Accuracies of field CO$_2$–H$_2$O data from open-path eddy-covariance flux systems: assessment based on atmospheric physics and biological environment

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Abstract. Ecosystem CO$_2$–H$_2$O data measured by infrared gas analyzers in open-path eddy-covariance (OPEC) systems have numerous applications, such as estimations of CO$_2$ and H$_2$O fluxes in the atmospheric boundary layer. To assess the applicability of the data for these estimations, data uncertainties from analyzer measurements are needed. The uncertainties are sourced from the analyzers in zero drift, gain drift, cross-sensitivity, and precision variability. These four uncertainty sources are individually specified for analyzer performance, but so far no methodology exists yet to combine these individual sources into a composite uncertainty for the specification of an overall accuracy, which is ultimately needed. Using the methodology for closed-path eddy-covariance systems, this overall accuracy for OPEC systems is determined from all individual uncertainties via an accuracy model and further formulated into CO$_2$ and H$_2$O accuracy equations. Based on atmospheric physics and the biological environment, for EC150 infrared CO$_2$–H$_2$O analyzers, these equations are used to evaluate CO$_2$ accuracy (±1.22 mgCO$_2$ m$^{-3}$, relatively ±0.19 %) and H$_2$O accuracy (±0.10 gH$_2$O m$^{-3}$, relatively ±0.18 % in saturated air at 35 °C and 101.325 kPa). Both accuracies are applied to conceptual models addressing their roles in uncertainty analyses for CO$_2$ and H$_2$O fluxes. For the high-frequency air temperature derived from H$_2$O density along with sonic temperature and atmospheric pressure, the role of H$_2$O accuracy in its uncertainty is similarly addressed. Among the four uncertainty sources, cross-sensitivity and precision variability are minor, although unavoidable, uncertainties, whereas zero drift and gain drift are major uncertainties but are minimizable via corresponding zero and span procedures during field maintenance. The accuracy equations provide rationales to assess and guide the procedures. For the atmospheric background CO$_2$ concentration, CO$_2$ zero and CO$_2$ span procedures can narrow the CO$_2$ accuracy range by 40 %, from ±1.22 to ±0.72 mgCO$_2$ m$^{-3}$. In hot and humid weather, H$_2$O gain drift potentially adds more to the H$_2$O measurement uncertainty, which requires more attention. If H$_2$O zero and H$_2$O span procedures can be performed practically from 5 to 35 °C, the H$_2$O accuracy can be improved by at least 30 %: from ±0.10 to ±0.07 gH$_2$O m$^{-3}$. Under freezing conditions, the H$_2$O span procedure is impractical but can be neglected because of its trivial contributions to the overall uncertainty. However, the zero procedure for H$_2$O, along with CO$_2$, is imperative as an operational and efficient option under these conditions to minimize H$_2$O measurement uncertainty.
1 Introduction

Open-path eddy-covariance (OPEC) systems are used most in quantity to measure boundary-layer CO₂, H₂O, heat, and momentum fluxes between ecosystems and the atmosphere (Lee and Massman, 2011). For flux measurements, an OPEC system is equipped with a fast-response three-dimensional (3-D) sonic anemometer, to measure 3-D wind velocities and sonic temperature \( T_s \), and a fast-response infrared CO₂–H₂O analyzer (hereafter referred to as an infrared analyzer or analyzer) to measure CO₂ and H₂O concentrations or densities (Fig. 1). In this system, the analyzer is adjacent to the sonic measurement volume. Both anemometer and analyzer together provide synthesized high-frequency (e.g., 10 to 20 Hz) measurements, which are used to compute the fluxes at a location represented by the measurement volume (Aubinet et al., 2012). Given that the measurement conditions, which are spatially homogenous in flux sources/sinks and temporally steady in turbulent flows without advection, satisfy the underlying theory for eddy-covariance flux techniques (Katul et al., 2004; Finnigan, 2008), the quality of each flux data point primarily depends on the exactness of field measurements of the variables, such as CO₂, H₂O, \( T_s \), and 3-D wind, at the sensor sensing scales (Foken et al., 2012; Richardson et al., 2012), although the quality may also be degraded by other biases if not fully corrected. In an OPEC system, other biases are commonly sourced from the tilt of the vertical axis of the sonic anemometer away from the vertical vector of natural wind (Kaimal and Haugen, 1969), the spatial separation between the anemometer and the analyzer (Laubach and McNaughton, 1998), the line and/or volume averaging of measurements (Wyngaard, 1971; Andreas, 1981), the response delay of sensors to fluctuations in measured variables (Horst, 2000), the air density fluctuations due to heat and water vapor transfer (Webb et al., 1980), and the filtering in data processing (Rannik and Vesala, 1999). These biases are theoretically correctable through coordinate rotation corrections for the tilt (Tanner and Thurtell, 1969; Wilczak et al., 2001); covariance lag maximization for the separation (Moncrieff et al., 1997; Ibröm et al., 2007); low- and high-frequency corrections for the data filtering, line and/or volume averaging, and response delay (Moore, 1986; Lenschow et al., 1994; Massman, 2000; van Dijk, 2002); and Webb–Pearman–Leuning (WPL) corrections for the air density fluctuations (Webb et al., 1980). Even though these corrections are thorough for corresponding biases, errors in the ultimate flux data still exist due to uncertainties related to measurement exactness at the sensor sensing scales (Fratini et al., 2014; Zhou et al., 2018). These uncertainties are not only unavoidable because of actual or apparent instrumental drifts due to the thermal sensitivity of sensor path lengths, long-term aging of sensor detection components, and unexpected factors in field operations (Fratini et al., 2014), but they are also not mathematically correctable because their sign and magnitude are unknown (Richardson et al., 2012). The overall measurement exactness related to these uncertainties would be a valuable addition to flux data analysis (Goulden et al., 1996; Anthone et al., 2004).

In addition to flux computations, the data for individual variables from these field measurements can be important in numerous applications. Knowledge of measurement exactness is also required for an accurate assessment of data applicability (Csavina et al., 2017; Hill et al., 2017). The infrared analyzer in an OPEC system outputs CO₂ density (\( \rho_{\text{CO}_2} \)) and H₂O density (\( \rho_{\text{H}_2\text{O}} \)) with a CSAT3A sonic anemometer for three-dimensional (3-D) wind velocities and sonic temperature (\( T_s \)) in an open-path eddy-covariance flux system (Image credit: Campbell Scientific Inc., UT, USA).

![Figure 1. Integration of an EC150 infrared CO₂–H₂O analyzer for CO₂ density (\( \rho_{\text{CO}_2} \)) and H₂O density (\( \rho_{\text{H}_2\text{O}} \)) with a CSAT3A sonic anemometer for three-dimensional (3-D) wind velocities and sonic temperature (\( T_s \)) in an open-path eddy-covariance flux system.](https://doi.org/10.5194/gi-11-335-2022)
As comprehensively reviewed by Richardson et al. (2012), numerous previous studies including Goulden et al. (1996), Lee et al. (1999), Anthoni et al. (1999, 2004), and Flanagan and Johnson (2005) have quantified various sources of flux measurement errors and have attempted to attach confidence intervals to the annual sums of net ecosystem exchange. These sources include measurement methods (e.g., sensor separation and site homogeneity; Munger et al., 2012), data processing algorithms (e.g., data filtering, Rannik and Vesala, 1999, and data gap filling, Richardson and Hollinger, 2007), measurement conditions (e.g., advection; Finnigan, 2007), energy closure (Foken, 2008), and sensor body heating effects (Burba et al., 2008). Instead of quantifying the flux errors, Foken et al. (2004, 2012) assessed the flux data quality and divided it into nine grades (1 to 9) based on steady state, turbulence conditions, and wind direction in the sonic anemometer coordinate system. The lower the grade, the smaller the error in flux data (i.e., higher flux data quality); the higher grade, the greater the error in flux data (i.e., lower flux data quality). This grade matrix (Foken et al., 2004, 2012) has been adopted by AmeriFlux (2018) for their flux data quality assessments. To correct the measurement biases from infrared analyzers, Burba et al. (2008) developed a correction method for sensor body heating effects on CO₂ and H₂O fluxes, whereas Fratini et al. (2014) developed a method for correcting the raw high-frequency CO₂ and H₂O data using the interpolated zero and span coefficients of an infrared analyzer from the analyzer maintenance such as zero and span procedures under the same conditions but at the beginning and ending of each maintenance period. The corrected data were then used to re-estimate the fluxes. Nevertheless, no study so far has addressed the overall measurement exactness of ρH₂O or ρCO₂, which are related to the unavoidable and uncorrectable measurement uncertainties in the CO₂ and H₂O data from the infrared analyzers in OPEC systems, even though this overall measurement exactness is fundamental for data analysis in applications (Richardson et al., 2012). Therefore, instead for the overall exactness of an individual field CO₂ or H₂O measurement, the infrared analyzers are specified only for their individual CO₂ and H₂O measurement uncertainties sourced from their zero and gain drifts, cross-sensitivity to background H₂O/CO₂, and measurement precision variability (LI-COR Biosciences, 2021c; Campbell Scientific Inc., 2021b).

For any sensor, the measurement exactness depends on its performance as commonly specified in terms of accuracy, precision, and other uncertainty descriptors such as sensor hysteresis. Conventionally, accuracy is defined as a systematic uncertainty, while precision is defined as a random measurement error (ISO, 2012, where ISO is the acronym of International Organization for Standardization). Other uncertainty descriptors are also defined for specific reliabilities in instrumental performance. For example, CO₂ zero drift is one of the descriptors specified for the performance of infrared analyzers in CO₂ measurements (Campbell Scientific Inc., 2021b). Both accuracy and precision are universally applicable to any sensor for the specification of its performance in measurement exactness. Other uncertainty descriptors are more sensor-specific (e.g., cross-sensitivity to CO₂/H₂O is used for infrared analyzers in OPEC and CPEC systems, where CPEC is an acronym for closed-path eddy covariance).

Conventionally, sensor accuracy is the degree of closeness to which its measurements are to the true value in the measured variable; sensor precision, related to repeatability, is the degree to which repeated measurements under unchanged conditions produce the same values (Joint Committee for Guides in Metrology, 2008). Another definition advanced by the ISO (2012), revising the conventional definition of accuracy as trueness originally representing only systematic uncertainty, specifies accuracy as a combination of both trueness and precision. An advantage of this definition for accuracy is the consolidation of all measurement uncertainties. According to this definition, the accuracy is the range of composited uncertainty from all uncertainty sources in field measurements. For CPEC systems, Zhou et al. (2021) developed a method and derived a model to assess the accuracy of CO₂/H₂O mixing ratio measurements of infrared analyzers. Their model was further formulated as a set of equations to evaluate the defined accuracies for CO₂ and H₂O mixing ratio data from CPEC systems. Although the CPEC systems are very different from OPEC systems in their structural designs (e.g., measurements take place inside a closed cuvette vs. in an open space) and in output variables (e.g., CO₂/H₂O mixing ratio vs. CO₂/H₂O density), similarities exist between the two systems in measurement uncertainties as specified by their manufacturers (Campbell Scientific Inc., 2021a, b) because the infrared analyzers in both systems use the same physics theories and similar optical techniques for their measurements (LI-COR Biosciences, 2021b, c). Accordingly, the method developed by Zhou et al. (2021) for CPEC systems can be reasonably applied to their OPEC counterparts with rederivation of the model and reformulation of equations. Following the methodology of Zhou et al. (2021) and using the specifications of EC150 infrared analyzers in OPEC systems as an example (Campbell Scientific Inc., 2021b), we can derive the model and formulate equations to assess the accuracies of CO₂ and H₂O measurements by infrared analyzers in OPEC systems; discuss the usage of accuracies in flux analysis, data applications, and analyzer field maintenance; and ultimately provide a reference for the flux measurement community in order to specify the overall accuracy of field CO₂/H₂O measurements by infrared analyzers in OPEC systems.

