C1: The authors present a non-commercial automated chamber system for measurement of soil greenhouse gas fluxes and compare its performance to manual chamber measurements. This is a nice set-up and experimental design presented and such data regarding the performance of automated chamber systems are relevant since automated systems start to become more widespread in greenhouse gas flux studies. However, there are some details and information in the manuscript about the automated chamber system that are either missing or not explained in such a way that I understood them. Also, despite the authors having generated a very good dataset, the discussion could benefit from more depth. I recommend major revision to strengthen this paper for publication.

Answer C1: We really appreciate the Reviewer's comments to improve the quality of the manuscript. Changes in the text are highlighted in yellow.

General comments

C2: The objective of the paper is to present an "innovative non-commercial soil GHG measurement system". However, I did not understand what is exactly new about this system. The 'Queensland design' described has already been in use since 2000 and has been referenced e.g. in the "Nitrous oxide chamber methodology guidelines" by de Klein & Harvey (2015). Please highlight more the innovative updates to the system.

Answer C2: The innovation of our automated chamber system is based on the majority of the electronic components that control the system are devices based on the Arduino system that allows an easy integration in the R script (developed by ourselves) that controls the system. (L170-179)

"This R script, governed by the time taken by the analyser to process the sample, can be easily modified by setting the total number of chambers or, if it is necessary to work by blocks, by setting the number of blocks and the number of chambers per block. One of the advantages of this system is the self-made multiplexer that allows to modify the number of chambers easily compared to other multiplexers like Gasera Multipoint Sampler (Gasera Ltd, Finland) which has a close configuration of 8 or 12 channels. Moreover, the use of relay boards that could be configured by Arduino or easily integrated into the R script as the selected ones, as an alternative to control modules, for example, I-7060D (ICP DAS CO, LTD) that only have four channels per module, simplifies the configuration of the script, since just with one board it's possible to handle all the chambers."

C3: In the abstract and the last paragraph, the authors refer to Mediterranean conditions. I am not sure how important this is with regard to the chamber methodology itself. What are environmental conditions that the automated chambers still have to properly function in which are different from automated chamber studies from other regions? What is challenging about measuring soil GHG fluxes in Mediterranean conditions?

Answer C3: We agree with the Reviewer's comment that the climate conditions, such as Mediterranean conditions, are not an important issue in developing chamber's methodologies.

We modified the abstract and final paragraph of the introduction section. (L35; L92-98)

C4: Lines 268 – 277: This discussion is a bit too vague for me. The authors have started some really good discussion points, but they didn't really explore them further in depth with their data. Instead of saying that the chamber dimensions could explain flux differences, why not use the measurement data to further explore this subject, e.g. by calculating the Minimum Detectable Flux according to Christiansen et al. (2015) and Nickersen (2016). This would be especially interesting for CH4 with fluxes fluctuating around zero. The MDF specifically includes chamber design and chamber closure time. It also includes the analytical precision of the gas analysis system. This is a point I am completely missing here. The authors compare a photoacoustic multigas analyzer and a gas chromatograph which differ significantly in their analytical precision. Does this significantly impact the results? A question regarding the effect of air-mixing: Could the fans have flushed out a bit of air from the soil pore system, thus contributing to the higher flux estimates?

Answer C4: We appreciate the Reviewer's comment and we calculate the MDF for both chamber systems. MDF for the automated chamber system were 1.209 mg CO₂-C m⁻² day⁻¹, 0.012 mg CH₄-C m⁻² day⁻¹ and 0.059 mg N₂O-N m⁻² day⁻¹, while for the manual chamber system, MDFs values were 14.050 mg CO₂-C m⁻² day⁻¹, 0.143 mg CH₄-C m⁻² day⁻¹ and 0.071 mg N₂O-N m⁻² day⁻¹.

Regarding the possible effects of fans on the fluxes estimation due to a flush phenomenon that forces the air coming from the soil to the chamber, in the development test carried out during the chamber set-up, we didn't find a clear effect of using fans or not on fluxes estimation. As we show in the next figure (Fig.1R), for more than 30 measurements, there is no clear effect of using fans against not using them on soil CO_2 , CH_4 and N_2O fluxes. These results are in line with the results published by Maier et al. (2022) in a guideline for soil gas measurements with non-steady-state chambers.

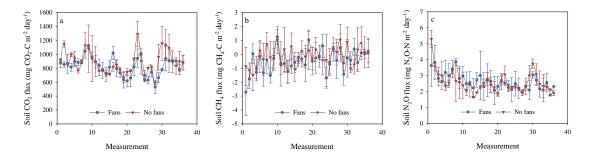


Fig. 1R. Effects of using or not using fans on soil a) CO_2 , b) CH_4 and c) N_2O fluxes. Blue line represents fluxes measurement with chamber fans activated. Red line represents fluxes measurement with chamber fans deactivated.

Moreover, we modified the discussion section to include the MDF as an explanation of the differences in emissions observed between chamber systems. (L299-309)

"In line with the previous explanation, the Minimum Detectable Flux (MDF) following the equation presented by Nickersen (2016) was calculated for methodologies. The MDF method not only considered the accuracy of the analyser but also considered the area and volume of the chamber and the enclosure time, factors that are different between both methodologies compared in this work. The MDFs for the automated chamber system were 1.209 mg CO₂-C m⁻² day⁻¹, 0.012 mg CH₄-C m⁻² day⁻¹ and 0.059 mg N₂O-N m⁻² day⁻¹, while for the manual chamber system, MDFs values were 14.050 mg CO₂-C m⁻² day⁻¹, 0.143 mg CH₄-C m⁻² day⁻¹ and 0.071 mg N₂O-N m⁻² day⁻¹. MDF was greater for the automated chamber system for the three gases, considering a similar enclosure time of 20 minutes and an average air temperature during the experiment of 20° C. The differences in MDF found between both methodologies was another factor that explained the greatest fluxes values observed under the automated chamber system. " Nickerson, N. (2016). Evaluating gas emission measurements using Minimum Detectable Flux (MDF). Eosense Inc., Dartmouth, Nova Scotia, Canada.

Maier, M., Weber, T. K., Fiedler, J., Fuß, R., Glatzel, S., Huth, V., Sabine Jordan, S.;Jurasinski, G.; Kutzbach, L.; Schäfer, K.; Weymann, D. & Hagemann, U. (2022). Introduction of a guideline for measurements of greenhouse gas fluxes from soils using non-steady-state chambers. Journal of Plant Nutrition and Soil Science, 185(4), 447-461.

Specific comments

C5: Lines 29f.: I disagree with this sentence. It is possible to resolve short-term emission events with manual chambers. The common low sampling frequency is simply a result of the high labor-intensity of this method. You explain this point very well in the introduction.

Answer C5: We agree with Reviewer's comment and we modified the abstract to clarify it. (L29-32)

"However, manual chambers are characterised by low sampling frequency, typically one sample per day is considered a high sampling frequency. Therefore, a great deal of effort is required to monitor short-term emission events such as fertilisation or rewetting"

C6: Lines 39ff.: Maybe include some numbers in the abstract, e.g. how much higher were the measured fluxes.

Answer C6: We modified the abstract as the Reviewer suggested. (L40-41)

"The automated system reported soil GHG fluxes up to 58 and 40% greater for CO_2 and N_2O fluxes compared to the manual chamber system"

C7: Line 47: Use the latest IPCC assessment report from 2023. There the entire AFOLU sector is listed with 22 % contribution.

Answer C7:We modified the text following the Reviewer's suggestion. (L48-49)

C8: Lines 83 - 86: I would include two more aspects here: 1) As a result of the constraints lower spatial coverage compared to manual chambers, and 2) also more and more companies start selling automated chambers systems; it is becoming a market

Answer C8: We have included both aspects suggested by the Reviewer. (L85-91).

"However, this method requires costly equipment and skilled operators and implies different infrastructure constraints, factors that result in lower spatial coverage compared to what can be achieved with manual systems. Moreover, these automated chamber systems are beginning to be manufactured and distributed by companies dedicated to the manufacture of gas analysers, with the limitation of being close systems to be modified. Based on that situation, over recent decades, several groups have crafted automated systems (Lognoul et al., 2017, Lawrence and Hall, 2020)." *C9: Lines* 176*ff.*: *Despite the reference, it would be good to include information if a collar was used with the manual chambers and the insertion depth.*

Answer C9: We have included in the text detailed information about manual chamber collars as the Reviewer suggested. (L195-196)

"Each chamber was placed same diameter PVC collar inserted 0.05 m into the soil"

C10: Lines 190ff.: Include the source for the climate data.

Answer C10: We have added the climate data source to the text following the Reviewer's comment. (L210-211)

"The meteorological data were obtained from a meteorological station situated at 0.5 km from the experimental site."

C11: Lines 209ff.: There are some words mixed up/writing mistakes which make this paragraph a bit hard to read.

Answer C11: We rewrite the text to clarify it. (L228-233).

