Response to Reviewer 2 Comments

Thank you for your decision and constructive comments on my manuscript. We have revised the manuscript carefully according to the reviewers' comments. Point–to–point responses are given below. The original comments are black in color, while our responses are in blue. The revised parts in the manuscript are marked in red. All the page number and line number are referred to the revised manuscript.

Detailed comments:

1. Fig. R1. I suggest changing the legend of "slope of the ratio of O_3 to normalized NO_2" to "ratio of O_3 to normalized NO_2", because "slope" always represents the slope derived from regression, and here it means the ratio for each hour. It's very confusing. I also suggest revise the y-label to "ratio" too.

Response 1: Thanks for your suggestion, following the referee's suggestion, the legend of Fig.R1 was corrected. Please refer to Fig.7 in the manuscript.

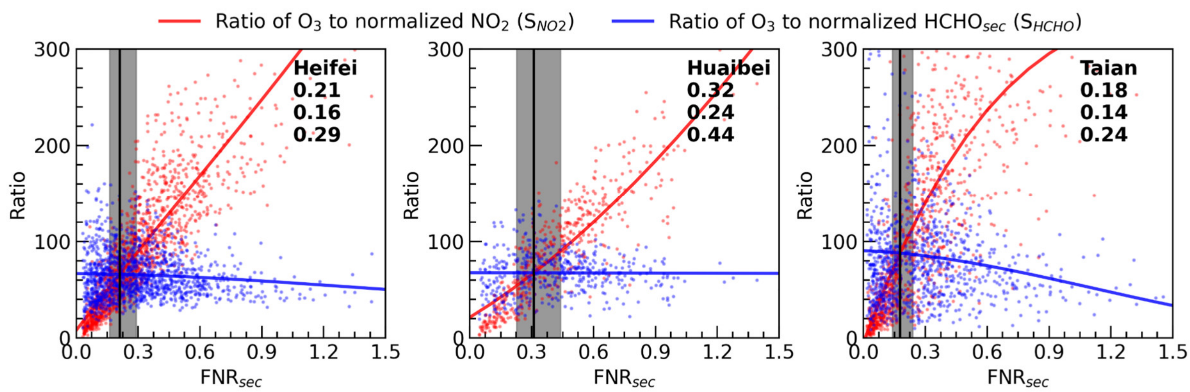

Fig.R1. Three–order fitting of ratios of O_3 VMRs versus normalized NO_2 VMRs and ratios of O_3 VMRs versus normalized secondary HCHO VMRs in different FNR_{sec} values in Hefei, Huaibei, and Tai'an during May–September based on MAX–DOAS observations. The intersect at FNR_{sec} indicated by the black solid line. The vertical shadow indicates the relative difference between the ratios of O_3 VMRs versus normalized NO_2 VMRs and ratios of O_3 VMRs versus secondary HCHO VMRs within 25% (transition regime). The labels at the top right of each panel represent the intersect FNR_{sec} values and the thresholds for the NO_x–limited regime (high) and VOC–limited regime (low) in Hefei, Huaibei, and Tai'an, respectively.

2. Response #7: the sensitivity of TROPOMI always peaks in upper troposphere, and lower in near surface, as represented by averaging kernel. This is true, but it's not fair to say this is the

reason for the underestimation of HCHO concentrations in TROPOMI. Fitting errors, a priori model bias, cloud and aerosols can all contribute to such bias. I suggest authors revising such statement carefully.

Response 2: Thanks for your suggestion. We have followed this suggestion and deleted the previous statements, and the corrected expression is "Generally, the NO_2 and HCHO VCD observed by TROPOMI were smaller than those observed by MAX–DOAS, and the difference may be caused by fitting errors, a priori model bias, cloud and aerosols, and spatio–temporal resolution." Please refer to Page 4 Line 29–32 in the manuscript.

