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

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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 compare it with a manual chamber 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 chamber dimension and shape in the development of chamber systems, as well as sampling frequency and sampling hour, for manual chamber system.

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. Subsequently, the 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.

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

99   also presented.

100 **2. Materials and Methods**
101   *2.1. Automated system description*

102   In this section, we present an automated chamber system tailored for monitoring soil gas

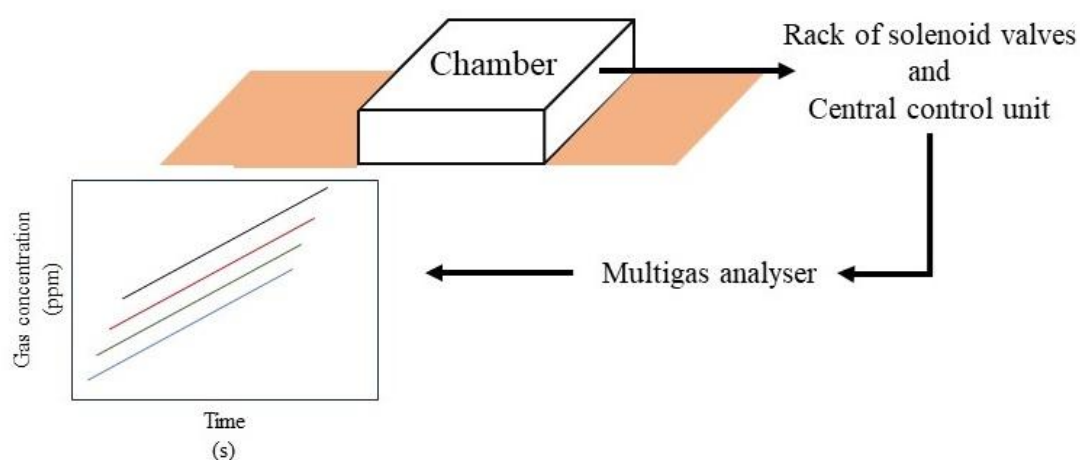
103 emissions. By integrating openness, cost-effectiveness, and versatility, this system facilitates

104 precise and dynamic measurements of soil GHG fluxes. Our design principles focused on building

105 an adaptable configuration and real-time functionality, alluding to its potential importance in

106 agricultural and environmental research. The system consists of three main parts: the chambers,

107 the set of solenoid valves controlled by a computer (central control unit) and the multigas analyser

108 (Figure 1).

109
110 Figure 1. General scheme of the automated soil GHG measurement system.
111

112   *2.2. Soil chamber design*

113   Soil chambers, 'Queensland' design, have been built following a model provided by the

114 Terrestrial Bio-Geo-Chemistry Division (Institute of Meteorology and Climate Research, Atmos.

115 Environ.al Research (IMK-IFU), Karlsruhe Institute of Technology (KIT)). Chambers consisted

116 of an aluminum structure of 0.50 x 0.50 m length and width and 0.15 m height closed with

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 90º 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.

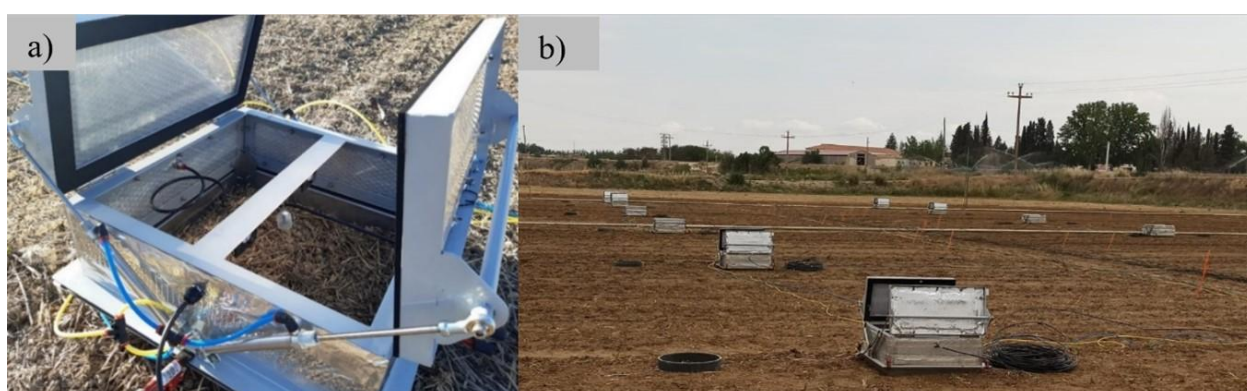



Figure. 2. (a) Open automated chamber deployed in the field trial ('Queensland' design). (b) Set of chambers deployed in the field trial. Dark rings next to chambers are the bases for manual chambers.

