Response to Reviewer #2

General comments

This paper reports a method for analyzing three greenhouse gases simultaneously using a relatively simple GC system. The strength of this paper is that the developed method enables us to separate and quantify CH4, CO2, and N2O in air samples on a single column with a single detector. This technique would reduce sample size, time, and resources for the gas analyses. A shortcoming of this paper is that the precision or repeatability of the method is insufficient for atmospheric monitoring at background concentration level. In this regard, I think the title is misleading and should be revised to mean that the method is most suitable for source gases such as soil emission. Another concern is that the results of experiments for optimizing the GC setting are mainly discussed in the context of CV without further consideration of sensitivity of the detector. I believe combination of split ratio and sample size affect the amount/concentration of the target species delivered to the detector. For example, split ratio of 1 with 1-mL sample loop should give peak area that is equal to the area obtained at split ratio of 3 with 2-mL loop. In Table 1, I see results of CO2 and N2 are consistent with this idea, but it is not the case for other gases.

In summary, I recommend the publication of this paper after the authors address the issues above and specific points below.

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. Yes, definitely we proposed inappropriate title for this manuscript, this will be changed to: **"Simultaneous measurement of greenhouse gases (CH_4, CO_2 and N_2O) using a gas chromatography system".** Our initial idea was to test this system for ambient air measurements and although so far the precision is not sufficient for precisely measure the small atmospheric variations, it can be very well applied for measurements of atmospheric fluxes. We missed to review our title before the final submission.

The answer for questions regarding the sensitivity of the BID detector is based on the analysing S/N (signal/noise) ratio for the selected peak. Generally, S/N above 3 allows for identification of the peak, whereas S/N above 10 allows for quantitative determination of concentration. For 339 ppb N_2O analysis at split ratio 5 we achieved the ratio S/N usually between 12-15. The S/N ratio for 50 ppm N_2O standard was usually above 250. The method how we calculated SD and CV [%] is described in the detailed answers to Reviewer's comments. We presented the equations and method of obtaining the CV [%] for this data. The very high peak area of O_2 (Table 1, sample loop 2 ml, split 1) was incorrect (mistake during preparation of the final table) and the corrected value 4513907 will be inserted in the table, which is similar to value 4317080 obtained with split 1 and sample loop 1.

Generally, transferring of the sample from the columns should be very fast to avoid the flattening of the peaks. The sample is transported from the sample loop to the column at total flow speed. Total flow is mainly dependent on the split value: total flow = column flow + split ratio x column flow + purge flow (3ml/min). Therefore, the larger the split value, the faster the sample reaches the column. The narrower band in which the sample hits the column makes the peaks narrower and higher than with lower split values, even though less sample hits the column. However, this is one of the rules that must be checked experimentally each time to find appropriate values for the experiment being conducted.

In this method we also consider the amount of water vapour, which is transferred to the column. It is important to find the ideal compromise between the appropriate amount of gas supplied to the column and obtaining a strong signal, especially for the lowest concentrations using BID. Therefore, we assume that the peak area are not consistent with idea of the Reviewer mainly due to the difference in the speed of transferring through the columns. The additional calculation is showed below to compare all uncertainties. The difference between obtained peak areas is showed in the table as column C, and its absolute value in column D. Then in column E we showed that the value A (difference of the peak area expressed in %) is much higher for smaller peaks (CH_4 and N_2O, 23.30 and 28.66%, respectively). For larger peaks of CO_2, O_2 and N_2 the difference E is equalled around 5%. Therefore, it is very important to monitor parameter of S/N ratio when analysing low concentration samples.

	A	B	C	D	E [%]
Gas	Peak area at split 1 sample loop 1mL	Peak area at split 3 sample loop 2mL	C=A-B	Absolute value of C	E=(A*100)/D
CH_4	33294	25535	7759	7759	23.30
CO_2	10900323	10274295	626028	626028	5.74
N_2O	7801	5565	2236	2236	28.66
O_2	4317080	4513507	-196427	196427	4.55
N_2	16522678	17338000	-815322	815322	4.93

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

Specific comments

L40–41. I think "the most modern techniques and devices" should be adopted only if they provide results with precision and accuracy that are sufficient for the purpose.