Response to Reviewer 3 Comments

We truly grateful for the reviewers for the valuable and constructive comments, which are very useful for the improvement of the manuscript. We have revised the manuscript carefully according to the reviewers' comments. Point–to–point responses are given below. The original comments are black in color, while our responses are in blue. The revised parts in the manuscript are marked in red. All the page number and line number are referred to the revised manuscript.

Major comments:

Point 1: MAX-DOAS observations only conducted in three typical cities in eastern China, whether the shift in ozone formation sensitivity from early morning VOC–limited regime to midday NOx–limited regime is widespread in most eastern Chinese cities? Since the satellite observations employed in this study, why not use satellite-derived FNR to diagnose each city's ozone formation sensitivity?

Response 1: Thanks for your constructive comments! We have followed the reviewer's comments and use satellite–derived FNR to diagnose each city's ozone formation sensitivity. Owing to the limitations of the observational data, the analysis of diurnal transitions in surface O_3 formation sensitivity is limited to three cities in eastern China. Here, other cities in eastern China were further investigated using satellite observations, and we construct conventional FNR using TROPOMI observed NO_2 and HCHO VCD from May to September 2018–2022. In order to avoid the misjudgment of O_3 formation sensitivity caused by arbitrary selection of FNR thresholds, A third–order polynomial model was applied to investigate the empirical relationship between TROPOMI FNR and surface O_3 volume mixing ratios (VMRs, ppb), which has been widely used in other studies (Ren et al., 2022). Since the TROPOMI observed surface O_3 VMRs can be obtained after November 2021 in China, we only collected the relationship between TROPOMI FNR and surface O_3 VMRs from May to September, 2022. The third–order polynomial fitting relationship between surface O_3 VMRs and TROPOMI FNR is shown in Fig. R1a, assuming that the peak of the curve (with a slope of 0) marks the transition from the VOC–limited regime to the NO_x–limited regime, the transition regime is defined as a range of slopes between -3 and +3 (Ren et al., 2022). Through the third–order polynomial model, the TROPOMI FNR threshold in eastern China was determined, which are FNR <2.1 for VOC–limited regime, FNR>3.2 for NO_x–limited regime (Fig.R1a).

Figure R2 shows the occurrence probabilities of the VOC–limited regime, transition limited regime, and NO_x–limited regime spatial distributions derived from TROPOMI observations in eastern China during May–September, 2018–2022. Since the TROPOMI satellite usually transits around 13:30, it can represent the spatial distribution of midday O_3 formation sensitivity in eastern China. Apparently, the midday O_3 formation sensitivity of most cities in eastern China is under NO_x–limited regime, only several cities in the northern part of the NCP and Yangtze River Delta are mainly controlled by VOC–limited regime. In addition, Fig. R1b–d shows the trend of the area proportion of VOC–limited regime, transition regime, and NO_x–limited regime in the eastern China, in which the area proportion of VOC–limited regime and transition regime decreases at a rate of 0.62% and 0.18% per year, respectively. While the NO_x–limited regime area proportion increased at a rate of 0.80% per year. More importantly, although there is a significant monthly variation in the area proportion of O_3 formation sensitivity, it is usually below 50% in May and September, and below 25% in June–August, that is, NO_x–limited regime dominates the midday O_3 formation sensitivity in eastern China. Due to China's strict control of NO_x emissions in recent years, the surface O_3 formation sensitivity in many areas of China has shown a transition from the VOC–limited regime to the transition regime or NO_x–limited regime.

In conclusion, significant diurnal transitions in surface O_3 formation sensitivity primarily stem from fluctuations in O_3 precursors. Early morning conditions (08:00–09:00) are mainly VOC–limited regime, shifting to a NO_x–limited regime by midday (12:00–14:00). In addition, the area proportion of VOC–limited regime was also declining, while the NO_x–limited regime area proportion was increasing. Consequently, the substantial reduction in NO_x emissions across eastern China has led to pronounced opposite trends in the low (increased) and peak (decreased) surface O_3 concentrations, and the surface O_3 formation sensitivity to VOCs is generally weakened year by year. Accordingly, the O_3 improvement benefits of VOCs emission reduction may become weaker, while the O_3 improvement benefits of NO_x emission reduction become larger. Furthermore, the long–distance transport of VOCs has a diminished impact on O_3 concentrations due to chemical losses from OH radical oxidation during transport, highlighting NO_x emission reductions as pivotal for intercity and even long–distance efforts to mitigate regional O_3 pollution (Wang et al., 2023). We have added this statement to the manuscript, please refer to Page 5 Line 14–18, Page 13 Line 13–34, Page 14 Line 1–13.

