC}_\text{A}}{\text{VOC}_\text{B}}\right) \right] \right)} \quad (\text{S3})$$

Where C_{OH} represents the ambient OH concentration; $k_{\text{A,OH}}$ and $k_{\text{B,OH}}$ represent the reaction rate of compound A and B with OH radical, respectively; t represents the reaction time of species i in the ambient.

In previous work (Shao et al., 2011; Zhan et al., 2021), the selection of ethylbenzene and xylene as tracers was justified for calculating ambient OH exposure under the following conditions: 1) the concentrations of xylene and ethylbenzene were well correlated (Figure S9), which indicated that they were simultaneously emitted; 2) they had different degradation rates in the atmosphere; and 3) the calculated PICs were in good agreement with those calculated using other tracers (Shao et al., 2011; Zhan et

al., 2021).

In this study, the ethylbenzene/xylene pair was used to calculate ambient OH exposure. As shown in Figure S9, the concentrations of xylene and ethylbenzene are well correlated, which indicates that they are simultaneously emitted. In addition, we compared the PICs according to xylene/ethylbenzene with that using toluene/benzene (Figure S10). The calculated PICs ratio ($\text{PIC}_{\text{Xylene/Ethylbenzene}} / \text{PIC}_{\text{Toluene/Benzene}}$) varied from 0.5 to 1.5 with a mean value of 0.96. This means the calculated initial VOCs was in good agreement when using different tracers. The mean ratio (0.52, from 0.45 to 0.66) of ethylbenzene/xylene before sunrise was taken as the initial ratio of ethylbenzene/xylene. Sensitivity tests showed that the uncertainty of PICs caused by the OH exposure (from -10% to +10%) ranged from 0.55 to 1.57 (Table S4). Variations of air mass may also affect the VOC ratio. Figure S11 A-D shows the mean concentration distribution of ethylbenzene and xylene in the early morning and the whole day based on potential source contribution function (PSCF) analysis. Xylene showed similar patterns to ethylbenzene in different air mass trajectories and different periods. These results indicate that the emissions of xylene and ethylbenzene were constant throughout the day and variations of air mass should have little influence on the initial ratio of VOCs. The hourly concentrations of ethylbenzene and xylene were used to calculate the concentration of initial VOCs. The initial VOC was calculated by adding the measured VOC concentration and the calculated photochemical loss. Figure S12 shows the diurnal variations of the observed and initial VOCs concentrations from 2014 to 2016. Photochemical loss of VOC occurred mainly during the daytime.

It should be noted that the lifetimes ($1/k_{2\text{COH}}$) of highly reactive VOCs, such as isoprene, greatly depend on the OH exposure. The photochemical ages of isoprene were 0.01–6.21 h (1.26 ± 1.12 h). This value is comparable with previously reported photochemical ages (Shao et al., 2011; Gao et al., 2018). However, the initial concentrations of highly reactive VOCs may be overestimated due to their short lifetimes and should be taken as the upper limits. On the other hand, isoprene is a biogenic VOC, while xylene and ethylbenzene are anthropogenic VOCs. If they do not share the same air mass histories, an additional uncertainty is inevitable for the PICs of

isoprene. As shown in Figure S11, isoprene showed similar patterns to that of xylene and ethylbenzene, which means VOC emissions are evenly distributed in Beijing during our observations. This can be ascribed to the fact that our observation site is a typical urban station. Although isoprene and xylene/ethylbenzene different sources, both them are non-point sources on a city scale. Therefore, the photochemical clock calculated using xylene and ethylbenzene is able to correct the photochemical loss of biogenic VOCs to some extent. It should be noted that uncertainty is inevitable when we estimating the photochemical age (Parrish et al., 2007). However, the aim of this work is to test whether the ML-model can reflect the influence of photochemical loss of VOCs species on O₃ modelling. The PICs should provide additional information for understanding O₃ formation in the atmosphere.”.

Q2: Line 50-75: It is easier to read if you divide the paragraph appropriately, e.g., Line50, Line53, Line59, Line64, Line75.

Reply: Thank you. To make it is readable, we have started a new paragraph in line 54 before “The observed indicators can be utilized to quickly diagnose the sensitivity regime...” and in line 76 before “Compared to traditional methods, machine learning (ML) is able to capture the” in the revised manuscript.

Q3: Line 118-129 and S1: As the composition of VOC species varies greatly from year to year as shown in Fig. 1(F), the analytical reliability is important. Information about VOC measurement in this article is insufficient to understand the reliability. Further information such as observation period and the reason, sampling time or cycle, calibration using standard gas, and method of quality control should be described.