2 Specification implications

An OPEC system for this study includes, but is not limited to, a CSAT3A sonic anemometer and an EC150 infrared analyzer (Fig. 1). The system operates in a T_a range from −30 to...
to 50°C and in a P range from 70 to 106 kPa. Within these operational ranges, the specifications for CO₂ and H₂O measurements (Campbell Scientific Inc., 2021b) are given in Table 1.

In Table 1, the top limit of 1553 mgCO₂ m⁻³ in the calibration range for CO₂ density in dry air is more than double the atmospheric background CO₂ density of 767 mgCO₂ m⁻³, or 419 µmolCO₂ mol⁻¹, where mol is the unit for dry air, reported by the Global Monitoring Laboratory (2022) with a Tₐ of 20°C under a P of 101.325 kPa (i.e., normal temperature and pressure, Wright et al., 2003). The top limit of 44 gH₂O m⁻³ in the calibration range for H₂O density is equivalent to a 37°C dew point, higher than the highest 35°C dew point ever recorded under natural conditions on Earth (National Weather Service, 2022).

The measurement uncertainties from infrared analyzers for CO₂ and H₂O in Table 1 are specified by individual uncertainty components along with their magnitudes: zero drift, gain drift, cross-sensitivity to CO₂/H₂O, and precision variability. Zero drift uncertainty is an analyzer non-zero response to zero air/gas (i.e., air/gas free of CO₂ and H₂O). Gain drift uncertainty is an analyzer trend-deviation response to zero air/gas (i.e., air/gas free of CO₂ and H₂O). Cross-sensitivity is an analyzer random response to minor unexpected factors. For CO₂ and H₂O, these four components should be composited as an overall uncertainty in order to evaluate the accuracy, which is ultimately needed in practice.

Precision variability is a random error, and the other specifications can be regarded as trueness. Zero drifts are primarily impacted by Tₐ, and so are gain drifts (see the “Note” column in Table 1 and also Fratini et al., 2014). Additionally, each gain drift is also positively proportional to the true magnitude of CO₂/H₂O density (i.e., true ρCO₂ or true ρH₂O) under measurements. Lastly, cross-sensitivity to CO₂/H₂O is related to the background amount of H₂O/CO₂ as indicated by its units: mgCO₂ m⁻³ (gH₂O m⁻³)⁻¹ for CO₂ measurements and gH₂O m⁻³ (mgCO₂ m⁻³)⁻¹ for H₂O measurements.

Accordingly, beyond statistical analysis, the accuracy of CO₂/H₂O measurements should be evaluated over a Tₐ range of −30 to 50°C, a ρH₂O range of up to 44 gH₂O m⁻³, and a ρCO₂ range of up to 1553 mgCO₂ m⁻³.

3 Accuracy model

The measurement accuracy of infrared analyzers is the possible maximum range of overall measurement uncertainty from the four uncertainty sources as specified in Table 1: zero drift, gain drift, cross-sensitivity, and precision variability. The four uncertainties interactively or independently contribute to the overall uncertainty in a measured value. Given the true α density (ραT), where subscript α can be either CO₂ or H₂O) and measured α density (ρα), the difference between the true and measured α densities (Δρα) is given by

$$\Delta \rho_\alpha = \rho_\alpha - \rho_\alpha T.$$  \hspace{1cm} (1)

The analyzer overestimates the true value if Δρα > 0, exactly estimates the true value if Δρα = 0, and underestimates the true value if Δρα < 0. The measurement accuracy is the maximum range of Δρα (i.e., an accuracy range). According to the analyses of Zhou et al. (2021) for CPEC infrared analyzers, as mathematically shown in Appendix A, this range is interactionally contributed by the zero drift uncertainty (Δρα₀), gain drift uncertainty (Δρα₁), and cross-sensitivity uncertainty (Δρα₂) along with an independent addition from the precision uncertainty (Δρα₃). However, any interactional contribution from a pair of uncertainties is 3 orders smaller in magnitude than each individual contribution in the pair. The contribution to the accuracy range due to interactions can be reasonably neglected. Therefore, the accuracy range can be simply modeled as a sum of the absolute values of the four component uncertainties. From Eq. (A7) in Appendix A, the measurement accuracy of α density from OPEC systems by infrared analyzers is defined in an accuracy model as

$$\Delta \rho_\alpha = \pm \left( |\Delta \rho_{\alpha,0}^z| + |\Delta \rho_{\alpha,1}^g| + |\Delta \rho_{\alpha,2}^C| + |\Delta \rho_{\alpha,3}^p| \right).$$ \hspace{1cm} (2)

Assessment of the accuracy of field CO₂ or H₂O measurements is, by the use of known and/or estimable variables, the formulation and evaluation of the four terms on the right side of this accuracy model.

4 Accuracy of CO₂ density measurements

Based on accuracy Model (2), we define the accuracy of field CO₂ measurements from OPEC systems by infrared analyzers (ΔρCO₂) as

$$\Delta \rho_{\text{CO}_2} = \pm \left( |\Delta \rho_{\text{CO}_2}^z| + |\Delta \rho_{\text{CO}_2}^g| + |\Delta \rho_{\text{CO}_2}^C| + |\Delta \rho_{\text{CO}_2}^p| \right),$$ \hspace{1cm} (3)

where ΔρCO₂ is CO₂ zero drift uncertainty, ΔρCO₂ is CO₂ gain drift uncertainty, ΔρCO₂ is cross-sensitivity-to-H₂O uncertainty, and ΔρCO₂ is CO₂ precision uncertainty. CO₂ precision (σCO₂) is the standard deviation of ρCO₂ random errors among repeated measurements under the same conditions (Joint Committee for Guides in Metrology, 2008). The random errors generally have a normal statistical distribution (Hoel, 1984). Therefore, using this deviation, the precision uncertainty for an individual CO₂ measurement at a 95% confidence interval (P value of 0.05) can be statistically formulated as

$$\Delta \rho_{\text{CO}_2}^p = \pm 1.96 \times \sigma_{\text{CO}_2}.$$ \hspace{1cm} (4)
Table 1. Measurement specifications for EC150 infrared CO$_2$–H$_2$O analyzers (Campbell Scientific Inc., UT, USA).

| CO$_2$ | H$_2$O | Note |
|-------|-------|------|
| **Notation** | **Value** | **Unit** | **Notation** | **Value** | **Unit** | **Note** |
| Calibration range | 0–1553 | mgCO$_2$ m$^{-3}$ | 0–44 | gH$_2$O m$^{-3}$ | For CO$_2$ up to 4500 mgCO$_2$ m$^{-3}$ if specially needed. |
| Zero drift | $d_{cz}$ | ±0.55 | mgCO$_2$ m$^{-3}$ | $d_{wz}$ | ±0.04 | gH$_2$O m$^{-3}$ | Zero/gain drift is the possible maximum range within the system operational ranges in ambient air temperature ($T_a$) and atmospheric pressure. The actual drift depends more on $T_a$. |
| Gain drift | $d_{cg}$ | ±0.10%$^a$ | true $\rho_{CO_2}$ | $d_{wg}$ | ±0.30%$^b$ | true $\rho_{H_2O}$ | |
| Cross-sensitivity to H$_2$O | $s_{H_2O}$ | ±2.69 $\times$ 10$^{-7}$ | mgCO$_2$ m$^{-3}$ | (gH$_2$O m$^{-3}$)$^{-1}$ | n/a | |
| Cross-sensitivity to CO$_2$ | $s_{CO_2}$ | ±4.09 $\times$ 10$^{-5}$ | gH$_2$O m$^{-3}$ | (mgCO$_2$ m$^{-3}$)$^{-1}$ | n/a | |
| Precision | $\sigma_{CO_2}$ | 0.200 | mgCO$_2$ m$^{-3}$ | $\sigma_{H_2O}$ | 0.004 | gH$_2$O m$^{-3}$ | |

$^a$ 0.10% is the CO$_2$ gain drift percentage denoted by $\Delta CO_2_{g,c}$ in the text, and $\rho_{CO_2}$ is CO$_2$ density. $^b$ 0.30% is the H$_2$O gain drift percentage denoted by $\Delta H_2O_{g,c}$ in the text, and $\rho_{H_2O}$ is H$_2$O density. n/a denotes “not applicable”.

The other uncertainties, due to CO$_2$ zero drift, CO$_2$ gain drift, and cross-sensitivity to H$_2$O, are caused by the inability of the working equation inside the analyzer operating system (OS) to adapt to the changes in analyzer-internal and ambient environmental conditions, such as internal housing CO$_2$ and/or H$_2$O levels and ambient air temperature. From the derivations in the “Theory and operation” section in LI-COR Biosciences (2001, 2021b, c), a general model of the working equation for $\rho_{CO_2}$ is given by

$$
\rho_{CO_2} = P \sum_{i=1}^{5} a_{ci} \left( 1 - \frac{A_c}{A_{cs}} \right) \left( \frac{1}{\Delta c_{z}} \right)^i \left( \frac{G_c}{P} \right)^i \left( \frac{1 - A_w}{A_{ws}} \right) Z_c^i, \quad (5)
$$

where subscripts c and w indicate CO$_2$ and H$_2$O, respectively; $a_{ci}$ ($i = 1, 2, 3, 4, 5$) is a coefficient of the 5-order polynomial for the terms inside curly brackets; $A_{cs}$ and $A_{ws}$ are the power values of analyzer source lights at the chosen wavelengths for CO$_2$ and H$_2$O measurements, respectively; $A_c$ and $A_w$ are their respective remaining power values after the source lights pass through the measured air sample; $S_w$ is cross-sensitivity of the detector to H$_2$O while detecting CO$_2$ at the wavelength for CO$_2$ measurements (hereafter referred to as sensitivity to H$_2$O); $Z_c$ is the CO$_2$ zero adjustment (i.e., CO$_2$ zero coefficient); and $G_c$ is the CO$_2$ gain adjustment (i.e., commonly known as the CO$_2$ span coefficient). For an individual analyzer, the parameters $a_{ci}$, $Z_c$, $G_c$, and $S_w$ in Model (5) are statistically estimated in the production calibration against a series of standard CO$_2$ gases at different concentration levels over the ranges of $\rho_{H_2O}$ and $P$ (hereafter referred to as calibration). Since the estimated parameters are specific for the analyzer, Model (5) with these estimated parameters becomes an analyzer-specific CO$_2$ working equation. The working equation is used internally by the infrared analyzer to compute $\rho_{CO_2}$ as the closet proxy for true $\rho_{CO_2}$ from field measurements of $A_c$, $A_{cs}$, $A_w$, $A_{ws}$, and $P$.

The analyzer-specific working equation is deemed to be accurate immediately after the calibration through estimations of $a_{ci}$, $Z_c$, $G_c$, and $S_w$ in production, while $Z_c$ and $G_c$ can be re-estimated in the field (LI-COR Biosciences, 2021c). However, as used internally by an optical instrument under changing environments vastly different from its calibration conditions by its manufacturer, the working equation may not be fully adaptable to the changes, which might be reflected through CO$_2$ zero and/or gain drifts of the deployed infrared analyzer. In the working equation for $\rho_{CO_2}$ from Model (5), the parameter $Z_c$ is related to CO$_2$ zero drift; $G_c$ to CO$_2$ gain drift; and $S_w$ to sensitivity to H$_2$O. Therefore, the analyses of $Z_c$ and $G_c$, along with $S_w$, aid in understanding the causes of CO$_2$ zero drift, CO$_2$ gain drift, and sensitivity to H$_2$O. Such understanding is necessary to formulate $\Delta \rho_{CO_2}^Z$, $\Delta \rho_{CO_2}^S$, and $\Delta \rho_{CO_2}^G$ in Model (3).