We agree with this comment and we are aware it is not suitable for measuring minimal changes in greenhouse gas concentrations in ambient air over time (and such measurements are required for monitoring climate change). The advantage of our method is that it determines measurements in a wide range of concentrations (up to 4000 ppm, according to specifications of BID). Therefore, we will change the title, which in the original version is misleading and confusing for the readers. In the corrected version of the article, we will not specify limitations of the method only for ambient gases. Our aim is to show novel method of separation CH_4, CO_2 and N_2O with single detector and one column.

L46. I think a chapter from an e-book is referred here. Correct the citation information in the References section.

You have right. This is a chapter from the e-book. Citation will be corrected:

Zaman, M., Kleineidam, K., Bakken, L., Berendt, J., Bracken, C., Butterbach-Bahl, K., Cai, Z., Chang, S.X., Clough, T., Dawar, K., Ding, W.X., Dörsch, P., dos Reis Martins, M., Eckhardt, C., Fiedler, S., Frosch, T., Goopy, J., Görres, C.-M., Gupta, A., Henjes, S., Hofmann, M.E.G., Horn, M.A., Jahangir, M.M.R., Jansen-Willems, A., Lenhart, K., Heng, L., Lewicka-Szczebak, D., Lucic, G., Merbold, L., Mohn, J., Molstad, L., Moser, G., Murphy, P., Sanz-Cobena, A., Šimek, M., Urquiaga, S., Well, R., Wrage-Mönnig, N., Zaman, S., Zhang, J., Müller. C., 2021. Methodology for Measuring Greenhouse Gas Emissions from Agricultural Soils using Non-Isotope techniques. 11-209. In: Zaman M, Kleineidam K, Bakken L, Berendt J, Bracken C, Butterbach-Bahl K, Cai Z, Chang SX, Clough T, Dawar K, Ding WX, Dörsch P, dos Reis Martins M, Eckhardt C, Fiedler S, Frosch T, Goopy J, Görres C-M, Gupta A, Henjes S, Hofmann MEG, Horn MA, Jahangir MMR, Jansen-Willems A, Lenhart K, Heng L, Lewicka-Szczebak D, Lucic G, Merbold L, Mohn J, Molstad L, Moser G, Murphy P, Sanz-Cobena A, Šimek M, Urquiaga S, Well R, Wrage-Mönnig N, Zaman S, Zhang J, Müller C (2021) Measuring Emission of Agricultural Greenhouse Gases and Developing Mitigation Options Using Nuclear and Related Techniques Springer ISBN 978-3-030-55395-1, https://doi.org/10.1007/978-3-030- 55396-8.

L53–55. I think mass spectrometer is one of the detectors used in gas chromatography. I cannot understand why the mass spectrometry is specifically noted.

You have right, we will delete the part of the sentence “gas chromatography and/or gas chromatography coupled with mass spectrometry (GC-MS)”. Corrected version will be as below:

Thus the most reliable methods for checking samples in a very wide range of concentrations are chromatographic methods (Ekeberg et al., 2004).

L56–63. This paragraph is difficult to read because there is a lot of duplication. It seems that the authors try to list several types of “systems”, but they just mention detectors and GC columns.

You have right. We will correct the paragraph to avoid duplication. The new paragraph will be:

Gas chromatography with automated sampling injections is very common and user friendly. The most common GHG measurement systems have been developed with: a thermal conductivity detector (TCD) (measurement of CH_4 and CO_2), flame ionisation detector - FID (measurement of CH_4 and CO_2 using a methaniser), electron capture detector - ECD (for N_2O measurement) (Hedley et al., 2006; Loftfield et al., 1997; ; Wang and Wang, 2003).

L64. What does “natural wear” mean? Because the half-life of the radiation source Ni-63 is 100 years, I wonder other factors are meant.

The ECD detector cell is a consumable part. The cells should be replaced every 2-5 years. Moreover, the ECD is very sensitive to oxygen, which oxidizes the nickel foil. Using poor quality nitrogen, e.g. 5.0, which contains trace amounts of oxygen, is enough to shorten the cell's life. Before the ECD, oxygen traps are used that must be replaced regularly. In addition, the ECD gets dirty with the stationary phase from the column. In general, the thicker the film inside the chromatography column, the faster the cell wears out. The ECD also gets dirty simply with the measured analytes. The ECD cell can no longer be disassembled and cleaned. Theoretically, it can be sent to service for cleaning, but the price is so prohibitive that it is not worth doing (the price of cleaning ~ the price of buying a new cell). The ECD can only be annealed. On the other hand, the BID is a maintenance-free detector, by definition it does not get dirty due to the dielectric barrier.