"The second step of the evaluation experiment consisted of assessing the impact of the sampling time (i.e. hour of the day) and sampling frequency (i.e. 16 daily measurements vs 1 daily measurement for the automated and the manual chamber system, respectively) on the estimation of the soil gas fluxes. For that propose, from 22 of May 2023 to 29 of June 2023, soil CO₂, CH₄ and N₂O fluxes were measured simultaneously by the manual and automated chamber systems in the same field experiment "

C12: Line 345: Was there a specific reason for sampling at 6:00 GMT?

Answer C12: 6:00 GMT corresponds to 08:00 am in Spain, during summer time. There are two main reasons to perform soil gas sampling at 08:00. The First reason is related to the schedule of other important agricultural practices such as irrigation. In terms of reducing the impact of irrigation on maize photosynthesis, irrigation is applied in the early morning hours (when nighttime irrigation is not possible), starting at 08:00 am and lasting up to 6 hours when water requirements reach maximum values. The second reason is due to in summer months, at midday, air temperature can reach values higher than 35-40 °C. These high temperatures are not comfortable to work in the field, and as a general recommendation, fieldwork at that hour should be avoided if possible. Therefore, in other to maintain homogeneity in the sampling hour, this is set according to the most restrictive period, in this case, the summer period.

C13: Lines 346f.: Wu et al. (2021) state 10:00 am. Do you consider 6:00 really close to that?

Answer C13: As we explained in the comment before, 6:00 GMT correspond to 08:00 am during summer time in Spain. From our point of view, a two-hour difference, it's no such a time difference and for that reason, we consider that our sampling time is close to the sampling time of Wu et al. (2021). Moreover, we specify in the text that 6 GMT correspond to 8 am. (L395)

C14: Lines 357f.: You don't say anything about the costs in your manuscript. Compared to what is your system more affordable?

Answer C14: We had some information about the cost of the system following the Reviewer's recommendation. (L142-143).

"The cost of each chamber, including the solenoid valve and the sampling line is $600 \notin$."

C15: Section 2.5: I presume you used a linear fit in equation 1? The molar weights in the brackets are not correctly displayed. You have to write C-CO2, C-CH4, and N-N2O. The R version used is the same as mentioned previously in the manuscript? Did you use any special R packages for the flux calculation or just the base packages?

Answer C15: Yes, we used a linear fit to calculate the fluxes and we didn't use any specific packages for that purpose, just the base packages. R version is the same for fluxes calculations and for running the script that controls the system.

We have corrected the error related to molar weight and rewrote the text to clarify this section according to the Reviewer's comment. (L253-262).

"where Fit represents the linear increase of gas concentration in the chamber over the enclosure time, MW is the molar weight of the atom in the gas molecule (i.e. 12 g mol \neg -1 for CO2-C and CH4-C and 28 g mol \neg -1 for N2O-N), p is the atmospheric pressure in Pa, h is the chamber height in m, R is the ideal gas constant in J K \neg -1 mol \neg -1, T is the chamber air temperature in K, fT is the correction factor of time units, 1440 minutes day \neg -1 and fU is the unit correction factor, 10 \neg 3. Cumulative soil CO2, CH4 and N2O emissions were calculated using the trapezoid rule (Levy et al., 2017). Comparison between systems was done by linear fitting considering only soil gas fluxes that presented a R2 higher than 0.8. Moreover, comparison in cumulative emissions between chamber system over one month was evaluated by one-way ANOVA. All analyses were done using the R statistical software version 4.2.2 (R Core Team, 2022)."

C16: Figure 3: In this figure it looks like the system is not a closed-loop system but the air drawn from the chambers is simply discarded to the atmosphere. Could this be one contributing factor to the higher fluxes measured with the automated chambers, e.g. pressure fluctuations despite the installed chamber vent? How long were the sampling lines and how long were your purge times?

Answer C16: As the Reviewer properly appreciate, the system is an open-loop that after the sample passthrough the analyser it's discarded. We did not test the chamber system in a close-loop, so we cannot guarantee that this could be a possible reason for the higher fluxes observed for the automated chamber system.

However, Hutchinson and Livingston (2001) stabilized that including a vent is the solution to avoid pressure or volume changes in non-steady state chambers. The inclusion of a vent reduces the disturbance associated with the pressure or volume changes that are responsible for changes in the soil diffusion process between soil and the internal chamber atmosphere, which may result in significant changes in the mass flow that governs the soil fluxes.

Sampling lines are 50 m long, yielding 630 mL. The purge time of each sampling is 90 seconds. The sampling line only needs 15 seconds to be purged, however, our purge time or specifically the time that each line is active corresponds to the analyser frequency, one analysis each 90 seconds. As we showed in Figure S1, each valve was open 30 seconds before the analyser was

ready, giving the system enough time to purge the line and thus avoid contamination with the dead volume of the sampling line.

Hutchinson, G. L., & Livingston, G. P. (2001). Vents and seals in non-steady-state chambers used for measuring gas exchange between soil and the atmosphere. European Journal of Soil Science, 52(4), 675-682.

C17: Line 370: I don't see how you can easily modify the number of chambers (also compared to other automated system). It is not only about the chamber number itself. What about power consumption, adjustment of the sampling protocol, length of tubing in the field, quick movability in case of field operations?

Answer C17: Modify the number of chambers it's just a matter of activating more o fewer channels in the relay board and also modifying the number of chambers per block in the R script. Compared to other systems like Gasera Multipoint Sampler (Gasera Ltd, Finland), which has a close configuration of 8 or 12 channels, our system allows to work with a higher number of chambers just replacing the 16 channels relay board for another relay board with extra channels. In terms of power consumption, including more chambers has a low impact, since solenoid valves have a small consumption only when activated. As shown in Figure S1, including an extra chamber per block will modify the total analysis time, but this system also allows to work of chambers independently not needing to be grouped in blocks if the total analysis time of one block exceeds the desired times.

Regarding the length of tubbing, this is independent of the number of chambers, since each chamber has its sampling line. In terms of movability during field operation, this probably is the main weakness of the system, it's clear that for every field operation that requires machinery, the system must be dismantled previously. However, this system can be fully dismantled in less than one day by two persons.

Finally, we modify the Material and Method section to explain better how the number of chambers can be modified in our system and compare it to other systems for controlling automated chamber systems. (L170-179).

"This R script, governed by the time taken by the analyser to process the sample, can be easily modified by setting the total number of chambers or, if it is necessary to work by blocks, by setting the number of blocks and the number of chambers per block. One of the advantages of this system is the self-made multiplexer that allows to modify the number of chambers easily compared to other multiplexers like Gasera Multipoint Sampler (Gasera Ltd, Finland) which has a close configuration of 8 or 12 channels. Moreover, the use of relay boards that could be configured by Arduino or easily integrated into the R script as the selected ones, as an alternative to control modules, for example, I-7060D (ICP DAS CO, LTD) that only have four channels per module, simplifies the configuration of the script, since just with one board it's possible to handle all the chambers."

| <u>Time valve on (s)</u> | Time valve off (s) | <u>Chamber</u> | | <u>Gasera (s)</u> |
|--------------------------|--------------------|----------------|----------------------|-------------------|
| 0 | 0 | | Close block 1 | 0 |
| 10 | 28 | 1 | | 0 |
| 28 | 111 | 2 | | 83 |
| 111 | 194 | 3 | | 166 |
| 194 | 277 | 4 | | 249 |
| 277 | 360 | 1 | | 332 |
| 360 | 443 | 2 | | 415 |
| 443 | 526 | 3 | | 498 |
| 526 | 609 | 4 | | 581 |
| 609 | 692 | 1 | | 664 |
| 692 | 775 | 2 | | 747 |
| 775 | 858 | 3 | | 830 |
| 858 | 941 | 4 | | 913 |
| 941 1024 | 1024 | 1 2 | | 996 1070 |
| 1024 | 1107 1190 | 2 3 | | 1079 1162 |
| 1107 | 1273 | 4 | | 1245 |
| 1273 | 1356 | 4 | | 1328 |
| 1356 | 1439 | 2 | | 1411 |
| 1439 | 1522 | 3 | | 1494 |
| 1522 | 1605 | 4 | | 1577 |
| | | | | |
| 1800 | 1800 | | Close block 2 | 1800 |
| 1810 | 1828 | 5 | | 1800 |
| 1828 | 1911 | 6 | | 1883 |
| 1911 | 1994 | 7 | | 1966 |
| 1994 | 2077 | 8 | | 2049 |
| 2077 | 2160 | 5 | | 2132 |
| 2160 | 2243 | 6 | | 2215 |
| 2243 | 2326 | 7 | | 2298 |
| 2326 2409 | 2409 2492 | 8 5 | | 2381 2464 |
| 2409 2492 | 2575 | 6 | | 2404 2547 |
| 2575 | 2658 | 7 | | 2630 |
| 2658 | 2741 | 8 | | 2713 |
| 2741 | 2824 | 5 | | 2796 |
| 2824 | 2907 | 6 | | 2879 |
| 2907 | 2990 | 7 | | 2962 |
| 2990 | 3073 | 8 | | 3045 |
| 3073 | 3156 | 5 | | 3128 |
| 3156 | 3239 | 6 | | 3211 |
| 3239 | 3322 | 7 | | 3294 |
| 3322 | 3405 | 8 | | 3377 |
| 2600 | 2600 | | Close block 3 | 3600 |
| 3600 3610 | 3600 3628 | 9 | <u>Close block 5</u> | 3600 |
| 3628 | 3711 | 10 | | 3683 |
| 3711 | 3794 | 10 | | 3766 |
| 3794 | 3877 | 12 | | 3849 |
| 3877 | 3960 | 9 | | 3932 |
| 3960 | 4043 | 10 | | 4015 |
| 4043 | 4126 | 11 | | 4098 |
| 4126 | 4209 | 12 | | 4181 |
| 4209 | 4292 | 9 | | 4264 |
| 4292 | 4375 | 10 | | 4347 |
| 4375 | 4458 | 11 | | 4430 |
| 4458 | 4541 | 12 | | 4513 |
| 4541 | 4624 | 9 | | 4596 |
| 4624 | 4707 | 10 | | 4679 |
| 4707 | 4790 | 11 | | 4762 |
| 4790 | 4873 | 12 | | 4845 |
| 4873 | 4956 | 9 | | 4928 |
| 4956 | 5039 | 10 | | 5011 |
| 5039 | 5122 | 11 | | 5094 |
| 5122 | 5205 | 12 | | 5177 |

