1 **Measurement of greenhouse gas fluxes in agricultural soils with a flexible, open-design**
2 **automated system**

3 Samuel Franco-Luesma [1*], María Alonso-Ayuso [1,2], Benjamin Wolf [3], Borja Latorre [1],
4 Jorge Álvaro-Fuentes [1]

5 [1] Soil and Water Department, Experimental Station of Aula Dei, Spanish National Research Council
6 (CSIC), Zaragoza, Spain

7 [2] Agricultural Technological Institute of Castilla y León, Valladolid, Spain.

8 [3] Institute of Meteorology and Climate Research, Atmos. Environ.al Research (IMK-IFU), Karlsruhe
9 Institute of Technology (KIT), Garmisch-Partenkirchen, Germany

13 *Corresponding author: sfrancoluesma@gmail.com

17 Keywords:

18 Greenhouse gas emissions; manual chamber system; automated chamber system

Abstract

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 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 last one capable to assess different treatment at the same site. Manual chambers are the most common one. 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. For this reason, automated chamber systems are an opportunity to improve soil gas flux determination, but their distribution is still scarce due to the cost and challenging technical implementation. The objective of this study was to develop an automated chamber system for agricultural systems under Mediterranean conditions and compare it with a manual chamber system. A comparison between manual and automated chamber systems was conducted to evaluate the soil gas fluxes obtained by the automated system. Moreover, over a period of one month the soil gas fluxes were determined by both systems to compare their capabilities to capture the temporal variability of soil gas emissions. 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. Additionally, the higher sampling frequency of the automated chamber system allowed to capture the daily flux variations, resulting in a more accurate estimation of cumulative soil gas emissions. Furthermore, the assessment of various sampling intervals for single-day measurements indicated that soil gas sampling between 10:00 and 12:00 was the optimal time interval for obtaining representative daily emissions. The study emphasises the importance of

47   chamber dimension and shape in the development of chamber systems, as well as

48   sampling frequency and sampling hour, for manual chamber system.

49

1. Introduction

Agriculture and land-use changes are significant contributors to climate change, accounting for a 22% of total global emissions of greenhouse gases (GHG) (IPCC, 2023). Moreover, agricultural emissions are expected to increase along with food demand (Wiebe et al., 2019). 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 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 great influence on soil GHG emissions (Oertel et al., 2016). By accurately measuring soil GHG emissions, it is possible to identify the major sources and understand the impact associated with various farming practices. This valuable information can be provided to policymakers and regulators to develop science-based policies and regulations that incentivize farmers to adopt more sustainable practices. Thus, measuring soil GHG emissions in agriculture is crucial to promote sustainable farming practices, that can mitigate climate change.

The use of manual chambers is one of the most widespread methods for studying soil GHG emissions at small spatial and temporal scales (Collier et al., 2014). Chambers are designed to establish an enclosed environment, facilitating the periodic collection of gases emitted from or 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 the concentration of GHG within the chamber headspace and allow the calculation of emission rates based on the change in gas concentration over a given time span. This method is characterized 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 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.

For instance, their measurement frequency is restricted due to the time-intensive nature of manual 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 frequency affects annual GHG estimations (Barton et al., 2015). For this reason, efforts are often 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 every 1 to 4 weeks (or even sometimes not considered). Another aspect to consider involves the notable soil disruption caused when samples need to be collected, such as after an irrigation event.

In contrast to manual chambers, the utilization of automated chambers coupled with an in-situ gas analyser allows sampling at a higher temporal frequency. Consequently, these automated systems more comprehensively capture temporal variations, enhancing insight into the dynamics 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 difficult access, and reducing the impact of soil disturbance on measurements. 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).

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.

100 A, a comparison between this automated system and the manual static chamber methodology is

101 also presented.

2. Materials and Methods

2.1. Automated system description

In this section, we present an automated chamber system tailored for monitoring soil gas emissions. By integrating openness, cost-effectiveness, and versatility, this system facilitates 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 agricultural and environmental research. The system consists of three main parts: the chambers, the set of solenoid valves controlled by a computer (central control unit) and the multigas analyser (Figure 1).

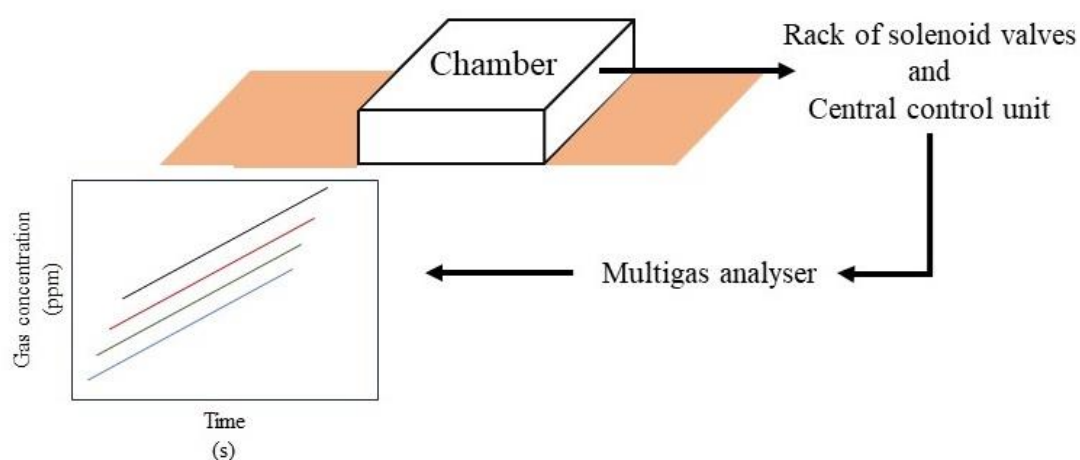



Figure 1. General scheme of the automated soil GHG measurement system.