L78. It is not clear what “and/or” means. In a certain case, both the two-column system and the single- column system are required?

You have right, this I misleading phrase. We will delete “and/or” and leave only word “or”.

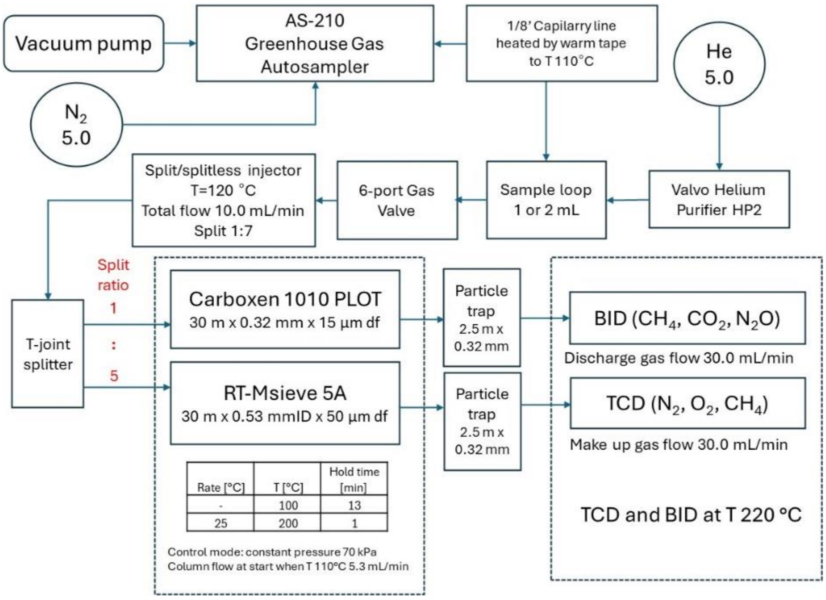
L81–83. This sentence is difficult to understand. For example, what is compared using "as well as"?

We will correct this sentence (confusing part of the sentence will be deleted). The corrected version of the sentence is:

This set-up using single column and single BID detector is commonly used for determination of CH_4 and CO_2 at very low atmospheric concentrations (Gruca-Rokosz et al., 2020).

L95. I recommend to add a schematic figure showing the GC system.

Thank you, this is a very good idea. We will add such scheme of the system to the revised manuscript.



L101–102. "warmed" at what temperature?

It was 110°C. This information will be added to the text and is showed on scheme of the GC system.

L102–103. This means gas sample with high moisture (e.g., soil gas) might cause problems. Is the system designed for already dried samples or does it withstand moist samples?

We tested Messer standard which doesn't contain water vapour as well environmental samples with natural, high moisture (collected from the soil after rainfall etc.). Generally for samples with significantly higher concentrations of CH_4, CO_2 and N_2O presence of moisture does not significantly affect the measurement. However, for samples with ambient concentrations of N_2O and with high moisture the baseline (and noise) should be checked to be sure that the signal of N_2O is enough to measure the concentrations. Shimadzu recommends that S/N (signal/noise) ratio should be above 10 to be sure that determination is correct. For 339 ppb N_2O analysis at split ratio 5 we achieved the ratio S/N usually between 12-15. The S/N ratio for 50 ppm N_2O standard was usually above 250.

The analysis of gas samples with natural moisture will lead to faster decay of the column filling (film) and accumulation of the solid parts in the particle trap, as a result, to a rise of the baseline, which has the greatest impact on the determination of samples with extremely low concentrations. For prevention we are actually testing different moisture traps (connected to ta capillary between GC and autosampler). This is to minimize the presence of water vapour inside the system (such as the sample loop).

L107–110. I guess the length and inner diameter of the columns are described here, but the splitting ratio of 1:5 cannot be achieved with the dimensions shown here. Add other parameters such as thickness of the inner coating of the columns. Also, combination of column and detector should be clearly described or shown using a figure. Is the TCD connected to the molecular sieve column?

