Author Response to Anonymous Reviewer #3

We would like to thank Reviewer #3 for the careful reading of the manuscript, and dedication to evaluating this study. We also appreciate Reviewer #3's insightful comments and valuable suggestions which are very helpful for further improving the quality of our manuscript. Please find below our point-by-point responses to the comments and a highlight to the changes made to the manuscript. Changes to the revised manuscript are marked in blue.

Scientific Comments：

1. Line 25: "with more detailed categories, accurate emission rate intervals and representative". The observational accuracy is determined in the measurement. It has nothing to do with more detailed categories and emission rate intervals. Therefore, the method in this paper probably can't give more accurate emission emissions than previous studies.

Response:

Thank you for your insightful comment.

As you said, the observational accuracy is determined in the measurement. The foundation of our statistical method to determine representative emission rates was the reliable original emission rate observations, as suggested by Niinemets et al. (2011). This has been described in Section of Evaluation. It is also both important and challenging to estimate emission rates accurately when developing emission inventories. On this basis, we focused on exploring scientific methods for the accurate estimation of plant species-specific representative BVOC emission rates.

In previous inventories, the sources and estimations of emission rates varied, yielding different results for individual plant species among studies. Different studies reported distinguished values with large uncertainties due to the use of different sampling techniques and sample sizes (Guenther et al., 1994). Even if the most accurate observations were screened or conducted, it would be still necessary to find a straightforward method to determine one emission rate value for a plant species when compiling an emission inventory. Therefore, some studies have used emission categories to determine emission intensities and rates (Guenther et al., 1994; Simpson et al., 1999; Klinger et al., 2002; Wang et al., 2007). By this means, discrete emission categories (e.g., negligible, low, moderate, and high) were defined based on the emission intensity of vegetation, with a representative rate and a range of ±50%. For each plant species, the emission rate was determined based on the tendency of

the reported emission rates to fall within certain categories. This method improved the accuracy of the final emission rates to a large extent in comparison with assigning one observation value or the average of different observations for each plant species. **However, the process of determining emission categories, representative emission rates, and ranges was not straightforward, and lacked theoretical evidence. Furthermore, some studies used both distinct emission categories and representative values, resulting in different emission rates for specific plants. Some studies used coarse classifications (usually three to six classes) of emission intensity, which might underestimate emission rates of plants with high emission potentials or overestimate emission rates of plants with low emission potentials. Additionally, for China, the previous studies have based on less local quantitative measurements.** This has been described in Section of Introduction.

For the drawbacks described above, it is essential and urgent to develop detailed emission categories and accurate representative values and ranges to determine emission rates accurately based on statistical analysis. It is particularly important to use local measurements of emission rates from plants, especially for China, a country with a large vegetated land area and high species diversity.

In our study, we first performed field measurements of BVOC emissions from 50 plant species using our established semi-static enclosure system, and obtained more local observations with higher accuracy. Then, we developed the theoretically effective approach to estimate emission rates used as basic data for BVOC emission inventories development and air quality modeling. We summarized our field measurements and reported emission rates from China and abroad to establish emission intensity categories. Our emission categories, emission intervals, and representative rates were different from those in previous studies. We included more categories, accurate emission rate intervals and representative rates. It should be noted that the added local accurate observations used to produce emission categories were still not sufficient, so the difference between our study and previous studies were not obvious. Future studies integrating more emission measurements with different intensities will create more detailed categories, accurate emission rate intervals and representative rates. Thus, the accuracy in the determination of representative emission rates for each plant will be improved to a larger extent with enhanced measurements. In the future, we will perform more measurements for further improvement of the approaches and accuracy of estimating representative emission rates.

References:

Guenther, A., Zimmerman, P., and Wildermuth, M.: Natural volatile organic-compound

emission rate estimates for United-States woodland landscapes, Atmos. Environ., 28,1197-1210, doi: 10.1016/1352-2310(94)90297-6, 1994.