2.2. Soil chamber design

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

119   methacrylate panels and two lids 0.50 x 0.25 m width and length that are controlled by four

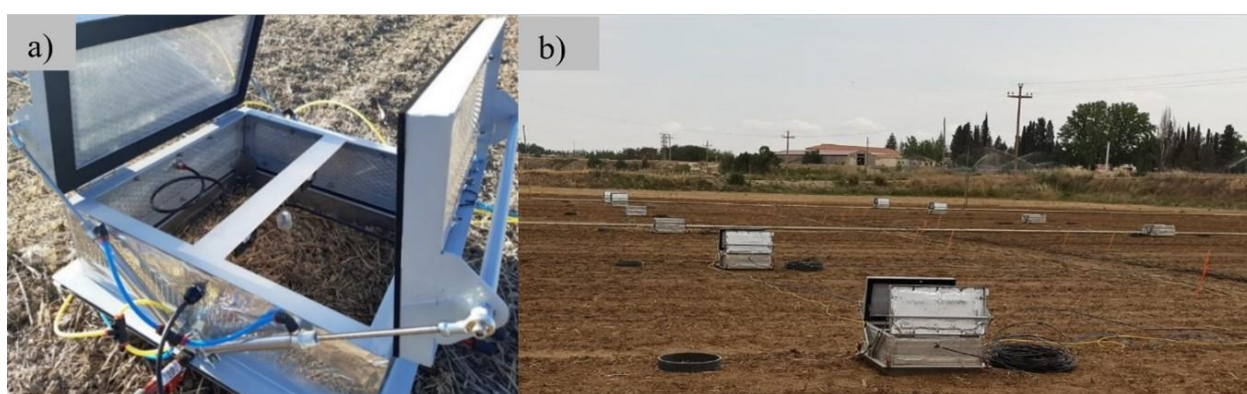
120   pneumatic actuators, two per lid (Figure 2a). Besides, lids open at a 90º angle allowing rainfall or

121   irrigation water supply to reach the soil surface of the area covered by the chambers. All

122   methacrylate panels were coated with an aluminum bubble foil to keep the internal chamber

123   temperature homogeneous during the enclosure time. Moreover, a rubber seal was fixed to the lids

124   and the bottom part of each chamber to ensure a hermetic close and avoid gas leakage during the

125   sampling process.

126
127   Figure. 2. (a) Open automated chamber deployed in the field trial ('Queensland' design). (b) Set
128   of chambers deployed in the field trial. Dark rings next to chambers are the bases for manual
129   chambers.
130

131   The gas sample line (polyethene coated aluminum tube, Eaton Sinflex. 6/4mmm external

132   internal diameter, respectively) entered each chamber via one of the side panels, positioned

133   approximately halfway up. In the central area of the chamber, the tube was bent facing downwards

134   and the tip was protected by a small PVC funnel to prevent water condensation at the tube inlet. A

135   vent (matching the material and diameter of the gas sampling line) was positioned on the opposite

136   side panel to equalize pressure between the chamber's interior and exterior during flux

137   measurements. Moreover, each chamber has two small fans (60x60x25 mm 12V; 4000 rpm.

138   EVERCOOL EC6025L12EA) to promote air mixing inside the chamber.

139

140 Three chambers were equipped with a threaded cable gland on a lateral methacrylate panel

141 for mounting a thermistor (107, Campbell Scientific Ltd., UK) to monitor internal chamber

142 temperature. Chambers were attached by clamps to stainless steel bases (0.5 x 0,5 x 0.1 m) with

143 sharp edges at the bottom that were inserted 0.10 m into the soil . Plants (crop and weeds) growing

144 inside the chambers were cut since the crop during this experiment was maize (*Zea mays* L.)

145 (Figure 2b). The cost of each chamber, including the solenoid valve and the sampling line is 600

146 €.

147 ### *2.3. Automated chamber operation*

148 The chambers opened and closed by means of pneumatic actuators. This setup comprised

149 an air compressor delivering pressure to the pneumatic actuators. Inside a shed located next to the

150 field trial, three solenoid valves installed in a panel, received air from the compressor (6 bar) and

151 directed compressed air to the chambers. Routing of compressed air was facilitated by an external

152 relay controller (8 relay board, 24V 6.5A, YWBL-WH) directly linked to the computer. In the

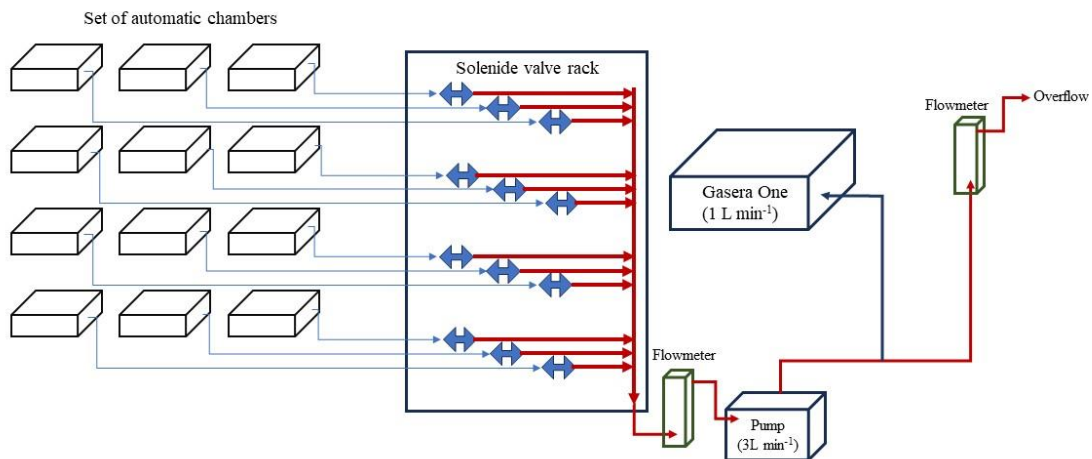
153 configuration of this study, three sets of four chambers each opened and closed simultaneously.

154 Similarly, each sampling line from each chamber was connected to a two-way solenoid valve that

155 regulated the entry of the gas sample from each of the chambers to the photoacoustic multi-gas

156 analyser (Gasera One, Gasera Ltd, Finland). The two-way solenoid valves were connected to a

157 relay board (16 relay board, 24V 6.5A, YWBL-WH) that controlled which valve was activated

158 (Figure 3).

