









#### **Highlights**

- 31 1. A new multiport profile system simplifies examining the  $CO<sub>2</sub>$  and H<sub>2</sub>O storage terms.
- 2. Neglecting canopy storage terms leads to inaccuracies in crop energy balance closure.
- 3. Energy closure is improved if canopy storage is considered.
- 4. The multiport system is necessary for eddy covariance-derived fluxes over maize canopy.

#### **Abstract**

36 The significance of canopy storage of CO<sub>2</sub>, latent energy and sensible heat within agricultural crops has not been fully examined. Reported canopy storage terms are consistently smaller than found for a forest ecosystem, such that they are often neglected. A novel multiport profile system has been developed to examine these storage terms. The system sequentially samples air from four heights to a single non-dispersive Infrared Gas Analyzer (IRGA). Following extensive 41 laboratory testing, the system was used to measure  $CO<sub>2</sub>$  and H<sub>2</sub>O within an eastern Tennessee maize canopy in 2023. The storage of latent and sensible heat was large enough to merit incorporation with conventional field measurements. The new system will enable profile 44 measurements of  $CO<sub>2</sub>$  sufficient to quantify canopy storage terms as are needed in agricultural field campaigns.

 **Keywords:** Multi-port system, vertical canopy profile, storage terms, energy balance closure, maize, carbon sequestration

**1 Introduction**

 In the last few decades, significant work has been conducted to improve understanding of gaseous exchanges between soils, plants, and the atmosphere. These improvements have been rapidly incorporated into land-surface models and numerical-based weather prediction as well as assessment of atmospheric fluxes of carbon dioxide (Lamas Galdo et al., 2021), water vapor (Wang et al., 2023), and heat over vegetated landscapes (e.g., Tilden and Steven, 2004). Eddy 54 covariance (EC) is a widely accepted method to measure the fluxes of  $CO<sub>2</sub>$ , H<sub>2</sub>O, and heat in the ecosystem (Nicolini et al., 2018). Routine EC measurements are now made at more than 650 locations, distributed globally (Fluxnet; Baldocchi, 2003).

 At most forest experimental sites, the measured energy budget is not always close to the balance calculated by the conventional method expressed by Eq. (1) (Wilson et al., 2002). An important





 factor emerging from forest ecosystem studies is that storage terms contribute substantially to the energy closure of forests and to the quantification of evapotranspiration (McCaughy and Saxton, 1988). In most forest studies, storage terms are ignored in consideration of the energy balance equation:

### 63  $R_n - G = H + LE$  (1)

Here, *R<sup>n</sup>* is net radiation, *G* is soil heat flux, *H* is sensible heat flux and *LE* is latent heat flux*.*

65 Storage measurement is challenging due to temporal changes in  $CO<sub>2</sub>$ , H<sub>2</sub>O, and heat (Yang et al., 1999). Globally, only a few sites (less than 30 %) apply a profile measurement system to calculate the temporal variations and storage terms (Papale, 2006). Many studies have reported that energy balance closure is an unsolved problem for a variety of vegetation types: the sum of sensible and latent heat flux is found to be 10-30% lower than the available energy (Wilson et al.,2002; Twine et al.,2000; Leuning et al. 2012; Russell et al. 2015; Liu et al. 2017; Raza et al., 2023a). There are several possible reasons for energy closure errors resulting from EC experimentation, such as neglecting the canopy and soil storage terms, loss of low- or high- frequency flux components, and the use of inappropriate averaging times, etc. (Massman, 2000; Meyers and Hollinger, 2004). Measurement procedures to test energy balance closure vary by researchers and there is no standardized way to address the issues that arise.

 In the case of agricultural cropping systems, storage terms are considered small and are often ignored (Raza et al., 2024; Nicolini et al., 2018). Studies on the assessment of storage terms within agricultural ecosystems are few, but the matter is well documented by researchers in the case of forest ecosystems studies (Mayocchi and Bristow, 1995; Wilson et al., 2002).