Figure S1 Scheme of sampling sequence for 3 block with 4 chambers per block

Answer C18: Thank you to the Reviewer for pointing out that error. We modified Figure 4 to correct the error.

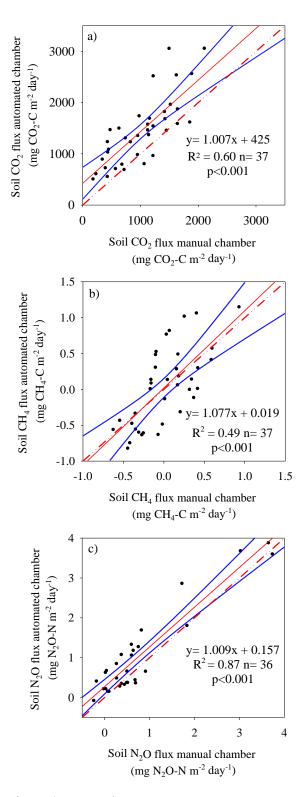


Figure 4 corrected

C19: Figure 5: What are the cumulative soil gas emissions in this figure (sorry, maybe I just don't get it for whatever reason; or are these average fluxes or do you mean scaling up from hourly to daily fluxes)? The color description in the caption is the wrong way around (also in Fig. 6). I am missing error bars. How certain are your flux estimates? I know error bars can make a plot unreadable, but at least include some information about the uncertainty range in the caption.

Answer C19: Data presented in Figure 5 are the soil gas fluxes obtained with both chamber systems from May 22nd to June 29th. Fluxes were upscaled from hourly to daily emissions. Moreover, the left panel represent the fluxes obtained over 24 hours with the automated chamber system on the days that the manual chamber sampling was performed.

We thank the Reviewer for pointed out the error related to the color description in the caption. We modified it in both figures. Besides, following the Reviewer suggestion, we had the standard error as a bar plot in Figure 5 to include information about the uncertainty of our measurement.

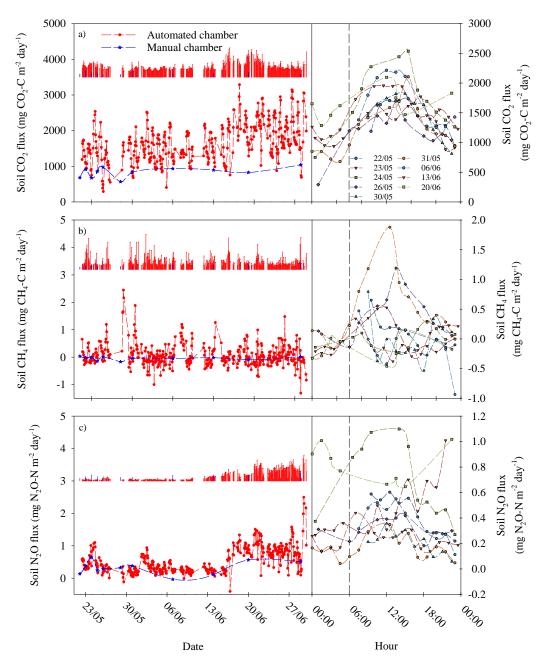


Figure 5 corrected

C20: Figure 6: Why is CO2 in Mg and the other gases in kg? There is one "soil" too many in the first sentence of the caption. What statistical test did you use?

Answer C20: CO₂ cumulative emissions are expressed in Mg rather than kg just to avoid having values of 600 kg CO₂-C ha⁻¹ while CH₄ and N₂O emissions, values were below 1. kg ha⁻¹. Comparison between systems was done by one-way ANOVA. We also include this information in the Material and Method section. (L260-261)

"Moreover, comparison in cumulative emissions between chamber system over one month was evaluated by one-way"

| 1 2 | Measurement of greenhouse gas fluxes in agricultural soils with a flexible, open-design automated system |
|--------|--|
| 3 4 | Samuel Franco-Luesma ^{1*} , María Alonso-Ayuso ^{1,2} , Benjamin Wolf ³ , Borja Latorre ¹ , Jorge Álvaro-Fuentes ¹ |
| 5 6 | ¹ Soil and Water Department, Experimental Station of Aula Dei, Spanish National Research Council (CSIC), Zaragoza, Spain |
| 7 | ² Agricultural Technological Institute of Castilla y León, Valladolid, Spain. |
| 8 9 | ³ Institute of Meteorology and Climate Research, Atmos. Environ.al Research (IMK-IFU), Karlsruhe Institute of Technology (KIT), Garmisch-Partenkirchen, Germany |
| 10 | |
| 11 | |
| 12 | |
| 13 | *Corresponding author: sfrancoluesma@gmail.com |
| 14 | |
| 15 | |
| 16 | |
| 17 | Keywords: |
| 18 | Greenhouse gas emissions; manual chamber system; automated chamber system |
| 19 | |
| 20 | |
| 21 | |
| 22 | |

Abstract

24 Over the last decades and due to the current climate change situation, the study of the impacts of human activities on climate has reached great importance, being agriculture one 25 26 of the main sources of soil greenhouse gas. There are different techniques to quantify the soil gas fluxes, such as micrometeorological techniques or chamber techniques, being the 27 last one capable to assess different treatment at the same site. Manual chambers are the 28 most common one. However, manual chambers are characterised by low sampling 29 frequency, typically one sample per day is considered a high sampling frequency. 30 Therefore, a great deal of effort is required to monitor short-term emission events such as 31 fertilisation or rewetting. For this reason, automated chamber systems are an opportunity 32 to improve soil gas flux determination, but their distribution is still scarce due to the cost 33 and challenging technical implementation. The objective of this study was to develop an 34 automated chamber system for agricultural systems under Mediterranean conditions and 35 compare it with a manual chamber system. A comparison between manual and automated 36 chamber systems was conducted to evaluate the soil gas fluxes obtained by the automated 37 system. Moreover, over a period of one month the soil gas fluxes were determined by both 38 systems to compare their capabilities to capture the temporal variability of soil gas 39 emissions. The automated system reported soil GHG fluxes up to 58 and 40% greater for 40 CO₂ and N₂O fluxes compared to the manual chamber system. Additionally, the higher 41 sampling frequency of the automated chamber system allowed to capture the daily flux 42 variations, resulting in a more accurate estimation of cumulative soil gas emissions. The 43 study emphasises the importance of chamber dimension and shape in the development of 44 45 chamber systems, as well as sampling frequency and sampling hour, especially when manual chamber system is the selected measurement system. 46

47 1. Introduction

Agriculture and land-use changes are significant contributors to climate change, accounting 48 for a 22% of total global emissions of greenhouse gases (GHG) (IPCC, 2023). Moreover, 49 agricultural emissions are expected to increase along with food demand (Wiebe et al., 2019). 50 51 Microbial activity is the primary driver of the production and emission of different soil GHG. Microbial processes are influenced by several abiotic factors such as soil water content, soil 52 53 temperature or nutrient availability. The different farming practices - i.e. crop rotation, fertilization, irrigation – have a significant impact on these factors, and, therefore, they can have a 54 great influence on soil GHG emissions (Oertel et al., 2016). By accurately measuring soil GHG 55 emissions, it is possible to identify the major sources and understand the impact associated with 56 various farming practices. This valuable information can be provided to policymakers and 57 regulators to develop science-based policies and regulations that incentivize farmers to adopt more 58 59 sustainable practices. Thus, measuring soil GHG emissions in agriculture is crucial to promote sustainable farming practices, that can mitigate climate change. 60