159
160 Figure. 3. Description of the automated chamber system.
161
162   To bring the gas from the chamber to the gas analyser, an external diaphragm pump (KNF

163 NMP830KNDC 12V, KNF Neuberger, Inc, Freiburg im Breisgau, Germany) was coupled to the

164 two-way solenoid valve bank. This pump continuously drew air from the activated sampling line,

165 maintaining a flow rate of 3L min^{-1}. The gas analyser (Analysis cell volume 30 mL) drew sample

166 gas from this primary line at a rate of 1 L min^{-1} for a duration of six seconds every one and a half

167 minutes (Figure 3c). Two flowmeters were attached to the main line. The initial one, positioned

168 after the pump and preceding the gas analyser, regulated the gas flow delivered to the analyser.

169 The second flowmeter ensured a continuous overflow greater than 1 L min^{-1}, guaranteeing

170 sufficient gas flow from the active sampling line to the gas analyser (Figure 3).

171   The solenoid valve banks, pneumatic system, chamber sampling lines, and gas analyser

172 were all managed through a custom script created using R statistical software version 4.2.2 (R

173 Core Team, 2022). This R script, governed by the time taken by the analyser to process the sample,

174 can be easily modified by setting the total number of chambers or, if it is necessary to work by

175 blocks, by setting the number of blocks and the number of chambers per block. One of the

176 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. For this field experiment, the current setup consists of 3 blocks of four chambers each block. This configuration responds to the needs of the current experimental design, however, since it is an open system, the configuration is variable and can be individualised for each of the chambers.

2.4. Evaluation of the automated measurement system

Over the last decade, the current research team members have successfully conducted several GHG flux studies using a manual closed chamber system (Álvaro-Fuentes et al., 2016, 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 system against the conventional manual chamber system used regularly by the research group. 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 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 pre-evacuated glass vial (Exetainer Labco®). The concentrations of CO_2, CH_4 and N_2O 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 10/05/2023 under irrigation conditions. The soil is a *Typic Xerofluvent* (Soil Survey Staff, 2015) with a silty loam texture, characterized by a basic pH of 8, a calcium carbonate content ($CaCO_3$) 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 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 evapotranspiration (ETo) of 1,243 mm. The meteorological data were obtained from a meteorological station situated at 0.5 km from the experimental site.

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 08:00 to 09:30 06:00 to 07:30 GMT. On June 21st and June 28th, chambers were sampled four times between 08:00 to 14:00 06:00 to 12:00 GMT. Conseqeuntly, 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.

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 CO_2, CH_4 and N_2O 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 system was the same as it was used during the step one of the evaluation experiments. The twelve chambers were grouped in three set of four chambers each, being sampling every five minutes for 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 of three gas samples at time 0, 20 and 40 minutes after closing the chamber. The sampling frequency followed a daily frequency over the first five days and, afterwards, weekly measurements till the end of the experiment. For both chamber systems, the measuring instrument (i.e. photoacoustic multi-gas analyser and gas chromatography for automated and manual chamber systems, respectively) were calibrated by using 4 different ultra-high purity gas standards (Carburos Metálicos, Barcelona, Spain, standard 1, 400 ppm CO_2, 1.5 ppm CH_4, 0.3 ppmN_2O, standard 2, 800 ppm CO_2, 2 ppm CH_4, 1 ppmN_2O, standard 3, 1500 ppm CO_2, 4 ppm CH_4, 3 ppmN_2O, standard 4, 3000 ppm CO_2, 6 ppm CH_4, 6 ppmN_2O) in order to standardize the concentration values obtained.

2.5. Data analysis

Soil gas flux (mg of gas m^2 day^1) of CO_2, CH_4 and N_2O, i.e., f_{CO2}, f_{CH4} and f_{N2O} was calculated using the following equation (Eq. 1)

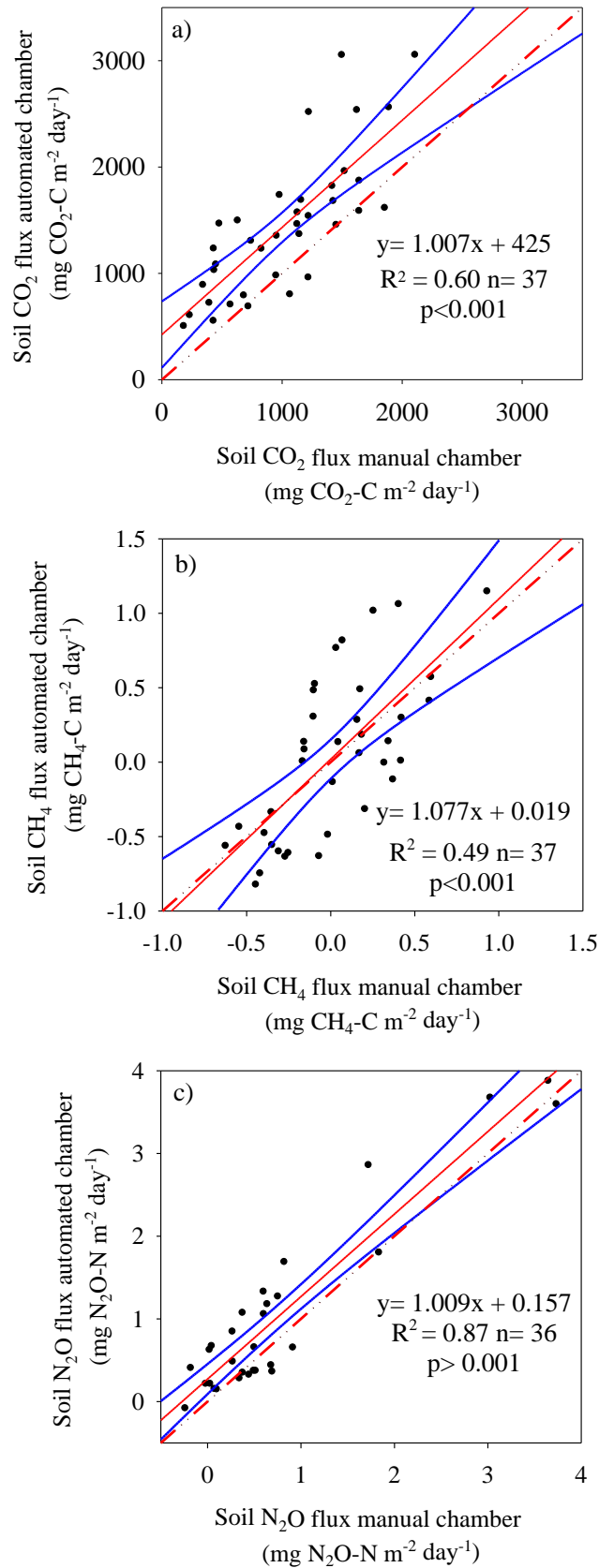
$$f_{gas} = \frac{Fit * MW * p * h}{R * T} * fT * fU \quad (Eq.\,1)$$