 Storage terms quantification is challenging because of its requirement for measurements both within and above the canopy (Yang et al., 1999). Finnigan (2006) reported that the storage term is underestimated when the average sampling time is large. Neglecting canopy storage 83 terms in studies of Net Ecosystem Exchange (NEE) can also cause substantial errors (Raza et al., 2023b). To understand the role of the storage terms in energy balance closure and NEE, new measurement and analysis approaches are required (Irmak et al, 2014).

 In the most recent series of field experiments conducted by the present research team, 87 as now reported, the emphasis has also been on fluxes of carbon dioxide ( $CO<sub>2</sub>$ ). The field site is





 large enough to warrant the use of EC measurement systems without fears of fetch and/or footprint limitations (q.v., Foken et al., 2017). Measurement procedures followed the recommendations of FLUXNET (Wilson et al., 2002) and ICOS (Montagnani et al., 2018). A key aspect 91 of the research program was the requirement for CO<sub>2</sub> concentration measurements at several 92 heights within the plant canopy, to permit examination of (1) flux interactions with pooled  $CO<sub>2</sub>$ 93 at night; (2) the CO<sub>2</sub> storage term derived from EC observations; and (3) sub-canopy mixing.

 The purpose of the present paper is to describe a measurement system specifically designed to provide observations for assessing the quantities contributing to the diurnal heat cycle, including the various storage terms and net ecosystem exchange. The instrumentation now described will be used to extend the analysis into the inter-canopy airspace, using eddy covariance observations as a basis for assessing storage terms. The protocols recommended by the ICOS community (e.g., Montagnani et al., 2018) have been used as guidance.

### **2 Methodology/Configuration**

#### **2.1 Apparatus design, operation, and measurement**

 Field experiments have repeatedly shown that the need for an uninterrupted series of observations of difficult–to–measure variables impose technical requirements that are often difficult to satisfy. In practice, the more complicated a measurement system, the more likely the desired continuous records will be interrupted by instrumentation malfunctions or by a variety of other unanticipated issues. Such interruptions have been a challenge in the many studies of maize crops conducted by the University of Tennessee (O'Dell et al, 2014; Hicks et al., 2020) in their series of field experiments These field experiments (in Lesotho and Zimbabwe as well as in Tennessee and Ohio in the USA) have demonstrated the need for a reliable yet technically simple measurement system to measure profiles of the quantities of interest, within and above a growing crop. To satisfy the basic requirements for time continuity and reliability of the data record, a multi-port sampling system has been developed. The intent is to facilitate the routine acquisition of temperature, humidity, and carbon dioxide data within and above a maize canopy.

 Analysis of the recorded observations requires attention to gradients of the variables measured and well as to the variables themselves. To minimize consequences of individual sensor offsets when gradients are computed, the new system is designed to use a single detection system (an





 IRGA —LI-COR-850, CO2/H2O gas analyzer). In the application considered here, the system was used to measure four heights, two within a maize canopy and two above.

 Figure 1 presents a schematic description of the apparatus. The system is designed to maintain continuous airflow through all intake tubes, to cycle through all heights of measurement every minute and to minimize the switching time between samplings. The system consists of two small pumps [Model TD-3LSA, Brailsford & CO., INC. Antrium. NH, USA], one pump (purge pump) draws in the sampling air to maintain constant flow to minimize hygroscopic interactions along the tube wall while the other pump pushes the drawn air to the IRGA. The sampling pump is mounted close to the IRGA so that air smoothly enters the IRGA at ambient pressure. The airflow rate through the sampling tubes is regulated by a flow meter [LZQ-7 flowmeter, 101.3 KPa, Hilitland] at 700 ml/min; the flow rate through the IRGA is maintained 1000 ml/min. The switching between heights is controlled by four three-way solenoid valves [231Y-6, Ronkonkoma, NY, USA]. The body material of the solenoid is brass, and the internal component material is stainless steel as is required when water vapor is present.

