

## Response to Reviewer #1

Thank you very much for your positive evaluation on our manuscript and the critical comments which helped us to prepare the improved version of our work.

Please find below our responses and clarifications (black font) and the proposed changes that will be made in the manuscript (blue font).

Page 3, line 89

*What SRI stand for? please write first*

This is the name of the producer, we will clarify this:

AS-210 Greenhouse Gas Autosampler (SRI Instruments Europe GmbH, Bad Honnef, Germany)

Page 3, line 90

*Molecular sieve*

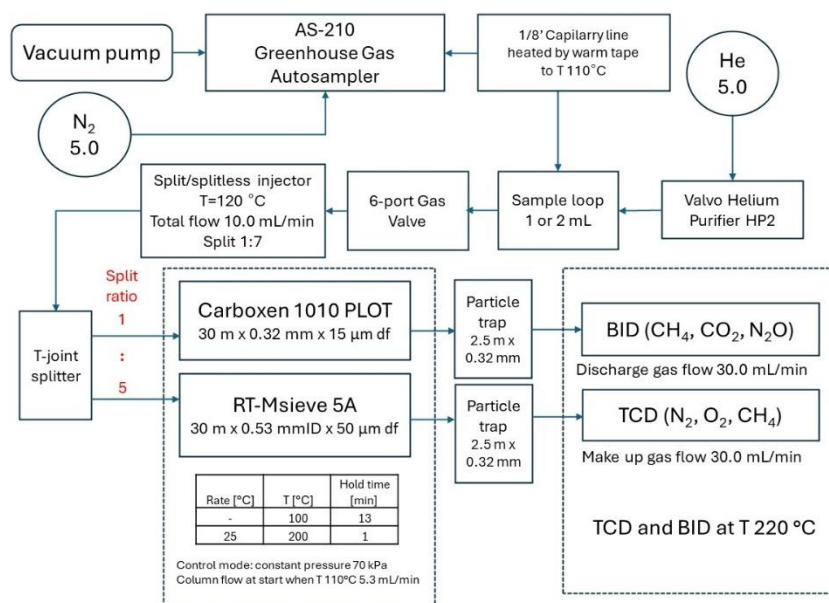
Yes, the own name of the column was used. This sentence will be corrected with precise information :

The GC separation columns used in this study were performed with a porous layer open tubular column (Carboxen 1010 PLOT) and a molecular sieve column (RT-MSieve 5A), which assured the full separation of the analysed gases.

Page 3, line 95

*The schematic configuration of GC system for simultaneously measurement of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O should be provided to get better understanding of the this measurement*

Thank you for this suggestion, this will be definitely helpful for the readers. The following scheme will be added to Section 2.1, as Figure 1



Page 3, line 115

*The statement of high sensitivity of BID and the usage of discharge flow, is there any references? (please cited in this statement)*

This is information from Shimadzu Instruction Manual. The respective citation will be added: Barrier Discharge Ionization Detector for GC-2010 Plus BID-2010 Plus Instruction Manual. Shimadzu Corporation 2013

Page 4, line 99

*Liquid N2 (LN2)*

It will be corrected.

Page 4, line 107 and 108

*Column has length 30 m, 0.32 mm inner diameter (i.d). Please provide also the information of thickness of stationery phase?*

This missing information will be added. Sentence will be corrected as below:

Additionally, using a t-joint, the injection sample was then divided between two porous layer open tubular capillary columns filled molecular sieve 5A (RT-MSieve 5A 30 m x 0.32 mm x 50 µm, Restek, USA, #18284) and fused silica (Carboxen 1010 PLOT 30 m x 0.53 mm x 0.15 µm, Supelco, USA, #24246).

Page 4, line 113

*Porous-layer open-tubular?*

Yes, phrase will be corrected to “the porous layer open tubular (PLOT) capillary column”

Page 4, line 124

*Please express with the consistence significant figures of the mL value (two digit or one digit behind coma)*

The values will be corrected to one digit behind coma.

Page 4, line 128

*the standard gas mixtures used in this study, is the certified standard gas mixtures or in-house standard gas mixtures developed by your institute?*

We used in-house standard of compressed air from Wrocław (Poland), which contained natural moisture (vapour) in the 10 liters gas cylinder. The second standard was ordered in Messer Polska Sp. z o.o. The special gas mixture is the commercially product prepared in Switzerland according to the norm ISO6141:2015. This standard was prepared in pure N<sub>2</sub>, without moisture, in volume of 8 liters. Based on information from Messer each of the standard contain filter F10, which protects outer valve to possible vapour or solid particles.