4.1 $Z_c$ and $\Delta \rho_{CO_2}^Z$ (CO$_2$ zero drift uncertainty)

In production, an infrared analyzer is calibrated for zero air/gas to report zero $\rho_{CO_2}$ plus an unavoidable random error. However, when using the analyzer in measurement environments that are different from calibration conditions, the ana-
lyzer often reports this zero $\rho_{\text{CO}_2}$, while exposed to zero air, as a value that migrates gradually away from zero and possibly beyond $\pm \Delta \rho_{\text{CO}_2}$, which is known as CO$_2$ zero drift. This drift is primarily affected by a combination of three factors: (i) the temperature surrounding the analyzer away from the calibration temperature, (ii) traceable CO$_2$ and H$_2$O accumulations, such as during use, inside the analyzer light housing due to an inevitable, although small, leaking exchange of housing air with the ambient air (hereafter referred to as housing CO$_2$–H$_2$O accumulation), and (iii) aging of analyzer components (Richardson et al., 2012).

Firstly, the dependency of analyzer CO$_2$ zero drift on ambient air temperature arises due to a thermal expansion/contraction of analyzer components that slightly changes the analyzer geometry (Fratini et al., 2014). This change in geometry can deviate the light path length for measurement a little away from the length under manufacturer calibration, contributing to the drift. Additionally, inside an analyzer, the performance of the light source and absorption detector for measurement, as well as the electronic components for measurement control, can vary slightly with temperature. In production, an analyzer is calibrated to compensate for the ensemble of such dependencies as assessed in a calibration chamber. The compensation algorithms are implemented in the analyzer OS, which is kept as proprietary by the analyzer manufacturer. However, the response of an analyzer to a temperature varies as conditions change over time (Fratini et al., 2014). Therefore, manufacturers typically specify an expected range of typical or maximal drift per °C (see Table 1 and also see the section for analyzer specifications in Campbell Scientific Inc., 2021b). Secondly, the housing CO$_2$–H$_2$O accumulation is caused by unavoidable small leaks in the light housing of an infrared analyzer. The housing is technically sealed to keep housing air close to zero air by introducing scrubber chemicals into the housing to absorb any CO$_2$ and H$_2$O that may sneak into the housing through an exchange with any ambient air (LI-COR Biosciences, 2021c). Over time, the scrubber chemicals may be saturated by CO$_2$ and/or H$_2$O or lose their active absorbing effectiveness, which can result in housing CO$_2$–H$_2$O accumulations. Thirdly, as optical components, the light source may gradually become dim, and the absorption detector may gradually become less sensitive. The accumulation and aging develop slowly and less obviously in the relatively long term (e.g., months or longer), whereas the dependencies of drift on ambient air temperature can occur quickly and more clearly as soon as an analyzer is deployed in the field (Richardson et al., 2012). Apparently, the drift with ambient air temperature is a major concern if an analyzer is maintained as scheduled as soon as an analyzer is deployed in the field (Richardson et al., 2012). Over time, the scrubber chemicals may be exchanged with any ambient air (LI-COR Biosciences, 2021c). Over time, the scrubber chemicals may be saturated by CO$_2$ and/or H$_2$O or lose their active absorbing effectiveness, which can result in housing CO$_2$–H$_2$O accumulations. Thirdly, as optical components, the light source may gradually become dim, and the absorption detector may gradually become less sensitive. The accumulation and aging develop slowly and less obviously in the relatively long term (e.g., months or longer), whereas the dependencies of drift on ambient air temperature can occur quickly and more clearly as soon as an analyzer is deployed in the field (Richardson et al., 2012). Apparently, the drift with ambient air temperature is a major concern if an analyzer is maintained as scheduled as soon as an analyzer is deployed in the field (Richardson et al., 2012).

Due to the CO$_2$ zero drift, the working equation needs to be adjusted through its parameter re-estimation to adapt the ambient air temperature near which the system is running, housing CO$_2$–H$_2$O accumulation, and analyzer component aging. This adjustment technique is the zero procedure, which brings the $\rho_{\text{CO}_2}$ and $\rho_{\text{H}_2\text{O}}$ in zero air/gas measurement back to zero as closely as possible. In this section, our discussion focuses on CO$_2$, and the same application to H$_2$O will be described in the following sections. In the field, the zero procedure should be feasibly operational using one air/gas benchmark to re-estimate one parameter in the working equation. This parameter must be adjustable to output zero $\rho_{\text{CO}_2}$ from the zero air/gas benchmark. By setting the left side of Model (5) to zero and rearranging it, it is clear that $Z_c$ is such a parameter that can be adjusted to result in a zero $\rho_{\text{CO}_2}$ value for zero air/gas:

$$Z_c = \left[ A_{c0} + S_w \left( 1 - \frac{A_{w0}}{A_{ws}} \right) \right]^{-1},$$

where $A_{c0}$ and $A_{w0}$ are the counterparts of $A_c$ and $A_w$ for zero air/gas, respectively. For an analyzer, the zero procedure for CO$_2$ is thus to re-estimate $Z_c$ in balance of Eq. (6).

If $Z_c$ could continually balance Eq. (6) after the zero procedure, the CO$_2$ zero drift would not be significant; however, this is not the case. Similar to its performance after the manufacturer calibration, an analyzer may still drift after the zero procedures due to frequent changes in ambient air temperature, housing CO$_2$–H$_2$O accumulation, and/or analyzer component age. Nevertheless, the $Z_c$ value needed for an analyzer to be punctually adaptable for these changes is unpredictable because these changes are not foreseeable. Assuming on-schedule maintenance (i.e., the scrubber chemicals inside the analyzer light housing are replaced following the manufacturer’s guidelines), the housing CO$_2$–H$_2$O accumulation should not be a concern. While the ambient temperature surrounding the infrared analyzer is not controlled, the CO$_2$ zero drift is therefore mainly influenced by $T_a$ and can be $\pm 0.55$ mg CO$_2$ m$^{-3}$ at most within the operational ranges in $T_a$ and $P$ for the EC150 infrared analyzers in OPEC systems (Table 1).

Given that an analyzer performs best almost without zero drift at the ambient air temperature for the calibration/zeroing procedure ($T_a$) and that it possibly drifts while $T_a$ gradually changes away from $T_a$, then the further away $T_a$ is from $T_c$, the more it possibly drifts in the CO$_2$ zero. Over the operational range in $P$ of the EC150 infrared analyzers used for OPEC systems, this drift is more proportional to the difference between $T_a$ and $T_c$ but is still within the specifications (Campbell Scientific Inc., 2021b). Accordingly, CO$_2$ zero drift uncertainty at $T_a$ can be formulated as

$$\Delta \rho_{\text{CO}_2}^z = \frac{d_{cz}}{T_{th} - T_{tl}} \times \abs{ \begin{array}{cc} T_a - T_c & T_c < T_a < T_{th} \\ T_c - T_a & T_a > T_c > T_{tl} \end{array} },$$

where, over the operational range in $T_a$ of EC150 infrared analyzers used for OPEC systems, $T_{th}$ is the highest-end value ($50^\circ$C) and $T_{tl}$ is the lowest-end value ($-30^\circ$C, Table 1). $\Delta \rho_{\text{CO}_2}^z$ from this equation has the maximum range, as specified in Table 1, equal to $d_{cz}$ in magnitude as if $T_a$ and $T_c$
were separately at the two ends of operational range in \( T_a \) of OPEC systems.

### 4.2 \( G_c \) and \( \Delta \rho_{\text{CO}_2}^{g} \) (CO\(_2\) gain drift uncertainty)

An infrared analyzer was also calibrated against a series of standard CO\(_2\) gases. The calibration sets the working equation from Model (5) to closely follow the gain trend of change in \( \rho_{\text{CO}_2} \). As was determined with the zero drift, the analyzer, with changes in housing CO\(_2\)-H\(_2\)O accumulation, ambient conditions, and age during its deployment, could report CO\(_2\) gradually drifting away from the real gain trend of the change in \( \rho_{\text{CO}_2} \), which is specifically termed CO\(_2\) gain drift. This drift is affected by almost the same factors as the CO\(_2\) zero drift (Richardson et al., 2012; Fratini et al., 2014; LI-COR Biosciences, 2021c).

Due to the gain drift, the infrared analyzer needs to be further adjusted, after the zero procedure, to tune its working equation back to the real gain trend in \( \rho_{\text{CO}_2} \), of measured air as closely as possible. This is done with the CO\(_2\) span procedure. This procedure can be performed through use of either one or two span gases (LI-COR Biosciences, 2021c). If two are used, one span gas is slightly below the ambient CO\(_2\) density and the other is at a much higher density to fully cover the CO\(_2\) density range by the working equation. However, commonly, like the zero procedure, this procedure is simplified by the use of one CO\(_2\) span gas, as a benchmark, with a known CO\(_2\) density (\( \rho_{\text{CO}_2} \)) around the typical CO\(_2\) density values in the measurement environment. If one CO\(_2\) span gas is used, only one parameter in the working equation is available for adjustment. Weighing the gain of the working equation more than any other parameter, this parameter is the CO\(_2\) span coefficient (\( G_c \)) (see Model 5). The CO\(_2\) span gas is used to re-estimate \( G_c \) to satisfy the following equation (for details, see LI-COR Biosciences, 2021c):

\[
\left| \rho_{\text{CO}_2} - \rho_{\text{CO}_2} (G_c) \right| \leq \min \left| \rho_{\text{CO}_2} - \rho_{\text{CO}_2} \right|
\]

(8)

Similar to the zero drift, the CO\(_2\) gain drift continues after the CO\(_2\) span procedure. Based on a similar consideration for the specifications of CO\(_2\) zero drift, the CO\(_2\) gain drift is specified by the maximum CO\(_2\) gain drift percentage (\( \delta_{\text{CO}_2 \rho_{\text{CO}_2}} = 0.10 \% \)) associated with \( \rho_{\text{CO}_2} \) as \( \pm 0.10 \% \times \) (true \( \rho_{\text{CO}_2} \)) (Table 1). This specification is the maximum range of CO\(_2\) measurement uncertainty due to the CO\(_2\) gain drift within the operational ranges in \( T_a \) and \( P \) of the EC150 infrared analyzers in OPEC systems.