We will modify the description in the text as well showed basic information on GC scheme. The corrected text will be as below:

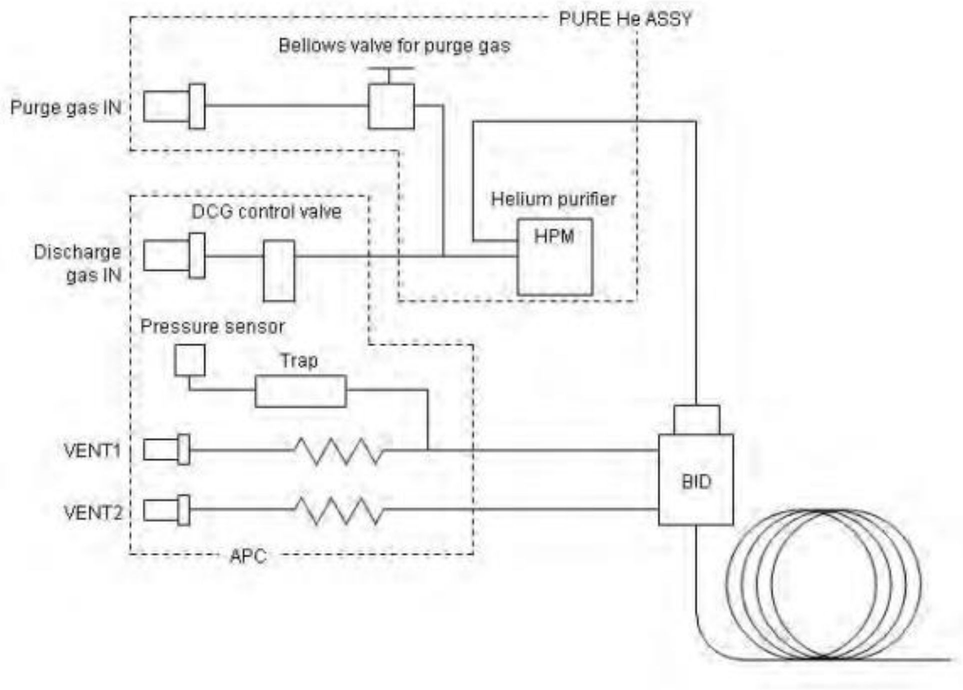
Additionally, using a t-joint, the injection sample was then divided between two porous layer open tubular capillary columns filled molecular sieve 5A (RT-MSieve 5A 30 m x 0.32 mm x 50 µm, Restek, USA, #18284) and fused silica (Carboxen 1010 PLOT 30 m x 0.53 mm x 0.15 µm, Supleco, USA, #24246). The dimensions of the columns were selected to achieve a splitting ratio of 1:5, directing most of the sample to the Carboxen 1010 PLOT and BID. Corresponding calculations were performed in Shimadzu AFT (Advanced Flow Technology) software.

L111. Quantitative information should be given instead of "extremely low baseline noise".

For example the baseline noise for measurement of 339 ppb N_2O with split 5 is 27.53 and S/N is equalled 11.65.

L115–117. It is not clear at which position the discharge gas is added to the flow system.

Discharge gas is connected and passed from the top, it is used to create plasma, below is a technical scheme from Shimadzu manual instruction:



Please see also link to the Schimadzu website BID | Research & Development | SHIMADZU CORPORATION with details regarding BID.

L117. I cannot understand what this sentence means.

On the TCD channel satisfactory sensitivity was achieved with standard settings - current 80 mA value and make-up gas 8 mL/min. Generally, in TCD, sensitivity can be adjusted by changing the type of carrier gas, make-up and current.

This will be clarified in the manuscript.