This information will be added to standards description.

Page 4, line 129:

Concentrations are the same as showed in the second columns in the Tables 1 and 2. The link to the values in respective tables will be added (Exact values in Table 1 and 2).

Gas	Concentration [% or ppm]
CH <sub>4</sub>	1.895 ppm
CO <sub>2</sub>	411 ppm
N <sub>2</sub> O	0.339 ppm
O <sub>2</sub>	20.946 %
N <sub>2</sub>	78.084 %

Page 5, line 149

*The peak label (name) for identification of gas component cannot be seen clearly (too small) both in the picture and inset of picture*

The previous version contained the picture obtained using GC Software Lab Solutions dedicated for GC made by Shimadzu. In the response for Reviewer's comments the data of chromatograms were exported from Lab Solutions as ASCII file and therefore converted to prepare new plots using Grapher Golden Software. Here we present the new Figure 2A and 2B (zoomed Figure 2A) which will be added to the revised article.

Figure 2A – presented below

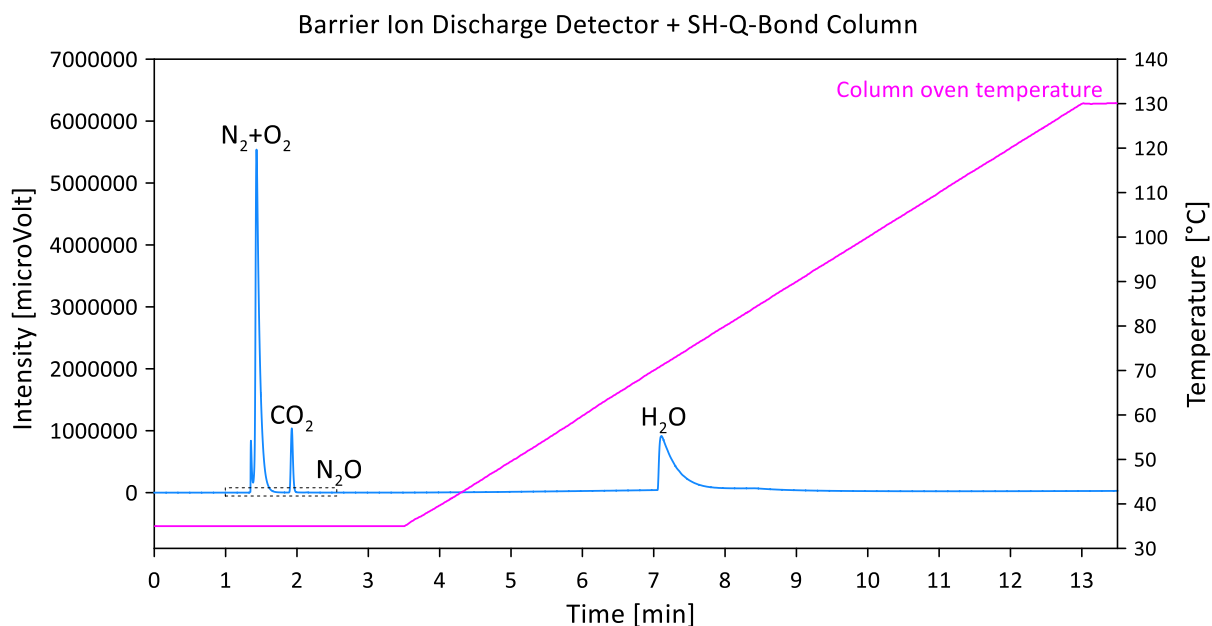
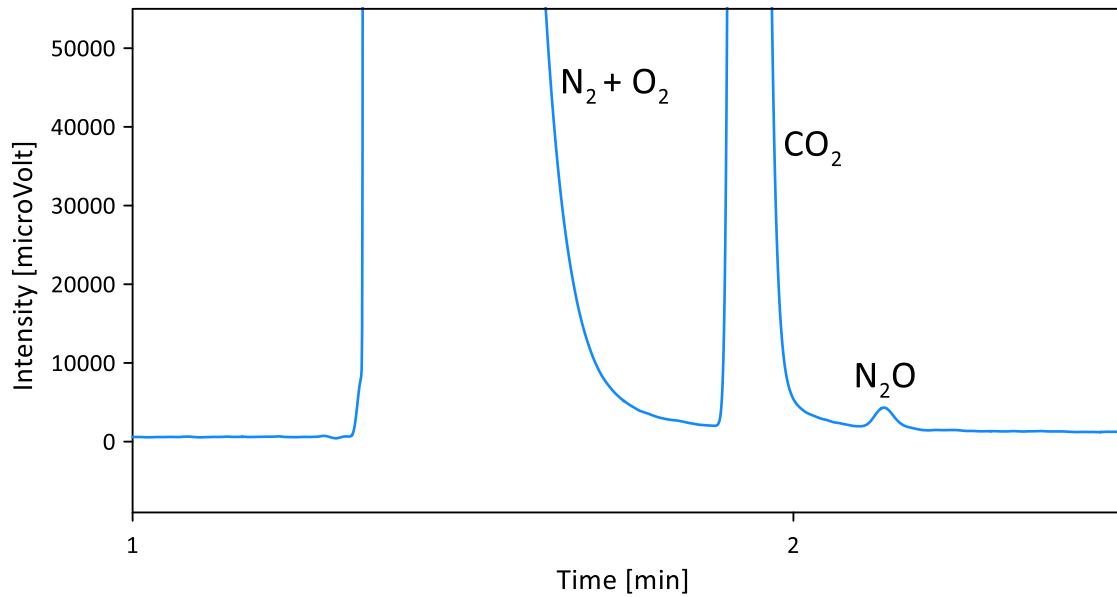