 Each sampling tube is 10.5 m long to ensure each sampling height has the same transit time. The purge pump manifold and all sampling tubes are of the same kind of urethane [BEV-A-LINE, Polyethylene material, Cole Parmer]. Before passing through the analyzer, the air is passed through a 1-µm pore filter [LI-6262, LI-COR NE, USA] to avoid the drifting of the analyzer and pumps during the time of measurement due to the accumulation of debris, dirt, particulates, etc., that can cause blockage in the analyzer optical cells. The air outlet of the purge pump and IRGA are open directly to the atmosphere.

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Figure 1abc (a) Schematic diagram of the manifold for profile sampling of CO<sub>2</sub>, water vapor (H<sub>2</sub>O), (b) analyzer, pump, and manifold system, (c) data logger for data collection

# 146 **2.2 Sampling time**

147 To determine the sampling time of the multiport system for accurate measurement of  $CO<sub>2</sub>$  and 148 H2O, the system was first evaluated in the laboratory. The apparatus was first flushed with 149 nitrogen (N2) gas to create a zero-carbon dioxide (0 ppm) environment. Subsequently, a known





150 concentration of  $CO<sub>2</sub>$  (430 ppm) at ambient pressure was fed through the intake tubes and 151 system outputs were measured, with results as shown in Table 1 and Fig. 2. This process allowed

152 determination of the minimum amount of time reach a stable measurement reading.

 To derive a continuous record of concentrations at each of the heights of interest (in the present experiment, four of them) switching between heights was set at every 7.5 seconds allowing each of the heights to be sampled twice a minute. Figure 2 shows the delays associated with the switching; these are confirmed by consideration of the known travel length and flow rate in the tubes. The delay (3.2 seconds) in reading by the IRGA was due to the presence of residual air in the previous sampling tube and other components of the apparatus, including the solenoid and manifold (refer to Fig. 1). This delay indicates how much time the system takes to purge the shared air in the manifold system. The sampling pump has a flow rate of 1 L/min, optimized to maximize cycling time and minimize any water vapor surface interaction in the urethane tubes. 3.2 seconds were ignored, and the remaining 4.3 seconds were recorded by the datalogger.

163 The laboratory tests showed that as the IRGA received known [CO<sub>2</sub>], it took approximately 164 1.8 seconds to achieve a steady output. During the laboratory evaluation period, the recorded 165 error was less than 0.5% in [CO<sub>2</sub>] between sampling heights as shown in Table 1. An accuracy 166 error of less than 1% is well within the acceptable range for the IRGA now used, according to the 167 specifications provided by the manufacturer. Montagnani et al. (2012) found 11% error for a set 168 of measurements when estimating  $CO<sub>2</sub>$  storage flux using the ICOS method.

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170 **Table 1** IRGA output for multiport air sampling system for CO<sub>2</sub> conc. (430 ppm) fed through the

- **Sampling tube Mean CO<sup>2</sup> concentration (ppm) SD No. of samples Error %** Intake 1 430 10.474 23 0.00 Intake 2 431 0.196 15 0.20 Intake 3 431 16 0.167 16 0.20 Intake 4 432 119 13 0.46
- 171 sampling manifold at ambient pressure.







 **Figure 2** The time-dependent relationship between the infrared gas analyzer (IRGA) in the 177 multiport air sampling apparatus for a gas concentration of 430 ppm  $CO<sub>2</sub>$  flowing at <1 L/min. The switching between the intakes occurs every 7.5 seconds. Blue corresponds to sampling intake height 1, green to height 2, black to height 3, and red to height 4. The vertical lines demarcate the stable, equilibrium regions where the measurements were suitable to be recorded. Here the lines were at 4.9 seconds but were further improved to 3.2 seconds.

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182 3 Field measurement setup
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 Following laboratory testing, the system was deployed in a field study conducted at Loudon, Tennessee, in 2023. In this study, four intake sampling tubes were positioned at heights (m) of 0.11, 0.5h, 1+h, and 2+h, where h is maize canopy height above the soil surface. Note that one height was permanently set at 0.11 m and three of these heights were adjusted as the crop grew. Sampling intakes were positioned on a 10 m steel mast at the respective positions. Thermocouples at the same height were used to measure temperature within and above the





- canopy; these thermocouples were aspirated within a white PVC pipe of 1.9 cm diameter (Figure
- 3) that also served as a radiation shield.