where *Fit* represents the linear increase of gas concentration in the chamber over the enclosure time, *MW* is the molar weight of the atom in the gas molecule (i.e. 12 g mol^{-1} for CO_2-C and CH_4-C and 28 g mol^{-1} for N_2O-N), *p* is the atmospheric pressure in Pa, *h* is the chamber 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 the correction factor of time units, 1440 minutes day^{-1} and *fU* is the unit correction factor, 10^3. Cumulative soil CO_2, CH_4 and N_2O 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 R^2 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).

.

3. Results and Discussion

3.1. Automated system comparison

The comparison between the automated and manual measurement systems showed a linear response for the three gases compared. In the case of soil CO_2, the automated system presented an average flux 58% greater compared to the manual system with a minimal flux difference of 425 mg CO_2-C m^2 day^1 (Figure 4a). Data exhibited moderate dispersion (R^2=0.60) revealing increased accuracy when manual fluxes were greater than 500 mg CO_2-C m^2 day^1 (Figure 4a). Regarding CH_4 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, the lowest data dispersion between both measurement systems was obtained for soil N_2O fluxes (R^2> 0.87) but as observed for the other two gases, the automated chamber system reported fluxes values 40% greater than the manual chamber system (Figure 4c).

278
279 Figure 4. Comparison of soil gas flux between automated and manual chamber systems for carbon
280 dioxide (CO_2) fluxes (a), methane (CH_4) fluxes (b) and nitrous oxide (N_2O) fluxes (c). Blue solid
281 lines represent 95% confidence intervals. Red dotted lines represent 1:1 line.
282

283  These differences between both measurement systems in flux magnitude and for the three

284 studied gases may probably be a consequence of the different chamber shapes and dimensions ~~that~~

285 ~~presented both systems~~. Hoffmann et al. (2018) found that the shape and dimension of the chamber

286 have a significant effect on CO_2 fluxes, observing that small and cylindrical chambers tend to

287 result in higher underestimation of CO_2 fluxes compared with large and squared chambers. In line

288 with the previous authors, Pihlatie et al. (2013) also found a significant effect of the chamber shape

289 and dimension on soil CH_4 flux determination. Similarly, Rochette and Eriksen-Hamel (2008) also

290 concluded that chamber shape and dimensions are critical factors in the estimation of GHG fluxes.

291  All previous studies agreed that the area/perimeter ratio is a key factor in soil gas flux

292 estimation and, hence, they recommended a ratio greater than 0.10 m (Clough et al., 2020). In our

293 work, the two types of chambers compared presented different area/perimeter ratios with values

294 of 0.125 and 0.089 m for the automated and the manual chamber systems, respectively. This

295 difference in the area/perimeter ratio could explain the greater CO_2, CH_4 and N_2O fluxes measured

296 by the automated chamber system compared with the manual system. Moreover, the use of fans to

297 mix the internal air of the automated chambers might have also explained the higher fluxes

298 measured in this system compared with the manual system. Air-mixing by fans is ~~highly~~

299 recommended to homogenize the internal air of the chamber, ensuring that the air sample aliquot

300 is representative of the chamber headspace air (Clough et al., 2020).

301  In line with the previous explanation, the Minimum Detectable Flux (MDF) following the

302 equation presented by Nickersen (2016) was calculated for methodologies. The MDF method not

303 only considered the accuracy of the analyser but also considered the area and volume of the

304 chamber and the enclosure time, factors that are different between both methodologies compared

305 in this work. The MDFs for the automated chamber system were 1.209 mg CO_2-C m^{-2} day^{-1}, 0.012

306 mg CH_4-C m^{-2} day^{-1} and 0.059 mg N_2O-N m^{-2} day^{-1}, while for the manual chamber system, MDFs

307 values were 14.050 mg CO_2-C m^{-2} day^{-1}, 0.143 mg CH_4-C m^{-2} day^{-1} and 0.071 mg N_2O-N m^{-2} day^{-}

308 [1]. MDF was greater for the automated chamber system for the three gases, considering a similar

309 enclosure time of 20 minutes and an average air temperature during the experiment of 20º C. The

310 differences in MDF found between both methodologies was another factor that explained the

311 greatest fluxes values observed under the automated chamber system.

312

313 *3.2. Sampling time and frequency comparison*

314 The effect of sampling time and frequency on cumulative soil gas emissions was compared

315 between the automated and the manual measurement systems. This analysis was performed during

316 one month in which the automated chamber system ran continuously over the entire month, while