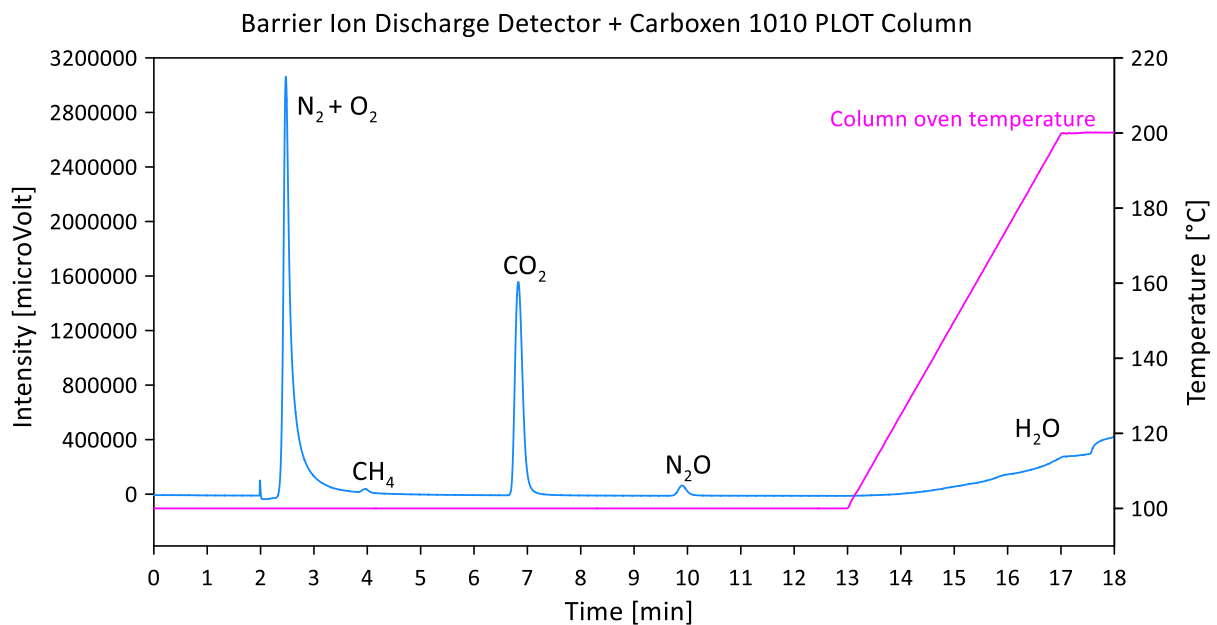
Figure 2B – zoomed figure 2A



Page 6, line 163

*The peak label (name) for identification of gas component cannot be seen clearly (too small) both in the picture and inset of picture*

New Figure 3 will be corrected as below:



Page 6, line 164

*Is the compressed air standard mixtures contained the moisture (dry or wet compressed air standard mixtures).*

*How the compressed air standard mixtures prepared should be explained in Materials and method section?*