 **Figure 3ab** Aspiration of CO<sup>2</sup> intake tubes and thermocouples and their application in the maize canopy.

 To provide the measurements necessary to interpret the gradient observations, a tripod tower was used to support an eddy covariance system and supporting micrometeorological variables 196 — an IRGASON [CO<sub>2</sub>/H<sub>2</sub>O] open path gas analyzer system, [Campbell Scientific, Logan, Utah], a net radiometer [Kipp & Zonen SR# 103660, OTT HydroMet B.V. Delft, Netherland], infrared radiometers [IRs-S1-111-SS, Apogee Instruments Inc, USA], and type T thermocouples [Omega, USA]. A schematic diagram of the system is shown in Fig. 1. The system was visually inspected every week for any leakage, condensation, and contamination.

**3.1 Experimental site** 

 The field study was conducted near Philadelphia, in Loudon County Tennessee (35.6729° N, 84.4651° W). The study area is twenty-three hectares of agricultural farmland cultivated with a maize cropping system. The red point on the map represents the location of the site where the 205 system was installed. The mean annual temperature and precipitation of the site are 12-15  $\degree$ C and 132-142 cm respectively. The elevation and slope of the site are 280 m (Figure 4A) and 2-5%





- (Figure 4B) respectively. The soil was classified as Alcoa Loam (Rhodic Paleudult) according to the
- USDA classification scheme (Soil Taxonomy, 1976).



**Figure 4** Soil elevation and slop overview of the test site in rural Philadelphia Tennessee, USA.

A) The red point on the map shows the instrumentation location.

## **3.2 Calculation of storage terms**

In accordance with other studies of the surface energy budget using EC systems, storage terms refer to

214 depletion or accumulation of scalar quantities ( $CO<sub>2</sub>$ , H<sub>2</sub>O, etc.) in a hypothetical control volume beneath

- the height of EC flux measurement. A storage flux is defined as the rate of change of dry molar
- concentrations of the same variables within the same control volume. Both concepts relate most directly
- 217 to the conditions of "perfect" micrometeorology. In practice, natural complexities of surroundings and





 exposures interfere to the extent that will necessarily be site-specific. Moreover, the covariances that are central in related deliberations are statistical quantities, with well-recognized error margins associated with every quantification of them. During this study, the storage fluxes of scalar quantities 221 (CO<sub>2</sub>, water vapor, etc.) were calculated using the ICOS methodology (Montagnani et al., 2018). For the case of CO2,

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J_c = \overline{\rho_d} \sum_{i=1}^{N} \left( \frac{\Delta c}{\Delta t} \right)_i \Delta z_i.
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 (2)

 Here*, J<sup>c</sup>* is the storage term of CO<sup>2</sup> within the *ith* layer over which Δc is measured, Δz<sup>i</sup> is the 227 thickness of this layer and  $\Delta t$  is the measurement time step;  $\bar{p_d}$  is dry air density, and N is the number of layers.

### **4** R**esults and discussion**

### **4.1 Vertical profile of CO<sup>2</sup> within a maize canopy**

231 Previous experiments revealed the ubiquity of nocturnal pooling of  $CO<sub>2</sub>$  because the presence of the maize canopy and the development of a strongly stable atmospheric surface layer that 233 permits CO<sub>2</sub> emitted by the soil biota to accumulate overnight. Fig. 5 presents average diurnal 234 cycles of  $CO<sub>2</sub>$  concentrations measured at four heights, two within the canopy and two above. 235 The concentrations of  $CO<sub>2</sub>$  observed low in the canopy exceed those elsewhere. Moreover, note that the increasing concentrations within the pool closely parallel each other, providing support 237 for the assumptions made elsewhere about  $CO<sub>2</sub>$  profile linearity within the pools. The fact that 238 concentrations drop below ambient ( $\approx$ 425 ppm) suggests that photosynthesis is ongoing which rapidly reduces the canopy concentrations.