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

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

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

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

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

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

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

144   €.

145   *2.3. Automated chamber operation*

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

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

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

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

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

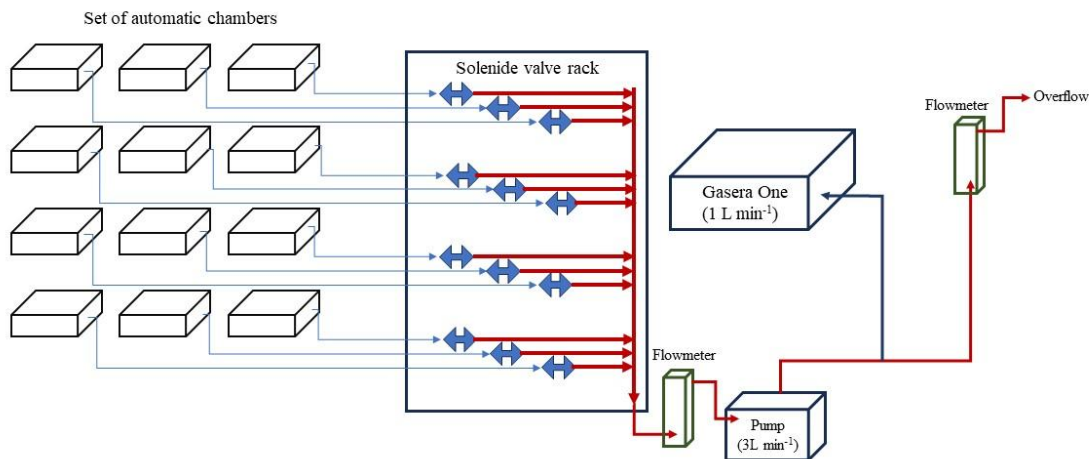
151   configuration of this study, three sets of four chambers each opened and closed simultaneously.

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

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

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

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

156   (Figure 3).

157
158 Figure. 3. Description of the automated chamber system.
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160   To bring the gas from the chamber to the gas analyser, an external diaphragm pump (KNF

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

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

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

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

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

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

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

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

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

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

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

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

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

174 advantages of this system is the self-made multiplexer that allows to modify the number of

175 chambers easily compared to other multiplexers like Gasera Multipoint Sampler (Gasera Ltd,

176 Finland) which has a close configuration of 8 or 12 channels. Moreover, the use of relay boards

177 that could be configured by Arduino or easily integrated into the R script as the selected ones, as

178 an alternative to control modules, for example, I-7060D (ICP DAS CO, LTD) that only have four

179 channels per module, simplifies the configuration of the script, since just with one board it's

180 possible to handle all the chambers. For this field experiment, the current setup consists of 3 blocks

181 of four chambers each block. This configuration responds to the needs of the current experimental

182 design, however, since it is an open system, the configuration is variable and can be individualised

183 for each of the chambers.

184

185 *2.4. Evaluation of the automated measurement system*

186 Over the last decade, the current research team members have successfully conducted

187 several GHG flux studies using a manual closed chamber system (Álvaro-Fuentes et al., 2016,

188 Franco-Luesma et al., 2019,2020a, 2020b, 2022). Based on that, an evaluation experiment was

189 carried out to compare the soil gas fluxes obtained via the newly developed automated chamber

190 system against the conventional manual chamber system used regularly by the research group.

191 This evaluation experiment was aimed to evaluate the impact of i) the chamber design and ii) the

192 sampling frequency and time on the differences in soil GHG fluxes between a manual and an

193 automated chamber measurement system.

194 Manual chambers consisted of a Polyvinyl Chloride (PVC) cylinder of 0.315 m diameter

195 and 0.2 m height coated by white thermal paint to avoid internal air temperature increasing during

196 the deployed time. Each chamber was placed same diameter PVC collar inserted 0.05 m into the

197 soil. A rubber septum was affixed atop the chamber to enable gas sampling via a plastic syringe

198 equipped with a needle. Gas samples from each chamber were transferred to a 12 mL pre-

199 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. On June 21st and June 28th, chambers were sampled four times between 08:00 to 14:00. 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.