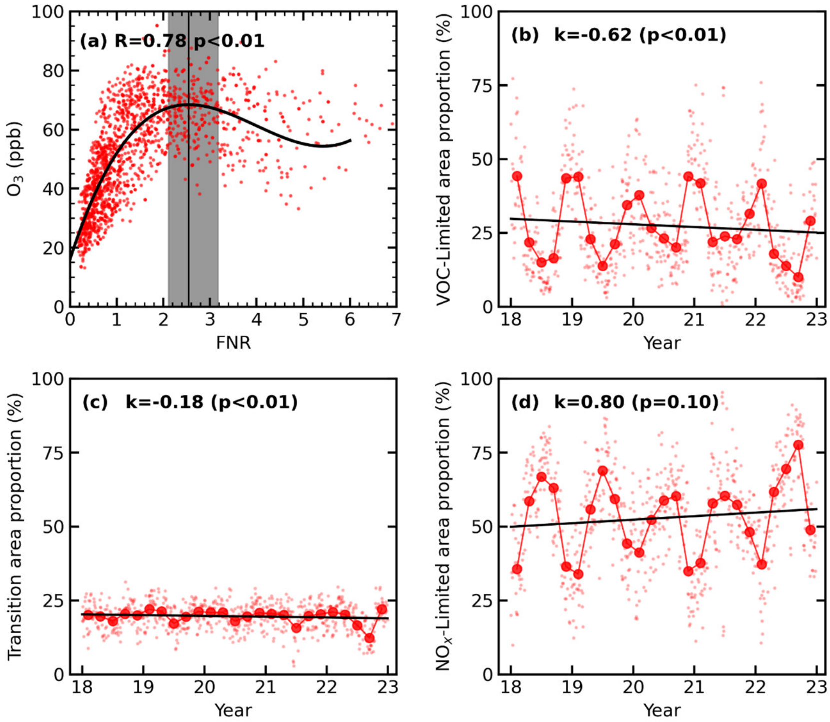

Fig. R1 (a) Variation of monthly mean O_3 VMRs (~13:30) with monthly mean TROPOMI FNR in eastern China during May–September 2022. The solid line represents third–order polynomial fitting. The vertical line represents the maximum value of the fitted curve, and the vertical shadow represents the range of the curve slope from −3 to +3 (transition regime). Trends of TROPOMI observed area proportion for (b) VOC–limited regime, (c) Transition regime, and (c) NO_x–limited regime over eastern China during May–September 2018–2022. The light red dots in (b–d) represent the daily values, and the solid red dots are monthly mean values.