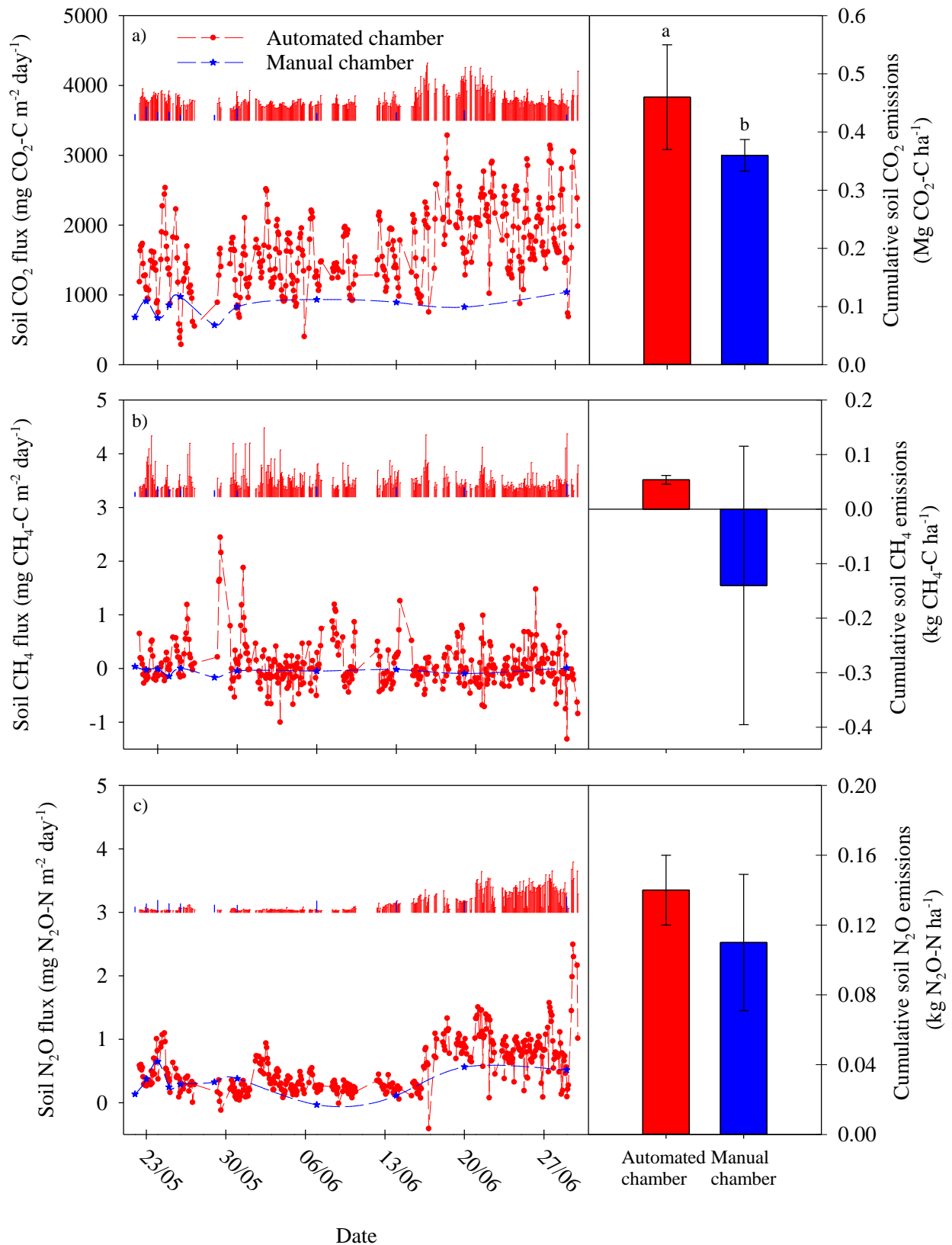
317 in the manual chamber system sampling was only performed on nine different dates.

318 As expected, the automated chamber system was able to capture daily flux fluctuations, a

319 fact that was not possible for the manual chamber system, because only one gas sampling was

320 done for each of the selected dates (Figure 5). However, when fluxes temporal dynamics for each

321 gas were evaluated, it had been observed differences for each gas.

322

323
324 Figure 5. Comparison of soil gas flux and cumulative soil gas emissions between the automated
325 (red line and bar) and the manual (blue line and bar) chamber system for carbon dioxide (CO_2)
326 fluxes (a), methane (CH_4) fluxes (b) and nitrous oxide(N_2O) fluxes (c). Vertical solid lines
327 represent standard error SE (left panel) and cumulative soil emissions for the automated chamber
328 systems (red bar)and manual chamber system (blue bar) (right panel).

329   Soil CO_2 and CH_4 fluxes determined by the manual chamber system showed similar

330 behaviour, presenting a low variation in the fluxes magnitude over the evaluated period, being

331 more pronounced for soil CH_4 fluxes (Figure 5a, 5b). For example, this was clearly observed in

332 the CH_4 in which the automated system captured flux peaks greater than 2 mg CH_4-C m^{-2} day^{-1}

333 while the manual fluxes were close to 0 mg CH_4-C m^{-2} day^{-1} over the entire measuring period

334 (Figure 5b). Interestingly, the manual system was able to capture the temporal emission trend

335 shown by the automated system for soil N_2O fluxes, the gas that showed the greatest temporal

336 variability over the period studied (Figure 5c).

337   The cumulative soil gas emissions of the three gases tended to be greater for the automated

338 than the manual measurement system (Fig. 5). For example, cumulative soil CO_2 emissions

339 presented significant differences between both sampling systems. The automated chamber system

340 showed average values 16% more than the manual chamber system (Fig 5a). Indeed, this

341 difference was even greater in CH_4 (more than 3-fold greater cumulative emissions in the

342 automated than in the manual measurement system, Fig. 5b). Cumulative CH_4 emissions showed

343 positive values for the automated chamber system while the average value for the manual chamber

344 system was negative. However, the variability observed for the manual chamber system was 10

345 times greater rather than for the automated chamber system, a fact that resulted in the absence of

346 significant differences between both sampling systems. Cumulative soil N_2O emissions did not

347 show significant differences between sampling systems despite that the average cumulative N_2O

348 emissions were 20% greater for the automated chamber system (Fig. 5c). As occurred with

349 cumulative CH_4 emissions, the manual chamber system showed a greater variability than the

350 automatic chamber system, reason that could explain the absence of significant differences

351 between sampling systems.