Given that an analyzer performs best, almost without gain drift, at the ambient air temperature for calibration/span procedures (also denoted by \( T_c \) because zero and span procedures should be performed under similar ambient air temperature conditions) but also drifts while \( T_a \) gradually changes away from \( T_c \), then the further away \( T_a \) is from \( T_c \), the greater potential that the analyzer drifts. Accordingly, the same approach to the formulation of CO\(_2\) zero drift uncertainty can be applied to the formulation of the approximate equation for CO\(_2\) gain drift uncertainty at \( T_a \) as

\[
\Delta \rho_{\text{CO}_2}^{g} = \pm \frac{\delta_{\text{CO}_2 \rho_{\text{CO}_2}} \rho_{\text{CO}_2} T}{T_{\text{th}} - T_{\text{rl}}} \times \left\{ \begin{array}{ll}
T_a - T_c & T_c < T_a < T_{\text{th}} \\
T_c - T_a & T_c > T_a > T_{\text{rl}}
\end{array} \right.
\]

(9)

where \( \rho_{\text{CO}_2} \) is the true CO\(_2\) density unknown in measurement. Given that the measured value of CO\(_2\) density is represented by \( \rho_{\text{CO}_2} \), by referencing Eq. (1), \( \rho_{\text{CO}_2} \) can be expressed as

\[
\rho_{\text{CO}_2} = \rho_{\text{CO}_2} - (\Delta \rho_{\text{CO}_2}^{g} + \Delta \rho_{\text{CO}_2}^{\rho} + \Delta \rho_{\text{CO}_2}^{C})
\]

(10)

The terms inside the parentheses in this equation are the measurement uncertainties for \( \rho_{\text{CO}_2} \) that are smaller in magnitude, by at least 2 orders, than \( \rho_{\text{CO}_2} \), whose magnitude in atmospheric background under the normal temperature and pressure as used by Wright et al. (2003) is 767 mgCO\(_2\) m\(^{-3}\) (Global Monitoring Laboratory, 2022). Therefore, \( \rho_{\text{CO}_2} \) in Eq. (10) is the best alternative, with the greatest likelihood, to \( \rho_{\text{CO}_2} \) for the application of Eq. (9). As such, \( \rho_{\text{CO}_2} \) in Eq. (9) can be reasonably approximated by \( \rho_{\text{CO}_2} \) for equation applications. Using this approximation, Eq. (9) becomes

\[
\Delta \rho_{\text{CO}_2}^{g} = \pm \frac{\delta_{\text{CO}_2 \rho_{\text{CO}_2}} \rho_{\text{CO}_2} T}{T_{\text{th}} - T_{\text{rl}}} \times \left\{ \begin{array}{ll}
T_a - T_c & T_c < T_a < T_{\text{th}} \\
T_c - T_a & T_c > T_a > T_{\text{rl}}
\end{array} \right.
\]

(11)

With \( \rho_{\text{CO}_2} \) being measured, this equation is applicable in estimating the CO\(_2\) gain drift uncertainty. The gain drift uncertainty (\( \Delta \rho_{\text{CO}_2}^{g} \)) from this equation has the maximum range of \( \pm \delta_{\text{CO}_2 \rho_{\text{CO}_2}} \rho_{\text{CO}_2} \), as if \( T_a \) and \( T_c \) were separately at the two ends of operational range in \( T_a \) of OPEC systems. With the greatest likelihood, this maximum range is the closest to \( \pm \delta_{\text{CO}_2 \rho_{\text{CO}_2}} \rho_{\text{CO}_2} \) as specified in Table 1.

### 4.3 \( S_w \) and \( \Delta \rho_{\text{CO}_2}^{s} \) (sensitivity-to-H\(_2\)O uncertainty)

The infrared wavelength of 4.3 \( \mu \text{m} \) for CO\(_2\) measurements is minorly absorbed by H\(_2\)O (LI-COR Biosciences, 2021c; Campbell Scientific Inc., 2021b). This minor absorption slightly interferes with the absorption by CO\(_2\) in the wavelength (McDermitt et al., 1993). The power of the same measurement light (i.e., \( A_c \)) as a steady value in the CO\(_2\) working equation from Model 5) through several gas samples with the same CO\(_2\) density, but different backgrounds of H\(_2\)O densities, is detected with different values of \( A_c \) in the working equation from Model 5). Without parameter \( S_w \) and its joined term in the working equation, different \( A_c \) values must result in significantly different \( \rho_{\text{CO}_2} \) values, although they are actually the same. In case of the same CO\(_2\) density in the airflows under different H\(_2\)O backgrounds, the different values of \( A_c \) to report similar \( \rho_{\text{CO}_2} \) are accounted for by \( S_w \) associated with \( A_w \) and \( A_{ws} \) in the working equation from

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Model (5). Similar to $Z_c$ and $G_c$ in the CO$_2$ working equation, $S_w$ is not perfectly accurate and can have uncertainty in the determination of $\rho_{CO_2}$. This uncertainty for EC150 infrared analyzers is specified by sensitivity to H$_2$O ($s_{H_2O}$) as $\pm 2.69 \times 10^{-7}$ mgCO$_2$ m$^{-3}$ (gH$_2$O m$^{-3}$)$^{-1}$ (Table 1). As indicated by its unit, this uncertainty is linearly related to $\rho_{H_2O}$. Assuming the analyzer for CO$_2$ works best, without this uncertainty, in dry air, $\Delta \rho_{CO_2}$ could be formulated as

$$\Delta \rho^s_{CO_2} = s_{H_2O}\rho_{H_2O} \quad 0 \leq \rho_{H_2O} \leq 44 \text{gH}_2\text{O m}^{-3},$$

(12)

where 44 gH$_2$O m$^{-3}$, as addressed in Sect. 2, is the top limit of H$_2$O density measurements. Accordingly, $\Delta \rho^s_{CO_2}$ can be in the range of

$$\Delta \rho^s_{CO_2} \leq 44 \left| s_{H_2O} \right| .$$

(13)

4.4 $\Delta \rho_{CO_2}$ (CO$_2$ measurement accuracy)

Substituting Eqs. (4), (7), (11), and (13) into Model (3), $\Delta \rho_{CO_2}$ for an individual CO$_2$ measurement from OPEC systems by infrared analyzers can be expressed as

$$\Delta \rho_{CO_2} = \pm \left[ 1.96s_{CO_2} + 44 \left| s_{H_2O} \right| \right]$$

$$+ \frac{|d_{lz}| + \delta_{CO_2,g}\rho_{CO_2}}{T_{rh} - T_{rl}}$$

$$\times \left\{ \begin{array}{ll}
T_a - T_c & T_c < T_a < T_{rh} \\
T_c - T_a & T_c > T_a > T_{rl} 
\end{array} \right\} .$$

(14)

This is the CO$_2$ accuracy equation for the infrared analyzers within OPEC systems. It expresses the accuracy of a field CO$_2$ measurement from the OPEC systems in terms of the analyzer specifications $s_{CO_2}$, $s_{H_2O}$, $d_{lz}$, $\delta_{CO_2,g}$, and the OPEC system operational range in $T_a$ as indicated by $T_{rh}$ and $T_{rl}$, measured variables $\rho_{CO_2}$ and $T_a$, and a known variable $T_c$. Given the specifications and the known variable, this equation can be used to evaluate the CO$_2$ accuracy as a range in relation to $T_a$ and $\rho_{CO_2}$.

4.5 Evaluation of $\Delta \rho_{CO_2}$

Given the analyzer specifications, the accuracy of field CO$_2$ measurements from an infrared analyzer after calibration, zero, and/or span at $T_c$ can be evaluated using the CO$_2$ accuracy Eq. (14) over a domain of $T_a$ and $\rho_{CO_2}$. To visualize the relationship of accuracy with $T_a$ and $\rho_{CO_2}$, the accuracy is presented better as the ordinate along the abscissa of $T_a$ for $\rho_{CO_2}$ at different levels and must be evaluated within possible maximum ranges of $T_a$ and $\rho_{CO_2}$ in ecosystems. In evaluation, the $T_a$ is limited to the $-30$ to $50$ °C range within which EC150 infrared analyzers used for OPEC systems operate, $T_c$ can be assumed to be $20$ °C (i.e., standard air temperature as used by Wright et al., 2003), and $\rho_{CO_2}$ can range according to its variation in ecosystems.

4.5.1 $\rho_{CO_2}$ range

The upper measurement limit of CO$_2$ density by the infrared analyzers can reach up to 1553 mgCO$_2$ m$^{-3}$. In the atmosphere, its background CO$_2$ mixing ratio is currently 419 mmolCO$_2$ mol$^{-1}$ (Global Monitoring Laboratory, 2022). Under normal temperature and pressure conditions (Wright et al., 2003), this background mixing ratio is equivalent to 767 mgCO$_2$ m$^{-3}$ in dry air. The CO$_2$ density in ecosystems commonly ranges from 650 to 1500 mgCO$_2$ m$^{-3}$ (LI-COR Biosciences, 2021c), depending on biological processes (Wang et al., 2016), aerodynamic regimes (Yang et al., 2007), and thermodynamic states (Ohkubo et al., 2008). In this study, this range is extended from 600 to 1600 mgCO$_2$ m$^{-3}$ as a common range within which $\Delta \rho_{CO_2}$ is evaluated. Because of the dependence of $\Delta \rho_{CO_2}$ on $\rho_{CO_2}$ (Eq. 14), to show the accuracy at different CO$_2$ levels, the range is further divided into five grades of 600, 767 (atmospheric background), 1000, 1300, and 1600 mgCO$_2$ m$^{-3}$ for evaluation presentations as in Fig. 2.

According to a brief review by Zhou et al. (2021) on the plant physiological threshold in air temperature for growth and development and the soil temperature dynamic related to CO$_2$ from microorganism respiration and/or wildlife activities in terrestrial ecosystems, $\rho_{CO_2}$ at any grade of 1000, 1300, or 1600 mgCO$_2$ m$^{-3}$ should, at 5 °C, start to converge asymptotically to the atmospheric CO$_2$ background (767 mgCO$_2$ m$^{-3}$ at $-30$ °C, Fig. 2). Without an asymptotical function for the convergence curve, conservatively assuming the convergence has a simple linear trend with $T_a$ from 5 to $-30$ °C, $\Delta \rho_{CO_2}$ is evaluated up to the magnitude of $\rho_{CO_2}$ along the trend (Fig. 2).

4.5.2 $\Delta \rho_{CO_2}$ range

At $T_a = T_c$, the CO$_2$ accuracy is best at its narrowest range to be the sum of precision and sensitivity-to-H$_2$O uncertainties ($\pm 0.39$ mgCO$_2$ m$^{-3}$). However, away from $T_c$, its range near-linearly becomes wider. The $\Delta \rho_{CO_2}$ range can be summarized as $\pm 0.40$ to $\pm 1.22$ mgCO$_2$ m$^{-3}$ over the domain of $T_a$ and $\rho_{CO_2}$ (Fig. 2a and CO$_2$ columns in Table 2). The maximum CO$_2$ relative accuracy at the different levels of $\rho_{CO_2}$ is in a range of $\pm 0.07$ % at 1600 mgCO$_2$ m$^{-3}$ to 0.19 % at 600 mgCO$_2$ m$^{-3}$ (from data for Fig. 2b).

5 Accuracy of H$_2$O density measurements

Model (2) defines the accuracy of field H$_2$O measurements from OPEC systems by infrared analyzers ($\Delta \rho_{H_2O}$) as

$$\Delta \rho_{H_2O} = \pm \left( \left| \Delta \rho^p_{H_2O} \right| + \left| \Delta \rho^s_{H_2O} \right| + \left| \Delta \rho^m_{H_2O} \right| + \left| \Delta \rho^c_{H_2O} \right| \right) .$$

(15)
where $\Delta \rho_{H_2O}^H$ is H$_2$O zero drift uncertainty, $\Delta \rho_{H_2O}^g$ is H$_2$O gain drift uncertainty, $\Delta \rho_{H_2O}^p$ is cross-sensitivity-to-CO$_2$ uncertainty, and $\Delta \rho_{H_2O}^m$ is H$_2$O precision uncertainty. Using the same approach as for $\Delta \rho_{CO_2}^p$, $\Delta \rho_{H_2O}^p$ is formulated as

$$\Delta \rho_{H_2O}^p = \pm 1.96 \times \sigma_{H_2O},$$

(16)

where $\sigma_{H_2O}$, as defined in Table 1, is the precision of the infrared analyzers for H$_2$O measurements. The other uncertainty terms in Model (15) can be understood and formulated using a similar approach for their counterparts in Model (3).