Reply: Thank you so much for your good suggestion. To clarify the analytical radiality, we have added more information about VOC measurement, including sampling time, data quality control, calibrations using standard gas. The details are shown in Text S1 in the SI.

“Text S1. Field observations

VOCs were measured in May and June from 2014 to 2016 by an online

commercial instrument (GC-866, Chromatotec, France), which consisted of two independent analyzers for C₂-C₆ and C₆-C₁₂ hydrocarbons. Both analyzers were equipped with a preconcentration system, a chromatographic column, and a flame ionization detector. The analyzers are located in an air-conditioned room and the sample tubes are wrapped with a heating jackets and insulation to ensure that the temperature remains stable between 22 and 27°C.

The samples were injected into the low carbon (C₂-C₆) analyzer and the high carbon (C₆-C₁₂) analyzer, respectively. Isoprene was detected in the components of C₂-C₆, while α -pinene and β -pinene were detected along with other VOCs of C₆-C₁₂. In the low carbon analyzer, the samples were adsorbed by a capture tube at -8 °C. The capture tube was then rapidly heated to 220 °C. The samples were introduced into a chromatographic column (id=0.53mm, length=25m) with hydrogen as the carrier gas and detected by a flame ionization detector (FID) detector. In the high carbon analyzer, the samples were adsorbed by a capture tube at room temperature; then the capture tube was heated to 380 °C, introduced into a chromatographic column (id=0.28mm, length=30m) with hydrogen as the carrier gas and finally detected by the same FID detector. The material in the column was Al₂O₃/Na₂SO₄.

The signals of VOCs were converted into chromatograms for qualitative and quantitative analysis. Before quantitative analysis, the retention time of each component was carefully checked using the chromatographic analysis software. The instruments were calibrated using both internal and external calibrations. Internally calibration was carried out twice every 24 hours using n-butane, n-hexane and benzene at different flow rates. External calibration was performed monthly using standard gas mixtures of volatile organic compounds (PAMS and TO-14, Linde gas, USA). The concentrations of each species were calculated according to the corresponding working curves with six concentration levels. In this study, total of 51 VOCs (including 21 alkanes, 13 alkenes, 1 alkyne and 16 aromatics) were analyzed within a limit of quantification of 0.002-0.05 ppbv as shown in Table S4. The relative standard derivations (RSDs) were within 10% for each compound among seven replicates.”.

Q4: Line 129 and S2: Explanation about PIC is insufficient in this article although PIC is important for the results. To calculate PIC, the initial ratio of Ethylbenzene and xylene must be constant. However, they may be emitted from several sources, e.g. painting, mobile exhaust, etc. Please explain why you can use these compounds in this study. And please describe the VOC sampling time which is also important to calculate PIC, because chemical reactions in the air are different in daytime and nighttime.

Reply: Thank you very much for your suggestions. We added explanations about PIC calculations in Text S2. Meanwhile, the xylene/ethylbenzene was selected as tracer for the following reasons: 1) the concentrations of xylene and ethylbenzene are well correlated, which indicates that they are simultaneously emitted; 2) they have different degradation rates in the atmosphere; 3) the calculated initial VOCs are in good agreement with those calculated using other tracers, such as toluene/benzene. As shown in Figure R1 or Figure S9, the concentrations of xylene and ethylbenzene correlated well during our observations in this work. In addition, we compared the ratio of the initial concentrations calculated according to the ratio of xylene/ethylbenzene with that using the ratio of toluene/benzene (Figure R2 or S9). Except for several compounds, the ratio of the PICs for most of these VOCs varied within 1.0 ± 0.1 . This means the calculated photochemical initial concentrations (PICs) are in good agreement when using different tracers. Sensitivity tests showed that the uncertainty caused by the OH exposure (from -10% to $+10\%$) ranged from 0.55 to 1.57 (Table R1 or Table S4). Figure R3 or Figure S12 shows the calculated diurnal curves of the PICs from 2014 to 2016. Photochemical losses of VOCs occurred prominently during the daytime.

Potential source contribution function (PSCF) analysis has been further carried out to evaluate the possible influence of air mass on the emission ratio of ethylbenzene and xylene. As shown in Figure R4A-D or Figure S11, xylene showed similar pattern to ethylbenzene in the early morning or in the whole day. These results indicate that variations of air mass should have little influence on their initial ratio. In addition, isoprene showed similar patterns to that of xylene and ethylbenzene (Figure R4G-H), which means VOC emissions are evenly distributed in Beijing. This can be ascribed to the fact that our observation site is a typical urban station. Although isoprene and

xylene/ethylbenzene are from biogenic sources and anthropogenic sources, both them are non-point sources on a city scale.