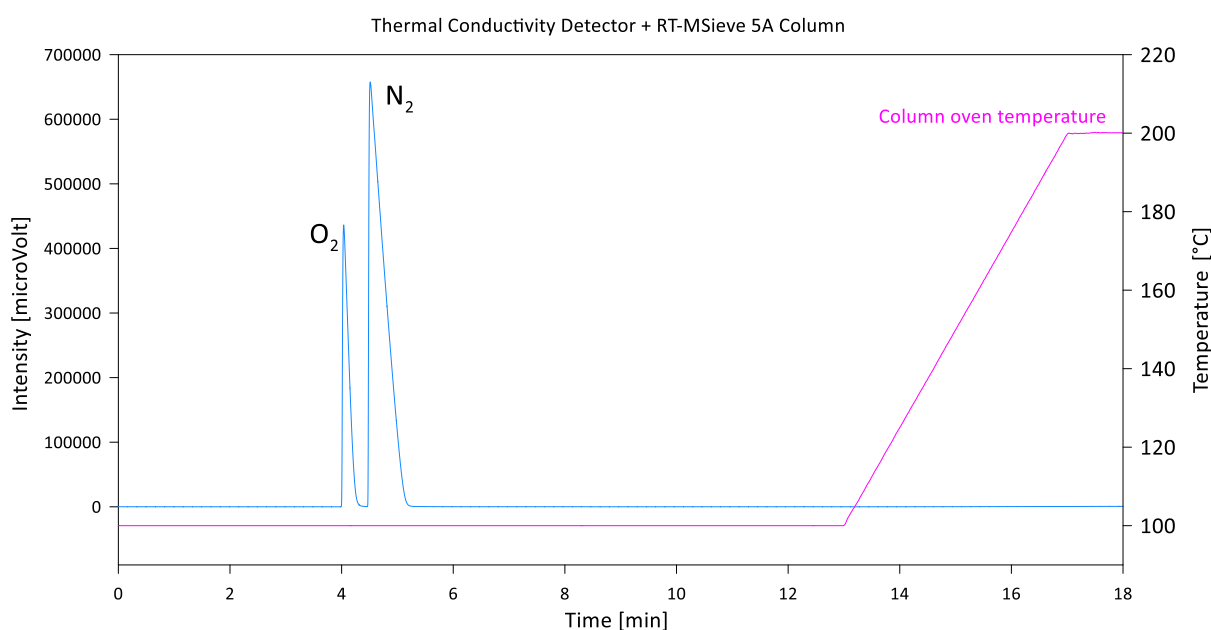
The compressed air contained natural moisture (water vapour). We analysed standard with natural moisture, because every sample collected from the natural conditions (field, soil, studies) has natural moisture (vapour). Our method is dedicated for such type of samples. This will be clarified in compressed air description.

Page 6, line 178

*In this section, can O<sub>2</sub> and N<sub>2</sub> be separated well by the GC system and detected by TCD? because in section 3.1, the O<sub>2</sub> and N<sub>2</sub> peaks overlapped when analyzed with GC BID as seen in the chromatogram in Figure 2.*

*Are the conditions and setup of the GC system in sections 3.1 and 3.2 different?*

Yes, in all configurations the system allow for separation of O<sub>2</sub> and N<sub>2</sub> by molecular sieve 5 A connected to TCD. The chromatogram with separation using this column will be added to manuscript as below:



The sections 3.1 contains chromatogram for tested configuration with using of the column SH-Q-BOND. The GC setup for preliminary tests of the SH-Q-BOND column connected to BID detector was different than GC setup for using Carboxen 1010 PLOT. Configuration of system with Carboxen 1010 PLOT was in details showed in the section 2.1, and was used to obtain results described in section 3.1, 3.2, 3.3, 3.4 and 3.5. We didn't describe the details of configuration with SH-Q-BOND column in the submission, because we didn't present any results regarding the accuracy of measurements using SH-Q-BOND column. On Figure 1 we showed example of the chromatogram (Figure 1) from SH-Q-BOND column and briefly described the analytical problems related to the separation of CO<sub>2</sub> and N<sub>2</sub>O and the lack of visibility of CH<sub>4</sub> in atmospheric concentration in the text. Conditions and setup of testing with SH-Q-BOND were exactly the same (injector, TCD, BID configuration, presence of MSieve 5A, the splitting), the only difference was oven temperature programme which was as below:

Rate	Temperature	Hold Time
-	35.0	3.50
10.00	130.0	0.50

We will add basic information of the setup with SH-Q-BOND as well specific conditions used during testing as an attachment Supplementary Materials.