### 5.1 $\Delta \rho_{H_2O}^H$ (H$_2$O zero drift uncertainty) and $\Delta \rho_{H_2O}^g$ (H$_2$O gain drift uncertainty)

The model of the analyzer working equation for $\rho_{H_2O}$ is similar to Model (5) for $\rho_{CO_2}$ in formulation, given also by the derivations in the “Theory and operation” section in LI-COR Biosciences (2001, 2021b, c):

$$\rho_{H_2O} = P \sum_{i=1}^{3} a_{wi} \left[ 1 - \left( \frac{A_w}{A_{ws}} \right) \right] \left( \frac{G_w}{P} \right) \left( 1 - \frac{A_c}{A_{cs}} \right) Z_w \left\{ 1 + S_c \left[ 1 - \frac{A_c}{A_{cs}} \right] \right\},$$

(17)

### Table 2. Accuracies of field CO$_2$ and H$_2$O measurements from open-path eddy-covariance systems by EC150 infrared CO$_2$–H$_2$O analyzers (Campbell Scientific Inc., UT, USA) on the major background values of ambient air temperature, CO$_2$, and H$_2$O in ecosystems. (Atmospheric pressure: 101.325 kPa. Calibration ambient air temperature: 20 °C.)

| Ambient air temperature °C | CO$_2$ | H$_2$O | H$_2$O |
|----------------------------|--------|--------|--------|
|                             | 767 mgCO$_2$ m$^{-3}$ | 1600 mgCO$_2$ m$^{-3}$ | 60 % Relative humidity | Saturated |
| 0                           | 1.215  | 0.16   | n/a    | 0.065      | 32.00 | 0.066 | 19.27 |
| 5                           | 1.133  | 0.15   | 0.063  | 18.92      | 0.065 | 11.42 |
| 10                          | 1.051  | 0.14   | 0.061  | 11.41      | 0.061 | 6.90  |
| 15                          | 0.968  | 0.13   | 0.059  | 7.00       | 0.059 | 4.26  |
| 20                          | 0.886  | 0.12   | 0.056  | 4.38       | 0.057 | 2.67  |
| 25                          | 0.804  | 0.10   | 0.054  | 2.78       | 0.056 | 1.70  |
| 30                          | 0.721  | 0.09   | 0.052  | 1.78       | 0.054 | 1.10  |
| 35                          | 0.639  | 0.08   | 0.049  | 1.22       | 0.051 | 0.75  |
| 40                          | 0.557  | 0.07   | 0.047  | 0.83       | 0.049 | 0.51  |
| 45                          | 0.474  | 0.06   | 0.044  | 0.57       | 0.045 | 0.35  |
| 50                          | 0.392  | 0.05   | 0.040  | 0.38       | 0.040 | 0.23  |

where 767 mgCO$_2$ m$^{-3}$ is the atmospheric background CO$_2$ density (Global Monitoring Laboratory, 2022). b 1600 mgCO$_2$ m$^{-3}$ is assumed to be the maximum CO$_2$ density in ecosystems. c CO$_2$ density in ecosystems is assumed to be lower than 1600 mgCO$_2$ m$^{-3}$ when ambient air temperature is below 5 °C. d H$_2$O density in saturated air above 37 °C is out of the measurement range of EC150 infrared CO$_2$–H$_2$O analyzers (0–44 gH$_2$O m$^{-3}$). e H$_2$O density in air of 60 % relative humidity above 48 °C is out of the measurement range of EC150 infrared CO$_2$–H$_2$O analyzers (0–44 gH$_2$O m$^{-3}$). n/a denotes “not applicable”.

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Because of the similarities in model principles and parameter implications between Models (5) and (17), following the same analyses and rationales as for \( \Delta \rho_{CO_2}^s \) and \( \Delta \rho_{CO_2}^c \), \( \Delta \rho_{H_2O}^g \) is formulated as

\[
\Delta \rho_{H_2O}^g = \frac{d_{wz}}{T_{rh} - T_{rl}} \times \left\{ \begin{array}{ll}
T_a - T_c & T_c < T_a < T_{rh} \\
T_c - T_a & T_c > T_a > T_{rl} 
\end{array} \right., \tag{18}
\]

and \( \Delta \rho_{H_2O}^g \) is formulated as

\[
\Delta \rho_{H_2O}^g = \pm \frac{\delta_{H_2O,g} \rho_{H_2O}}{T_{rh} - T_{rl}} \times \left\{ \begin{array}{ll}
T_a - T_c & T_c < T_a < T_{rh} \\
T_c - T_a & T_c > T_a > T_{rl} 
\end{array} \right.. \tag{19}
\]

### 5.2 \( \Delta \rho_{H_2O}^s \) (sensitivity-to-CO\(_2\) uncertainty)

The infrared light at wavelength of 2.7 µm for H\(_2\)O measurement is traceably absorbed by CO\(_2\) (see Fig. 4.7 in Wallace and Hobbs, 2006). This absorption interferes slightly with the H\(_2\)O absorption at this wavelength (McDermitt et al., 1993). As such, the power of identical measurement lights (i.e., \( A_{wz} \) as a steady value in the H\(_2\)O working equation from Model 17) through several air standards with the same H\(_2\)O density but different backgrounds of CO\(_2\) amounts would result in different values of \( A_w \) in the H\(_2\)O working equation from Model (17). In this equation, without parameter \( S_c \) and its joined term, different \( A_w \) values will result in significantly different \( \rho_{H_2O}^s \) values, although \( \rho_{H_2O} \) is essentially the same. In case of the same H\(_2\)O amount in the airflows under different CO\(_2\) backgrounds, different values of \( A_w \) reporting the same \( \rho_{H_2O} \) are accounted for by \( S_c \) associated with \( A_c \) and \( A_{cs} \) in the H\(_2\)O working equation from Model (17). However, \( S_c \) is not perfectly accurate either, having uncertainty in the determination of \( \rho_{H_2O} \). This uncertainty in the EC150 infrared analyzer is specified by the sensitivity to CO\(_2\) (\( s_{CO_2} \)) as the maximum range of \( \pm 4.09 \times 10^{-3} \) g H\(_2\)O m\(^{-3}\) (mg CO\(_2\) m\(^{-3}\))\(^{-1}\) (Table 1). Assuming the infrared analyzers for H\(_2\)O have the lowest sensitivity-to-CO\(_2\) uncertainty for airflow with an atmospheric background CO\(_2\) amount (i.e., 767 mgCO\(_2\) m\(^{-3}\)), \( \Delta \rho_{H_2O}^s \) could be formulated as

\[
\Delta \rho_{H_2O}^s = s_{CO_2} (\rho_{CO_2} - 767) \leq 1553 \text{ mg CO}_2 \text{ m}^{-3}. \tag{20}
\]

Accordingly, \( \Delta \rho_{H_2O}^s \) can be reasonably expressed as

\[
\left| \Delta \rho_{H_2O}^s \right| \leq 786 \text{ mg CO}_2. \tag{21}
\]

### 5.3 \( \Delta \rho_{H_2O} \) (H\(_2\)O measurement accuracy)

Substituting Eqs. (16), (18), (19), and (21) into Model (15), \( \Delta \rho_{H_2O} \) for an individual H\(_2\)O measurement from OPEC sys-
tems by infrared analyzers can be expressed as

$$\Delta \rho_{\text{H}_2\text{O}} = \pm \left[ 1.966 \sigma_{\text{H}_2\text{O}} + 786 |\delta_{\text{CO}_2}| \right]$$

$$\times \frac{|d_{\text{rv}}| + \delta_{\text{H}_2\text{O}, g} \rho_{\text{H}_2\text{O}}}{T_{\text{th}} - T_{\text{rl}}} \times \left\{ \frac{T_a - T_c}{T_c - T_a} \text{ if } T_c < T_a < T_{\text{th}} \right\}.$$ (22)

This equation is the H$_2$O accuracy equation for the OPEC systems with infrared analyzers. It expresses the accuracy of H$_2$O measurements from the OPEC systems in terms of the analyzer specifications $\sigma_{\text{H}_2\text{O}}$, $\sigma_{\text{CO}_2}$, $d_{\text{rv}}$, $\delta_{\text{H}_2\text{O}, g}$, $T_{\text{th}}$, and $T_{\text{rl}}$; measured variables $\rho_{\text{H}_2\text{O}}$ and $T_a$; and a known variable $T_c$. Using this equation and the specification values as in Table 1 for EC150 infrared analyzers, the accuracy of field H$_2$O measurements can be evaluated as a range for OPEC systems with such analyzers. For an OPEC system with another model of open-path infrared analyzer, such as the LI-7500 series (LI-COR Biosciences, NE, USA) or IRGASON (Campbell Scientific Inc., UT, USA), its corresponding specification values are used.

5.4 Evaluation of $\Delta \rho_{\text{H}_2\text{O}}$

H$_2$O accuracy ($\Delta \rho_{\text{H}_2\text{O}}$) can be evaluated using the H$_2$O accuracy equation over a domain of $T_a$ and $\rho_{\text{H}_2\text{O}}$. Similar to the CO$_2$ accuracy equation in Fig. 2, $\Delta \rho_{\text{H}_2\text{O}}$ is presented as the ordinate along the abscissa of $T_a$ at different $\rho_{\text{H}_2\text{O}}$ levels within the ranges of $T_a$ and $\rho_{\text{H}_2\text{O}}$ in ecosystems (Fig. 3). As with the evaluation of $\Delta \rho_{\text{CO}_2}$, $T_a$ is limited from $-30$ to $50^\circ$C and $T_c$ can be assumed to be $20^\circ$C. The range of $\rho_{\text{H}_2\text{O}}$ at $T_a$ needs to be determined using atmospheric physics (Buck, 1981).

5.4.1 $\rho_{\text{H}_2\text{O}}$ range

The EC150 analyzers were calibrated for H$_2$O density from 0 to 44 gH$_2$O m$^{-3}$ due to the reason addressed in Sect. 2. The highest limit of measurement range for H$_2$O density by other models of analyzers also should be near 44 gH$_2$O m$^{-3}$. However, due to the positive exponential dependence of air water vapor saturation on $T_a$ (Wallace and Hobbs, 2006), $\rho_{\text{H}_2\text{O}}$ has a range that is wider at higher $T_a$ and narrower at lower $T_a$. Below $37^\circ$C at 101.325 kPa, $\rho_{\text{H}_2\text{O}}$ is lower than 44 gH$_2$O m$^{-3}$, and its range becomes narrower and narrower, reaching 0.34 gH$_2$O m$^{-3}$ at $-30^\circ$C. To determine the H$_2$O accuracy over the same relative range of air moisture, even at different $T_a$, the saturation water vapor density is used to scale air moisture to 20%, 40%, 60%, 80%, and 100% (i.e., relative humidity or RH). For each scaled RH value, $\rho_{\text{H}_2\text{O}}$ can be calculated at different $T_a$ and $P$ (Appendix B) for use in the H$_2$O accuracy equation. In this way, over the range of $T_a$, H$_2$O accuracy can be shown as curves, along each of which RH is equal (Fig. 3).

5.4.2 $\Delta \rho_{\text{H}_2\text{O}}$ range

In the same way as with CO$_2$ accuracy, the H$_2$O accuracy at $T_a = T_c$ is best at its narrowest as the sum of precision and sensitivity-to-CO$_2$ uncertainties ($< 0.040$ gH$_2$O m$^{-3}$ in magnitude). However, away from $T_c$, its range non-linearly becomes wider, very gradually below this $T_c$ value but more abruptly above because, as $T_a$ increases, $\rho_{\text{H}_2\text{O}}$ at the same RH increases exponentially (Eqs. B1 and B2 in Appendix B), while $\Delta \rho_{\text{H}_2\text{O}}$ increases linearly with $\rho_{\text{H}_2\text{O}}$ in the H$_2$O accuracy Eq. (22). This range can be summarized as the widest at 48$^\circ$C as $\pm 0.099$ gH$_2$O m$^{-3}$ for air with 60% RH (Fig. 3a and H$_2$O columns in Table 2). The number can be rounded up to $\pm 0.10$ gH$_2$O m$^{-3}$ for the overall accuracy of field H$_2$O measurements from OPEC systems by the EC150 infrared analyzers.

Figure 3b shows an interesting trend of H$_2$O relative accuracy with $T_a$. Given the RH range, as shown in Fig. 3b, the relative accuracy diverges with a $T_a$ decrease and converges with a $T_a$ increase. The H$_2$O relative accuracy varies from 0.17% for saturated air at $37^\circ$C to 96% for 20% RH air at $-30^\circ$C (data for Fig. 3b) and, at this low $T_a$, can be much greater if RH goes further lower. The H$_2$O relative accuracy in magnitude is $< 1\%$ while $\rho_{\text{H}_2\text{O}} > 5.00$ gH$_2$O m$^{-3}$, $< 5\%$ while $\rho_{\text{H}_2\text{O}} > 1.20$ gH$_2$O m$^{-3}$, and $> 10\%$ while $\rho_{\text{H}_2\text{O}} > 0.60$ gH$_2$O m$^{-3}$.