249   *2.5. Data analysis*

250   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

251   calculated using the following equation (Eq. 1)

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

253   where *Fit* represents the linear increase of gas concentration in the chamber over the

254   enclosure time, *MW* is the molar weight of the atom in the gas molecule (i.e. 12 g mol^{-1} for CO_2-

255   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

256   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

257   the correction factor of time units, 1440 minutes day^{-1} and *fU* is the unit correction factor, 10^3.

258   Cumulative soil CO_2, CH_4 and N_2O emissions were calculated using the trapezoid rule (Levy et

259   al., 2017). Comparison between systems was done by linear fitting considering only soil gas fluxes

260   that presented a R^2 higher than 0.8. Moreover, comparison in cumulative emissions between

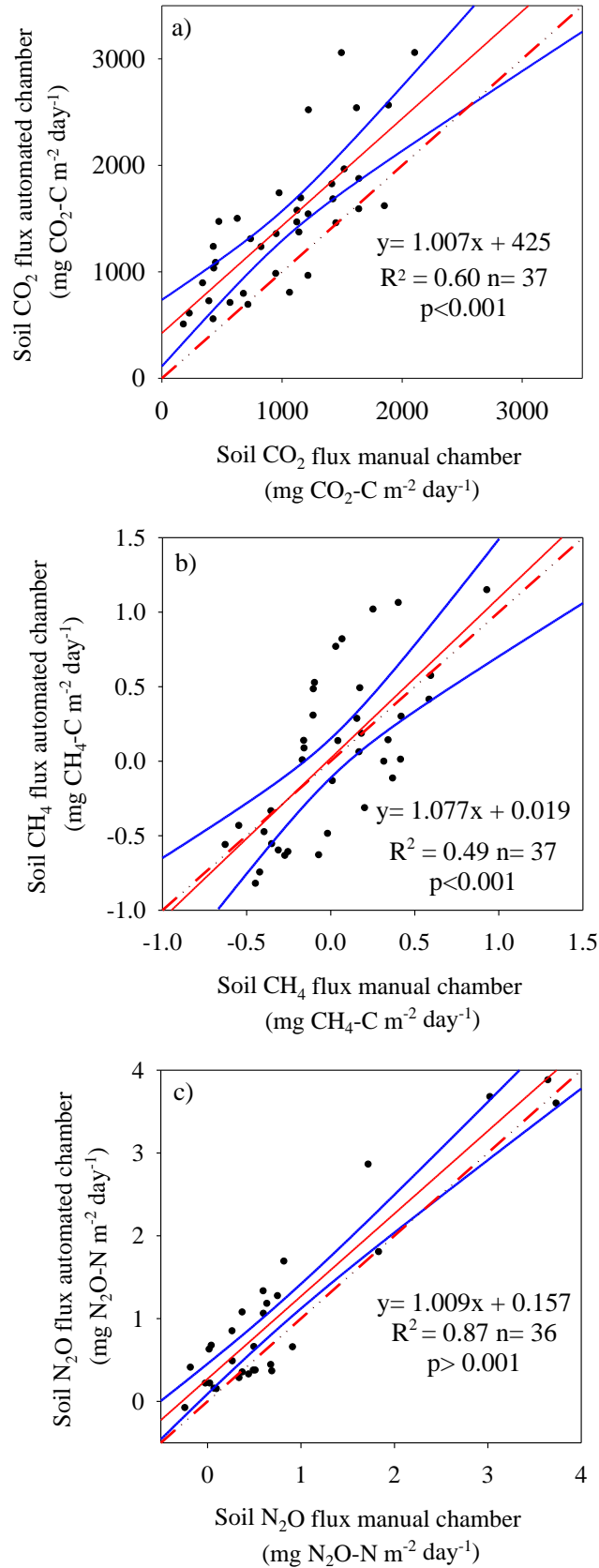
261   chamber system over one month was evaluated by one-way ANOVA. All analyses were done

262   using the R statistical software version 4.2.2 (R Core Team, 2022).

263   .

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).

276
277 Figure 4. Comparison of soil gas flux between automated and manual chamber systems for carbon
278 dioxide (CO_2) fluxes (a), methane (CH_4) fluxes (b) and nitrous oxide (N_2O) fluxes (c). Blue solid
279 lines represent 95% confidence intervals. Red dotted lines represent 1:1 line.
280

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

282   studied gases may probably be a consequence of the different chamber shapes and dimensions.