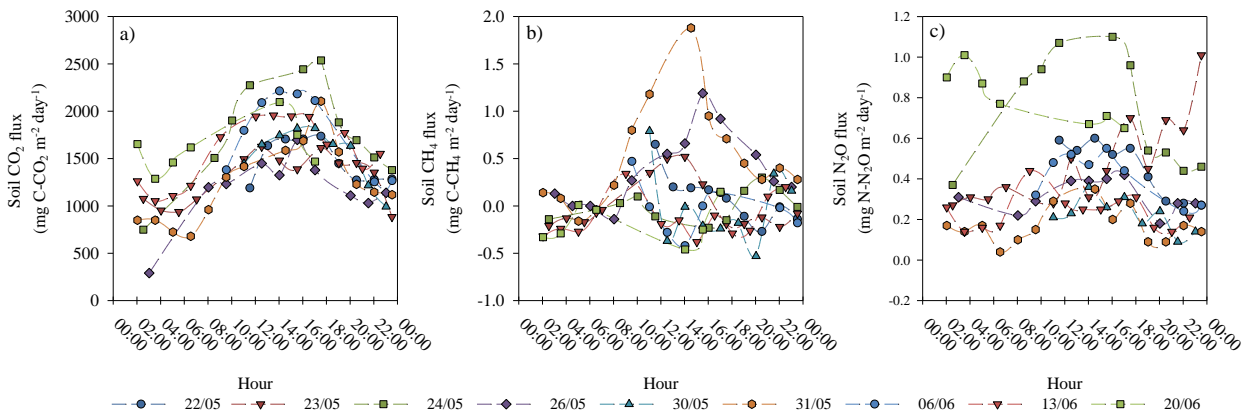
352

353   Differences in the different cumulative emissions found between measurement systems
354   might have been explained by the next three points: (i) construction differences, (ii) the sampling
355   time in the manual system, and (iii) the height/enclosure time ratio (Clough et al., 2020). The
356   automated chamber presented higher area/perimeter ratios and air-mixing by fans which could
357   contribute to the greater fluxes found in this system compared with the manual system. Regarding
358   the sampling time, this was especially critical for CO_2. Manual sampling was performed at 08:00
359   ~~GMT (08:00 am, GMT+2),~~ resulting in an underestimation of the average daily emission
360   (Pumpanen et al., 2003, Yu et al.,2013). In contrast, for N_2O, underestimation was lower since
361   08:00 ~~06:00 GMT~~ is considered a sampling time close to the optimal time for this gas (Wu et al.,
362   2021). Finally, height/enclosure time ratio is also an important factor that affect the sensibility of
363   the flux determination. As a recommendation, height/enclosure time ratio greater than 0.40 m hour^{-1}
364   is suggested to increase the minimum detectable flux and to reduce the impacts on air humidity,
365   temperature and the gas diffusion process, variables that govern the soil gas fluxes between soil
366   and atmosphere (Clough et al., 2020). In our study, the automated system resulted in
367   height/enclosure ratios of 0.60 m hour^{-1}, while in the manual system the ratios dropped to 0.30 m
368   hour^{-1}, explaining the lower cumulative emissions reported by the manual system.

369

370   Moreover, when the daily emission pattern of the automated chamber was, it was observed
371   that soil CO_2 fluxes presented the maximum fluxes rate between 10:00 and 16:00, a daily pattern
372   thar respond to the changes in air and soil temperature, similar to the results reported by Pumpanen
373   et al. (2003) and Yu et al. (2013). Differences between maximum and minimum daily fluxes
374   (Figure 6a). Soil CH_4 fluxes did not show a clear daily pattern, excepted for some dates for (May
375   26th and 31st). Differences between the maximum and the minimum CH_4 fluxes were lower since
376   soil CH_4 fluxes only ranged between -0.5 to 0.5 mg CH_4-C m^{-2} day^{-1} for most of the nine selected

377 dates, expected for May 26th and 31st when soil CH4 fluxes above 1 mg CH$_4$-C m^{-2} day^{-1} were

378 observed at midday (Figure 6b).

379
380 Figure 6. Daily soil gas flux determined by the chamber system for carbon dioxide (CO$_2$) (a),
381 methane (CH$_4$) fluxes (b) and nitrous oxide(N$_2$O) fluxes (c). Vertical solid bars represent the two-
382 hour intervals 08:00 to 10:00 (red), 10:00 to 12:00 (purple) and 12:00 to 14:00 (green), selected
383 for evaluating the daily bias between sampling hours.

384

385   Soil N$_2$O fluxes also presented a daily emission pattern characterized by reaching the

386 maximum soil N$_2$O from 10:00 to 18:00 and the minimum during nighttime, but not being as clear

387 as emission pattern observed for soil CO$_2$ fluxes (Figure 5c). This daily emission pattern was also

388 observed by Wu et al. (2021) in a metanalysis which evaluated global daily N$_2$O emission patterns.

389 A possible explanation to the daily pattern observed in all three gases would be the temperature

390 dependence of the biological process that governs the production and emission of soil GHG (Lloyd

391 and Taylor, 1994, Smith and Dobbie, 2001, Davidson and Janssens, 2006,). This dependence

392 would explain the higher emissions observed during daytime compared to nighttime (Fig. 6c).

393   To evaluate the effect of the selected sampling time for single day measurements could

394 have over the soil fluxes estimation, three two intervals, 08:00-10:00, 10:00-12:00 and 12:00-

395 14:00, were selected. For cumulative soil CO$_2$ emissions, the selected interval had a large impact

396 on the estimation of the emissions, reporting cumulative emissions 23% greater for the 12:00-

397 14:00 intervals against doing the gas sampling between 08:00 and 10:00 (Table 1). Cumulative

soil CH4 emissions presented the highest values for the 08:00-10:00 time interval, however differences in absolute values were too low, indicating that sampling hour could have a lower impact on emissions estimation compared to CO_2 emissions for example (Table 1). Finally, time interval also has an impact on cumulative soil N_2O emissions, observing the greatest emissions for 10:00-12:00 time interval. The large difference what found between 08:00-10:00 and 10:00-12:00 time interval, with a difference of 7.45% in cumulative emissions (Table 1).

Table 1. Cumulative soil emissions (carbon dioxide, CO_2, methane, CH_4, nitrous oxide, N_2O) at three different time intervals (08:00-10:00, 10:00-12:00, 12:00-14:00).