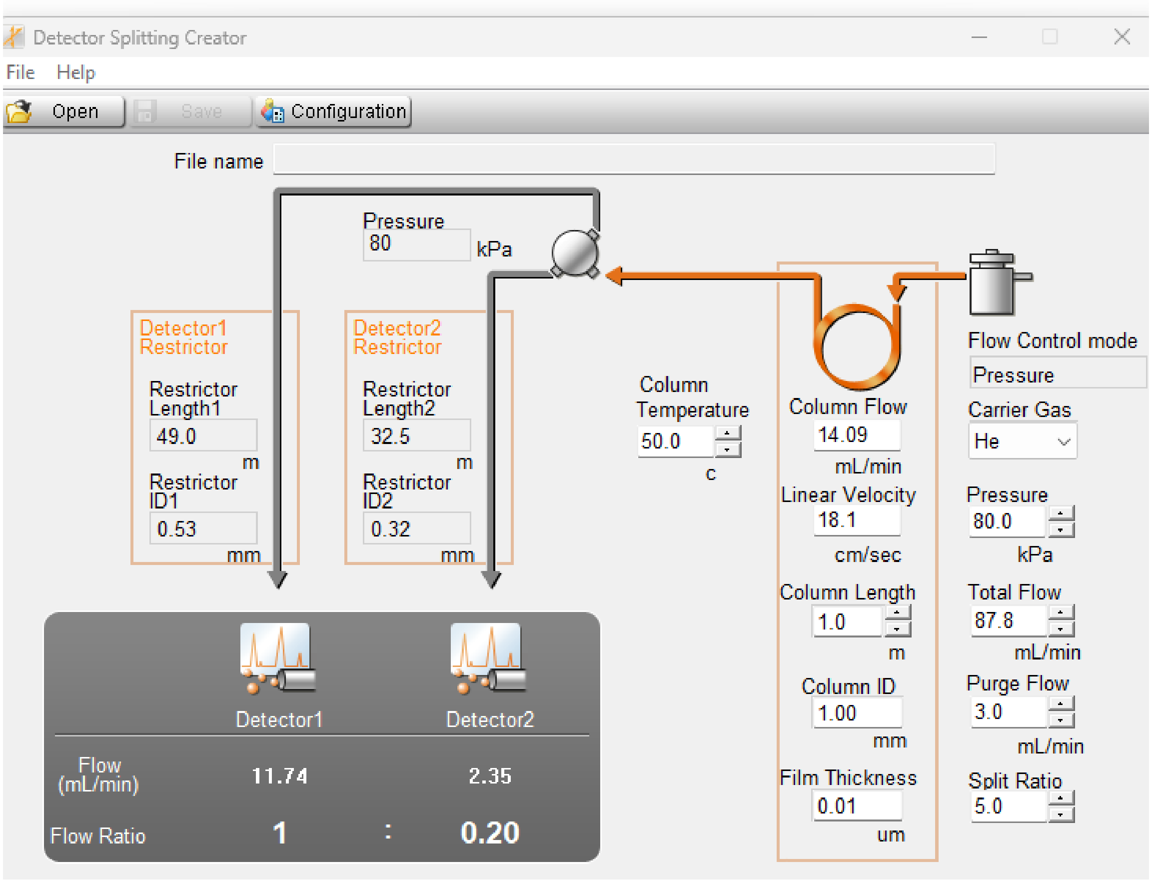
L121–122. Do the authors mean the final temperature of 200C is kept for 1 min? Revise the sentence.

Yes. The final temperature is called "hold time". The temperature program is also now showed on the figure with GC Scheme.

L123–124. As described in the previous section, the flow after sample injection was divided into two columns. Are these flow parameters common to them?

It is necessary to add 2.5m particle traps with a diameter of 0.32mm to the columns. For a column with a diameter of 0.32mm, we added 2.5m which gives 32.5m. The column of 0.53mm should be theoretically extended by 19m, therefore 2.5m x 0.32mm gives the same resistance as 19m x 0.53mm, therefore the second column has a entered length of 49m. The flow parameters are very close to those showed on picture:

This will be added in the manuscript:



File name

Pressure 80 kPa

Restrictor Length1 49.0 m

Restrictor ID1 0.53 mm

Restrictor Length2 32.5 m

Restrictor ID2 0.32 mm

Column Temperature 50.0 c

Column Flow 14.09 mL/min

Linear Velocity 18.1 cm/sec

Column Length 1.0 m

Column ID 1.00 mm

Film Thickness 0.01 um

Flow Control mode Pressure

Carrier Gas He

Pressure 80.0 kPa

Total Flow 87.8 mL/min

Purge Flow 3.0 mL/min

Split Ratio 5.0

	Detector1		Detector2
Flow (mL/min)	11.74		2.35
Flow Ratio	1	:	0.20

L140. Decrease from what temperature?

What we mean here is a quick stabilization of the oven temperature. Temperature stabilization. 35° is the lowest temperature that can be practically achieved in our laboratory without using liquid nitrogen for cooling. The temperature reduction that we mention here concerned the standard temperature of 40°C (at which we most often tested the SH-Q-Bond column).