283   Hoffmann et al. (2018) found that the shape and dimension of the chamber have a significant effect

284   on CO_2 fluxes, observing that small and cylindrical chambers tend to result in higher

285   underestimation of CO_2 fluxes compared with large and squared chambers. In line with the

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

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

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

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

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

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

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

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

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

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 recommended

297   to homogenize the internal air of the chamber, ensuring that the air sample aliquot is representative

298   of the chamber headspace air (Clough et al., 2020).

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

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

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

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

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

304   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

305   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^{-}

306 [1]. MDF was greater for the automated chamber system for the three gases, considering a similar

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

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

309 greatest fluxes values observed under the automated chamber system.

310

311 *3.2. Sampling time and frequency comparison*

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

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

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

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

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

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

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

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

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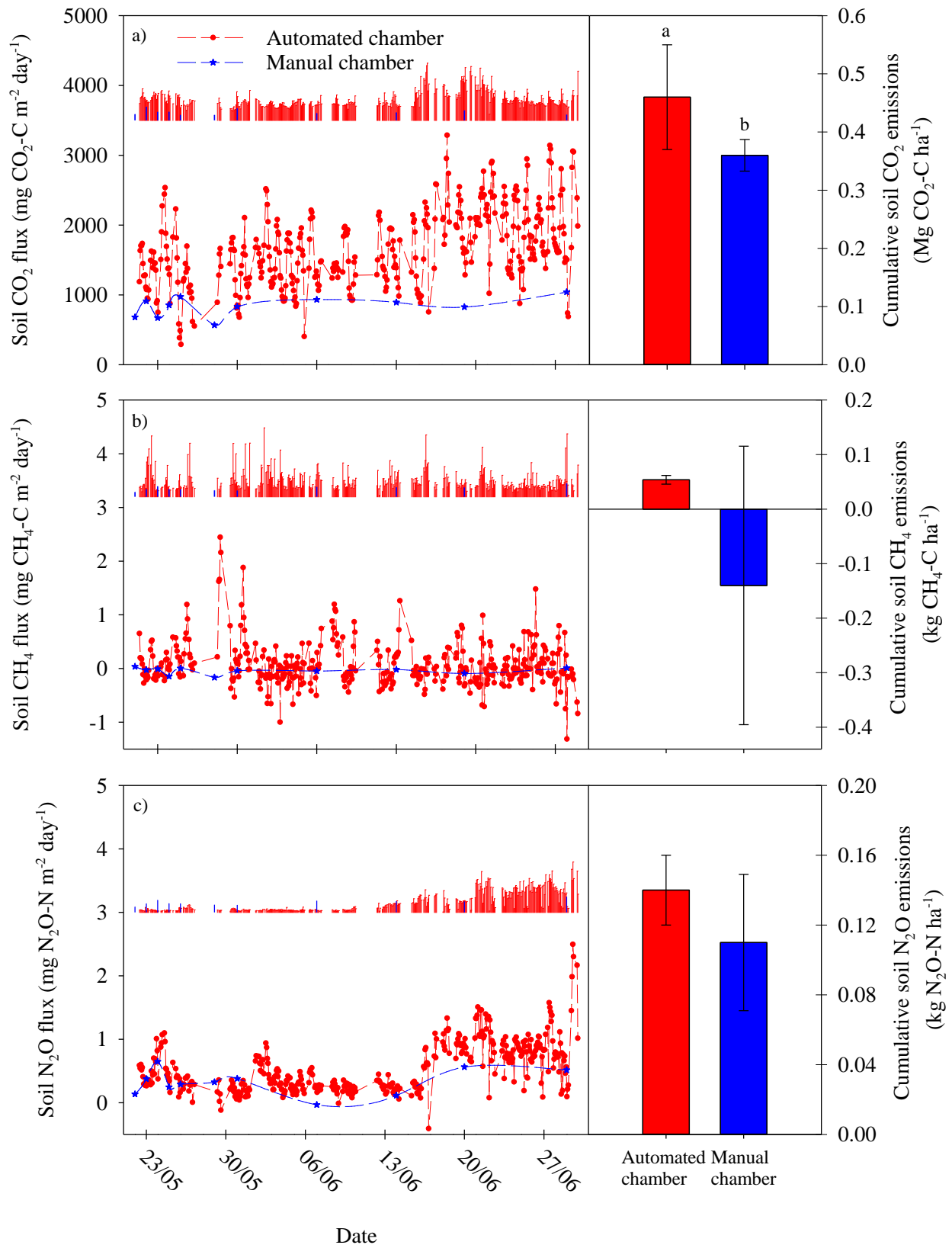