The use of manual chambers is one of the most widespread methods for studying soil GHG 61 emissions at small spatial and temporal scales (Collier et al., 2014). Chambers are designed to 62 establish an enclosed environment, facilitating the periodic collection of gases emitted from or 63 64 consumed in the soil using syringes. Subsequently, the gathered gas samples are subjected to laboratory analysis through gas chromatography (Harvey et al., 2020). These analyses determine 65 66 the concentration of GHG within the chamber headspace and allow the calculation of emission 67 rates based on the change in gas concentration over a given time span. This method is characterized 68 by its simplicity and versatility as chambers are relatively simple to use and can be employed across diverse ecosystems and soil types (de Klein et al., 2020). Manual chambers are relatively 69 70 simple to construct and can be tailored to fit specific research requirements. Besides, compared to alternative methods, they entail relatively low cost. However, they have as well some limitations. 71

For instance, their measurement frequency is restricted due to the time-intensive nature of manual 72 73 sampling and subsequent analysis, making high-frequency sampling impractical. Usually, sampling frequency is not higher than one sampling per day, but it's well stablished that sampling 74 frequency affects annual GHG estimations (Barton et al., 2015). For this reason, efforts are often 75 76 concentrated on intense sampling frequencies during short periods (hours to days) when significant emissions peaks are expected, but later, during the rest of the campaign, samplings are carried out 77 every 1 to 4 weeks (or even sometimes not considered). Another aspect to consider involves the 78 notable soil disruption caused when samples need to be collected, such as after an irrigation event. 79

In contrast to manual chambers, the utilization of automated chambers coupled with an in-80 situ gas analyser allows sampling at a higher temporal frequency. Consequently, these automated 81 systems more comprehensively capture temporal variations, enhancing insight into the dynamics 82 83 of soil GHG emissions on a daily and seasonal basis (Grace et al., 2020). Automation also ensures capturing fluxes linked to unexpected events (such as rainstorms), obtaining data in areas of 84 difficult access, and reducing the impact of soil disturbance on measurements. However, this 85 method requires costly equipment and skilled operators and implies different infrastructure 86 constraints, factors that result in lower spatial coverage compared to what can be achieved with 87 manual systems. Moreover, these automated chamber systems are beginning to be manufactured 88 and distributed by companies dedicated to the manufacture of gas analysers, with the limitation of 89 being close systems to be modified. Based on that situation, over recent decades, several groups 90 have crafted automated systems (Lognoul et al., 2017, Lawrence and Hall, 2020). 91

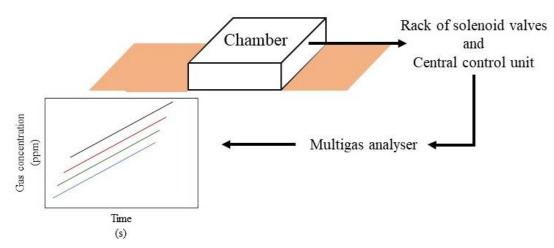
To date, the number of experiences using automated chambers coupled with in situ gas analysers is scarce and, as far as we have been able to find out, none of these previous studies used chamber systems consisting of a total of 12 individual chambers. The objective of this paper is to present an innovative non-commercial soil GHG measurement system based on automated chambers linked to an in situ photoacoustic multigas analyser and describe its operational details.

A, a comparison between this automated system and the manual static chamber methodology is 97 98 also presented.

2. Materials and Methods 99

2.1. Automated system description 100

In this section, we present an automated chamber system tailored for monitoring soil gas 101 emissions. By integrating openness, cost-effectiveness, and versatility, this system facilitates 102 103 precise and dynamic measurements of soil GHG fluxes. Our design principles focused on building an adaptable configuration and real-time functionality, alluding to its potential importance in 104 agricultural and environmental research. The system consists of three main parts: the chambers, 105 the set of solenoid valves controlled by a computer (central control unit) and the multigas analyser 106 107 (Figure 1).



108 Figure 1. General scheme of the automated soil GHG measuring system. 110

109

2.2. Soil chamber design 111

Soil chambers, 'Queensland' design, have been built following a model provided by the 112 Terrestrial Bio-Geo-Chemistry Division (Institute of Meteorology and Climate Research, Atmos. 113 Environ.al Research (IMK-IFU), Karlsruhe Institute of Technology (KIT)). Chambers consisted 114 of an aluminum structure of 0.50 x 0.50 m length and width and 0.15 m height closed with 115

methacrylate panels and two lids 0.50 x 0.25 m width and length that are controlled by four pneumatic actuators, two per lid (Figure 2a). Besides, lids open at a 90° angle allowing rainfall or irrigation water supply to reach the soil surface of the area covered by the chambers. All methacrylate panels were coated with an aluminum bubble foil to keep the internal chamber temperature homogeneous during the enclosure time. Moreover, a rubber seal was fixed to the lids and the bottom part of each chamber to ensure a hermetic close and avoid gas leakage during the sampling process.

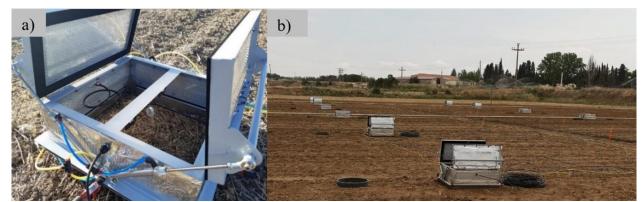


Figure. 2. (a) Open automated chamber deployed in the field trial ('Queensland' design). (b) Set of chambers deployed in the field trial. Dark rings next to chambers are the bases for manual chambers.

127

123

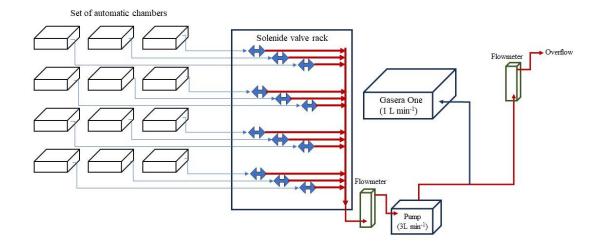
The gas sample line (polyethene coated aluminum tube, Eaton Sinflex. 6/4mmm external 128 internal diameter, respectively) entered each chamber via one of the side panels, positioned 129 approximately halfway up. In the central area of the chamber, the tube was bent facing downwards 130 and the tip was protected by a small PVC funnel to prevent water condensation at the tube inlet. A 131 vent (matching the material and diameter of the gas sampling line) was positioned on the opposite 132 side panel to equalize pressure between the chamber's interior and exterior during flux 133 measurements. Moreover, each chamber has two small fans (60x60x25 mm 12V; 4000 rpm. 134 135 EVERCOOL EC6025L12EA) to promote air mixing inside the chamber.

Three chambers were equipped with a threaded cable gland on a lateral methacrylate panel for mounting a thermistor (107, Campbell Scientific Ltd., UK) to monitor internal chamber temperature. Chambers were attached by clamps to stainless steel bases ($0.5 \ge 0.5 \ge 0.1 = 0.1 = 0.10$

144

2.3. Automated chamber operation

The chambers opened and closed by means of pneumatic actuators. This setup comprised 145 146 an air compressor delivering pressure to the pneumatic actuators. Inside a shed located next to the field trial, three solenoid valves installed in a panel, received air from the compressor (6 bar) and 147 directed compressed air to the chambers. Routing of compressed air was facilitated by an external 148 149 relay controller (8 relay board, 24V 6.5A, YWBL-WH) directly linked to the computer. In the configuration of this study, three sets of four chambers each opened and closed simultaneously. 150 Similarly, each sampling line from each chamber was connected to a two-way solenoid valve that 151 regulated the entry of the gas sample from each of the chambers to the photoacoustic multi-gas 152 analyser (Gasera One, Gasera Ltd, Finland). The two-way solenoid valves were connected to a 153 154 relay board (16 relay board, 24V 6.5A, YWBL-WH) that controlled which valve was activated (Figure 3). 155



157 Figure. 3. Description of the automated chamber system.

156

158

To bring the gas from the chamber to the gas analyser, an external diaphragm pump (KNF 159 160 NMP830KNDC 12V, KNF Neuberger, Inc, Freiburg im Breisgau, Germany) was coupled to the two-way solenoid valve bank. This pump continuously drew air from the activated sampling line, 161 maintaining a flow rate of 3L min⁻¹. The gas analyser (Analysis cell volume 30 mL) drew sample 162 gas from this primary line at a rate of 1 L min⁻¹ for a duration of six seconds every one and a half 163 minutes (Figure 3c). Two flowmeters were attached to the main line. The initial one, positioned 164 after the pump and preceding the gas analyser, regulated the gas flow delivered to the analyser. 165 166 The second flowmeter ensured a continuous overflow greater than 1 L min⁻¹, guaranteeing sufficient gas flow from the active sampling line to the gas analyser (Figure 3). 167

The solenoid valve banks, pneumatic system, chamber sampling lines, and gas analyser were all managed through a custom script created using R statistical software version 4.2.2 (R Core Team, 2022). This R script, governed by the time taken by the analyser to process the sample, can be easily modified by setting the total number of chambers or, if it is necessary to work by blocks, by setting the number of blocks and the number of chambers per block. One of the advantages of this system is the self-made multiplexer that allows to modify the number of

chambers easily compared to other multiplexers like Gasera Multipoint Sampler (Gasera Ltd, 174 Finland) which has a close configuration of 8 or 12 channels. Moreover, the use of relay boards 175 that could be configured by Arduino or easily integrated into the R script as the selected ones, as 176 an alternative to control modules, for example, I-7060D (ICP DAS CO, LTD) that only have four 177 channels per module, simplifies the configuration of the script, since just with one board it's 178 possible to handle all the chambers. For this field experiment, the current setup consists of 3 blocks 179 of four chambers each block. This configuration responds to the needs of the current experimental 180 design, however, since it is an open system, the configuration is variable and can be individualised 181 for each of the chambers. 182

183

184

2.4. Evaluation of the automated measurement system

Over the last decade, the current research team members have successfully conducted 185 several GHG flux studies using a manual closed chamber system (Álvaro-Fuentes et al., 2016, 186 187 Franco-Luesma et al., 2019,2020a, 2020b, 2022). Based on that, an evaluation experiment was carried out to compare the soil gas fluxes obtained via the newly developed automated chamber 188 system against the conventional manual chamber system used regularly by the research group. 189 190 This evaluation experiment was aimed to evaluate the impact of i) the chamber design and ii) the sampling frequency and time on the differences in soil GHG fluxes between a manual and an 191 192 automated chamber measurement system.