240 Following dawn (or sunrise as indicated in Fig. 5) the accumulated concentrations of  $CO<sub>2</sub>$  drop rapidly as convection starts to mix surface air with that aloft and as photosynthesis commences. Concentrations decrease to about 350 ppm, due to the maize photosynthetic requirement for  $CO<sub>2</sub>$  from the air. After sunset, concentrations of  $CO<sub>2</sub>$  rise uniformly with little evidence of a separation between sub-canopy and upper-canopy concentration regimes. Note, however, that there is evidence of early effects of soil emissions, such that the 11–cm trend departs from the others soon after solar noon.





247 Furthermore, at all four heights, CO<sub>2</sub> concentrations were greatest during late night and early morning until 0600 local time (LT), after which concentrations declined rapidly and reached a relatively constant level of approximately 350 ppm in the afternoon (1200 to 1800 LT). The 350 250 ppm observation is 70 ppm less than current ambient  $CO<sub>2</sub>$  due to photosynthetic demand. 251 Subsequently, CO<sub>2</sub> concentrations increased again, with a more pronounced increase during late night. Soil respiration, photosynthesis, and temperature contribute to this trend. During the late 253 night, the surface atmosphere stabilizes and wind speeds decrease allowing emitted  $CO<sub>2</sub>$  to accumulate. Moreover, in many climatic regions like our experimental site, nighttime soil temperatures remain high enough to sustain microbial and soil respiration activities, resulting in CO<sub>2</sub> accumulation in the stratified air above the ground. As the sun rises, increased light availability increases stomatal activities, leading to higher photosynthesis rates.



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 **Figure 5** Average diurnal vertical cycle of CO<sup>2</sup> for over two months of maize canopy growth/monitoring. Times of sunrise and sunset are shown.

## **4.2 Vertical profile of H2O in a maize canopy**

As in Fig. 5, Fig. 6 shows 15-minute H2O concentration observations have been used to construct

an average diurnal cycle for the two-month period exemplified shown here. During daytime, H2O





- concentrations were significantly higher when compared to nighttime, peaking between 1200 LT and 1400 LT and then gradually decreasing. Notably, after 2000 LT, we recorded a rapid decline 266 in H<sub>2</sub>O concentration. At 0600 LT, the H<sub>2</sub>O reached its minimum concentration throughout the 267 cycle, followed by a sharp increase in the first hour. The  $H_2O$  concentration decreased as the height increased for both day and nighttime because at both times a source of water vapor is the soil surface, with crop evapotranspiration adding in the daytime. A comparison of the diurnal cycles shown in Figs. 5 and 6 indicates considerably different cycles 271 of  $CO<sub>2</sub>$  and H<sub>2</sub>O cases. At night, Fig. 5 shows that the  $CO<sub>2</sub>$  profile appears to be stronger than in 272 the daytime. The opposite is seen, for H<sub>2</sub>O, in Fig. 6. The reason is presumed to be that  $CO<sub>2</sub>$ 273 continues to be emitted from the soil at night, whereas there is no parallel process influencing the H2O concentrations. This is a feature made apparent by the profile sampling system. The processes of evaporation from the soil surface and evapotranspiration from leaves are linked with solar radiation. Overall, the study highlights the vertical distribution of water vapor concentration and its temporal variability, indicating that factors such as height and diurnal variations significantly influence the profile/gradient and temporal patterns of water vapor in the canopy profile.
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283 **Figure 6** Diurnal vertical profile pattern of water vapor averaged over two months as in Fig. 5.

### 284 **4.3 Latent heat, sensible heat and CO<sup>2</sup> storage fluxes of maize profile**

285 The vertical profile data were also used to investigate how various storage fluxes influence 286 the energy balance closure of the maize crop. The diurnal average behavior of these storage 287 fluxes is shown in Fig. 7.  $CO<sub>2</sub>$  storage (Fig. 7a) exhibited higher values at nighttime as compared 288 to daytime, due to the  $CO<sub>2</sub>$  pooling effect. During both early morning and late night,  $CO<sub>2</sub>$  storage 289 increased at a rate of approximately 1  $\mu$ mol m<sup>-2</sup> s<sup>-1</sup>, after which it gradually decreased until 0730-290 0800 LT when it became negative.  $CO<sub>2</sub>$  storage started to increase again, remaining close to zero 291 until the following day. This trend indicates that CO<sub>2</sub> storage was significantly higher during early 292 morning and late night as compared to daytime when photosynthesis processes actively utilized 293  $CO<sub>2</sub>$  within the canopy. During nighttime and morning, these processes were reversed, leading to 294 CO<sub>2</sub> storage.