This will be clarified in the manuscript.

Figures 1 and 2. Labels on the x and y axis are difficult to read.

The Figures are corrected with larger size fonts.

L158. Does "vapour" mean water vapor? Please specify. Also, do the authors mean that the retention time of H2O peak shown in Figure 2 changes depending on the amount of water in the sample?

Yes, vapour means water vapour (natural moisture). The H_2O peak appeared usually when the oven temperature reached 115°C – it is not perfectly visible because the oven temperature was rising (and thus the baseline level too).

L165. It is not clear to me for what purpose the authors made experiments with different combinations of split ratio and sample size. I think the amount of sample (and water vapor) injected to the column is determined by the two parameters. For example, if 1 mL sample is processed with split ratio of 1, the amount of sample injected to the column is 1×1/(1+1) = 0.5 mL. If 2 mL sample is processed with split ratio of 3, the amount would be 2×1/(1+3) = 0.5 mL, which is the same as the first case.

We tested different split settings and loop volumes to find a compromise between the amount of sample analyzed and the speed of sample transport to the chromatography column. If we use a 2 mL loop, we can dose a larger amount of sample onto the column, which we want to transport to the column as quickly as possible. If we do it slowly, then the peaks will be broad and low, we will lose sensitivity.

L177 and elsewhere. Since TCD, FID, and ECD are acronyms of "xxx detector", notation like "TCD detector" is awkward.

Thank you for this comment. We will correct these mistakes.

Table 1. It seems "SD" does not show the standard deviation of peak area, because dividing this value with "area" gives much smaller CV value. This is also the case for Tables 2 and 3. Please correct.

You have right. We suppose that these ambiguities resulted from the different way for presentation of the data (SD and CV) and lack of a clear presentation of the used calculation method in the table's legends. In the original manuscript SD showed the standard deviation of the calculated concentration. First, we measured the same standard 3, 4, 5, 10 or 20 times. Then, this raw data of measured peak area was used for calculation of mean peak area typical for concentration at different and known levels (calibration). Concentrations were calculated according to equation:

Concentration [%] = (measured peak area * known concentration of the standard) / (calculated mean peak area from 3, 4, 5, 10 or 20 analyses)

SD = standard deviation of concentrations calculated for 3, 4, 5, 10 or 20 analyses

CV = (SD * 100) / (mean peak area from 3, 4, 5, 10 or 20 analyses)

However, we corrected tables according to the idea proposed by the Reviewer. Tables 1, 2 and 3 after correction and re-calculation to present SD of the measured area are at the end of the response to Reviewer 2. We will add clarification regarding calculations (SD, CV) used for this study at the bottom of each table. We will also modify sentences, where the range of CV needs to be revised (line 169- phrase "and ranged from 0.57 to 1.87 % for the 2 mL sample loop" and line 170 – phrase "and ranged from 7.09 to 12.67 %, compared with the 1 mL sample loop"). These changes do not affect the conclusions from the obtained results.

L185. Specify "the main atmospheric gases".

We mean O_2 and N_2. We will correct the paragraph because the measurement of these two compounds was performed with TCD – in our system is dedicated to a gases of higher concentrations than 0.2% (2000 ppm). Therefore the comparison of the SD obtained from BID which is much more sensitive in our opinion it is not recommended. New paragraph will be as below:

The gases analysed using the TCD detector, O_2 and N_2, were characterised by a narrow CV ranging from 0.10 to 0.39 %. The highest CV (0.39 %) was observed for the N_2 measurement with the sample loop 2 mL, where the peak area was very large. The results of the measurement (peak area, SD, CV) are presented in Table 1.

L202. What does "reportable results" mean?

This was a mistake, most probably made by autocorrection. We should use the phrase "repeatable results" – the achieved precision of N_2O analysis is considered as sufficient for determining environmental gas samples, e.g. from soil experiments and measurements of gas emissions from natural sources such as peat bogs.

L212–214. If the authors use the system for soil gases, should the sample be dried before analysis?

No, we recommend to use original sample and eventually trap the water moisture (using sorbents) – but these sorbents needs to be tested in order to check potential influence on the concentrations of other gases (e.g. sorption of CO_2 or N_2O). The best way is to analyse pure samples, and find the conditions when water moisture does not affect the precision of GC measurements.