Manual chambers consisted of a Polyvinyl Chloride (PVC) cylinder of 0.315 m diameter and 0.2 m height coated by white thermal paint to avoid internal air temperature increasing during the deployed time. Each chamber was placed same diameter PVC collar inserted 0.05 m into the soil. A rubber septum was affixed atop the chamber to enable gas sampling via a plastic syringe equipped with a needle. Gas samples from each chamber were transferred to a 12 mL preevacuated glass vial (Exetainer Labco®). The concentrations of CO₂, CH₄ and N₂O in the gas samples were determined by gas chromatography Agilent 7890B (Agilent, Santa Clara, CA,
United States) equipped with an autosampler (PAL3 autosampler, Zwingen, Switzerland). Soil gas
fluxes were determined based on the increase of the gas concentration during the deployment
period. Further details of the gas chromatography method and manual chamber design could be
found in Franco-Luesma et al. (2022).

The evaluation experiment took place in a maize (Zea mays L.) field trial sown on 204 10/05/2023 under irrigation conditions. The soil is a *Typic Xerofluvent* (Soil Survey Staff, 2015) 205 with a silty loam texture, characterized by a basic pH of 8, a calcium carbonate content (CaCO₃) 206 of 48%, a total organic carbon content of 0.6% and a bulk density of 1.33 g cm⁻³ in the first 0.25 207 208 m soil depth. The area is characterized by a Mediterranean semiarid climate with a mean annual air temperature of 14.1 °C, mean annual precipitation of 298 mm and mean annual reference 209 evapotranspiration (ETo) of 1,243 mm. The meteorological data were obtained from a 210 meteorological station situated at 0.5 km from the experimental site. 211

The evaluation experiment had two different steps. The first step consisted of simultaneous gas sampling with both manual and automated chamber systems on four different dates (i.e. 19/06/2023, 20/06/2023, 21/06/2023 and 28/06/2023). On June 19th and 20th, chambers were sampled once during 06:00 to 07:30 GMT. On June 21st and June 28th, chambers were sampled four times between 06:00 to 12:00 GMT. Consequently, a total of ten samplings were performed, covering four different days and different hours of the day to capture the possible diurnal variation of soil gas emission.

219

In this short time experiment, two chambers of each block were selected to compared with the manual chambers. The sampling sequence for the automated system was programmed to sample each chamber every five minutes, with a total enclosure time of 28 minutes. However, due to the sequence configuration, the computable time for determining the soil gas fluxes was 20
minutes as described in the sequence diagram (Figure S1). The two manual chambers of each block
were closed at the same time as the automated chamber and gas sampling was done at time 0 (first
automated chamber sampling), at time 10 minutes and at time 20 minutes (coinciding with the last
automated chamber sampling).

The second step of the evaluation experiment consisted of assessing the impact of the sampling time (i.e. hour of the day) and sampling frequency (i.e. 16 daily measurements vs 1 daily measurement for the automated and the manual chamber system, respectively) on the estimation of the soil gas fluxes. For that propose, from 22 of May 2023 to 29 of June 2023, soil CO2, CH4 and N2O fluxes were measured simultaneously by the manual and automated chamber systems in the same field experiment

During this period, the sampling frequency and configuration of the automated chamber 234 system was the same as it was used during the step one of the evaluation experiments. The twelve 235 236 chambers were grouped in three set of four chambers each, being sampling every five minutes for 237 28 minutes, resulting in a total of 5 sampling points per chamber (Figure S1). However, the procedure followed in the manual chamber system was different and it consisted of the collection 238 of three gas samples at time 0, 20 and 40 minutes after closing the chamber. The sampling 239 frequency followed a daily frequency over the first five days and, afterwards, weekly 240 measurements till the end of the experiment. For both chamber systems, the measuring instrument 241 (i.e. photoacoustic multi-gas analyser and gas chromatography for automated and manual chamber 242 systems, respectively) were calibrated by using 4 different ultra-high purity gas standards 243 (Carburos Metálicos, Barcelona, Spain, standard 1, 400 ppm CO₂, 1.5 ppm CH₄, 0.3 ppmN₂O, 244 standard 2, 800 ppm CO₂, 2 ppm CH₄, 1 ppmN₂O, standard 3, 1500 ppm CO₂, 4 ppm CH₄, 3 245 ppmN₂O, standard 4, 3000 ppm CO₂, 6 ppm CH₄, 6 ppmN₂O) in order to standardize the 246 concentration values obtained. 247

249 2.5. Data analysis

Soil gas flux (mg of gas $m^2 day^1$) of CO₂, CH₄ and N₂O, i.e., f_{CO2}, f_{CH4} and f_{N2O} was calculated using the following equation (Eq. 1)

252
$$f_{gas} = \frac{Fit * MW * p * h}{R * T} * fT * fU \quad (Eq.1)$$

where Fit represents the linear increase of gas concentration in the chamber over the 253 enclosure time, MW is the molar weight of the atom in the gas molecule (i.e. 12 g mol⁻¹ for CO₂-254 C and CH₄-C and 28 g mol⁻¹ for N₂O-N), p is the atmospheric pressure in Pa, h is the chamber 255 height in m, R is the ideal gas constant in J K⁻¹ mol⁻¹, T is the chamber air temperature in K, fT is 256 the correction factor of time units, 1440 minutes day⁻¹ and fU is the unit correction factor, 10^3 . 257 Cumulative soil CO₂, CH₄ and N₂O emissions were calculated using the trapezoid rule (Levy et 258 al., 2017). Comparison between systems was done by linear fitting considering only soil gas fluxes 259 that presented a R^2 higher than 0.8. Moreover, comparison in cumulative emissions between 260 chamber system over one month was evaluated by one-way ANOVA. All analyses were done 261 using the R statistical software version 4.2.2 (R Core Team, 2022). 262

263

.

264 **3. Results and Discussion**

265 *3.1. Automated system comparison*

266 The comparison between the automated and manual measurement systems showed a linear response for the three gases compared. In the case of soil CO₂, the automated system presented an 267 average flux 58% greater compared to the manual system with a minimal flux difference of 425 268 mg CO₂-C m² day¹ (Figure 4a). Data exhibited moderate dispersion (R^2 =0.60) revealing increased 269 accuracy when manual fluxes were greater than 500 mg CO₂-C m² day¹ (Figure 4a). Regarding 270 271 CH₄ fluxes, the automated chamber system showed values greater than the fluxes obtained in the manual chamber system, showing a better fitting when fluxes were positive (Figure 4b). However, 272 273 the lowest data dispersion between both measurement systems was obtained for soil N2O fluxes $(R^2 > 0.87)$ but as observed for the other two gases, the automated chamber system reported fluxes 274 values 40% greater than the manual chamber system (Figure 4c). 275

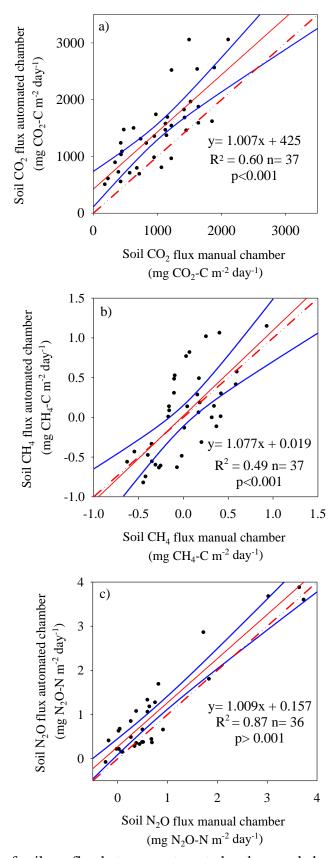


Figure 4. Comparison of soil gas flux between automated and manual chamber systems for carbon dioxide (CO₂) fluxes (a), methane (CH₄) fluxes (b) and nitrous oxide (N₂O) fluxes (c). Blue solid

279 lines represent 95% confidence intervals. Red dotted lines represent 1:1 line.

