

We appreciate constructive comments on the manuscripts from the anonymous referees. We addressed the points that each referee raised in the submitted revised manuscript. We described the revision by responding the comments line by line.

#### Anonymous Referee #2

I have no further technical problems with the revised manuscript. I do think that the heading of 3.2, 3.3 are too long.

We shortened the headings in the revised manuscript.

#### Anonymous Referee #4

This manuscript describes the photochemical box model simulations constrained to observations of ozone precursors to explore radical photochemistry and ozone production regimes at the Taehwa forest site in South Korea. The impact of isoprene chemistry mechanism and elevated concentrations of HONO was studied.

I find that critical comments and recommendation given by the previous two reviewers are often not taken into account by the authors seriously and that the points that the authors noticed important are not adequately discussed even in the latest revised manuscript. The most fatal three points are as follows:

1) Although Dr. Mueller warned that the OH yield of 2.6 is not any more the consensus of the research community and recommended more than 10 times lower value, the authors just continued to use the original value that is outdated. Also, it is nonsense that combination of (1) OH recycle from the isoprene peroxy radical + HO<sub>2</sub> reaction and (2) HPALD chemistry is tested (Scenario IV). The two mechanisms are separately proposed in the past to explain high OH levels observed during GABRIEL campaign (likely affected by interference) and therefore the combination should overpredict OH even for the GABRIEL measurements. The interference issue in the used instrument (e.g., Novelli et al., AMT, 2014) also needs to be taken into account seriously.

As the referee suggested, we have eliminated the model calculation scenario with the excess OH recycling from the HO<sub>2</sub> + RO<sub>2</sub> reaction. In addition, we refer to recent study results indicating the invalidity of the recycling pathway as the referee suggested.

2) If the authors still believe that such high OH yield takes place, RO<sub>2</sub> + HO<sub>2</sub> reaction rates, likely dominated by isoprene peroxy radical + HO<sub>2</sub> reaction, need to be categorized to "radical recycling" process in section 3.3. The authors seem to have recognized this issue because they mentioned in the latest manuscript (lines 495-497) that "we may need to reconsider R4 as a radical recycling process"; surprisingly however, they continued to follow the conventional

classification in the analysis. The logic here is clearly self-inconsistent.

As we no longer present peroxy radical reactions as a major OH recycling pathway, we have deleted the inconsistent argument.

3) The authors used photostationary state analysis for NO and NO<sub>2</sub> (line 524 of the latest manuscript) trying to explain observed [NO]/[NO<sub>2</sub>] ratio that is extraordinary low (<0.1, calculated from [NO]=0.6 ppb and [NO<sub>2</sub>]= 6 ppb at around 10 KST as read from Figure 1). When I assume that the JNO<sub>2</sub> value is about  $5 \times 10^{-3} \text{ s}^{-1}$  (for which no observational or simulation information is provided in the manuscript!) and the [O<sub>3</sub>], [HO<sub>2</sub>], and [RO<sub>2</sub>] levels shown in Figure 1 and Table 4, the [NO]/[NO<sub>2</sub>] ratio can be 0.25 for the morning period, but not as low as 0.1. Only if the JNO<sub>2</sub> value is as low as  $2 \times 10^{-3} \text{ s}^{-1}$  (as UV actinic flux is highly blocked by the forest?), the observed low [NO]/[NO<sub>2</sub>] might be reproduced. The even lower [NO]/[NO<sub>2</sub>] ratio in the afternoon (around only 0.016, as calculated from [NO]=0.05 ppb and [NO<sub>2</sub>]=3 ppb at around 14 KST shown in Figure 1) is much more difficult to be reconciled with the photostationary state theory. The authors should have used the equation (labeled as R7, although this is not chemical reaction!) to test their hypothesis given in the lines 526-534 quantitatively. I may suspect that the NO<sub>2</sub> measurements suffered from interference from NO<sub>z</sub> species. The authors at least need to describe which type of converter was used in the NO<sub>x</sub> measurements. If NO<sub>2</sub> measurements are incorrect, all calculation of the radical concentrations and the regime determination may be false. To remove my doubt, the authors need to provide information of J value measurements and their treatment in the model, the type of converter is used for NO<sub>2</sub> measurements, and quantitative explanation why the observed [NO]/[NO<sub>2</sub>] ratios were so low.

Mannschreck et al. (2004) thoroughly discussed the NO-NO<sub>2</sub>-O<sub>3</sub> photostationary state by presenting three extensive datasets from the Hohenpeissenberg GAW Station, Germany. The results showed that the photostationary state parameter ( $\phi$ ) is in the range of 2.5 – 5.7, which is consistent with our observed results. Even with consideration of peroxy radical chemistry presented in the manuscript, only 13-32 % of data points fall into the photostationary state regime. The authors presented further discussion on reasons of not achieving photostational state as 1) local NO<sub>2</sub> sources near the measurement site, 2) local NO or ozone sinks near the measurement site, 3) rapid changes in JNO<sub>3</sub> and ozone, and 4) measurement errors. In our case, 1) and 4) should be considered among the potential reasons. The proximity to SMA may provide sources for fresh NO<sub>2</sub>. In addition, as NO<sub>2</sub> observations were conducted by Thermo Environmental NO<sub>2</sub> analyzer with Mo-converter, thermally unstable organic nitrate species may become artifacts in NO<sub>2</sub> quantifications. We added the above discussion in the revised manuscript.