6 Application

The primary objective of this study is to develop an assessment methodology to evaluate the overall accuracies of field CO$_2$ and H$_2$O measurements from the infrared analyzers in OPEC systems by compositing their individual measurement uncertainties as specified with four uncertainty descriptors: zero drift, gain drift, sensitivity to CO$_2$/H$_2$O, and precision variability (Table 1). Ultimately, the overall accuracies (i.e., $\Delta \rho_{\text{CO}_2}$ and $\Delta \rho_{\text{H}_2\text{O}}$) make uncertainty analyses possible for the various applications of CO$_2$ and H$_2$O data, and the composited accuracy equations (i.e., Eqs. 14 and 22) make the field maintenance rationale for infrared analyzers.

6.1 Application of $\Delta \rho_{\text{CO}_2}$ and $\Delta \rho_{\text{H}_2\text{O}}$ to the uncertainty analyses for CO$_2$ and H$_2$O flux data

As discussed in Introduction, the uncertainty in each flux data point is contributed by numerous sub-uncertainties in the processes of measurements and computations, among which $\Delta \rho_{\text{CO}_2}$ and $\Delta \rho_{\text{H}_2\text{O}}$ are two fundamental uncertainties in the measurements from infrared analyzers. For this study topic, assuming 3-D wind speeds are accurately measured by a sonic anemometer, Appendix C demonstrates that neither $\Delta \rho_{\text{CO}_2}$ nor $\Delta \rho_{\text{H}_2\text{O}}$ brings an uncertainty into the covariance of vertical wind speed ($u$) with $\rho_{\text{CO}_2}$, $\rho_{\text{H}_2\text{O}}$, or $T_a$ even after coordinate rotations, lag maximization, and low- and high-frequency corrections, given by Eqs. (C8) and (C9) in Ap-
where the overbar is a Reynolds’ averaging operator, prime denotes the fluctuations in a variable away from its mean (e.g., \( w' = w - \bar{w} \)), subscript T indicates “true” value (see Appendix C for the implication of true value), and subscript rmf indicates that the covariance was corrected through coordinate rotations (r), lag maximization (m), and low- and high-frequency corrections (f). The three equalities in Eq. (23) that are proved in Appendix C prove that the measured covariance of \( w \) with \( \rho_{CO_2}, \rho_{H_2O}, \) or \( T_a \) is not affected by corresponding \( \Delta \rho_{CO_2}, \Delta \rho_{H_2O}, \) or \( \Delta T_a \) (i.e., accuracy of \( T_a \)), being equal to the true covariance. Further, through WPL corrections, the three terms on the left side of Eq. (23) can be used to derive an analytical equation for measured CO\(_2\) or H\(_2\)O flux, whereas the three terms on the right side of this equation can be used to derive an analytical equation for true CO\(_2\) or H\(_2\)O flux. The comparison of both analytical equations can demonstrate the partial effects of \( \Delta \rho_{CO_2} \) and \( \Delta \rho_{H_2O} \) on the uncertainty in CO\(_2\) or H\(_2\)O flux data.

### 6.1.1 Roles of \( \Delta \rho_{CO_2} \) and \( \Delta \rho_{H_2O} \) in the uncertainty in CO\(_2\) flux data

Using the terms on the left side of Eq. (23), through the WPL corrections for CO\(_2\) flux from \( \left( w' \rho_{CO_2}' \right)_{\text{rmf}} \) (Webb et al., 1980), the measured CO\(_2\) flux \( \left( F_{CO_2} \right) \) is given by

\[
F_{CO_2} = \left( w' \rho_{CO_2}' \right)_{\text{rmf}} + \frac{\mu}{\rho_d} \left( \frac{\rho_{CO_2}'}{\rho_d w} \right)_{\text{rmf}} + \left( 1 + \mu \frac{\rho_{H_2O}}{\rho_d} \right) \frac{\bar{\rho}_{CO_2}}{\bar{T}_{aK}} \left( w'T_a \right)_{\text{rmf}},
\]

(24)

where \( \mu \) is the ratio of dry air to water molecular weight, \( \rho_d \) is dry air density, and \( T_{aK} \) is air temperature in kelvin. According to Eqs. (C1) and (23), this equation can be written as

\[
F_{CO_2} = \left( w' \rho_{CO_2}' \right)_{\text{rmf}} + \frac{\mu}{\rho_d} \left( \frac{\rho_{CO_2}'}{\rho_d w} \right)_{\text{rmf}} + \left( 1 + \mu \frac{\rho_{H_2O}}{\rho_d} \right) \frac{\bar{\rho}_{CO_2}}{\bar{T}_{aK}} \left( w'T_a \right)_{\text{rmf}},
\]

(25)

where \( \Delta T_a \) is the accuracy of \( T_{aK} \). \( \Delta T_a \) is well defined as \( \pm 0.20 \) K in compliance with the WMO standard (WMO, 2018). According to Eqs. (23) and (24), from \( \left( w' \rho_{CO_2}' \right)_{\text{rmf}} \), the nominal true CO\(_2\) flux \( \left( F_{CO_2T} \right) \) can be given by

\[
F_{CO_2T} = \left( w' \rho_{CO_2}' \right)_{\text{rmf}} + \frac{\mu}{\rho_d} \left( \frac{\rho_{CO_2}'}{\rho_d w} \right)_{\text{rmf}} + \left( 1 + \mu \frac{\rho_{H_2O}}{\rho_d} \right) \frac{\bar{\rho}_{CO_2}}{\bar{T}_{aK}} \left( w'T_a \right)_{\text{rmf}},
\]

(26)

From Eqs. (25) and (26), the uncertainty in CO\(_2\) flux \( \left( \Delta F_{CO_2} \right) \) can be expressed as

\[
\Delta F_{CO_2} = F_{CO_2} - F_{CO_2T}
\]

\[
= \mu \left( \frac{\bar{\rho}_{CO_2}}{\bar{T}_{aK}} - \frac{\bar{\rho}_{H_2O}}{\bar{T}_{aK}} \right) \left( \frac{\rho_{CO_2}'}{\rho_d T} \right)_{\text{rmf}} + \left( 1 + \mu \frac{\rho_{H_2O}}{\rho_d} \right) \frac{\bar{\rho}_{CO_2}}{\bar{T}_{aK}} \left( w'T_a \right)_{\text{rmf}} - \left( 1 + \mu \frac{\rho_{H_2O}}{\rho_d} \right) \frac{\bar{\rho}_{CO_2}}{\bar{T}_{aK}} \left( w'T_a \right)_{\text{rmf}}.
\]

(27)

This derivation provides a conceptual model for the partial effects of \( \Delta \rho_{CO_2} \) and \( \Delta \rho_{H_2O} \) on the uncertainty in CO\(_2\) flux data. This uncertainty is added by \( \Delta \rho_{CO_2} \) and \( \Delta \rho_{H_2O} \) interactively with the density effect due to H\(_2\)O flux (i.e., the term with \( \left( w' \rho_{H_2O}' \right)_{\text{rmf}} \) in Eq. 27) and temperature flux (i.e., the term with \( \left( w'T_a' \right)_{\text{rmf}} \) in Eq. 27).
6.1.2 $\Delta \rho_{H_2O}$ on uncertainty in H$_2$O flux data

Using the same approach to Eq. (27), the uncertainty in H$_2$O flux ($\Delta F_{H_2O}$) can be expressed as

$$\Delta F_{H_2O} = \mu \left( \frac{\partial \overline{p_{H_2O}}}{\partial T} - \delta \overline{p_{H_2O}} - \frac{\partial \overline{p_{H_2O}}}{\partial T} \right) (w' \rho_{H_2O})_{rmf} + \left[ \left( 1 + \mu \frac{\partial \overline{p_{H_2O}}}{\partial T} - \delta \overline{p_{H_2O}} \right) \frac{\partial \overline{p_{H_2O}} + \delta \overline{p_{H_2O}}}{\partial T} + \Delta T_a \right]$$

$$- \left( 1 + \mu \frac{\partial \overline{p_{H_2O}}}{\partial T} \right) \frac{\partial \overline{p_{H_2O}}}{\partial T} (w'T_a)_{rmf}.$$ \hspace{5cm} (28)

This formulation provides a conceptual model for the partial effects of $\Delta \rho_{H_2O}$ on the uncertainty in H$_2$O flux data. This uncertainty is added only by $\Delta \rho_{H_2O}$ also interactively with the density effect due to H$_2$O flux (i.e., the term with $(w' \rho_{H_2O})_{rmf}$ in Eq. 28) and temperature flux (the term with $(w'T_a)_{rmf}$ in Eq. 28). Further analysis and more discussion about Eqs. (27) and (28) go beyond the scope of this study.

6.2 Application of $\Delta \rho_{H_2O}$ to the uncertainty analysis for high-frequency air temperature

The measured variables $\rho_{H_2O}$, along with $T_s$ and $P$, can be used to compute high-frequency $T_a$ in OPEC systems (Swiakie, 2018). If $T_a(\rho_{H_2O}, T_s, P)$ were an exact function from the theoretical principles, it would not have any error itself. However, in our applications, variables $\rho_{H_2O}$, $T_s$, and $P$ are measured from the OPEC systems experiencing seasonal climates. As addressed in this study, the measured values of these variables have measurement uncertainty in $\rho_{H_2O}$ ($\Delta \rho_{H_2O}$, i.e., accuracy of field H$_2$O measurement), in $T_s$ ($\Delta T_s$, i.e., accuracy of field $T_s$ measurement), and in $P$ ($\Delta P$, i.e., accuracy of field $P$ measurement). The uncertainties from the measurements propagate to the computed $T_a$ as an uncertainty ($\Delta T_a$, i.e., accuracy of $T_a(\rho_{H_2O}, T_s, P)$). This accuracy is a reference by any application of $T_a$. It should be specified through the relationship of $\Delta T_a$ to $\Delta \rho_{H_2O}$, $\Delta T_s$, and $\Delta P$.

As field measurement uncertainties, $\Delta \rho_{H_2O}$, $\Delta T_s$, or $\Delta P$ are reasonably small increments in numerical analysis (Burden et al., 2016). As such, depending on all the small increments, $\Delta T_a$ is a total differential of $T_a(\rho_{H_2O}, T_s, P)$ with respect to $\rho_{H_2O}$, $T_s$, and $P$, which are measured independently by three sensors, given by

$$\Delta T_a = \frac{\partial T_a}{\partial \rho_{H_2O}} \Delta \rho_{H_2O} + \frac{\partial T_a}{\partial T_s} \Delta T_s + \frac{\partial T_a}{\partial P} \Delta P.$$ \hspace{5cm} (29)

In this equation, $\Delta \rho_{H_2O}$ from the application of Eq. (22) is a necessary term to acquire $\Delta T_a$. $\Delta T_s$ can be acquired from the specifications for 3-D sonic anemometers (Zhou et al., 2018), $\Delta P$ can be acquired from the specifications for the barometer used in the OPEC systems (Vaisala, 2020), and the three partial derivatives can be derived from the explicit function $T_a(\rho_{H_2O}, T_s, P)$. With $\Delta \rho_{H_2O}$, $\Delta T_s$, $\Delta P$, and the three partial derivatives, $\Delta T_a$ can be ranged as a function of $\rho_{H_2O}$, $T_s$, and $P$.