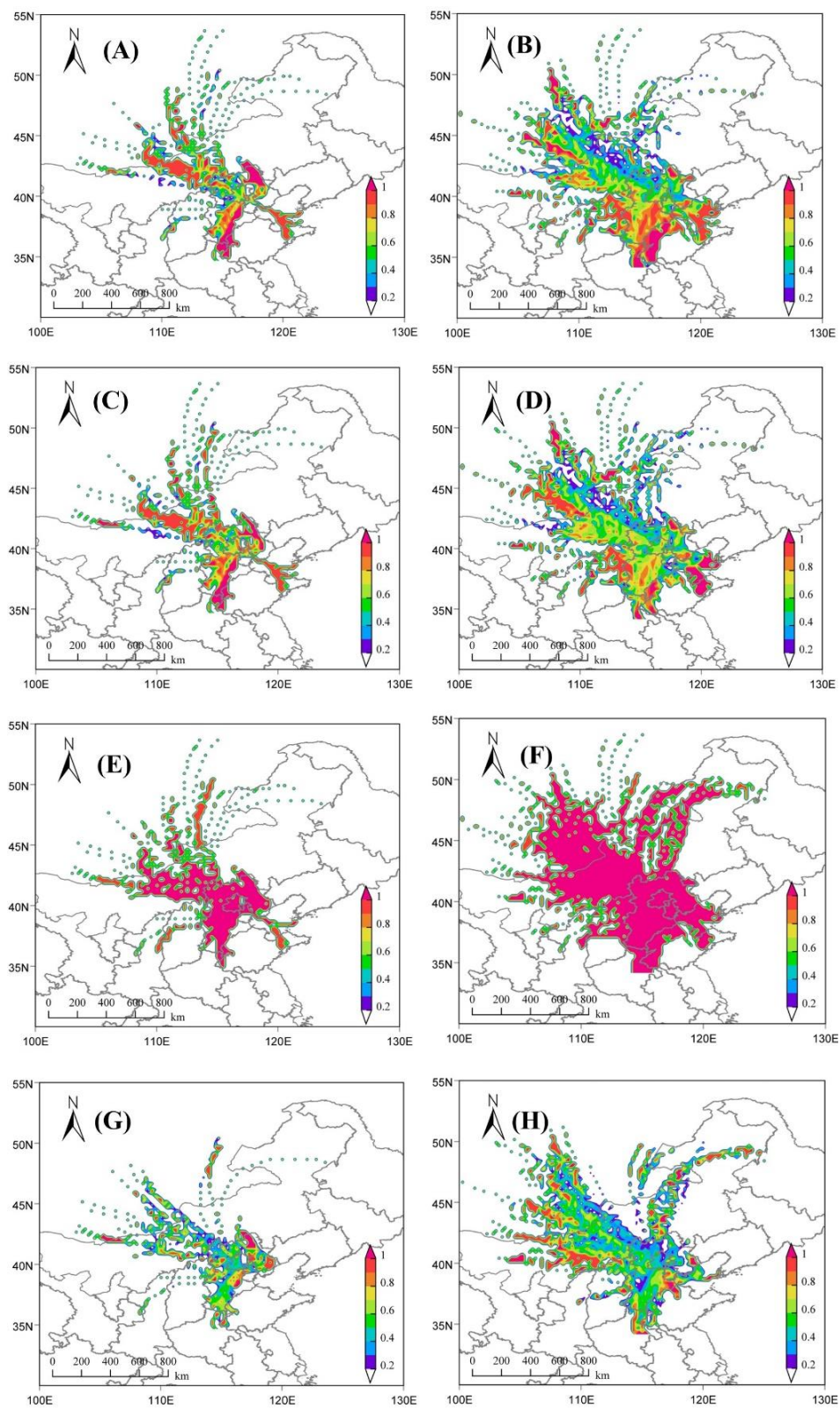


Figure R4. The potential source contribution function (PSCF) maps for ethylbenzene (A and B), xylene (C and D), ratio of xylene to ethylbenzene (E and F), and isoprene

(G and H) arriving in the observation site. The figures A, C, E and G are the results for the morning (05:00 and 06:00), and the figures of B, D, F and H are the results of the whole day (00:00-23:00).

Figure R3 or Figure S12 shows the diurnal variations of the observed and initial VOCs concentrations from 2014 to 2016. From Figure R3, it can be seen that photochemical loss of VOCs occurred prominently during the daytime. We have added information about the sampling time (“VOCs were measured in May and June from 2014 to 2016 by an online commercial instrument...”) in Text S1.

Q5: Figure 1: What are the red lines in (A)?

