

In this paper, the authors measure vertical profiles of ozone and its precursors concentrations. The authors measure directly net ozone production rate  $P(O_3)_{net}$  at ground level, and discuss ozone concentration variations in terms of both photochemical ozone production and physical transportation using measured  $P(O_3)_{net}$  and ozone concentrations. In addition, they compare observed and modeled values for  $P(O_3)_{net}$  and discuss the vertical distribution of  $P(O_3)_{net}$  and ozone production regimes calculated from the model. The discussion on the ozone budget and its vertical distribution is very important to mitigate ozone pollution problems, so that I recommend this paper to be published in ACP. However, I found several concerns to be published in the present form, so the authors should perform appropriate revisions sufficiently.

We thank the reviewer for the useful comments and suggestions, which will help us to provide a more accurate description of our work. Our responses are given below in red, after the reviewer's comments, which are in black. The changes in the text are marked in yellow.

Major comments:

Line 225:  $NO_2$  and  $NO_x$  concentrations measured by commercially available  $NO_x$  analyzer include  $NO_z$  species such as PAN and  $HNO_3$ . I think this is a large problem because  $NO_2$  and  $NO_x$  are important ozone precursors. If this is no problem for the authors, they should prove that there is no problem. For example, an intercomparison of  $NO_2$  concentrations measured by the CAPS and chemiluminescence methods should be performed.

Yes, we have used a commercially available chemiluminescent  $NO_x$  monitor with the interference of  $HNO_3$  and PANs on  $NO_2$  measurement. However, we compared the  $NO_2$  measured by the chemiluminescence  $NO_x$  monitor with that measured by the Cavity Attenuated Phase Shift (CAPS, which is considered to be the more reliable  $NO_2$  measurement technique without chemical interference) and found that a 5% bias could be caused by the chemiluminescence  $NO_x$  monitor as shown in Zhou et al (2025). Therefore, we simulated  $P(O_3)_{net}$  by reducing and increasing the mixing ratios of  $NO_2$  by 5% to check the interference caused by using the chemiluminescence  $NO_x$  monitor to modelled  $P(O_3)_{net}$ . The results show that increasing and decreasing  $NO_2$  by 5% resulted in a decrease in  $P(O_3)_{net}$  of 1.64% and 3.68%, respectively, which is much smaller than the bias caused by  $P(O_3)_{net}$  in the reference chamber ( $\sim 13.9\%$ ), these tests are shown in Hao et al. (2023). However, this won't affect the measured  $P(O_3)_{net}$  values, as we used a CAPS  $NO_2$  monitor (Aerodyne research, Inc., Billerica MA, USA) in the net photochemical ozone production rate (NPOPR) detection system to avoid such interference, and quantified  $O_x (=O_3+NO_2)$  differences in the reaction and reference chambers to correct the effects of fresh  $NO$  titration to  $O_3$ . We have specified the interference of  $NO_2$  measurements using the chemiluminescence technique on pages 9, lines 263-269 in the amended manuscript:

“According to our test (Zhou et al., 2025), a 5% overestimation could be caused in the  $NO_2$

measurement using the chemiluminescence technique compared to the CAPS technique, due to some  $\text{NO}_z$  species (i.e.,  $\text{HNO}_3$ , peroxyacetyl nitrate (PANs), HONO, etc.) (Dunlea et al., 2007), this will result in a decrease of the modelled  $P(\text{O}_3)_{\text{net}}$  by  $< 4\%$ , which is negligible compared to the bias caused by the  $P(\text{O}_3)_{\text{net}}$  in the reference chamber ( $\sim 14\%$ ) (Zhou et al., 2023)."

Fig. 5: Why are there significant  $P(\text{O}_3)_{\text{net}}$  (not zero) in the nighttime? What is the precision of  $P(\text{O}_3)_{\text{net}}$  measured by this instrument? This should be discussed. Since  $\text{O}_x$  concentrations derived from the reaction chamber and reference chamber are measured alternately by solenoid valves, large fluctuations in ambient  $\text{O}_x$  concentrations are expected to cause poor precision.