6.3 Application of accuracy equations in analyzer field maintenance

An infrared analyzer performs better if the field environment is near its manufacturing conditions (e.g., $T_a$ at 20 °C), which is demonstrated in Figs. 2a and 3a for measurement accuracies associated with $T_c$. As indicated by the accuracies in both figures, the closer to $T_c$ at 20 °C $T_a$ is, the better the analyzers perform. However, the analyzers are used in OPEC systems mostly for long-term field campaigns through four-seasonal climates vastly different from those in the manufacturing processes. Over time, an analyzer gradually drifts in some ways and needs field maintenance, although within its specifications.

The field maintenance cannot improve the sensitivity-to-CO$_2$/H$_2$O uncertainty and precision variability, but both are minor (their sum $< 0.392$ ngCO$_2$ m$^{-3}$ for CO$_2$, Eqs. 4 and 13; $< 0.045$ gH$_2$O m$^{-3}$ for H$_2$O, Eqs. 16 and 21) as compared to the zero or gain drift uncertainties. However, the zero and gain drift uncertainties are major in the determination of field CO$_2$/H$_2$O measurement accuracy (Figs. 2 to 4 and Eqs. 14 and 22), but they are adjustable, through the zero and/or span procedures, and can be minimized. Therefore, manufacturers of infrared analyzers have provided software and hardware tools for the procedures (Campbell Scientific Inc., 2021b) and scheduled the procedures using those tools (LI-COR Biosciences, 2021c). Fratini et al. (2014) provided a technique implemented into the EddyPro® Eddy Covariance Software (LI-COR Biosciences, 2021a) to correct the drift biases from a raw time series of CO$_2$ and H$_2$O data through post-processing. This study provides rationales for how to assess, schedule, and perform the zero and span procedures (Figs. 2a, 3a, and 4).

6.3.1 CO$_2$ zero and span procedures

Figure 4a shows that the CO$_2$ zero drift uncertainty linearly increases with $T_a$ away from $T_c$ over the full $T_a$ range within which OPEC systems operate; so, too, does CO$_2$ gain drift uncertainty increase for a given CO$_2$ concentration. As suggested by Zhou et al. (2021), both drifts should be adjusted near the $T_a$ value around which the system runs. The zero and gain drifts should be adjusted, through zero and span procedures, at a $T_a$ close to its daily mean around which the system runs. Based on the range of $T_a$ daily cycle, the procedures are set at a moderate instead of the highest or lowest moment in $T_a$. Given the daily cycle range is much narrower than 40 °C, an OPEC system could run at $T_a$ within ±20 °C of $T_c$, if the procedures are performed at a right moment of $T_a$. For our case study on atmospheric CO$_2$ background (left CO$_2$ column in Table 2), the procedures can narrow the widest possible range
of ±1.22 mgCO$_2$ m$^{-3}$ for field CO$_2$ measurement by at least 40% to ±0.72 mgCO$_2$ m$^{-3}$ (i.e., accuracy at 0 or 40°C when $T_c = 20°C$), which would be a significant improvement to ensure field CO$_2$ measurement accuracy through CO$_2$ zero and span procedures.

6.3.2 H$_2$O zero and span procedures

Figure 4b shows that the H$_2$O zero drift uncertainty increases as $T_a$ moves away from $T_c$ in the same trend as CO$_2$ zero drift uncertainty. Therefore, an H$_2$O zero procedure can be performed by the same technique as for the CO$_2$ zero procedure. H$_2$O gain drift uncertainty has a different trend. It exponentially diverges, as $T_a$ increases away from $T_c$, to ±5.0 × 10$^{-2}$ gH$_2$O m$^{-3}$ near 50°C and gradually converges to 2 orders smaller as $T_a$ decreases away from $T_c$, to ±6.38 × 10$^{-3}$ gH$_2$O m$^{-3}$ at −30°C (data for Fig. 4b). The exponential divergence results from the linear relationship of H$_2$O gain drift uncertainty (Eq. 19) with $\rho_{H_2O}$, which exponentially increases (Eq. B1) with a $T_a$ increase away from $T_c$ for the same RH (Buck, 1981). The convergence results from the linear relationship offset by the exponential decrease in $\rho_{H_2O}$ with a $T_a$ decrease for the same RH. This trend of H$_2$O gain drift uncertainty with $T_a$ is a rationale to guide the H$_2$O span procedure, which adjusts the H$_2$O gain drift.

The H$_2$O span procedure needs standard moist air with known H$_2$O density from a dew point generator. The generator is not operational near or below freezing conditions (LI-COR Biosciences, 2004), which limits the span procedure to be performed only under non-freezing conditions. This condition, from 5 to 35°C, may be considered for the generator to be conveniently operational in the field. Accordingly, the zero and span procedures for H$_2$O should be discussed separately for a $T_a$ above and below 5°C.

$T_a$ above 5°C

Looking at the right portion with $T_a$ above 5°C in Fig. 4b, H$_2$O gain drift has a more obvious impact on measurement uncertainty in a higher $T_a$ range (e.g., above $T_c$), within which the H$_2$O span procedure is most needed. In this range, the maximum accuracy range of ±0.10 gH$_2$O m$^{-3}$ can be narrowed by 30% to ±0.07 (assessed from data for Fig. 3a) if the zero and span procedures for H$_2$O can be sequentially performed as necessary in a $T_a$ range from 5 to 35°C.

$T_a$ below 5°C

Looking at the left portion with $T_a$ below 5°C in Fig. 4b, H$_2$O gain drift has a less obvious contribution to the measurement uncertainty in a lower $T_a$ range (e.g., below 5°C), within which the H$_2$O span procedure may be unnecessary. An H$_2$O gain drift uncertainty at 5°C is 50% of the H$_2$O zero drift uncertainty (dotted curve in Fig. 5). This percentage decreases to 3% at −30°C. On average, this percentage over a range of −30 to 5°C is 18% (assessed from data for the dotted curve in Fig. 5). Thus, for H$_2$O measurements over the lower $T_a$ range, it can be concluded that H$_2$O zero drift is a major uncertainty source, and H$_2$O gain drift is a minor uncertainty source.

A close examination of the other curves in Fig. 5 for the portion in the accuracy range from H$_2$O zero/gain drift makes this conclusion more convincing. Given $T_c = 20$°C, in the accuracy range, the portion from H$_2$O zero drift uncertainty is much greater (maximum 38% at −30°C) than that from H$_2$O gain drift uncertainty (maximum only 7% at 5°C). On average over the lower $T_a$ range, the former is 27% and the latter only 4%. Further, given $T_c = 5$°C, in the accuracy range, the portion from H$_2$O gain drift uncertainty is even smaller (maximum only 3% at −5°C); in contrast, the portion from zero drift uncertainty is more major (1 order higher, 30% at −30°C). On average over the lower $T_a$ range, the minor gain drift uncertainty is 1.7%, and the major zero drift uncertainty is 17%. Both percentages underscore that the H$_2$O span procedure is reasonably unnecessary under cold/dry conditions, and, under such conditions, the H$_2$O zero procedure is the only necessary option to efficiently minimize H$_2$O measurement uncertainty from the
In a cold and/or dry environment, H$_2$O zero procedures on a regular schedule would best minimize the impact of zero drifts on measurements. Under such an environment, the automatic zero procedure for CO$_2$ and H$_2$O together in CPEC systems is an operational and efficient option to ensure and improve field CO$_2$ and H$_2$O measurement accuracies (Campbell Scientific Inc., 2021a; Zhou et al., 2021).

7 Discussion

An assessment methodology to evaluate the overall accuracies of field CO$_2$ and H$_2$O measurements from the infrared analyzers in OPEC systems is developed using individual analyzer measurement uncertainties as specified using four uncertainty descriptors: zero drift, gain drift, sensitivity to CO$_2$/H$_2$O, and precision variability (Table 1). For the evaluation, these uncertainty descriptors are comprehensively composited into the accuracy Model (2) and then formulated as a CO$_2$ accuracy Eq. (14) and an H$_2$O accuracy Eq. (22) (Sects. 3 to 5 and Appendix A). The assessment methodology, along with the model and the equations, presents our development for the objective (Sects. 4.5 and 5.4).

7.1 Accuracy model

Accuracy Model (2) composites the four measurement uncertainties (zero drift, gain drift, sensitivity to CO$_2$/H$_2$O, and precision variability), specified for analyzer performance, as an accuracy range. This range is modeled as a simple addition of the four uncertainties. The simple addition is derived from our analysis assertion that the four measurement uncertainties interactionally or independently contribute to the accuracy range, but the contributions from the interactions inside any pair of uncertainties are negligible since they are 3 orders smaller in magnitude than an individual contribution in the pair (Appendix A). This derived model is simple and applicable, paving an approach to the formulation of accuracy equations that are computable for evaluating the overall accuracies of field CO$_2$ and H$_2$O measurements from the infrared analyzers in OPEC systems.

Additionally, included in the accuracy model, the four types of measurement uncertainty sources (i.e., zero drift, gain drift, sensitivity to CO$_2$/H$_2$O, and precision variability) to specify the performance of infrared CO$_2$–H$_2$O analyzers for OPEC systems have been consistently used over last 2 decades (LI-COR Biosciences, 2001, 2021b, c; Campbell Scientific Inc., 2021a, b). With the advancement of optical technologies, the number of these uncertainty sources for analyzer specifications is not expected to increase; rather some current uncertainty sources could be eliminated from the current specification list, even if not in the near future. If eliminated, in Models (3) and (15) and Eqs. (14) and (22), the parameters and variables related to the eliminated uncer-
tainty sources could be easily removed for the adoption of the new set of specifications for infrared CO$_2$–H$_2$O analyzers.

7.2 Formulation of uncertainty terms in Model (2) for accuracy equations

In Sects. 4 and 5, each of the four uncertainty terms in accuracy Model (2) is formulated as a computable sub-equation for CO$_2$ (Eqs. 4, 7, 11, and 13) and H$_2$O (Eqs. 16, 18, 19, and 21), respectively. The accuracy model, whose terms are replaced with the formulated sub-equations for CO$_2$, becomes a CO$_2$ accuracy Eq. (14) and, for H$_2$O, becomes an H$_2$O accuracy Eq. (22). In the formulation, approximation is used for zero drift, gain drift, and sensitivity to CO$_2$/H$_2$O, while statistics are applied for precision variability.

For the zero/gain drift, although it is well known that the drift is influenced more by $T_a$ if housing CO$_2$–H$_2$O accumulation is assumed to be minimized as insignificant under normal field maintenance (LI-COR Biosciences, 2021c; Campbell Scientific Inc., 2021b), the exact relationship of drift to $T_a$ does not exist. Alternatively, the zero/gain drift uncertainty is formulated by an approximation of drifts away from $T_a$, linearly in proportion to the difference between $T_a$ and $T_c$ within its maximum range over the operational range in $T_a$ of OPEC systems (Eqs. 7, 11, 18, and 19). A drift uncertainty equation formulated through such an approximation is not an exact relationship of drift to $T_a$, but it does represent the drift trend, as influenced by $T_a$, to be understood by users. The accuracy from this equation at a given $T_a$ is not exact either, but the maximum range over the full range, which is the greatest-likelihood estimation, is most needed by users.

In fact, the H$_2$O accuracy as influenced by the linear trend of zero and gain drifts with the difference between $T_a$ and $T_c$ is overshadowed by the exponential trend of saturated H$_2$O density with $T_a$ (Fig. 4b). Similarly, the CO$_2$ accuracy as influenced by the linear trend of zero and gain drifts with this difference is dominated by the CO$_2$ density of the ecosystem background with $T_a$, particularly in the low temperature range (Fig. 2). Ultimately, the assumed linear trend does not play a dominant role in the accuracy trends of CO$_2$ and H$_2$O, which shows the merits of our methodology in the uses of atmospheric physics and biological environment principles for the field data.