Reply: Thank you. The red lines (arrows) indicate the O₃ concentration exceed 74.6 ppbv according to the national ambient air quality standard. We have added an explanation in the caption of Figure 1 “**Figure 1.** Time series of air pollutants and meteorological parameters during observations in Beijing (In A, the red arrows represent the O₃ concentration exceed 74.6 ppbv according to the national ambient air quality standard)”.

Q6: Figure 2: It is difficult to find the difference in (A), (B), and (C). Something will be needed to make it clear.

Reply: Thank you. We revised these figures (bolded the lines and increased the color contrast) to make it clearer. Actually, Figure 2(D)-(F) can show their difference for the correlations between modeled and observed O₃ concentrations.

Q7: Line 203-205: It is unclear that this is what part about Figure 3A.

Reply: Thank you. We have adjusted the position of the label in Figure 3 (Figure R5) and the left part is Figure 3A.

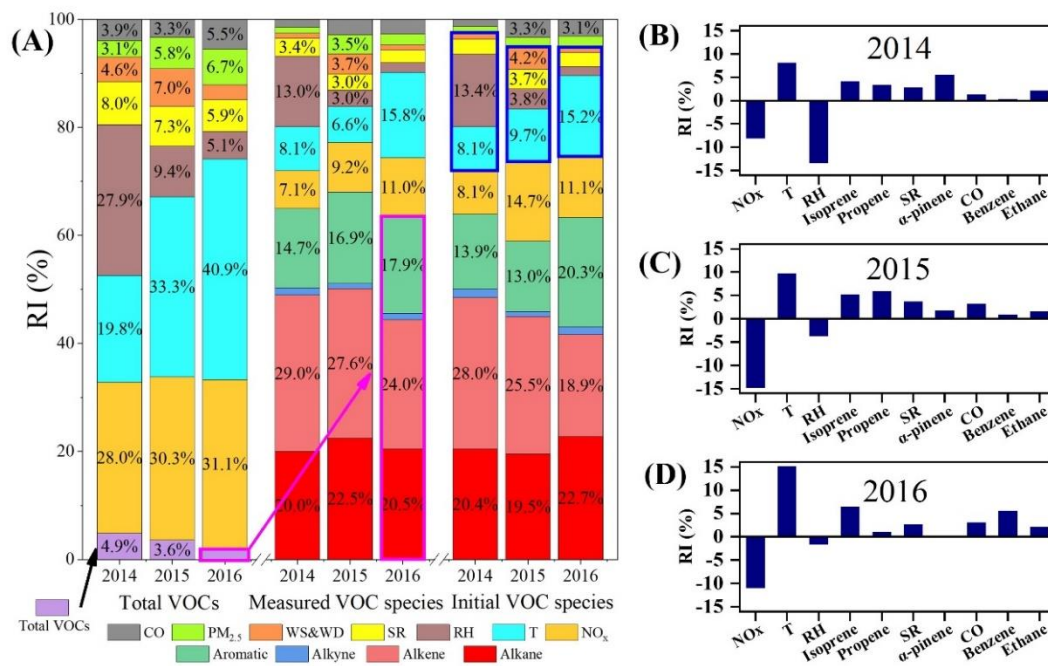


Figure R5. Percentage of RI for O₃ precursors and meteorological parameters (A) and the top 10 factors with high values of RI in 2014-2016 (B-D: using initial concentrations of VOC species).

Q8: Figure 3A: Please explain why RI does not change so much even though the composition of VOCs differs greatly between 2015 and 2016.

Reply: Thank you for your good comments. VOCs contributed 64.0%, 58.9%, and 63.3% to the RI, respectively, in 2014, 2015, and 2016. From Figure R5 or Figure 3, it did not change so much among the three years although VOCs concentrations changed obviously. We think this should be ascribed to the production of O₃ in Beijing was still in a VOCs-sensitive regime as shown in Figure R6. This is consistent with previous studies based on transport chemical model (Li et al. 2020) which found VOCs were the dominant contributors to O₃ formation in Beijing. This means that the sensitivity of RI to VOCs concentrations might be not so high. We suppose that it should be more prominent when O₃ formation shifts to a NO_x-sensitive regime. However, as shown in Figure R5 (Figure 3B-D), the RI of individual VOC species changed obviously among different years.