According to our measurement error description added in "S4. The measurement error of  $P(\text{O}_3)_{\text{net}}$  and the LOD of the NPOPR detection system", the uncertainty of the measured  $P(\text{O}_3)_{\text{net}}$  is determined by the measurement error of  $\text{O}_x$  of the CAPS- $\text{NO}_2$  monitor and the error caused by the light-enhanced loss of  $\text{O}_3$  in the reaction and reference chambers, which is higher at lower  $P(\text{O}_3)_{\text{net}}$  values (as shown in the updated Fig. 4). During the night,  $P(\text{O}_3)_{\text{net}}$  is close to zero, but with a high uncertainty due to the instrument measurement error. As there is no light-enhanced  $\text{O}_3$  loss in the reaction and reference chambers during the night, the uncertainty of the measured  $P(\text{O}_3)_{\text{net}}$  is mainly determined by the ambient  $\text{O}_x$  concentrations, which can be considered as the measurement precision, and is estimated as  $\sim 38\%$ . We have added the corresponding discussion on page 20, lines 535-543 in the revised manuscript:

"During nighttime,  $P(\text{O}_3)_{\text{net}}$  should be zero without sun radiation. The significant  $P(\text{O}_3)_{\text{net}}$  shown in Fig. 5 may be due to the measurement uncertainty of  $P(\text{O}_3)_{\text{net}}$ , which is determined by the measurement error of  $\text{O}_x$  of CAPS- $\text{NO}_2$  monitor and the error caused by the light-enhanced loss of  $\text{O}_3$  in the reaction and reference chambers (as discussed in Sect. S4). The measurement uncertainty of  $P(\text{O}_3)_{\text{net}}$  is higher at lower  $P(\text{O}_3)_{\text{net}}$  values (as shown in Fig. 4), which was mainly determined by the instrumental error of  $\text{O}_x$  measurement and the ambient  $\text{O}_x$  concentrations during nighttime. It was estimated to be  $\sim 38\%$  and can be considered as the measurement precision."

Figs. S2 and 6: For  $P(\text{O}_3)_{\text{net}}$ , there are cases where the model agrees with the observation and cases where it does not. Why? The authors should discuss in depth? For IOA, NMB, and NME, the authors state their values during the whole measurement period only. What about the values of these parameters for each episode? Episode I and III may be good, but are the other episodes adequately reproduced, as described in Lines 571-573? Also, I think the discussion on the accuracy also concern the accuracy of the discussion on the vertical profiles of ozone budgets

and ozone production regime described in Figs. 7 and 9.

We discussed the relationship between the average daily disparities of the measured and modelled  $P(O_3)_{net}$  ( $\Delta P(O_3)_{net}$ ) with the various average daily NO concentrations during different episodes and non-episodes, which is depicted in Fig. 6f. The related discussion can be found on page 23, lines 637-644 in the main text:

“The observed elevated  $\Delta P(O_3)_{net}$  at higher NO concentrations aligns with findings from previous studies, which suggest that multiple factors could contribute to these outcomes. For example, the reaction of OH with unknown VOCs (Tan et al., 2017), the lack of correction for the decomposition of  $CH_3O_2NO_2$ , the missing  $RO_2$  production from photolysis  $ClNO_2$  (Whalley et al., 2018; Tan et al., 2017), and the underestimation of OVOCs photolysis (Wang et al., 2022) in modelling approaches may lead to the underestimation of  $RO_2$ , thus underestimating the modelled  $P(O_3)_{net}$ .”

Parameters		P1	P2	P3	C1	C2
IOA	$P(O_3)_{net}$	0.89 [0.88,0.90]	0.89 [0.88,0.90]	0.96 [0.95,0.96]	0.86 [0.86,0.87]	0.91 [0.90,0.91]
	$O_3$	0.81 [0.80,0.82]	0.79 [0.78,0.73]	0.83 [0.81,0.84]	0.81 [0.80,0.82]	0.80 [0.79,0.80]
NMB	$P(O_3)_{net}$	-0.33 [-0.36,-0.32]	-0.31 [-0.32,-0.31]	-0.12 [-0.14,-0.11]	-0.45 [-0.45,-0.44]	-0.26 [-0.27,-0.26]
	$O_3$	0.23 [0.23,0.24]	0.28 [0.28,0.28]	0.29 [0.27,0.32]	0.24 [0.23,0.24]	0.27 [0.78,0.80]
NME	$P(O_3)_{net}$	0.44 [0.43,0.47]	0.43 [0.43,0.44]	0.25 [0.24,0.26]	0.56 [0.55,0.56]	0.4 [0.38,0.40]
	$O_3$	0.30 [0.29,0.30]	0.34 [0.34,0.34]	0.31 [0.29,0.34]	0.32 [0.31,0.33]	0.33 [0.33,0.33]

To better describe the IOA, NMB, and NME of the measured and modelled  $P(O_3)_{net}$  (or  $O_3$ ) values, we added the IOA, NMB, and NME values during different episodes and non-episodes, as shown in Table S3 in the modified supplementary material:

“Table S3. The median values of IOA, NMB, and NME between measured and modelled  $P(O_3)_{net}$  (or  $O_3$ ) for different episodes and non-episodes.