Table 3. Is the area for N2O at split ratio of 3 correct? It is extremely higher than those obtained at split ratio of 4 and 5.

Thank you for this comment. This is mistake. We will correct the table. The correct value of area= 5552, SD=30.6, CV [%]=9.02.

L234 split ratio of 4

It will be corrected.

L235–237. I cannot understand these sentences. Do the authors mean the "GC" results of CO2 obtained after 25/11/23 18:00 (Figure 3) have a systematic error due to a shift in sensitivity of the detector?

Yes, some shift occurred, eg. due to change in air moisture, this was Friday evening after all people left laboratory. But importantly, with new calibration the both measurements would stay in very good agreement.

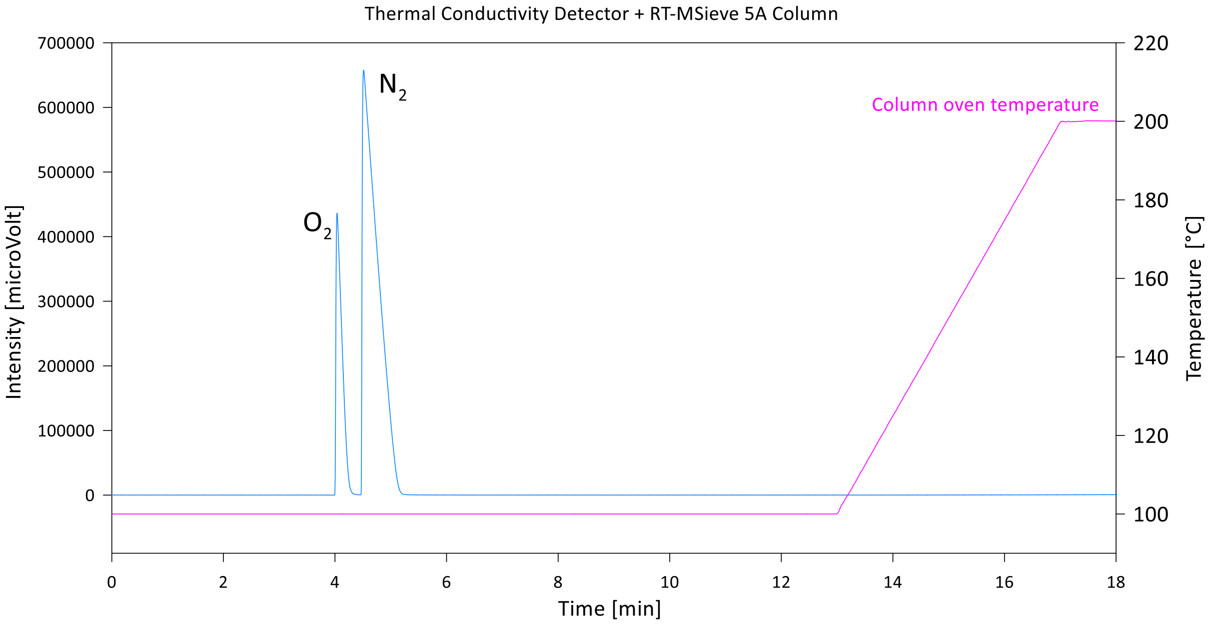
One of the reason why Picarro is much more precise could be amount of sample analysed. Picarro analyses at least 20mLof sample for constant measurement, which make a single measurement every few seconds. Our GC system is sampling air in the volume of 1 or 2 mL. By design, such a measurement will not be as accurate in the long-term run as a device specifically dedicated to analyzing CO_2 or N_2O fluctuations in the atmosphere. Our system is not limited to low concentrations of GHG's, which is why it stands out from other special devices.

L243–245. Although it is not clear what "typical N2O measurements" means, 5% error is NOT satisfactory if one would like to know diurnal/seasonal cycle or secular trend of atmospheric N2O at background level.

Yes, we agree with this comment. However, in soil sciences such error is accepted by scientific community.

L250–251. Since no TCD chromatogram is shown, this statement cannot be verified.

We will add the chromatogram with TCD to the manuscript as below:



L261. Consider other quantitative or scientific expression for "very good".