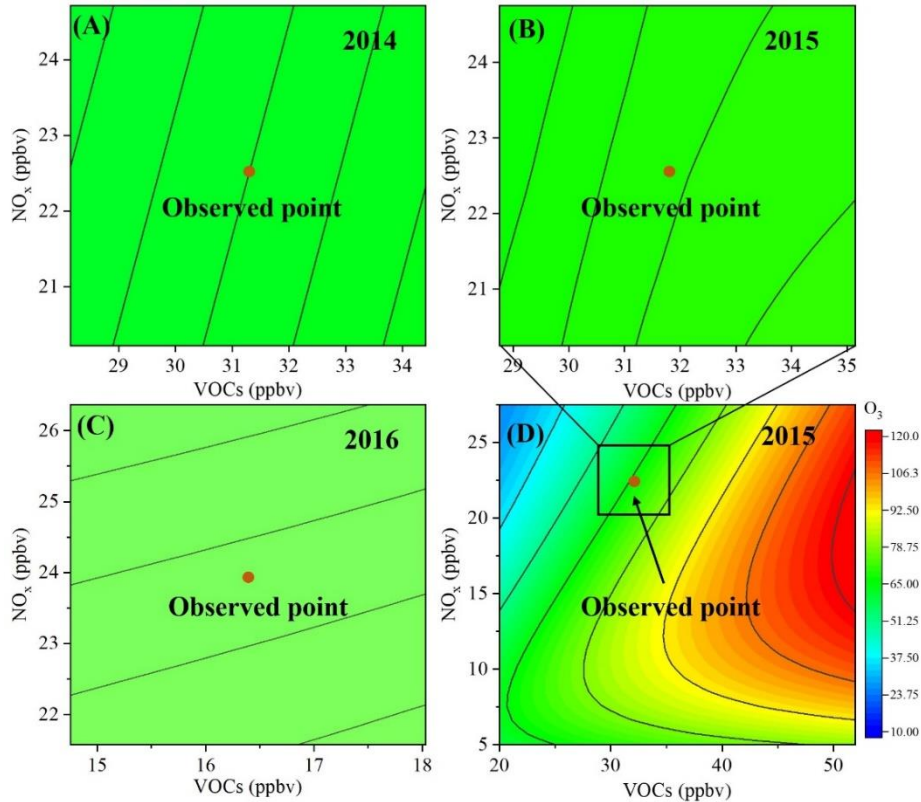


Figure R6. Ozone formation sensitivity curves from 2014-2016. (A, B, C: calculated by the RF model for 2014, 2015, and 2016, respectively. D: calculated by the OBM for 2015.)

Q9: Line 287-289: It is unclear why you can describe that the RF model is better than the box model from Figure S5.

Reply: Thank you. We have deleted Figure S5 and revised the statement to “We compared the relative error of simulated MDA8 O₃ calculated using the RF and OBM model in 2015, as shown in Figure S8. The mean relative error of simulated MDA8 O₃ between RF model and Box model was 15.6%. Hence, a combination of the RF model and initial VOCs species can well depict the sensitivity regime of O₃ formation, while the calculated RIs correlate well with the OFPs.” in lines 319-323.

References

- Carter, W.P.L. Development of the SAPRC-07 chemical mechanism. *Atmos. Environ.*, 44, 5324-5335, <https://doi.org/10.1016/j.atmosenv.2010.01.026>, 2010.
- Gao, J., Zhang, J., Li, H., Li, L., Xu, L., Zhang, Y., Wang, Z., Wang, X., Zhang, W., Chen, Y., Cheng, X., Zhang, H., Peng, L., Chai, F., Wei, Y. Comparative study of volatile organic compounds in ambient air using observed mixing ratios and initial mixing ratios taking chemical loss into account – A case study in a typical urban area in Beijing. *Sci. Total Environ.*, 628-629, 791-804, <https://doi.org/10.1016/j.scitotenv.2018.01.175>, 2018.
- Parrish, D.D., Stohl, A., Forster, C., Atlas, E.L., Blake, D.R., Goldan, P.D., Kuster, W.C., de Gouw, J.A. Effects of mixing on evolution of hydrocarbon ratios in the troposphere. *J. Geophys. Res. Atmos.*, 112, <https://doi.org/10.1029/2006JD007583>, 2007.
- Li, K., Jacob, D.J., Shen, L., Lu, X., De Smedt, I., Liao, H. Increases in surface ozone pollution in China from 2013 to 2019: anthropogenic and meteorological influences. *Atmos. Chem. Phys.*, 20, 11423-11433, [10.5194/acp-20-11423-2020](https://doi.org/10.5194/acp-20-11423-2020), 2020.
- Shao, M., Bin, W., Sihua, L., Bin, Y., Ming, W. Effects of Beijing Olympics Control Measures on Reducing Reactive Hydrocarbon Species. *Environ. Sci. Technol.*, 45, 514-519, [10.1021/es102357t](https://doi.org/10.1021/es102357t), 2011.