Response to Reviewer’s Comments

We are grateful for the reviewer’s comments and suggestions. We have addressed all of the referee’s comments below.

General comments:

It’s always very challenging to accomplish the high-precision and multi-gas measurements by any single detection technology. The present study at-tempts to simultaneously measure N_2O, CH_4, CO_2, and O_2 concentrations and fluxes based on the high-resolution multi-turn time-of-flight mass spectrometer (MULTUM)that attached to an automated chamber system. The authors emphasize a fundamental truth that “continuous multiple-gas flux and concentration measurements can be a powerful tool for tracking and understanding of underlying biological and physicochemical processes.” …...... The present study only prove the ability of multi-gas concentration rather than flux measurements by the MULTUM system. The other most important highlight is to notice the different response of CO_2 and N_2O fluxes to the first rainfall event in the present study. However, the authors draw the conclusion only from two hourly fluxes (two data points in Fig. 11), which have no spatial replicates (no error bars) and quality control processes.

The purpose of this manuscript is to describe a new atmospheric measurement technique for simultaneous multi-soil gas flux field observation with a unique portable high-resolution mass spectrometer as the AMT aims for. It is not for the discussion on soil science. Therefore, we do not report any “spatial replicates” of soil gas fluxes. We agree that such “spatial replicates” would be quite valuable when the present technique is used for the researches in soil and atmospheric sciences.

Specific comments:

1. The manuscript NEEDS a thorough editing for language. There are too many grammatical errors and obscure sentences.

   Although we had a language editing before proceeding to the AMTD, we will have another language editing after this interactive discussion.

2. I do not understand why the authors use different confidence levels (1 to 3 RSD) to calculate the limit of detection instrument precision, minimum detectable fluxes and minimum quantitative fluxes.

   We used 1 RSD as an instrumental precision for the measurement of atmospheric N_2O, CO_2, CH_4, O_2 concentrations, and 2 RSD for the rest of all measurements in this manuscript. As the reviewer pointed out, using two different confidence levels (1 and 2 RSDs) is not appropriate. We will set all confidence levels to 2 RSD.

3. The concentrations of ambient gases rather than calibration gases are used to evaluate the instrument precision, why? How to avoid the impacts of daily variations in ambient gas

concentrations, especially for CO_2. A better way to present the instrument performance is the continuous measurement of calibration gases in the field laboratory.

As discussed in the manuscript (Line 235-239), the observed variation in concentrations during ambient air measurement was considered to be instrumental one rather than natural one since the variations were quite similar to those obtained with standard gases (Line 235-239).
As the reviewer suggested, using standard gas rather than ambient air usually gives better instrumental accuracy since ambient air contains much more complicated gas species, including water vapor, which could affect mass spectrometric measurement performance. Our final goal in our instrumental development is to construct a new instrument for field observation. Soil gas flux is determined from the change in gas concentration in flux chamber relative to its atmospheric concentration. Due to these reasons, we thus considered that using ambient air measurement is more appropriate and practical for our research purpose.

4. How to do the quality control of flux data, e.g. the statistical significance test of linear fitting between gas concentrations and sampling times?

In Section 3.3, quality control of flux determination (linear regression analysis and its R^2) is discussed. We believe that adequate discussion is made there.

5. The future perspectives are absolutely arbitrary. "Coupling of proton transfer reaction (PTR) ionization sources with the MULTUM also makes it easier to observe BVOCs concentrations and soil-atmosphere fluxes." Do you have any data to support the perspective? "We consider that the improvement in the detection limit by one order of magnitude can be relatively easy by retrofitting a larger vacuum pump to the MULTUM (from 50 l/sec to 250 l/sec) and using a flux chamber with lower height (from 0.37 m to 0.2 m)." How to easily improve the detection limit when you measure the gas emissions from the soil-plant system rather than the bare soil?

The section "Future Perspectives" is to foresee how the current study is expected to impact future research. There is no need to show the actual result to support that since it is the "Future Perspective" section. However, proton-transfer-reaction mass spectrometer (PTR-MS) has been widely used in atmospheric VOC measurement [e.g., Yuan et al., 2017]. It is now a de facto standard for atmospheric VOCs measurement in high time resolution [e.g., Yuan et al., 2017]. We will cite some review papers regarding VOC measurements with PTR-MS for this part to show PTR-MULTUM is quite possible and promising. In fact, we are developing it now.

Yuan, B., Koss, A. R., Warneke, C., Coggon, M., Sekimoto, K. and de Gouw, J. A.: Proton-Transfer-Reaction Mass Spectrometry: Applications in Atmospheric Sciences, Chem. Rev., 117(21), 13187–13229, doi:10.1021/acs.chemrev.7b00325, 2017.

Currently, we only consider soil gas flux measurement. Gas emission from soil-plant system is beyond the scope of current instrumental development. We also find incorrect expression in this part, and we will correct "with lower height (from 0.37 m to 0.2 m)" (Line 335) to "lower ratio of height to the bottom area".

Technical corrections:

1. The descriptions about how to calculate the minimum quantitative fluxes (Lines 270-285) should be the part of Materials and methods.

   We moved the calculation method for the minimum quantitative fluxes to the part of Materials and methods, as suggested to the reviewer.

2. Please specify what are the targets for the laboratory flux measurements?

   It was to confirm whether our newly developed instrument could capture the changes of each gas flux and whether the response when water is added, which is a major fluctuation factor of soil gas flux, could be captured. We will add this brief explanation in the manuscript.

3. The conclusion is just a summary and repeated descriptions of results.

   We also thought that there are some simple repetitions in conclusion. We merged “3.5 Future perspectives” and “4 Conclusion” into “4 Conclusion and Future perspectives”. The content had been much improved in the revised ma