*The separation chromatogram for analysis in the GC system in section 3.2 can be displayed*

Yes, N<sub>2</sub> and O<sub>2</sub> in our GC system can be separated with application of RT-MSieve 5A column with detection using TCD. The range of detection is from 0.2 to 100% (for N<sub>2</sub> and O<sub>2</sub>). This is very important especially for analyses of microbial samples (cultivation experiments) to control the aerobic or anaerobic conditions in the headspace gas. Moreover, in our system we have potential to separate argon from ambient air using cryogenic option (decrease of the column oven temperature to e.g. 0°C by liquid nitrogen (LN<sub>2</sub>)), because RT-MSieve 5A column can work in temperature range of -100 to 300°C. However, if it is necessary to perform an analysis of O<sub>2</sub> concentration at lower concentration (below 0.2%) and detect with BID, Carboxen 1010 PLOT column should be unmounted from the GC system – because its minimal temperature of working is 25°C. It is also possible to separate N<sub>2</sub> from O<sub>2</sub> using SH-Q-Bond column which can work at minimal temperature of -60°C.

Page 7, line 194

*For the better understanding, the data can be added with split ratio of 1,2 at 2 mL sample loops*

We decided not to do it, because the amount of water vapour which can be transferred through the column after injection of 2 ml of ambient air sample would be destructive for the column's filling phase (will shorten its proper functioning). Material used for Carboxen columns is known as very sensitive for water vapour – in the past its filling was used as water adsorber – please see:

Fastyn P., et al. 2003: [Adsorption of water vapour from humid air in carbon molecular sieves: Carbosieve S-III and Carboxens 569, 1000 and 1001 - Analyst \(RSC Publishing\)](#)

Page 7, line 189

*The detection limit of simultaneous analysis N<sub>2</sub>O, CH<sub>4</sub>, CO<sub>2</sub> using GC BID can be provided further to get the information of the characteristics of this GC system*

In case of CH<sub>4</sub> and N<sub>2</sub>O we are working at very low levels for BID, almost at the limit of detectability. For CH<sub>4</sub> it is 1.8 ppm and for N<sub>2</sub>O 339 ppb. The precision error of N<sub>2</sub>O at such low concentration is 5%. We are aware that this precision is not really satisfactory for measuring slight variations of ambient levels, however can be very well applied to determine environmental fluxes. We are still working on improvements, and we will test few more modifications, e.g. installing additional valve to allow for more gas measurements combinations and temperature controlling of sample loop and injection valves to better control the water vapour level. With this manuscript we intended to publish the first idea of the system with Carboxen column and BID detector already applicable for many environmental studies. Hopefully in near future we can report better precision.

Page 7, line 194

*Why the special gas mixture used in this analysis do not contain the same matrices as compressed air or ambient air (it means the CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O is in air matrices)*

This reason is the process of preparing the calibration mixture by the manufacturer. To obtain the appropriate accuracy, the manufacturer uses pure gas that doesn't contain the analyte, which needs to be added and diluted for final concentration.

Our aim was to use the GC system also for samples from laboratory incubation studies with partially anoxic conditions. For such experiments it is important to determine the low oxygen levels, therefore we needed a gas standards with no and low O<sub>2</sub> concentration. To reduce the amount of necessary standards tanks we simultaneously varied O<sub>2</sub>/N<sub>2</sub> levels and levels of GHGs possibly widest range of concentrations of all gases with lowest amount of tanks.

Page 10, line 238

*How about the comparison of precision from this GC system and CRDS Picarro in CO<sub>2</sub> and CH<sub>4</sub> measurement (standard deviation, %relative standard deviation, error)?*

For these comparison measurements we could only determine % error, because we measured atmospheric ambient air and it shows natural diurnal variations, we compared the results point by point and not the means and standard deviations. This could be only done this way because CRDS Picarro is dedicated mostly to ambient air samples, and it is not possible to insert special gas samples.

Page 10, line 248

*Regarding the upper detection limit, How much the upper detection limit of this simultaneous measurement of CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>O by the GC system in this study?*

We can state at this moment that concentrations which can be measured using our GC system are:

CH<sub>4</sub> 1.8 ppm to 4000 ppm (using BID), and 0.2% to 100% (using TCD)

CO<sub>2</sub> 411 ppm to 4000 ppm (0.4%) – according to Shimadzu specifications of BID detector

N<sub>2</sub>O 0.330 ppm (339 ppb) to 4000 ppm – according to Shimadzu specifications of BID detector

Additional information:

O<sub>2</sub> – 0.2 to 100% (using TCD)

N<sub>2</sub> – 0.2 to 100% (using TCD)