Besides the above three points, I still find two more critical issues.

First point is on the judgment criteria of the ozone production regime. The authors cite Tonnesen and Dennis (2000) and used the ratio range ( $P(H_2O_2)/P(HNO_3)$ ) of 0.35 as the border range. However, I only found in Tonnesen and Dennis (2000) that the border lies with the ratio ( $P(H_2O_2)/P(HNO_3)$ ) of 0.06-0.07 in the daytime. The authors need to clarify this first. Also, such value determined for a different site and different season could not be valid for the campaign studied in this manuscript, because of the strong influence from the types of VOCs present in the atmosphere and J values. Especially, I do not understand why the regimes can be determined with the same criteria for scenarios II, IV, and V, where the isoprene chemistry mechanism was severely modified. Clearly different approach (e.g., model sensitivity experiments of ozone production rates on the amount of  $NO_x$  or VOCs) is recommended.

In the revised manuscript, we present a different yet more precise criterion to determine  $NO_x$  and VOC limited regimes. The previously presented criterion, determining ozone production regimes based on  $P(H_2O_2)/P(HNO_3)$ , has been widely applied in regional studies using air quality models such as CMAQ and WRF-Chem. The ozone isopleth is calculated based on the  $NO_x$  and VOC emissions and photochemical environments such as solar radiation. Therefore, it is difficult to apply this concept to the interpretation of an observed dataset. For this reason, different numbers have been applied for the determination of ozone production regimes. The ratio of 0.35 was adapted from Li et al., (2013) who presented investigation on ozone production chemistry in the Pearl River Delta region indicating similar photochemical environments with those of TRF. Cadelino and Chameides (1995) developed an observation-based model to determine the ozone production regime, which can be expressed as one simple equation for the identification of  $NO_x$  or VOC limited regimes (Kleinman, 2000 and references therein). We introduced this equation and applied it to assess ozone production regime in the revised manuscript.

Second, nighttime isoprene concentration levels as high as 1 ppbv have rarely been reported and thus more explanation should be provided. The cited literatures (Apel et al., 2002; Bryan et al., 2012) reported much lower nighttime levels. The authors need to discuss possibility of interference in the PTR-MS measurements during night and similar artifact in the daytime isoprene measurements.

As the referee suggested in the remote environments, the observed isoprene nighttime low is usually much lower than 1 ppb. However, isoprene observations in a suburban environment indicate occasional high isoprene levels reached a few ppb (e.g. Lu et al. 2012). In addition, as the referee suggested, there have been several reports on potential isobaric compounds detected as same mass as isoprene, especially, in the urban air (e.g. Yuan et al., 2014). We included this discussion in the revised manuscript.

Anonymous Referee #3

The manuscript has considerably improved but some previous comments have

not yet been reflected. The manuscript would be acceptable for publication after reconsidering the following points:

1) Line 255: Reviewer #1 strongly recommended that headline should be changed from 'results' into 'results and discussion' in the previous review. Please reconsider.

We corrected as the reviewer suggested in the revised manuscript.

2) Line 115: The citation method '... and reference therein' would not be recommended in this journal. Please cite appropriate references.

We added another reference instead in the revised manuscript.

3) Line 252: The places where specific parameters are mentioned have explained in the revised manuscript but it is still unclear what specific parameters are.

We added specific parameter information in the revised manuscript

4) Lines 301-302: The authors have added the description on the extent of the branch enclosure sampling method to the revised manuscript. However, data shown in Table 2 are all from sampling during the midday, i.e., the authors did not give information how the emissions develop 'throughout the day.'

In the method section of the revised manuscript, we included more specifics about the "continuous branch enclosure observations". We discussed the emission diurnal variation qualitatively in order to explain the BVOC diurnal patterns. More quantitative analysis is being prepared for a separate manuscript.

5) Line 338: Reviewer #1 objected that the authors treated MEK as AVOC. He wrote that MEK has both anthropogenic (industrial solvent) and biogenic (wounded and stressed plants) sources. Please reconsider.

As described in the manuscript, the diurnal variations of MEK and toluene are very similar, which indicates that observed MEK is dominated by anthropogenic emissions.

6) Line 381: I think that Reviewer #1 requested to insert 'simulations with' before 'observed HONO' in this line of the revised manuscript. Please try this assumption and reflect the comment if acceptable.

We corrected it as suggested.