Klinger, L. F., Li, Q. J., Guenther, A. B., Greenberg, J. P., Baker, B., and Bai, J. H.: Assessment of volatile organic compound emissions from ecosystems of China, J. Geophys. Res.-Atmos., 107, 4603, doi: 10.1029/2001jd001076, 2002.

Niinemets, Ü., Kuhn, U., Harley, P. C., Staudt, M., Arneth, A., Cescatti, A., Ciccioli, P., Copolovici, L., Geron, C., Guenther, A., Kesselmeier, J., Lerdau, M. T., Monson, R. K., and Peñuelas, J.: Estimations of isoprenoid emission capacity from enclosure studies: measurements, data processing, quality and standardized measurement protocols, Biogeosciences, 8, 2209-2246, doi:10.5194/bg-8-2209-2011, 2011.

Simpson, D., Winiwarter, W., Borjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, C. N., Janson, R., Khalil, M. A. K., Owen, S., Pierce, T. E., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrason, L., and Oquist, M. G.: Inventorying emissions from nature in Europe, J. Geophys. Res.-Atmos., 104, 8113-8152, doi: 10.1029/98JD02747, 1999.

Wang, Q. G., Han, Z. W., Wang, T. J., and Higano, Y.: An estimate of biogenic emissions of volatile organic compounds during summertime in China, Environ. Sci. Pollut. R., 14, 69-75, doi: 10.1065/espr2007.01.376, 2007.

2. Line 67: How many rotameters were used? Please describe it in more detail. Such as: type, company, what's the accuracy of the flow rate? How it controls the flow rate?

Response: Accepted.

Two rotameters were used in this study to monitor the flow rate of the zero air at 10 L $min^{-1}$and 2 L min^{-1}, respectively. They were made by Yuyao Zhenxing Instruments Co. in China. Their precision was 2.5% which was relatively low. But owing to limitations of the field experiment, we selected rotameters with portability instead of automatic mass flow controllers. Actually, the rotameter can only be used to monitor but not control the flow rate. In this study, the flow rates were calibrated and regulated respectively at 10 L min^{-1} and 2 L min^{-1} at the beginning of each experiment by a primary air flow calibrator (Gilian Gilibrator-2; Sensidyne, Inc., St. Petersburg, FL, USA), respectively, and were measured again at the end of each experiment. During one experiment, the flow rate scarcely changed. The flow rates could be controlled by the method described above.

We make a further explanation in the revised manuscript. Line 136-142, "Owing to limitations of the field experiment, rotameters were used to monitor and control the flow rate of the zero

air. Considering its relatively low accuracy, the flow rate had to be measured and calibrated with a primary air flow calibrator (Gilian Gilibrator-2; Sensidyne, Inc., St. Petersburg, FL, USA) at the beginning and end of each experiment." is changed to "Owing to limitations of the field experiment, two rotameters with different measuring range (LZB-4WB and LZB-6WB; Yuyao Zhenxing Instruments Co., Yuyao, China) were used to monitor the flow rate of the zero air. Considering relatively low accuracy (±2.5%), the rotameters had to be calibrated and regulated at the scheduled flow rate with a primary air flow calibrator (Gilian Gilibrator-2; Sensidyne, Inc., St. Petersburg, FL, USA) at the beginning of each experiment and measured again at the end of each experiment. There was almost no change between the flow rates measured at the beginning and end for one experiment.".

3. Line 120 and Figure 1: The measurement of PAR is not right. The PAR sensor should be placed in the Tedlar bag. Large observational errors from PAR measurement would be introduced to normalized emission rates, especially the measurements were carried out at different time. The transparence varied with solar zenith angle and the Tedlar surface. The normalized emission rates should be corrected. Please give the uncertainty of BVOC emission rates.

Response: Accepted.

Thank you for your insightful critique. We couldn't agree more with you.