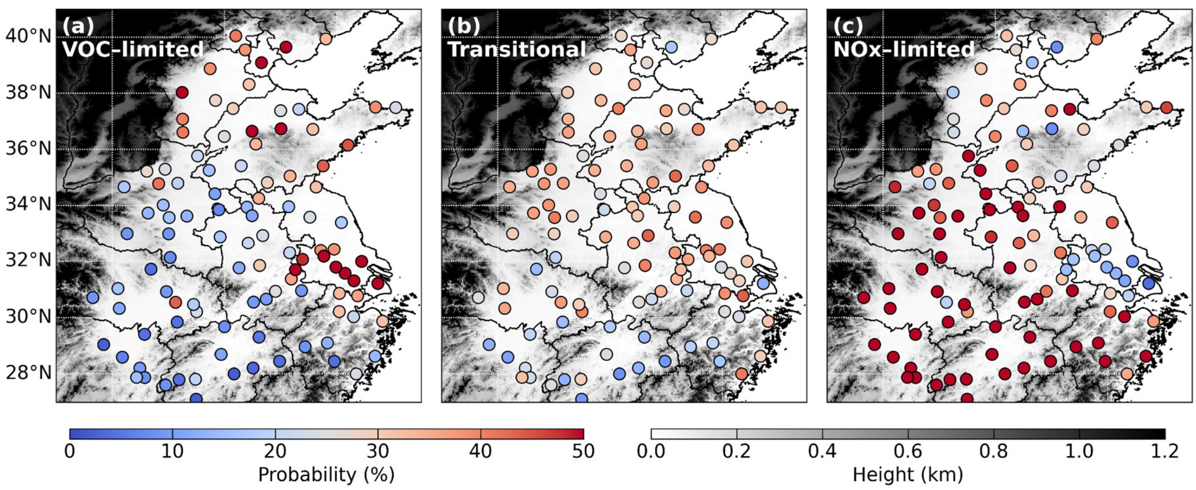

Fig. R2 Occurrence probabilities of the (a) VOC–limited regime, (b) transition limited regime, and (c) NO_x–limited regime spatial distributions in eastern China derived by TROPOMI observations during May–September 2018–2022.

Point 2: The secondary formaldehyde and NO_2 (secondary FNR) are employed to diagnose the diurnal variations in ozone formation sensitivity, what is the difference between conventional FNR and secondary FNR?

Response 2: We thank the reviewer for pointing out this issue. we used secondary FNR (defined as the ratio of secondary HCHO to NO_2; $FNR_{sec} = HCHO_{sec}/NO_2$) in the manuscript as an indicator of O_3 formation sensitivity. Compared with conventional FNR (defined as the ratio of HCHO to NO_2; FNR = $HCHO/NO_2$), FNR_{sec} eliminate background and primary HCHO interference, improve the accuracy of diagnosing O_3 formation sensitivity, and contribute to a better understanding of O_3 formation sensitivity (Lin et al., 2022; Xue et al., 2022). The secondary sources in ambient HCHO participated in the photochemical reaction directly, the non–negligible contributions of background and primary HCHO attribute errors to conventional FNR and reduce the accuracy in diagnosing O_3 formation sensitivity (Liu, et al., 2021). Hence FNR_{sec} was more favourable for indicating O_3 formation sensitivities (Su et al., 2019).

Detailed comments:

1. Section 2.4 Stepwise Multiple Linear Regression Model, confusion descriptions, Eq1 : Y(t) is the deseasonalized and detrended daily surface 98th or 2nd ozone percentile time series, the "detrended" is not correct here. While the author use the deseasonalized but not detrended data in the Eq2, it is corrected. The description of Eq1 seems meaningless and may mislead the reader.

Response 1: Thanks for your suggestion**.** We have followed the reviewer's comments and deleted the description of Eq1 in the previous manuscript. Please refer to our new manuscript for details.

2. How do you calculate the Regression Model for source separation in primary and secondary HCHO. Are you using the ground measurements for all years? Are you using the ground measurements in each hour? Please specify it.

Response 2: As described in Section 2.5 in the manuscript. CO and O_x ($O_x = O_3 + NO_2$) were selected as tracers to separate the primary and secondary sources of ambient HCHO. The HCHO was measured by ground–based MAX–DOAS, the system was operated only during the daytime (08:00–17:00 local time) with a temporal resolution of 15 min. CO and O_x was collected from the open website of Ministry of Ecology and Environment of China (MEE; https://www.mee.gov.cn; last access: January 7, 2024), and the temporal resolution is one hour. Thus, we first perform hourly averaging of HCHO data from MAX–DOAS observations to match CO and O_x data from MEE observations. Primary and secondary HCHO will then be separated for all available HCHO data from May to September in the MAX–DOAS measurement period. We have added this statement to the manuscript, please refer to Page 7 Line 13–15 in the manuscript.