Cumulative emissions	Time intervals			Bias between intervals (%)		
	08:00 - 10:00 (1)	10:00 - 12:00 (2)	12:00 - 14:00 (3)	1 vs 2	1 vs 3	2 vs 3
CO_2 (Mg CO_2-C ha^{-1})	0.40	0.48	0.53	16.12	23.60	8.92
CH_4 (g CH_4-C ha^{-1})	0.23	0.21	0.20	-8.81	-13.40	-4.22
N_2O (g N_2O-N ha^{-1})	0.91	0.99	0.95	7.45	3.79	-3.95

Based on the daily emissions pattern observed couple with the evaluation of the effect of different time interval, sampling time (i.e. hour) can have an impact on soil gases flux estimation, especially when only one sampling is done per day, as occurred with manual chamber systems. For soil CO_2 emissions, carried out the manual sampling at 08:00 supposed an underestimation of 43% respect to the mean daily flux estimated over 24 hours estimated with automated chamber system for the nine dates evaluated. Average soil CO_2 fluxes determined with the manual chamber system over the nine dates was 836 mg CO_2-C m^{-2} day^{-1}, while the 24 hours CO_2 flux for the same nine date measuring with the automated chambers system was 1469 mg CO_2-C m^{-2} day^{-1}. In contrast, sampling hour had a minimum impact on soil CH_4 fluxes, obtaining the similar average flux in both systems, 0.066 and 0.068 836 mg CH_4-C m^{-2} day^{-1} for the manual and the automated chamber system, respectively.

Regarding N_2O emissions, 08:00 resulted in an adequate sampling hour to obtain a representative daily emission. Average soil N_2O flux of the nine manual sampling was 0.38 mg N_2O-N m^{-2} day^{-1}, while the daily average for the same nine dates estimated with the automated chamber system was 0.41 mg N_2O-N m^{-2} day^{-1}, resulting the fluxes determined with the manual chambers in an underestimation of 7% compared to the daily average soil N_2O flux determined with the automated chambers. Perhaps, considering the evaluation of the three different time intervals, carrying out the soil gas sampling between 10:00 to 12:00 could be reduce this underestimation.

4. Conclusion

The presented system features an open design, cost-effective components, and adaptable configuration, offering benefits in flexibility, compatibility, and affordability, which in the end resulted in a more precise monitoring of the time flux variability. Moreover, it has been highlighted 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 height/enclosure time ratios greater than 0.10m and 0.40m h^{-1}, respectively. Likewise, in case there is not option to implement an automated system, the sampling time of the manual measurement system is critical resulting in significant over or underestimation. Our results showed that 08:00 ~~06:00GMT~~ was an optimal sampling time for soil N_2O emissions but resulted in an underestimation of soil CO_2 and CH_4 emissions, being more adequate performing the gas sampling between 10:00 to 12:00 to reduce emissions overestimation compared to the mean daily emissions, especially for CO_2. Therefore, based on the results presented in this work, automated chamber systems are a powerful tool for quantifying GHG fluxes from the soil, allowing to capture the large temporal variability that characterizes GHG emissions. However, when the implementation of automated measurement system was not possible, sampling time for manual chamber must be

443   considered to avoid underestimation of soil fluxes, being the time interval between 10:00 to 12:00

444   the most appropriate time interval.

Data availability

All raw data can be provided by the corresponding authors upon request.

Author contributions

SF-L: Conceptualization, formal analysis, software, data acquisition, writing—original draft, data curation, methodology, formal analysis, investigation. MA-A: Conceptualization, methodology, writing—review; editing. BW: Writing—review. BL: Conceptualization ,methodology, software, writing—review, funding acquisition. JA-F: Conceptualization ,methodology, writing—review; editing, supervision, project administration, resources, funding acquisition

Competing interests

The authors declare that they have no conflict of interest.

Acknowledgements

We are grateful to Valero Pérez Laguardia for assistance in the in the development, construction and maintenance of the manual and automated chamber systems.

Financial support

This work was supported by the project AgriGEI funded by the Regional Government of Aragon ("Proyectos de I+D+i en líneas prioritarias del Gobierno de Aragón", Ref. LMP185_21) and the project TED2021-130837B-I00 funded by MCIN/AEI/ /10.13039/501100011033 and by the "European Union NextGenerationEU/PRTR".

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 N_2O chamber methodology guidelines: Design considerations. J. Environ. Qual., 49(5), 1081-1091. https://doi.org/10.1002/jeq2.20117

Collier, S. M., Ruark, M. D., Oates, L. G., Jokela, W. E., & Dell, C. J. (2014). Measurement of greenhouse gas flux from agricultural soils using static chambers. JoVE, (90), e52110. https://doi.org/10.3791/52110

Davidson, E. A., & Janssens, I. A. (2006). Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. Nature, 440(7081), 165-173. 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

490   Ferrara, R. M., Carozzi, M., Decuq, C., Loubet, B., Finco, A., Marzuoli, R., Gerosa, G., Di

491   Tommasi, P., Magliulo, V. & Rana, G. (2021). Ammonia, nitrous oxide, carbon dioxide, and water

492   vapor fluxes after green manuring of faba bean under Mediterranean climate. Agric. Ecosyst.

493   Environ., 315, 107439. https://doi.org/10.1016/j.agee.2021.107439

494   Forte, A., Fiorentino, N., Fagnano, M., & Fierro, A. (2017). Mitigation impact of minimum

495   tillage on CO_2 and N_2O emissions from a Mediterranean maize cropped soil under low-water input

496   management. Soil Tillage Res., 166, 167-178. https://doi.org/10.1016/j.still.2016.09.014

497   Francis Clar, J. T., & Anex, R. P. (2020). Flux intensity and diurnal variability of soil N_2O

498   emissions in a highly fertilized cropping system. Soil Sci. Soc. Am. J., 84(6), 1983-1994.