The PAR sensor used in this study had to be leveled horizontally to make accurate measurements. It was not possible to place the sensor inside the bag in this way, so it was placed on the ground rather than in the Tedlar bag to monitor the PAR outside the bag. As you pointed out, the solar zenith angle and transparence of Tedlar bag would cause difference to the PAR in and outside the bag. To minimize the difference of monitored PAR in and outside bag, we chose the bag which was 50 μm thick and could be 90–95% transparent to PAR (Ortega et al., 2008). However, the uncertainty caused by the variation of solar zenith angle could not be evaluated. As it is reported, no systematic difference was observed with the varying solar angle (Yaman et al., 2015).

In the added uncertainty analysis in Section 5 in the revised manuscript, we make an explanation of the uncertainty introduced by the PAR measurements, in line 453-457, "Secondly, PAR sensor was placed horizontally on the ground to monitor PAR outside the bag due to limitation of actual operation, which resulted in a difference of 5–10% for PAR between inside and outside the bag (Ortega et al., 2008; Yaman et al., 2015). This would introduce uncertainties to BVOC normalized emission rates, 0.9–3.1% for isoprene and 0.2–2.4% for other compounds." is added.

Reference (Yaman et al., 2015) is added in the reference list.

References:

Yaman, B., Aydin, Y. M., Koca, H., Dasdemir, O., Kara, M., Altiok, H., Dumanoglu, Y., Bayram, A., Tolunay, D., Odabasi, M., and Elbir, T.: Biogenic volatile organic compound (BVOC) emissions from various endemic tree species in Turkey, Aerosol Air Qual. Res., 15(1), 345-356, doi: 10.4209/aaqr.2014.04.0082, 2015.

Ortega, J., Helmig, D., Daly, R. W., Tanner, D. M., Guenther, A. B., and Herrick, J. D.: Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques - part B: applications, Chemosphere, 72(3), 365-380, doi: 10.1016/j.chemosphere.2008.02.054, 2008.

4. Line 178: What's the uncertainty for isoprene, α-pinene, β-pinene and other species?

Response: Accepted.

We added the errors of isoprene, α-pinene, β-pinene and other species measurements by GC-MS/FID system in the revised manuscript.

Line 179-181, "A calibration was measured at 1 ppbv repeatedly for ten times to determine precision and detection limits." is added. Line 181-182, "The precision of the system for VOCs ranged from 0.5% to 4%." was modified to "The precision of the system for isoprene, α-pinene, β-pinene, and acetylene were 2.30%, 3.65%, 3.37%, and 1.11%, respectively; the precision for other VOC species ranged from 0.5% to 4%.".

5. Line 263: alkenes alkenes, please delete one alkenes.

Response: Accepted.

Line 281 in revised manuscript, one "alkenes" is deleted.

6. Line 308: … new interval were eliminated due to possible measurement errors. Many old intervals were removed. Does it mean there were large measurement errors in the measurements? What are the reasons for this?

Response: Accepted.

We considered the measured emission rates outside the 95% confidence interval (CI) of each

interval had large random errors of measurements. The explanation for it is as follows.

In our study, we firstly estimated a range of emission rates for each category according to the distribution. Because the measured values in each range displayed dispersed distributions with large standard deviations (SDs) relative to the mean, the mean could not represent the real emission for each isoprene emission category. Some observations falling in each category happened by chance. Therefore, we did additional statistics for all the values in each emission rate range separately. Using the *t*-test, we determined the 95% confidence interval (CI) of each range, which were considered to be the final emission rate interval for each emission category (Rivas-Ruiz et al., 2013). Here, the 95% CI was where the true emission rate of each emission category could locate with a large possibility of 95%. The true emission rate could locate outside the 95% CI with only a small possibility of 5%, which implied the values outside the 95% CI had lower reliability and larger errors. They could be considered as outliers and eliminated when doing statistics.