[x, y]: x, y represent 25% and 75% percentile values of IOA during different episodes and non-episodes, respectively.

The relevant discussion is added on page 23, lines 647-653 in the revised

manuscript:

“However, the derived IOA, NMB, and NME values from the modelled and observed  $P(O_3)_{net}$  (and  $O_3$ ) at 5 m ground level during different episodes and non-episodes indicate that the model proficiently reproduces the genuine  $P(O_3)_{net}$  at the observation site well (as shown in Table S3). Consequently, these results provide confidence in exploring the vertical and temporal variations of the  $P(O_3)_{net}$  and  $O_3$  formation sensitivities utilizing the outcomes from the modelling approach. Nonetheless, it is important to acknowledge and discuss the potential biases induced by the modelling methodology in this study.”

Other minor comments:

Line 61-63: The authors should explain ozone production regime in more detail.

Ok, we have added the definition of OBM-MCM on page 2-3, lines 63-67:

“A “NO<sub>x</sub>-limited” regime has higher VOCs/NO<sub>x</sub> ratios and the O<sub>3</sub> formation is sensitive to NO<sub>x</sub> concentration changes, while a “VOCs-limited” regime has lower VOCs/NO<sub>x</sub> ratios and the O<sub>3</sub> formation is sensitive to NO<sub>x</sub> concentration changes. In a “mixed-sensitive” regime, O<sub>3</sub> formation responds positively to changes in both NO<sub>x</sub> and VOC emissions (Wang et al., 2019).”

Line 100: The authors should define OBM-MCM.

We have added the definition of OBM-MCM on page 4, lines 104-107:

“To diagnose the net ozone production rate,  $P(O_3)_{net}$ , and O<sub>3</sub> formation sensitivities across various heights, we employed an observation-based model coupled with the Master Chemical Mechanism (MCM v3.3.1), hereafter referred to as OBM-MCM.”

Sections 2.1 and 2.2.1: I think it would be easier for the readers to understand if the authors explain the details of the SZMGT and sampling method at SZMGT, using schematic diagrams in supplement.

We agree with the reviewer. Further details of the SZMGT have been added on pages

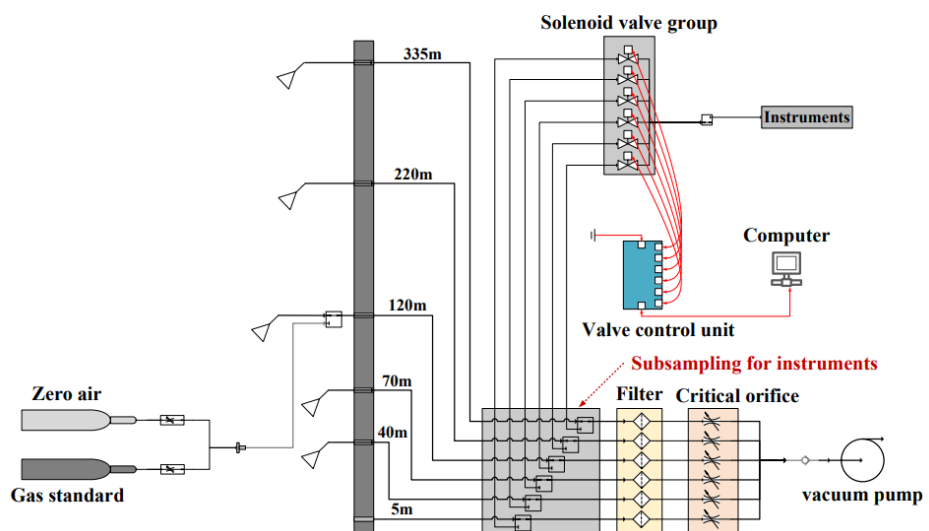
4, lines 125-128 in the revised manuscript:

“The SZMGT is 365 m high and is currently the tallest mast tower in Asia and the second tallest of this kind in the world. The main structure of the tower is made of steel, steel stay lines are used for fixing and securing the tower.”