3. Page 7 line 20, Are Regression Model reliable? as the correlation coefficients are not that high. Please specify it.

Response 3: Thanks for your constructive comments! The Regression Model is reliable. Although the correlation coefficients are not that high (0.55~0.66), were also comparable to the comparisons reported in previous studies (Lin et al., 2022; Sun et al., 2021). As other factors (e.g., meteorological conditions) can also affect the atmospheric HCHO concentration, regression models are difficult to obtain very consistent results. We have added this statement to the manuscript, please refer to Page 7 Line 16–18 in the manuscript.

4. Page 9 line 1-2, How about "typical" ozone concentrations?

Response 4: Thanks for your suggestion**,** the trend in typical O_3 concentrations in eastern China from May to September 2017–2022 ranging from -0.4 to 0.3 ppb/year (-0.8–0.8% per year), with about one third of the cities increasing and two thirds decreasing. We have added this statement to the manuscript, please refer to Page 8 Line 34 and Page 9 Line 1–2 in the manuscript.

5. Page 13 line "the relationship between the O_3 concentration and FNR_{sec} values from 08:00 to 13:00", why the correlation coefficient of exponential fitting was higher on ozone exceedance days

Response 5: This may be due to more dramatic daily variations in FNR_{sec} and ozone concentrations on ozone exceedance days. Fig.R3 (j–l) show the diurnal variation of surface FNR_{sec} during the whole observation in Hefei, Huaibei, and Tai'an, respectively. Fig.R3 (m–o) show the diurnal variation of surface FNR_{sec} during O_3 exceedance day in Hefei, Huaibei, and Tai'an, respectively. Compared to the entire observation period, FNR_{sec} on O_3 exceedance days exhibits a faster transition from 08:00 to 13:00 and prolonged persistence in the NO_x–limited regime. This indicates that the dependence of the O_3 production rate on its precursors rapidly shifts with increasing O_3 concentration, particularly on O_3 exceedance days.