To make it more clear, we make a further explanation in the revised manuscript. Line 323-329, "Using the *t*-test, we determined the 95% confidence interval (CI) of each range, which we considered to be the final emission rate interval for each emission category (Table 4)." is revised to "Using the *t*-test, we determined the 95% confidence interval (CI) of each range (Rivas-Ruiz et al., 2013). Here, the 95% CI was where the true emission rate of each emission category could locate with a large possibility of 95%. The true emission rate could locate outside the 95% CI with only a small possibility of 5%, which implied the values outside the 95% CI had lower reliability and larger errors. So we considered the determined 95% CI to be the final emission rate interval for each emission category (Table 4).". Line 329-331, "... outside the new interval were eliminated due to possible measurement errors ..." is modified to "... outside the new interval were eliminated due to possible large random errors of measurements ...".

Reference:

Rivas-Ruiz, R., Perez-Rodriguez, M., and Talavera, J. O.: Clinical research XV. From the clinical judgment to the statistical model. Difference between means. Student's t test, Revista medica del Instituto Mexicano del Seguro Social, 51(3): 300-3, 2013.

7. Line 354: Their use of fewer categories could result in underestimation of emission rates for plants with higher emission potentials. For example, the emission rate estimates of Eucalyptus, Quercus, Populus, and bamboo were much lower in previous studies than in our

study. What's the reason for this difference? which could result in an underestimation of 4.9–7.8 Tg C yr^{-1} for isoprene emissions in China. How can get 4.9–7.8 Tg C yr^{-1}?

Response: Accepted.

(1) We are sorry for our confused expression.

If fewer categories are used, such as three categories, emission of plants with "higher" or "lower" emission potential might be classified into "moderate" emission category, resulting in inexact representative emission rates. This might result in underestimation of emission rates for plants with higher emission potentials or overestimation of those for plants with lower emission potentials. However, there was a mistake here that the examples of *Eucalyptus*, *Quercus*, *Populus*, and bamboo were not the improper usage because their underestimations were mainly caused by using different emission categories and representative values.

To make it clear, we make a revision on this issue in the revised manuscript. Line 377-383, "Table 8 lists the isoprene emission categories and determined emission rates of some dominant tree species with higher emission potentials. In addition, previous studies used coarse emission intensity classifications (usually three to six classes) (Klinger et al., 2002; Yan et al., 2005; Wang et al., 2007), while we defined seven categories for the isoprene emission rates. Their use of fewer categories could result in underestimation of emission rates for plants with higher emission potentials. For example, the emission rate estimates of *Eucalyptus*, *Quercus*, *Populus*, and bamboo were much lower in previous studies than in our study (Klinger et al., 2002; Yan et al., 2005; Wang et al., 2007), which could result in an underestimation of 4.9–7.8 Tg C yr^{-1} for isoprene emissions in China, estimated using the methodologies described in Li et al. (2013) and Li and Xie (2014)." is modified to "In addition, previous studies used coarse emission intensity classifications (usually three to six classes) (Table 8), which could result in inexact estimation of emission rates. Table 8 lists the isoprene emission categories and determined emission rates of some dominant tree species with higher emission potentials. The emission rate estimates of *Eucalyptus*, *Quercus*, *Populus*, and bamboo were much lower in previous studies than in our study (Klinger et al., 2002; Yan et al., 2005; Wang et al., 2007), which could result in an underestimation of 4.9–7.8 Tg C yr^{-1} for isoprene emissions in China, estimated using the methodologies described in Li et al. (2013) and Li and Xie (2014).".

Line 88-90 in revised manuscript, "Some studies used coarse classifications of emission intensity, which might underestimate emission rates of plant species with high emission potentials." is modified to "Some studies used coarse classifications of emission intensity, which might result in overestimation or underestimation of emission rates.", accordingly.

(2) Here, "4.9–7.8 Tg C yr^{-1}" was estimated according to the methodologies described in Li et

al. (2013) and Li and Xie (2014), by using different emission rate of *Eucalyptus*, *Quercus*, *Populus*, and bamboo in previous studies and our study, respectively.