295 Sensible heat energy storage (Fig. 7b) was found lower than latent energy storage (Fig. 7c).





 The diurnal patterns of sensible (Fig. 7b) and latent energy storage (Fig. 7c) show similar characteristics. Sensible heat storage remained zero until after sunrise, eventually rising to a 298 maximum value (around 2.5 W  $m^{-2}$ ) recorded between 1200 LT and 1230 LT. After that, this sensible energy storage rate declined, reaching negative values until 2400 LT and returning to zero until 0700 LT the following day.

 Latent energy storage (Fig. 7c) exhibited a pattern like sensible energy storage but with 302 comparatively higher values. The maximum latent energy storage ( $>$  4 W m<sup>-2</sup>) occurred between 0700 LT and 0730 LT, followed by a rapid decrease and negative storage until 2000 UTC. After a 304 brief increase (presently unexplained, about 4 W  $m<sup>2</sup>$ ) for thirty minutes, rapid decline ensued, leading to negligible values during the late nighttime until the next morning. The diurnal variations in sensible and latent energy storage are influenced by several factors, including solar radiation, temperature fluctuations, and plant physiological processes. The variation in canopy density, structure, and microclimate within the canopy significantly changes the canopy storage which directly influences the daily integrated fluxes. Forest studies reported that the exchange of CO2 and H2O between plant and atmosphere is regulated by canopy density (e.g. LAI), surface conductance, etc. and these canopy characteristics change seasonally which influences the estimation of flux (Renchon et al., 2024; Chen et al., 2019). Therefore, consideration of canopy storage into our analysis can improve the accurate estimation of flux.

 The results provide valuable insights into the energy dynamics within the maize canopy and contribute to a deeper understanding of its environmental response to plants during different periods of the day. Latent and sensible heat storage are the two most important components of the energy balance of maize crops and are primarily influenced by important environmental conditions such as temperature, humidity, solar radiation, and wind.







**Figure 7abc** Diurnal pattern of CO<sub>2</sub> storge (µmol m<sup>-2</sup> s<sup>-1</sup>), sensible energy storage (J m<sup>-2</sup>s<sup>-</sup> 1 ) and latent energy storage (J m-2 s -1 ) of a mature maize crop, averaged over a two month period.

 Note that the definition of the heat storage used here (as in Eq. (2)) omits warming of the biomass. This omission accounts for the differences between the storage terms now computed and those published previously (e.g. Hicks et al., 2020), based on infrared measurements of





- biomass temperature in addition to changes in air temperature and humidity below the level of
- atmospheric measurement.

### **5 Conclusions and summary**

- 333 The new multi-port profile system demonstrated its effectiveness in the measurement of  $CO<sub>2</sub>$ 334 and  $H_2O$  concentrations at different heights. Its development significantly aids in understanding 335  $CO<sub>2</sub>$  and H<sub>2</sub>O concentration variations in the vertical profile of a rapidly growing maize crop, thereby facilitating precise assessments of their exchanges, storage, and overall balance within agricultural ecosystems. The new system is designed to provide the capability to change measurement heights simply, as crops grow in height, while relying on a single measurement device and thereby minimizing level-to-level biases.
- The 2023 field experience with the new system indicates that canopy data obtained from the vertical profile observations hold potential for many applications in future studies such as 342 evaluation of soil-plant-atmospheric models that rely on the precise estimation of CO<sub>2</sub>, heat, and H2O concentrations as well as future assessment of canopy nitrous oxide concentration.
- **Author contribution statement**
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