These differences between both measurement systems in flux magnitude and for the three 281 282 studied gases may probably be a consequence of the different chamber shapes and dimensions that presented both systems. Hoffmann et al. (2018) found that the shape and dimension of the chamber 283 have a significant effect on CO₂ fluxes, observing that small and cylindrical chambers tend to 284 result in higher underestimation of CO₂ fluxes compared with large and squared chambers. In line 285 with the previous authors, Pihlatie et al. (2013) also found a significant effect of the chamber shape 286 and dimension on soil CH₄ flux determination. Similarly, Rochette and Eriksen-Hamel (2008) also 287 concluded that chamber shape and dimensions are critical factors in the estimation of GHG fluxes. 288

All previous studies agreed that the area/perimeter ratio is a key factor in soil gas flux 289 estimation and, hence, they recommended a ratio greater than 0.10 m (Clough et al., 2020). In our 290 work, the two types of chambers compared presented different area/perimeter ratios with values 291 of 0.125 and 0.089 m for the automated and the manual chamber systems, respectively. This 292 difference in the area/perimeter ratio could explain the greater CO₂, CH₄ and N₂O fluxes measured 293 by the automated chamber system compared with the manual system. Moreover, the use of fans to 294 295 mix the internal air of the automated chambers might have also explained the higher fluxes 296 measured in this system compared with the manual system. Air-mixing by fans is highly recommended to homogenize the internal air of the chamber, ensuring that the air sample aliquot 297 is representative of the chamber headspace air (Clough et al., 2020). 298

In line with the previous explanation, the Minimum Detectable Flux (MDF) following the equation presented by Nickersen (2016) was calculated for methodologies. The MDF method not only considered the accuracy of the analyser but also considered the area and volume of the chamber and the enclosure time, factors that are different between both methodologies compared in this work. The MDFs for the automated chamber system were 1.209 mg CO₂-C m⁻² day⁻¹, 0.012 mg CH₄-C m⁻² day⁻¹ and 0.059 mg N₂O-N m⁻² day⁻¹, while for the manual chamber system, MDFs values were 14.050 mg CO₂-C m⁻² day⁻¹, 0.143 mg CH₄-C m⁻² day⁻¹ and 0.071 mg N₂O-N m⁻² day⁻¹ ¹. MDF was greater for the automated chamber system for the three gases, considering a similar
 enclosure time of 20 minutes and an average air temperature during the experiment of 20° C. The
 differences in MDF found between both methodologies was another factor that explained the
 greatest fluxes values observed under the automated chamber system.

310

311 3.2. Sampling time and frequency comparison

The effect of sampling time and frequency on cumulative soil gas emissions was compared between the automated and the manual measuring systems. This analysis was performed during one month in which the automated chamber system ran continuously over the entire month, while in the manual chamber system sampling was only performed on nine different dates.

As expected, the automated chamber system was able to capture daily flux fluctuations, a fact that was not possible for the manual chamber system, because only one gas sampling was done for each of the selected dates (Figure 5). However, when fluxes temporal dynamics for each gas were evaluated, it had been observed differences for each gas.

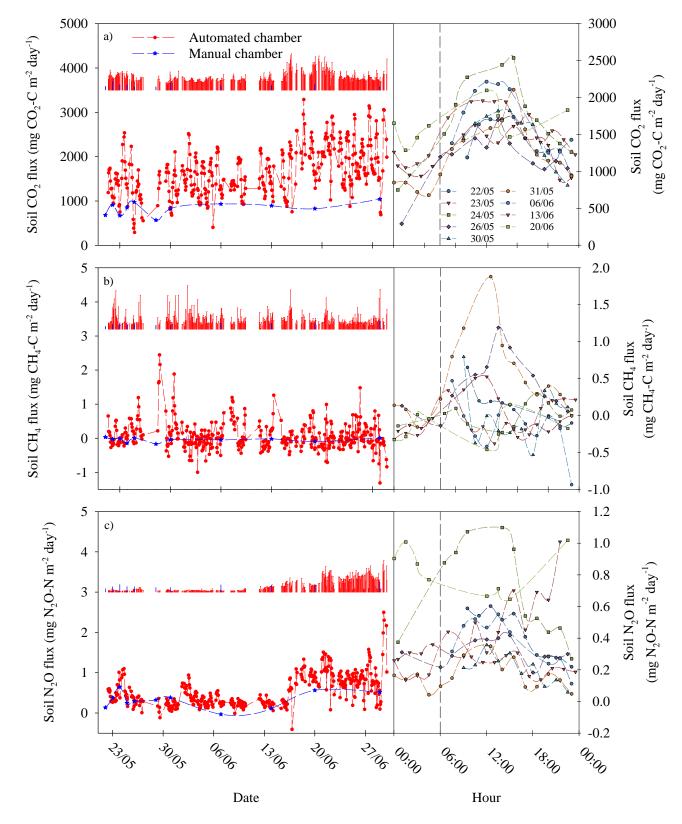


Figure 5. Comparison of soil gas flux and cumulative soil gas emissions between the automated (red line and bar) and the manual (blue line and bar) chamber system for carbon dioxide (CO₂) fluxes (a), methane (CH₄) fluxes (b) and nitrous oxide(N₂O) fluxes (c). Vertical solid lines represent standard error SE (left panel) and daily soil flux of the automated chamber systems on nine different dates Vertical dotted line indicates manual sampling hour (i.e., 6 GMT) (right panel).

Soil CO₂ and CH₄ fluxes determined by the manual chamber system showed similar 328 329 behaviour, presenting a low variation in the fluxes magnitude over the evaluated period, being more pronounced for soil CH₄ fluxes (Figure 5a, 5b). For example, this was clearly observed in 330 the CH₄ in which the automated system captured flux peaks greater than 2 mg CH₄-C m⁻² day⁻¹ 331 while the manual fluxes were close to 0 mg CH₄-C m⁻² day⁻¹ over the entire measuring period 332 (Figure 5b). Interestingly, the manual system was able to capture the temporal emission trend 333 shown by the automated system for soil N₂O fluxes, the gas that showed the greatest temporal 334 variability over the period studied (Figure 5c). 335

Moreover, when the daily emission pattern of the automated chamber was evaluated for 336 the manual sampling dates, it was observed that soil CO₂ fluxes presented the maximum fluxes 337 rate between 12:00 and 16:00 GMT, a daily pattern similar to the results reported by Pumpanen et 338 al. (2003) and Yu et al. (2013). The maximum soil CO_2 fluxes of one day were a factor of three 339 higher than the minimum fluxes measured (Figure 5a). Differences between the maximum and the 340 minimum CH₄ fluxes were lower since soil CH₄ fluxes only ranged between -0.5 to 0.5 mg CH₄-341 C m⁻² day⁻¹ for most of the nine selected dates, expected for May 26th and 31st when soil CH4 342 fluxes above 1 mg CH₄-C m⁻² day⁻¹ were observed at midday (Figure 5b). 343

Soil N₂O fluxes also presented a daily emission pattern characterized by reaching the 344 maximum soil N₂O from 08:00 to 16:00 GMT and the minimum during nighttime, but not being 345 as clear as emission pattern observed for soil CO₂ fluxes (Figure 5c). This daily emission pattern 346 was also observed by Wu et al. (2021) in a metanalysis which evaluated global daily N₂O emission 347 patterns. A possible explanation to the daily pattern observed in all three gases would be the 348 temperature dependence of the biological process that governs the production and emission of soil 349 350 GHG (Lloyd and Taylor, 1994, Smith and Dobbie, 2001, Davidson and Janssens, 2006,). This dependence would explain the higher emissions observed during daytime compared to nighttime 351 352 (Fig. 5c).

Based on the daily emissions pattern observed, right panels of Figure 5, the time of 353 354 sampling can have a very high impact on the gases flux estimation for manual chambers systems, especially when only one sampling is done per day. For CO₂ emissions, carried out the manual 355 sampling at 06:00 GMT suppose and underestimation of 43% respect to the mean daily flux 356 estimated over 24 hours with automated chamber system. Average soil CO2 fluxes determined 357 with the manual chamber system over the nine dates was 836 mg CO₂-C m⁻² day⁻¹, while the 24 358 359 hours CO2 flux for the same nine date measuring with the automated chambers system was 1469 mg CO₂-C m⁻² day⁻¹. In contrast, sampling hour had a minimum impact on soil CH₄ fluxes, 360 obtaining the similar average flux in both systems, 0.066 and 0.068 836 mg CH₄-C m⁻² day⁻¹ for 361 362 the manual and the automated chamber system, respectively.

Regarding N₂O emissions, 06:00 GMT resulted in an adequate sampling hour to obtain a representative daily emission. Average soil N₂O flux of the nine manual sampling was 0.38 mg N₂O-N m⁻² day⁻¹, while the daily average for the same nine dates estimated with the automated chamber system was 0.41 mg N₂O-N m⁻² day⁻¹, resulting the fluxes determined with the manual chambers in an underestimation of 7% compared to the N₂O fluxes determined with the automated chambers.