Line 380-383, "... an underestimation of 4.9–7.8 Tg C yr^{-1} for isoprene emissions in China." is revised to "... an underestimation of 4.9–7.8 Tg C yr^{-1} for isoprene emissions in China, estimated using the methodologies described in Li et al. (2013) and Li and Xie (2014).". Reference (Li et al., 2013) and (Li and Xie, 2014) have been included in the reference list.

References:

Li, L.Y., Chen, Y., and Xie, S. D.: Spatio-temporal variation of biogenic volatile organic compounds emissions in China, Environ. Pollut., 182, 157-168, doi: 10.1016/j.envpol.2013.06.042, 2013.

Li, L.Y. and Xie, S. D.: Historical variations of biogenic volatile organic compound emission inventories in China, 1981-2003, Atmos. Environ., 95, 185-196, doi: 10.1016/j.atmosenv.2014.06.033, 2014.

8. Table 4 and Table 5: emission rates for isoprene and monoterpenes are almost the same? Some old mission rate intervals were removed in Table 5, which may be more useful data to understand realistic BVOC emissions.

Response:

(1) The representative emission values for each category in Table 3 and 4 (here the tables are numbered again because we delete the original Table 1 in Response to Reviewer #1's Other Comment 3) have differences of 0–10% for isoprene and 0–25% for monoterpene.

We added a quantitation for their differences in the revised manuscript. Line 331-332, "The means for each emission category have also changed by 0–10% for isoprene and 0–25% for monoterpene." is added.

(2) About the reason why we eliminated the values outside the new interval when doing additional statistics, please **refer to our Response to Comment 6**.

9. Line 417: our emission rate categories were more detailed, and the emission rate interval and representative rates were more accurate. How can prove it?

Response: Accepted.

Please refer to our **Response to Comment 1**.

10. Table 6: What's the improvement for this study? Most of the normalized leaf-level isoprene and monoterpene emission rates in China are the same with the previous studies in the Table 6.

Response:

In our study, we have tried our best to collect the available original local measured data in China, but measurements were rare. So, sometimes we had to collect data from studies that only showed their estimated representative emission rates (e.g. 1, 70 μg C gdw^{-1} h^{-1} for isoprene and 3 μg C gdw^{-1} h^{-1} for monoterpene) for some plants using the traditional emission categories based on their original observations being not presented, such as studies of Klinger et al. (2002) and Guenther et al. (1996). This would inevitably influence the accuracy of our results. Although we performed field measurements of emission rates from 36 tree species in China using our established semi-static enclosure system and obtained 53 available emission samples to be used in the estimation of representative emission rates, the measured emission rates were not sufficient. If we can enhance the measurements and use the original data to estimate the emission intervals and representative rates in the future study, we will get different results from our current study. Our method can be improved constantly by more and more local reliable measurements. And the accuracy in the estimation of representative emission rates for each plant would be improved much with enhanced measurements.

We make an explanation to this issue in **Section 4.3 Comparison of representative emission rates** and also make an evaluation to our approach in **Section 5 Evaluation and uncertainty analysis** in the revised manuscript. Line 383-389, "Especially, from Table 8 and 5, representative values for some emission categories and determined leaf-level emission rates for some plants looked the same. Sometimes we had to collect data from studies that only showed their estimated representative emission rates (e.g. 1, 70 μg C gdw^{-1} h^{-1} for isoprene and 3 μg C gdw^{-1} h^{-1} for monoterpene) for some plants using the traditional emission categories based on their original observations being not presented, such as studies of Klinger et al. (2002) and Guenther et al. (1996), because the available original local measured data in China were relatively rare." is added. Line 419-424, "It is notable that the application of reported estimated representative emission rates for some plants using the traditional emission categories based on their original observations would influence the accuracy of our results unavoidably. Although we performed field measurements of emission rates in China and obtained 67 available emission samples to be used in the estimation of representative emission rates, it was still not enough." is added.

In our study, we believed that the estimation of representative emission rates applied in

emission inventory has been improved. About the improvement for our study, please refer to our **Response to Comment 1**.