499   https://doi.org/10.1002/saj2.20132

500   Franco-Luesma, S., Álvaro-Fuentes, J., Plaza-Bonilla, D., Arrúe, J. L., Cantero-Martínez,

501   C., & Cavero, J. (2019). Influence of irrigation time and frequency on greenhouse gas emissions

502   in a solid-set sprinkler-irrigated maize under Mediterranean conditions. Agric. Water Manage.,

503   221, 303-311. https://doi.org/10.1016/j.agwat.2019.03.042

504   Franco-Luesma, S., Cavero, J., Plaza-Bonilla, D., Cantero-Martínez, C., Tortosa, G.,

505   Bedmar, E. J., & Álvaro-Fuentes, J. (2020). Irrigation and tillage effects on soil nitrous oxide

506   emissions in maize monoculture. Agron. J., 112(1), 56-71. https://doi.org/10.1002/agj2.20057

507   Franco-Luesma, S., Cavero, J., Plaza-Bonilla, D., Cantero-Martínez, C., Arrúe, J. L., &

508   Álvaro-Fuentes, J. (2020). Tillage and irrigation system effects on soil carbon dioxide (CO_2) and

509   methane (CH_4) emissions in a maize monoculture under Mediterranean conditions. Soil Tillage

510   Res., 196, 104488. https://doi.org/10.1016/j.still.2019.104488

511   Franco-Luesma, S., Lafuente, V., Alonso-Ayuso, M., Bielsa, A., Kouchami-Sardoo, I.,

512   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 N_2O 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 N_2O chamber methodology guidelines: Recommendations for air sample collection, storage and analysis. J. Environ. Qual., 49(5), 1110-1125. https://doi.org/10.1002/jeq2.20129

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

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

536   Lloyd, J. and Taylor J, A. (1994). On the temperature dependence of soil respiration.

537   Functional Ecology, 8, 315–323. https://doi.org/10.2307/2389824

538   Lognoul, M., Theodorakopoulos, N., Hiel, M. P., Regaert, D., Broux, F., Heinesch, B., ...

539   & Aubinet, M. (2017). Impact of tillage on greenhouse gas emissions by an agricultural crop and

540   dynamics of N_2O fluxes: Insights from automated closed chamber measurements. Soil Tillage

541   Res., 167, 80-89. https://doi.org/10.1016/j.still.2016.11.008

542   Nickerson, N. (2016). Evaluating gas emission measurements using Minimum Detectable

543   Flux (MDF). Eosense Inc., Dartmouth, Nova Scotia, Canada.

544   Oertel, C., Matschullat, J., Zurba, K., Zimmermann, F., & Erasmi, S. (2016). Greenhouse

545   gas   emissions   from   soils—A   review.   Chem   Erde-Geochem.,   76(3),   327-352.

546   https://doi.org/10.1016/j.chemer.2016.04.002

547   Parkin, T. B. (2008). Effect of sampling frequency on estimates of cumulative nitrous oxide

548   emissions. J. Environ. Qual., 37(4), 1390–1395. https://doi.org/10.2134/jeq20 07.0333

549   Pihlatie, M. K., J. R. Christiansen, H. Aaltonen, J. F. J. Korhonen, A. Nordbo, T. Rasilo,

550   G. Benanti, M. Giebels, M. Helmy, J. Sheehy, S. Jones, R. Juszczak, R. Klefoth, R. Lobo-do-Vale,

551   A. P. Rosa, P. Schreiber, D. Serça, S. Vicca, B. Wolf, and J. Pumpanen. (2013). Comparison of

552   static chambers to measure CH_4 emissions from soils. Agric. For. Meteorol., 171, 124-136.

553   https://doi.org/10.1016/j.agrformet.2012.11.008

554   Pumpanen, J., Ilvesniemi, H., Perämäki, M., & Hari, P. (2003). Seasonal patterns of soil

555   CO_2 efflux and soil air CO_2 concentration in a Scots pine forest: comparison of two chamber

556   techniques. Glob. Change Biol., 9(3), 371-382. https://doi.org/10.1046/j.1365-2486.2003.00588.x

557   R Core Team (2022). R: A language and environment for statistical computing. R

558   Foundation for Statistical Computing, Vienna, Austria. Version 4.2.2. https://www.R-project.org/

559   Reeves, S., Wang, W., Salter, B., & Halpin, N. (2016). Quantifying nitrous oxide emissions

560   from sugarcane cropping systems: Optimum sampling time and frequency. Atmos. Environ., 136,

561   123-133. https://doi.org/10.1016/j.atmosenv.2016.04.008

562   Rochette, P., & Eriksen-Hamel, N. S. (2008). Chamber Measurements of Soil Nitrous

563   Oxide Flux: Are Absolute Values Reliable? Soil Sci. Soc. Am. J., 72(2), 331.

564   doi:10.2136/sssaj2007.0215

565   Savage, K., Phillips, R., & Davidson, E. (2014). High temporal frequency measurements

566   of greenhouse gas emissions from soils. Biogeosciences, 11(10), 2709-2720.

567   https://doi.org/10.5194/bg-11-2709-2014

568   Smith, K. A., & Dobbie, K. E. (2001). The impact of sampling frequency and sampling

569   times on chamber- based measurements of N2 O emissions from fertilized soils. Glob. Change

570   Biol., 7(8), 933–945. https://doi.org/10.1046/j.1354-1013.2001.00450.x

571   Yu, L., Wang, H., Wang, G., Song, W., Huang, Y., Li, S. G., Liang, N., Tang, Y. & He, J.

572   S. (2013). A comparison of methane emission measurements using eddy covariance and manual

573   and automated chamber-based techniques in Tibetan Plateau alpine wetland. Environ. Pollut., 181,

574   81-90. https://doi.org/10.1016/j.envpol.2013.06.018

575   Wang, Z.-P., & Han, X.-G. (2005). Diurnal variation in methane emissions in relation to

576   plants and environmental variables in the Inner Mongolia marshes. Atmos. Environ., 39(34),

577   6295–6305. https://doi.org/10.1016/j.atmosenv.2005.07.01

578   Wiebe, K., Robinson, S., & Cattaneo, A. (2019). Climate change, agriculture and food

579   security: impacts and the potential for adaptation and mitigation. Sustainable Food and

580   Agriculture, 55-74. https://doi.org/10.1016/B978-0-12-812134-4.00004-2

581   Wu, Y. F., Whitaker, J., Toet, S., Bradley, A., Davies, C. A., & McNamara, N. P. (2021).

582   Diurnal variability in soil nitrous oxide emissions is a widespread phenomenon. Glob. Change

583   Biol., 27(20), 4950-4966. https://doi.org/10.1111/gcb.15791

584

585