The cumulative soil gas emissions of the three gases tended to be greater for the automated 369 than the manual measuring system (Fig. 6). For example, cumulative soil CO₂ emissions presented 370 significant differences between both sampling systems. The automated chamber system showed 371 average values 16% more than the manual chamber system (Fig 6a). Indeed, this difference was 372 373 even greater in CH₄ (more than 3-fold greater cumulative emissions in the automated than in the manual measuring system, Fig. 6b). Cumulative CH₄ emissions showed positive values for the 374 375 automated chamber system while the average value for the manual chamber system was negative. However, the variability observed for the manual chamber system was 10 times greater rather than 376 for the automated chamber system, a fact that resulted in the absence of significant differences 377

between both sampling systems. Cumulative soil N_2O emissions did not show significant differences between sampling systems despite that the average cumulative N_2O emissions were 20% greater for the automated chamber system (Fig. 6c). As occurred with cumulative CH₄ emissions, the manual chamber system showed a greater variability than the automatic chamber system, reason that could explain the absence of significant differences between sampling systems.

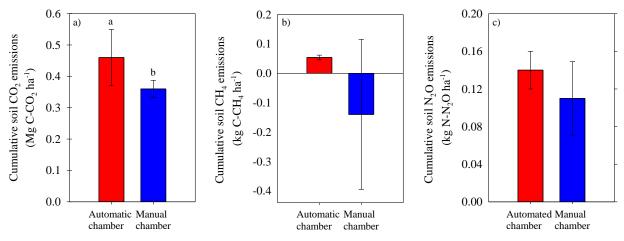


Figure 6. Comparison of soil cumulative soil gas emissions between the automated (red bar) and the manual (blue bar) chamber system for carbon dioxide (CO₂) (a), methane (CH₄) (b) and nitrous oxide(N₂O) (c). Error bars represent standard error. Different letters indicate significant differences at p< 0.05.

383

388 Differences in the different cumulative emissions found between measuring systems might 389 390 have been explained by the next three points: (i) construction differences, (ii) the sampling time in the manual system, and (iii) the height/enclosure time ratio (Clough et al., 2020). The automated 391 chamber presented higher area/perimeter ratios and air-mixing by fans which could contribute to 392 the greater fluxes found in this system compared with the manual system. Regarding the sampling 393 time, this was especially critical for CO₂. Manual sampling was performed at 06:00 GMT (08:00 394 am, GMT+2), resulting in an underestimation of the average daily emission (Pumpanen et al., 395 2003, Yu et al., 2013). In contrast, for N_2O , underestimation was lower since 06:00 GMT is 396 considered a sampling time close to the optimal time for this gas (Wu et al., 2021). Finally, 397 height/enclosure time ratio is also an important factor that affect the sensibility of the flux 398 determination. As a recommendation, height/enclosure time ratio greater than 0.40 m hour⁻¹ is 399 20

400 suggested to increase the minimum detectable flux and to reduce the impacts on air humidity, 401 temperature and the gas diffusion process, variables that govern the soil gas fluxes between soil 402 and atmosphere (Clough et al., 2020). In our study, the automated system resulted in 403 height/enclosure ratios of 0.60 m hour⁻¹, while in the manual system the ratios dropped to 0.30 m 404 hour⁻¹, explaining the lower cumulative emissions reported by the manual system.

405

406 **4.** Conclusion

407 The presented system features an open design, cost-effective components, and adaptable configuration, offering benefits in flexibility, compatibility, and affordability, which in the end 408 resulted in a more precise monitoring of the time flux variability. Moreover, it has been highlighted 409 410 that the shape, dimension, and configuration of the chamber system are critical factors that must be considered in the design of the chambers, being critical in setting area/perimeter and 411 height/enclosure time ratios greater than 0.10m and 0.40m h^{-1} , respectively. Likewise, in case there 412 is not option to implement an automated system, the sampling time of the manual measuring 413 system is critical resulting in significant over or underestimation. Our results showed that 414 06:00GMT was an optimal sampling time for soil N₂O emissions but resulted in an 415 underestimation of soil CO₂ and CH₄ emissions. Therefore, based on the results presented in this 416 work, automated chamber systems are a powerful tool for quantifying GHG fluxes from the soil, 417 418 allowing to capture the large temporal variability that characterizes them. Moreover, open 419 configuration systems, such as the one presented in this study, are more suitable for use in agricultural systems, allowing the number of chambers to be easily modified to cover as much 420 421 variability as possible.

| 423 | Data availability |
|-----|--|
| 424 | All raw data can be provided by the corresponding authors upon request. |
| 425 | |
| 426 | Author contributions |
| 427 | SF-L: Conceptualization, formal analysis, software, data acquisition, writing-original draft, data |
| 428 | curation, methodology, formal analysis, investigation. MA-A: Conceptualization, methodology, |
| 429 | writing-review; editing. BW: Writing-review. BL: Conceptualization ,methodology, software, |
| 430 | writing-review, funding acquisition. JA-F: Conceptualization ,methodology, writing-review; |
| 431 | editing, supervision, project administration, resources, funding acquisition |
| 432 | |
| 433 | Competing interests |
| 434 | The authors declare that they have no conflict of interest. |
| 435 | |
| 436 | Acknowledgements |
| 437 | We are grateful to Valero Pérez Laguardia for assistance in the in the development, |
| 438 | construction and maintenance of the manual and automated chamber systems. |
| 439 | Financial support |
| 440 | This work was supported by the project AgriGEI funded by the Regional Government of |
| 441 | Aragon ("Proyectos de I+D+i en líneas prioritarias del Gobierno de Aragón", Ref. LMP185_21) |
| 442 | and the project TED2021-130837B-I00 funded by MCIN/AEI/ $/10.13039/501100011033$ and by |
| 443 | the "European Union NextGenerationEU/PRTR". |

444 **References**

Álvaro-Fuentes, J., Arrúe, J. L., Cantero-Martínez, C., Isla, R., Plaza-Bonilla, D., & Quílez,
D. (2016). Fertilization Scenarios in Sprinkler-Irrigated Corn under Mediterranean Conditions:
Effects on Greenhouse Gas Emissions. Soil Sci. Soc. Am. J., 80(3), 662-671.
https://doi.org/10.2136/sssaj2015.04.0156

- Barton, L., Wolf, B., Rowlings, D., Scheer, C., Kiese, R., Grace, P., Stefanova, K.,
 Butterbach-Bahl, K. Sampling frequency affects estimates of annual nitrous oxide fluxes. Sci
 Rep2015, 5 (1), 15912. https://doi.org/10.1038/srep15912
- Clough, T. J., Rochette, P., Thomas, S. M., Pihlatie, M., Christiansen, J. R., & Thorman,
 R. E. (2020). Global Research Alliance N₂O chamber methodology guidelines: Design
 considerations. J. Environ. Qual., 49(5), 1081-1091. https://doi.org/10.1002/jeq2.20117
- 455 Collier, S. M., Ruark, M. D., Oates, L. G., Jokela, W. E., & Dell, C. J. (2014). Measurement
 456 of greenhouse gas flux from agricultural soils using static chambers. JoVE, (90), e52110.
 457 https://doi.org/10.3791/52110

458 Davidson, E. A., & Janssens, I. A. (2006). Temperature sensitivity of soil carbon
459 decomposition and feedbacks to climate change. Nature, 440(7081), 165-173.
460 https://doi.org/10.1038/nature04514

de Klein, C. A. M., Harvey, M. J., Clough, T. J., Petersen, S. O., Chadwick, D. R., &
Venterea, R. T. (2020). Global research alliance nitrous oxide chamber methodology guidelines:
Introduction, with health and safety considerations. J. Environ. Qual., 49(5), 1073-1080.
https://doi.org/10.1002/jeq2.20131