Figure 5. Comparison of soil gas flux and cumulative soil gas emissions between the automated (red line and bar) and the manual (blue line and bar) chamber system for carbon dioxide (CO_2) fluxes (a), methane (CH_4) fluxes (b) and nitrous oxide(N_2O) fluxes (c). Vertical solid lines represent standard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

328   Soil CO_2 and CH_4 fluxes determined by the manual chamber system showed similar behaviour, presenting a low variation in the fluxes magnitude over the evaluated period, being more pronounced for soil CH_4 fluxes (Figure 5a, 5b). For example, this was clearly observed in the CH_4 in which the automated system captured flux peaks greater than 2 mg CH_4-C m^{-2} day^{-1} while the manual fluxes were close to 0 mg CH_4-C m^{-2} day^{-1} over the entire measuring period (Figure 5b). Interestingly, the manual system was able to capture the temporal emission trend shown by the automated system for soil N_2O fluxes, the gas that showed the greatest temporal variability over the period studied (Figure 5c).

336   The cumulative soil gas emissions of the three gases tended to be greater for the automated than the manual measurement system (Fig. 5). For example, cumulative soil CO_2 emissions presented significant differences between both sampling systems. The automated chamber system showed average values 16% more than the manual chamber system (Fig 5a). Indeed, this difference was even greater in CH_4 (more than 3-fold greater cumulative emissions in the automated than in the manual measurement system, Fig. 5b). Cumulative CH_4 emissions showed positive values for the 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 for the automated chamber system, a fact that resulted in the absence of significant differences 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. 5c). As occurred with cumulative CH_4 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.

352   Differences in the different cumulative emissions found between measurement systems

353   might have been explained by the next three points: (i) construction differences, (ii) the sampling

354   time in the manual system, and (iii) the height/enclosure time ratio (Clough et al., 2020). The

355   automated chamber presented higher area/perimeter ratios and air-mixing by fans which could

356   contribute to the greater fluxes found in this system compared with the manual system. Regarding

357   the sampling time, this was especially critical for CO_2. Manual sampling was performed at 08:00,

358   resulting in an underestimation of the average daily emission (Pumpanen et al., 2003, Yu et

359   al.,2013). In contrast, for N_2O, underestimation was lower since 08:00 is considered a sampling

360   time close to the optimal time for this gas (Wu et al., 2021). Finally, height/enclosure time ratio is

361   also an important factor that affect the sensibility of the flux determination. As a recommendation,

362   height/enclosure time ratio greater than 0.40 m hour^{-1} is suggested to increase the minimum

363   detectable flux and to reduce the impacts on air humidity, temperature and the gas diffusion

364   process, variables that govern the soil gas fluxes between soil and atmosphere (Clough et al.,

365   2020). In our study, the automated system resulted in height/enclosure ratios of 0.60 m hour^{-1},

366   while in the manual system the ratios dropped to 0.30 m hour^{-1}, explaining the lower cumulative

367   emissions reported by the manual system.

368

369   Moreover, when the daily emission pattern of the automated chamber was, it was observed

370   that soil CO_2 fluxes presented the maximum fluxes rate between 10:00 and 16:00, a daily pattern

371   thar respond to the changes in air and soil temperature, similar to the results reported by Pumpanen

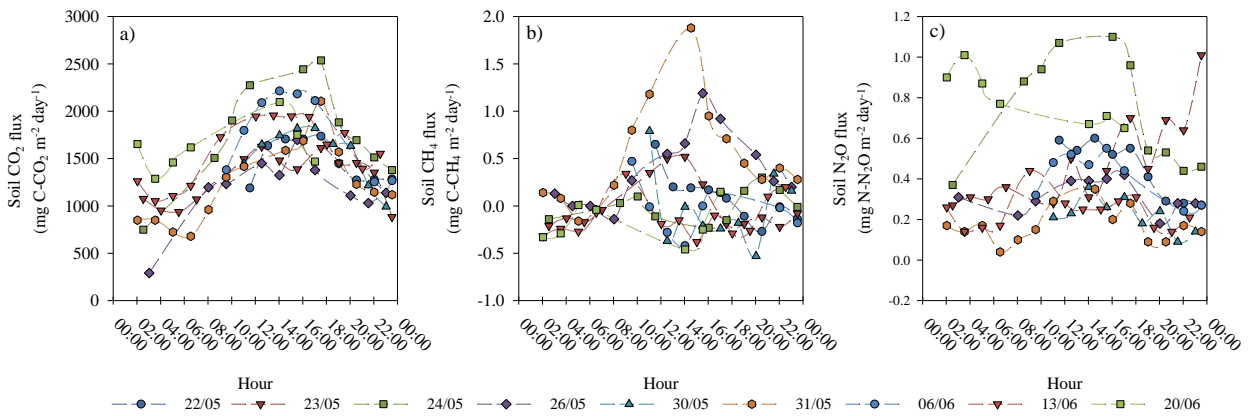
372   et al. (2003) and Yu et al. (2013). Differences between maximum and minimum daily fluxes