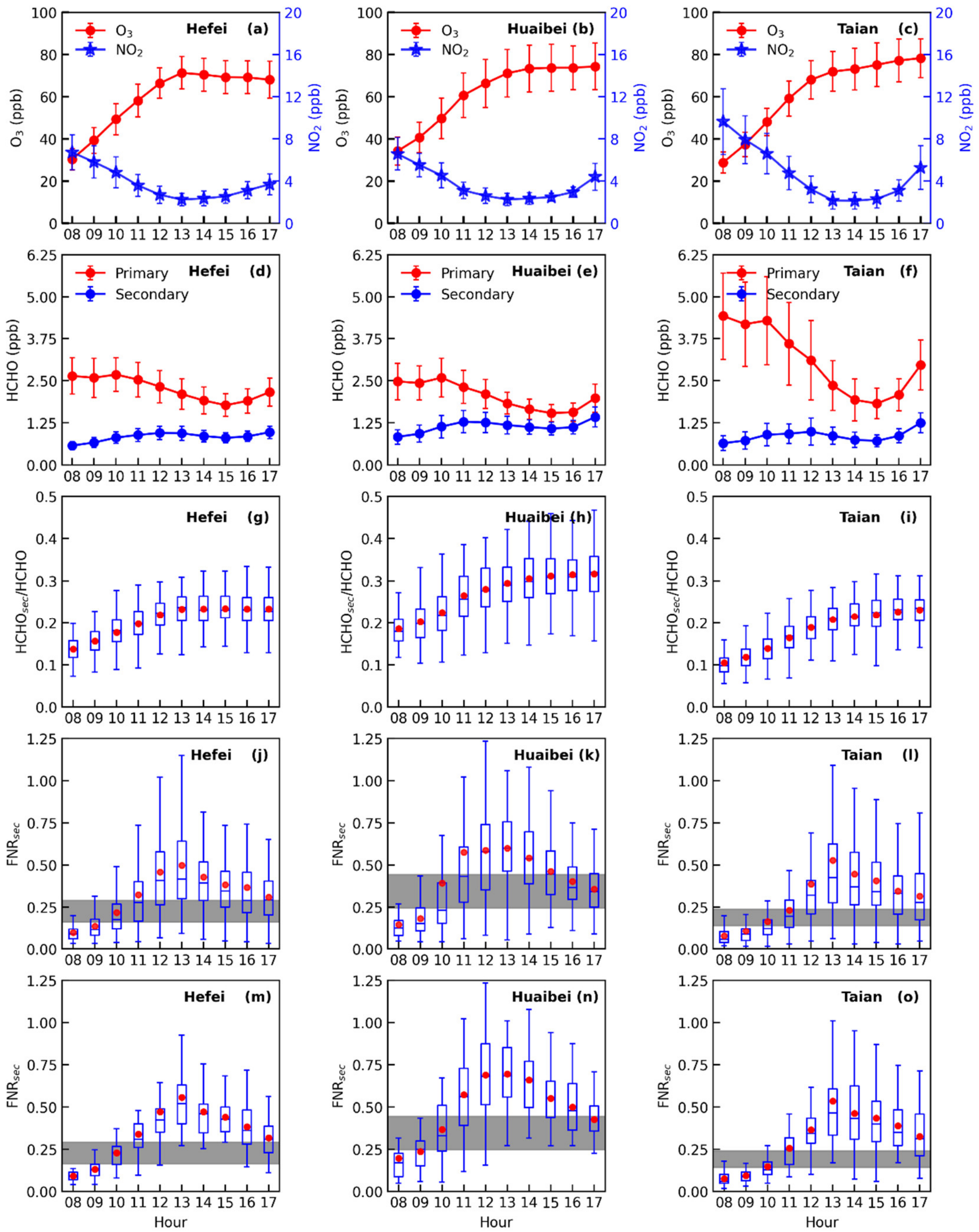

Fig.R3. Diurnal variation of surface (a–c) O_3 and NO_2 VMRs, (d–f) HCHO VMRs contributed by primary and secondary sources, (g–i) the ratio of secondary HCHO to total HCHO VMRs, (j–l) FNR_{sec} during the whole observation, and (m–o) FNR_{sec} during O_3 exceedance day in Hefei, Huaibei, and Tai'an during May–September, respectively. The vertical bars in (a–f) represent the one standard deviation. The dot within the box indicates the mean value, the positions of box plots represent the 5^{th}, 25^{th}, 50^{th}, 75^{th}, 95^{th} percentiles, respectively. The horizontal shadow in (j–o) represents the transition regime, the top of the shadow represents the NO_x–limited regime, and the bottom of the shadow represents the VOC–limited regime.

6. Page15 line 6-7, can you elaborate more on the "The RH at night increased slowly in eastern China during May–September of 2017–2021 (Fig.10b), and the nighttime RH in 2020 and 2021 was higher than that in other years"

Response 6: Thanks for your suggestion**,** it has been reported in previous studies (Hu et al., 2021), a general wetting trend has been detected in eastern China during the summer in recent years, which is largely related to the increase in summer Precipitation and decrease in summer Potential Evapotranspiration. We have added this statement to the manuscript, please refer to Page 16 Line 1–2 in the manuscript.

7. The discussion should point out the shortcomings in this study and future research perspectives.

Response 7: Thanks for your constructive comments! We have pointed out the shortcomings in this study in discussion section. "Owing to the limitations of the observational data, the analysis of surface O_3 precursors and O_3 formation sensitivity is limited to three cities in eastern China. Although other cities in eastern China were further investigated using satellite observations, TROPOMI only provides observation results for column concentrations at approximately 13:30 each day, which did not allow us to obtain diurnal variations in the O_3 formation sensitivity. Further observations must be extended to southern and coastal cities to investigate the relationship between O_3 and its precursors more comprehensively." We have added this statement to the manuscript, please refer to Page 16 Line 7–11 in the manuscript.

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