Ding, W., Cai, Z., & Tsuruta, H. (2004). Diel variation in methane emissions from the
stands of Carex lasiocarpa and Deyeuxia angustifolia in a cool temperate freshwater marsh. Atmos.
Environ., 38(2), 181-188. https://doi.org/10.1016/j.atmosenv.2003.09.066

| 468 | Ferrara, R. M., Carozzi, M., Decuq, C., Loubet, B., Finco, A., Marzuoli, R., Gerosa, G., Di |
|-----|--|
| 469 | Tommasi, P., Magliulo, V. & Rana, G. (2021). Ammonia, nitrous oxide, carbon dioxide, and water |
| 470 | vapor fluxes after green manuring of faba bean under Mediterranean climate. Agric. Ecosyst. |
| 471 | Environ., 315, 107439. https://doi.org/10.1016/j.agee.2021.107439 |
| 472 | Forte, A., Fiorentino, N., Fagnano, M., & Fierro, A. (2017). Mitigation impact of minimum |
| 473 | tillage on CO_2 and N_2O emissions from a Mediterranean maize cropped soil under low-water input |
| 474 | management. Soil Tillage Res., 166, 167-178. https://doi.org/10.1016/j.still.2016.09.014 |
| 475 | Francis Clar, J. T., & Anex, R. P. (2020). Flux intensity and diurnal variability of soil N_2O |
| 476 | emissions in a highly fertilized cropping system. Soil Sci. Soc. Am. J., 84(6), 1983-1994. |
| 477 | https://doi.org/10.1002/saj2.20132 |
| 478 | Franco-Luesma, S., Álvaro-Fuentes, J., Plaza-Bonilla, D., Arrúe, J. L., Cantero-Martínez, |
| 479 | C., & Cavero, J. (2019). Influence of irrigation time and frequency on greenhouse gas emissions |
| 480 | in a solid-set sprinkler-irrigated maize under Mediterranean conditions. Agric. Water Manage., |
| 481 | 221, 303-311. https://doi.org/10.1016/j.agwat.2019.03.042 |
| 482 | Franco-Luesma, S., Cavero, J., Plaza-Bonilla, D., Cantero-Martínez, C., Tortosa, G., |
| 483 | Bedmar, E. J., & Álvaro-Fuentes, J. (2020). Irrigation and tillage effects on soil nitrous oxide |
| 484 | emissions in maize monoculture. Agron. J., 112(1), 56-71. https://doi.org/10.1002/agj2.20057 |
| 485 | Franco-Luesma, S., Cavero, J., Plaza-Bonilla, D., Cantero-Martínez, C., Arrúe, J. L., & |
| 486 | Álvaro-Fuentes, J. (2020). Tillage and irrigation system effects on soil carbon dioxide (CO ₂) and |
| 487 | methane (CH ₄) emissions in a maize monoculture under Mediterranean conditions. Soil Tillage |
| 488 | Res., 196, 104488. https://doi.org/10.1016/j.still.2019.104488 |
| 489 | Franco-Luesma, S., Lafuente, V., Alonso-Ayuso, M., Bielsa, A., Kouchami-Sardoo, I., |
| 490 | Arrúe, J. L., & Álvaro-Fuentes, J. (2022). Maize diversification and nitrogen fertilization effects |

on soil nitrous oxide emissions in irrigated Mediterranean conditions. Front. Environ. Sci., 10,
914851. https://doi.org/10.3389/fenvs.2022.914851

Grace, P. R., van der Weerden, T. J., Rowlings, D. W., Scheer, C., Brunk, C., Kiese, R.,
Butterbach-Bahl, K., Rees, R. M., Robertson, G. P. & Skiba, U.M. (2020). Global Research
Alliance N₂O chamber methodology guidelines: Considerations for automated flux measurement.
J. Environ. Qual., 49(5), 1126-1140. https://doi.org/10.1002/jeq2.20124

Harvey, M. J., Sperlich, P., Clough, T. J., Kelliher, F. M., McGeough, K. L., Martin, R. J.,
& Moss, R. (2020). Global Research Alliance N₂O chamber methodology guidelines:
Recommendations for air sample collection, storage and analysis. J. Environ. Qual., 49(5), 11101125. https://doi.org/10.1002/jeq2.20129

Hoffmann, M., Pehle, N., Huth, V., Jurisch, N., Sommer, M. and Augustin, J. (2018). A 501 simple method to assess the impact of sealing, headspace mixing and pressure vent on airtightness 502 J. Plant Soil Sci., 36-40. 503 of manually closed chambers. Nutr. 181, https://doi.org/10.1002/jpln.201600299 504

Intergovernmental Panel on Climate Change, IPCC (2014). Climate Change 2014:
Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of
the Intergovernmental Panel on Climate Change (IPCC).

Isla, R., Castillo, M. G., Medina, E. T., Latorre, B., de Viteri, D. Q. S., & Cavero, J. (2022).
Greenhouse gas emissions associated to sprinkler-irrigated alfalfa under semi-arid Mediterranean
conditions. Span. J. Agric. Res., 20(3), 4. https://doi.org/10.5424/sjar/2022203-18416

Lawrence, N. C., & Hall, S. J. (2020). Capturing temporal heterogeneity in soil nitrous
oxide fluxes with a robust and low-cost automated chamber apparatus. Atmos. Meas. Tech., 13(7),
4065-4078. https://doi.org/10.5194/amt-13-4065-2020

| 514 | Lloyd, J. and Taylor J, A. (1994). On the temperature dependence of soil respiration |
|-----|--|
| 515 | Functional Ecology, 8, 315–323. https://doi.org/10.2307/2389824 |

- Lognoul, M., Theodorakopoulos, N., Hiel, M. P., Regaert, D., Broux, F., Heinesch, B., ...
 & Aubinet, M. (2017). Impact of tillage on greenhouse gas emissions by an agricultural crop and
 dynamics of N₂O fluxes: Insights from automated closed chamber measurements. Soil Tillage
 Res., 167, 80-89. https://doi.org/10.1016/j.still.2016.11.008
 Nickerson, N. (2016). Evaluating gas emission measurements using Minimum Detectable
- 521 Flux (MDF). Eosense Inc., Dartmouth, Nova Scotia, Canada.
- 522 Oertel, C., Matschullat, J., Zurba, K., Zimmermann, F., & Erasmi, S. (2016). Greenhouse
 523 gas emissions from soils—A review. Chem Erde-Geochem., 76(3), 327-352.
 524 https://doi.org/10.1016/j.chemer.2016.04.002
- Parkin, T. B. (2008). Effect of sampling frequency on estimates of cumulative nitrous oxide
 emissions. J. Environ. Qual., 37(4), 1390–1395. https://doi.org/10.2134/jeq20 07.0333
- Pihlatie, M. K., J. R. Christiansen, H. Aaltonen, J. F. J. Korhonen, A. Nordbo, T. Rasilo,
 G. Benanti, M. Giebels, M. Helmy, J. Sheehy, S. Jones, R. Juszczak, R. Klefoth, R. Lobo-do-Vale,
 A. P. Rosa, P. Schreiber, D. Serça, S. Vicca, B. Wolf, and J. Pumpanen. (2013). Comparison of
 static chambers to measure CH₄ emissions from soils. Agric. For. Meteorol., 171, 124-136.
 https://doi.org/10.1016/j.agrformet.2012.11.008
- Pumpanen, J., Ilvesniemi, H., Perämäki, M., & Hari, P. (2003). Seasonal patterns of soil
 CO₂ efflux and soil air CO₂ concentration in a Scots pine forest: comparison of two chamber
 techniques. Glob. Change Biol., 9(3), 371-382. https://doi.org/10.1046/j.1365-2486.2003.00588.x
- R Core Team (2022). R: A language and environment for statistical computing. R
 Foundation for Statistical Computing, Vienna, Austria. Version 4.2.2. <u>https://www.R-project.org/</u>

- Reeves, S., Wang, W., Salter, B., & Halpin, N. (2016). Quantifying nitrous oxide emissions
 from sugarcane cropping systems: Optimum sampling time and frequency. Atmos. Environ., 136,
 123-133. https://doi.org/10.1016/j.atmosenv.2016.04.008
- Rochette, P., & Eriksen-Hamel, N. S. (2008). Chamber Measurements of Soil Nitrous
 Oxide Flux: Are Absolute Values Reliable? Soil Sci. Soc. Am. J., 72(2), 331.
 doi:10.2136/sssaj2007.0215
- Savage, K., Phillips, R., & Davidson, E. (2014). High temporal frequency measurements
 of greenhouse gas emissions from soils. Biogeosciences, 11(10), 2709-2720.
 https://doi.org/10.5194/bg-11-2709-2014
- Smith, K. A., & Dobbie, K. E. (2001). The impact of sampling frequency and sampling
 times on chamber- based measurements of N2 O emissions from fertilized soils. Glob. Change
 Biol., 7(8), 933–945. https://doi.org/10.1046/j.1354-1013.2001.00450.x
- Yu, L., Wang, H., Wang, G., Song, W., Huang, Y., Li, S. G., Liang, N., Tang, Y. & He, J.
 S. (2013). A comparison of methane emission measurements using eddy covariance and manual
 and automated chamber-based techniques in Tibetan Plateau alpine wetland. Environ. Pollut., 181,
 81-90. https://doi.org/10.1016/j.envpol.2013.06.018
- Wang, Z.-P., & Han, X.-G. (2005). Diurnal variation in methane emissions in relation to
 plants and environmental variables in the Inner Mongolia marshes. Atmos. Environ., 39(34),
 6295–6305. https://doi.org/10.1016/j.atmosenv.2005.07.01
- Wiebe, K., Robinson, S., & Cattaneo, A. (2019). Climate change, agriculture and food security: impacts and the potential for adaptation and mitigation. Sustainable Food and Agriculture, 55-74. https://doi.org/10.1016/B978-0-12-812134-4.00004-2

Wu, Y. F., Whitaker, J., Toet, S., Bradley, A., Davies, C. A., & McNamara, N. P. (2021).
Diurnal variability in soil nitrous oxide emissions is a widespread phenomenon. Glob. Change
Biol., 27(20), 4950-4966. <u>https://doi.org/10.1111/gcb.15791</u>