Instead of the expression "very good" we will use: "time interval enabling measurement of each gas separately without the effect of peak overlapping"

L268. water vapour?

Yes, we will correct the sentence.

Table 1: Peak area, SD (standard deviation) and CV (coefficient of variation) of standard atmospheric gas measurements at split ratios 1, 2, 3, 4, and 5 with 1 mL and 2 mL sample loops

			Sample loop 1 mL					Sample loop 2 mL		
Gas	**Conc.**		**Split**					**Split**		
			1	**2**	**3**	**4**	**5**	**3**	**4**	**5**
		Repetitions	**n=3**	**n=10**	**n=20**	**n=20**	**n=20**	**n=10**	**n=10**	**n=10**
CH_4	**1.895 ppm**	**Area**	33294	24249	25271	20085	16269	25535	23901	23195
		SD	2580	802	1859	1365	1394	386	381	640
		CV [%]	7.75	3.31	7.36	6.79	8.57	1.51	1.59	2.76
CO_2	**411 ppm**	**Area**	10900323	8015901	5742835	4525868	3658827	10274295	8037126	6295494
		SD	99092	84289	162281	58578	79062	155997	45587	117747
		CV [%]	0.91	1.05	2.83	1.29	2.16	1.52	0.57	1.87
N_2O	**0.339 ppm**	**Area**	7801	4732	3572	2565	2080	5565	4470	3306
		SD	714	955	554	289	323	705	317	329
		CV [%]	9.15	20.19	15.51	11.26	15.55	12.67	7.09	9.95
O_2	**20.946%**	**Area**	4317080	3030077	2147582	1660466	1340040	4513907	3320157	2523219
		SD	9241	5136	7177	4196	2088	10598	3298	7454
		CV [%]	0.21	0.17	0.33	0.25	0.16	0.23	0.10	0.30
N_2	**78.084%**	**Area**	16522678	11587989	8205177	6343410	5119796	17338000	12767184	9709091
		SD	42456	21960	27025	16376	8251	31998	12603	38248
		CV [%]	0.26	0.19	0.33	0.26	0.16	0.18	0.10	0.39

Table 2: Peak area, SD (standard deviation) and CV (coefficient of variation) of special gas mixture measurements at split ratios 3, 4, and 5 with sample loops 1 mL and 2 mL

			Sample loop 1 mL			Sample loop 2 mL		
Gas	**Conc.**		**Split**			**Split**		
			3	**4**	**5**	**3**	**4**	**5**
		Repetitions	**n=5**	**n=4**	**n=3**	**n=10**	**n=10**	**n=10**
CH_4	**10 ppm**	**Area**	149922	118357	96007	278296	207227	161265
		SD	831	133	318	1067	707	2895
		CV [%]	0.55	0.11	0.33	0.38	0.34	1.79
CO_2	**1000 ppm**	**Area**	13522596	11079679	8993195	21485425	17323467	13525917
		SD	331786	341314	184053	337763	331554	435439
		CV [%]	2.45	3.08	2.05	1.57	1.91	3.22
N_2O	**50 ppm**	**Area**	629251	497331	402025	1171624	867747	673486
		SD	2801	1782	729	9975	11510	14360
		CV [%]	0.45	0.36	0.18	0.85	1.33	2.14

Table 3: Peak area, SD (standard deviation) and CV (coefficient of variation) of direct measurements of laboratory air at split ratios 3, 4, and 5 with sample loop 2 mL

			Sample loop 2 mL		
Gas	**Conc.**		**Split**		
			3	**4**	**5**
		Repetitions	**n=20**	**n=20**	**n=20**
CH_4	**1.895 ppm**	**Area**	27007	24995	23355
		SD	919	1047	957
		CV [%]	3.40	4.19	4.10
CO_2	**411 ppm**	**Area**	8297069	6787524	5351342
		SD	190315	89672	97529
		CV [%]	2.29	1.32	1.82
N_2O	**339 ppb**	**Area**	5736	4479	3359
		SD	232	139	111
		CV [%]	4.04	3.11	3.31
O_2	**20.95%**	**Area**	4466737	3319922	2493245
		SD	6357	4415	4366
		CV [%]	0.14	0.13	0.18
N_2	**78.08%**	**Area**	17054807	12671953	9517713
		SD	23464	15061	15702
		CV [%]	0.14	0.12	0.16