More details on the sampling method at SZMGT are added on page 5, lines 134-145 in the amended manuscript:

“A tower-based observation system for traces gases using long perfluoroalkoxy alkane (PFA) tubing (OD: 1/2") was used to sample the O<sub>3</sub> and O<sub>3</sub> precursors at six heights during the campaign, including 5, 40, 70, 120, 220, and 335 m above the ground. All six tubes were continuously drawn using a rotary vane vacuum pump to keep flushing with ambient air to reduce tube delay of the organic compounds, with the flow rate controlled by critical orifices (orifice diameter: 0.063"). A Teflon solenoid valve group was used to switch the air samples at specified time intervals so that the subsamples from these six heights could be sequentially drawn by instruments (see Fig. S1). Consequently, the flow rates of the air sample streams for the six tubes varied between 12.0 and 15.0 SLPM without subsampling and were less than 20 SLPM with subsampling. The residence time of the sample gas in the longest tube (~ 400 m) is less than 180 s at a flow rate of 13 SLPM.”

And added the sampling schematic scheme diagram at SZMGT in the supplementary material:



**Figure S1. A simple schematic illustration of the vertical observation system on the SMT and locations of the six sampling inlets for measuring atmospheric gaseous species (Li et al., 2023).**

Line 149:  $O_3 + NO = NO_2 \rightarrow O_3 + NO \rightarrow NO_2$  (This is a chemical reaction, not an equation)

We have changed “ $O_3 + NO = NO_2$ ” to “ $O_3 + NO \rightarrow NO_2$ ” in the modified manuscript on page 6, line 169-172:

“A stream of air from the two chambers was alternately introduced into an NO-reaction chamber every 2 min to convert  $O_3$  in the air to  $NO_2$  in the presence of high concentrations of NO ( $O_3+NO \rightarrow NO_2$ ), ...”

Section 2.2.3: What kinds of VOCs did the authors measure? Listed in Table S2? If so, the authors should refer to Table S2 in the text.

We have added the description of Table S2 on page 8, lines 254-256:

“A full list of all 56 non-methane hydrocarbons (NMHCs) can be found in the supplementary material (Table S2).”

Line 233: at 424 nm  $\rightarrow$  less than 424 nm?

We have changed the description on page 9, lines 274-276:

“The specific tropospheric  $O_3$  photochemical formation process involves the photolysis of  $NO_2$  at  $< 420$  nm (Sadanaga et al., 2017).”

Line 289: In order to investigated  $\rightarrow$  In order to investigate

We modified the description on page 11, lines 340:

“In order to investigate the influence of the photochemical reactions of different VOCs to photochemical O<sub>3</sub> formation, ...”

Fig. 1 and Table 1: How did the authors measure CO and TVOCs? And the authors should define TVOCs.

Ok. We have added the measurement method for CO on page 9, line 259-263 in the revised manuscript:

“O<sub>3</sub>, CO, and NO<sub>x</sub> concentrations were measured by a 2B O<sub>3</sub> monitor based on dual-channel UV-absorption (Model 205, 2B Technologies, USA), a gas filter correlation (GFC) CO analyzer (Model 48i, Thermo Fisher Scientific, USA), and a chemiluminescence NO<sub>x</sub> monitor (Model 42i, Thermo Fisher Scientific, USA), respectively.”

And defined TVOC on page 14-15, line 404-406:

“The mean concentrations of O<sub>3</sub> precursors, including CO, NO, NO<sub>2</sub>, and the total VOCs measured by PTR-TOF-MS (shown as TVOC in Fig. 1 and Table 1),...”

Line 363-365: Is this sentence made during the daytime?

Yes, we added “during daytime” to the sentence on page 15, line 430-432:

“From Fig. 2, minimal vertical gradients were observed during daytime in the concentration of all species—O<sub>3</sub>, NO<sub>x</sub>, O<sub>x</sub>, and TVOC—due to the rapid vertical mixing effects.”

Line 454: Sect. 3.3.1 → Sect. 3.1.1?

Yes, it should read “Sect. 3.1.1”. We have changed “Sect. 3.3.1” to “Sect. 3.1.1” on page 18, line 508-509:

“As concluded in Sect. 3.1.1, O<sub>3</sub> pollution episodes may be jointly affected by the

photochemical reactions and physical transport.”