373   (Figure 6a). Soil CH_4 fluxes did not show a clear daily pattern, excepted for some dates for (May

374   26th and 31st). Differences between the maximum and the minimum CH_4 fluxes were lower since

375   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

376 dates, expected for May 26th and 31st when soil CH4 fluxes above 1 mg CH_4-C m^{-2} day^{-1} were

377 observed at midday (Figure 6b).

378
379 Figure 6. Daily soil gas flux determined by the chamber system for carbon dioxide (CO_2) (a),
380 methane (CH_4) fluxes (b) and nitrous oxide(N_2O) fluxes (c). Vertical solid bars represent the two-
381 hour intervals 08:00 to 10:00 (red), 10:00 to 12:00 (purple) and 12:00 to 14:00 (green), selected
382 for evaluating the daily bias between sampling hours.

383

384 Soil N_2O fluxes also presented a daily emission pattern characterized by reaching the

385 maximum soil N_2O from 10:00 to 18:00 and the minimum during nighttime but not being as clear

386 as emission pattern observed for soil CO_2 fluxes (Figure 6c). This daily emission pattern was also

387 observed by Wu et al. (2021) in a metanalysis which evaluated global daily N_2O emission patterns.

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

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

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

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

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

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

394 14:00, were selected. For cumulative soil CO_2 emissions, the selected interval had a large impact

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

396 14:00 intervals against doing the gas sampling between 08:00 and 10:00 (Table 1). Cumulative

soil CH_4 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.

417   Regarding N_2O emissions, 08:00 resulted in an adequate sampling hour to obtain a

418   representative daily emission. Average soil N_2O flux of the nine manual sampling was 0.38 mg

419   N_2O-N m^{-2} day^{-1}, while the daily average for the same nine dates estimated with the automated

420   chamber system was 0.41 mg N_2O-N m^{-2} day^{-1}, resulting the fluxes determined with the manual

421   chambers in an underestimation of 7% compared to the daily average soil N_2O flux determined

422   with the automated chambers. Perhaps, considering the evaluation of the three different time

423   intervals, carrying out the soil gas sampling between 10:00 to 12:00 could be reduce this

424   underestimation.

425

426   **4. Conclusion**

427   The presented system features an open design, cost-effective components, and adaptable

428   configuration, offering benefits in flexibility, compatibility, and affordability, which in the end

429   resulted in a more precise monitoring of the time flux variability. Moreover, it has been highlighted

430   that the shape, dimension, and configuration of the chamber system are critical factors that must

431   be considered in the design of the chambers, being critical in setting area/perimeter and

432   height/enclosure time ratios greater than 0.10m and 0.40m h^{-1}, respectively. Likewise, in case there

433   is not option to implement an automated system, the sampling time of the manual measurement

434   system is critical resulting in significant over or underestimation. Our results showed that 08:00

435   ~~06:00GMT~~ was an optimal sampling time for soil N_2O emissions but resulted in an

436   underestimation of soil CO_2 and CH_4 emissions, being more adequate performing the gas sampling

437   between 10:00 to 12:00 to reduce emissions overestimation compared to the mean daily emissions,

438   especially for $CO_{2.}$. Therefore, based on the results presented in this work, automated chamber

439   systems are a powerful tool for quantifying GHG fluxes from the soil, allowing to capture the large

440   temporal variability that characterizes GHG emissions. However, when the implementation of

441   automated measurement system was not possible, sampling time for manual chamber must be

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

443   the most appropriate time interval.

Data availability

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

Code and data availability

The R code and notebooks of the automatic chamber system and the data used to compare and validate the function of the automatic chamber system can be found at https://zenodo.org/records/15189414. (Franco-Luesma et al., 2025).

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.

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