The sensitivity-to-CO$_2$/H$_2$O uncertainty can be formally formulated as Eqs. (20) or (12), but, if directly used, this formulation would add an additional variable to the CO$_2$/H$_2$O accuracy equation. Equation (12) would add H$_2$O density ($\rho_{H_2O}$) to the CO$_2$ accuracy Eq. (14), and Eq. (20) would add CO$_2$ density ($\rho_{CO_2}$) to the H$_2$O accuracy Eq. (22). For either accuracy equation, the additional variable would complicate the uncertainty analysis. According to the ecosystem environment background, the maximum range of sensitivity-to-CO$_2$/H$_2$O uncertainty is known, and as compared to the major uncertainty in zero/gain drift (Table 1), this range is narrow (Table 1 and Eqs. 13 and 21). Therefore, the sensitivity-to-CO$_2$/H$_2$O uncertainty is approximated as Eq. (21) or (13). This approximation widens the accuracy range slightly, in a magnitude smaller than each of major uncertainties from the drifts by at least 1 order; however, it eliminates the need for $\rho_{H_2O}$ in the CO$_2$ accuracy Eq. (14) and for $\rho_{CO_2}$ in the H$_2$O accuracy Eq. (22), which makes the equations easily applicable.

Precision uncertainty is statistically formulated as Eq. (4) for CO$_2$ and Eq. (16) for H$_2$O. This formulation is common practice based on statistical methods (Hoel, 1984).

7.3 Use of relative accuracy for infrared analyzer specifications

Relative accuracy is often used concurrently with accuracy to specify sensor measurement performance. The accuracy is the numerator of relative accuracy whose denominator is the true value of a measured variable. When evaluated for the applications of OPEC systems in ecosystems, CO$_2$ accuracy in magnitude is small in a range within 1 order (0.39–1.22 mgCO$_2$ m$^{-3}$, data for Fig. 2a), and so is H$_2$O accuracy (0.04–0.10 gH$_2$O m$^{-3}$, data for Fig. 3a). In ecosystems, CO$_2$ is naturally high, as compared to its accuracy magnitude, and does not change much in terms of a magnitude order (e.g., no more than 1 order from 600 to 1600 mgCO$_2$ m$^{-3}$, assumed in this study). However, unlike CO$_2$, H$_2$O naturally changes dramatically in its amount across at least 3 orders in magnitude (e.g., at 101.325 kPa, from 0.03 gH$_2$O m$^{-3}$ when RH is 10% at $-30^\circ$C to 40 gH$_2$O m$^{-3}$ when dew point temperature is 35 $^\circ$C at the highest as reported by the National Weather Service, 2022; under drier conditions, the H$_2$O amount could be even lower). Because, in ecosystems, CO$_2$ changes differently from H$_2$O in amount across magnitude orders, the relative accuracy behaviors in CO$_2$ differ from H$_2$O (Figs. 2b and 3b).

7.3.1 CO$_2$ relative accuracy

Because the small CO$_2$ accuracy magnitude relative to the natural CO$_2$ amount in ecosystems, the CO$_2$ relative accuracy magnitude varies within a narrow range of ±0.07 to ±0.19 % (Sect. 4.5.2). If the relative accuracy is used, either a range of ±0.07 to ±0.19 % or an inequality of ≤0.19 % in magnitude can be specified as the CO$_2$ relative accuracy for field CO$_2$ measurements. Both range and inequality would be equivalently perceived by users to be a fair performance of the infrared analyzers in OPEC systems. For simplicity, our study specifies the CO$_2$ relative accuracy for the EC150 infrared analyzers to be ±0.19 % after a manufacturing calibration (data shown in Fig. 2b).

7.3.2 H$_2$O relative accuracy

Although the H$_2$O accuracy magnitude is also small, the “relatively” great change in natural-air H$_2$O across several magnitude orders in ecosystems results in a much wider range of
the H$_2$O relative accuracy magnitude, from $\pm 0.23\%$ at maximum air moisture to $\pm 96\%$ when RH is 20\% at $-30^\circ$C (Fig. 3b and Sect. 5.4.2). H$_2$O relative accuracy can be much greater under dry conditions at low $T_a$ (e.g., $\pm 192\%$ for air when RH is 10\% at $-30^\circ$C). Accordingly, if the relative accuracy is used, either a range of $\pm 0.23\%$ to $\pm 192\%$ or an inequality of $\leq 192\%$ in magnitude can be specified as the H$_2$O relative accuracy for field H$_2$O measurements. Either the range or the inequality could be perceived by users intrinsically as a poor measurement performance of the infrared analyzers in OPEC systems, although either specification is conditionally right for fair H$_2$O measurement.

Apparently, the relative accuracy for H$_2$O measurements in ecosystems is not intrinsically interpretable by users to correctly perceive the performance of the infrared analyzers in OPEC systems. Instead, if H$_2$O relative accuracy is unconditionally specified just in an inequality of $\leq 192\%$ in magnitude, it could easily mislead users to wrongly assess the performance as unacceptable for H$_2$O measurements, although this performance of the infrared analyzers in OPEC systems is fair for air when RH is 10\% at $-30^\circ$C. Therefore, H$_2$O relative accuracy is not recommended to be used for specification of infrared analyzers for H$_2$O measurement performance. If this descriptor is used, the H$_2$O relative accuracy under a standard condition should be specified. This condition may be defined as saturated air at 35\°C (i.e., the highest natural dew point; National Weather Service, 2022) under normal $P$ of 101.325 kPa (Wright et al., 2003). For our case study, under such a standard condition, the H$_2$O relative accuracy can be specified within $\pm 0.18\%$ after a manufacturing calibration (data for Fig. 3b).

8 Conclusions

The accuracy of field CO$_2$/H$_2$O measurements from the infrared analyzers in OPEC systems can be defined as a maximum range of composited measurement uncertainty (Eqs. 14 and 22) from the specified sources: zero drift, gain drift, sensitivity to CO$_2$/H$_2$O, and precision variability (Table 1), all of which are included in the system specifications for infrared CO$_2$–H$_2$O analyzers currently used in field OPEC systems. The specified uncertainties interactationally or independently contribute to the overall uncertainty. Fortunately, the interactions between component uncertainties in each pair is 3 orders smaller than either component individually (Appendix A). Therefore, these specified uncertainties can be simply added together as the accuracy range in a general CO$_2$/H$_2$O accuracy model for the infrared analyzers in OPEC systems (Model 2). Based on statistics, bio-environment, and approximation, the specification descriptors of the infrared analyzers in OPEC systems are incorporated into the model terms to formulate the CO$_2$ accuracy Eq. (14) and the H$_2$O accuracy Eq. (22), both of which are computable to evaluate corresponding CO$_2$ and H$_2$O accuracies. For the EC150 infrared analyzers used in the OPEC systems over their operational range in $T_a$ at the standard $P$ of 101.325 kPa (Figs. 2 and 3 and Table 2), the CO$_2$ accuracy can be specified as $\pm 1.22$ mg CO$_2$ m$^{-3}$ (relatively within $\pm 0.19\%$, Fig. 2) and H$_2$O accuracy as $\pm 0.10$ g H$_2$O m$^{-3}$ (relatively within $\pm 0.18\%$ for saturated air at 35\°C at the standard $P$, Fig. 3).

Both accuracy equations are not only applicable for further uncertainty estimation for CO$_2$ and H$_2$O fluxes due to CO$_2$ and H$_2$O measurement uncertainties (Eqs. 27 and 28) and the error/uncertainty analyses in CO$_2$ and H$_2$O data applications (e.g., Eq. 29); they may also be used as a rationale to assess and guide field maintenance on infrared analyzers. Equation (14) as shown in Fig. 2a, along with Eqs. (7) and (11) as shown in Fig. 4a, guides users to adjust the CO$_2$ zero and CO$_2$ gain drifts, through the corresponding zero and span procedures, near a $T_a$ value that minimizes the $T_a$ departures, on average, during the period of interest if this period were not under extreme and hazard conditions (Fratini et al., 2014). As assessed on atmospheric CO$_2$ background, the procedures can narrow the maximum CO$_2$ accuracy range by 40\%, from $\pm 1.22$ to $\pm 0.72$ mg CO$_2$ m$^{-3}$ and thereby greatly improve the CO$_2$ measurement accuracies with these regular zero and span procedures for CO$_2$.

Equation (22) as shown in Fig. 3a, along with Eqs. (18) and (19) as shown in Fig. 4b, presents users with a rationale to adjust the H$_2$O zero drift of infrared analyzers in the same technique as for CO$_2$, but the H$_2$O gain drift under hot and humid environments needs more attention (see the right portion above $T_c$ in Figs. 3a and 4b); under cold and/or dry environments, it does not merit further concern (see the left portion below 0\°C in Fig. 4b). In a $T_a$ range above 5\°C, the maximum H$_2$O accuracy range of $\pm 0.10$ g H$_2$O m$^{-3}$ can be narrowed by 30\% to $\pm 0.07$ g H$_2$O m$^{-3}$ if both zero and span procedures for H$_2$O are performed as necessary. In a $T_a$ range below 5\°C, the H$_2$O zero procedure alone can narrow the maximum H$_2$O accuracy range of $\pm 0.066$ g H$_2$O m$^{-3}$ by 22\% to $\pm 0.051$ g H$_2$O m$^{-3}$. Under cold environmental conditions, the H$_2$O span procedure is found to be unnecessary (Fig. 5), and the H$_2$O zero procedure is proposed as the only, and prominently efficient, option to minimize H$_2$O measurement uncertainty from the infrared analyzers in OPEC systems. This procedure plays the same role under dry conditions. Under cold and/or dry environments, the zero procedure for CO$_2$ and H$_2$O together would be a practical and efficient option not only to warrant but also to improve measurement accuracy. In a cold environment, adjusting the H$_2$O gain drift is impractical because of the failure of a dew point generator under freezing conditions.

Additionally, as a specification descriptor for OPEC systems used in ecosystems, relative accuracy is applicable for CO$_2$ instead of H$_2$O measurements. A small range in the CO$_2$ relative accuracy can be perceived intuitively by users as normal. In contrast, without specifying the condition of air moisture, a large range in H$_2$O relative accuracy under cold

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and/or dry conditions (e.g., 100 %) can easily mislead users to an incorrect conclusion in interpretation of H2O measurement reliability, although it is the best achievement of the modern infrared analyzers under such conditions. If the H2O relative accuracy is used, the authors suggest conditionally defining it for saturated air at 35 °C relative accuracy is used, the authors suggest conditionally defining it for saturated air at 35 °C (i.e., 39.66 g H2O m⁻³ at 101.352 kPa). Ultimately, this study provides some scientific bases for the flux community to specify the accuracy of CO2–H2O measurements from the infrared analyzers in OPEC systems, although only one model of infrared analyzers (i.e., EC150) is used for this study.

Appendix A: Derivation of the accuracy model for infrared CO2–H2O analyzers

As defined in the Introduction, the measurement accuracy of infrared CO2–H2O analyzers is a range of the difference between the true a density (ρaT, where a can be either CO2 or H2O) and a density (ρa) measured by the analyzers. The difference is denoted by Δρa, given by Eq. (1) in Sect. 3. The range of this difference is contributed from the analyzer performance uncertainties, as specified by the use of the four descriptors: zero drift, gain drift, cross-sensitivity, and precision (LI-COR Biosciences, 2021c; Campbell Scientific Inc., 2021b).

According to the definitions in Sect. 2, zero drift uncertainty (Δρa) is independent of ρaT value and gain trend related to analyzer response; so, too, is cross-sensitivity uncertainty (Δρa)g, which depends upon the amount of background H2O in the measured air if a is CO2 and upon the amount of background CO2 in the measured air if a is H2O. In the case that both gain drift and precision uncertainties are zero, Δρa and Δρa are simply additive to any true value as a measured value, including zero drift and cross-sensitivity uncertainties (ρa_zs):

\[ \rho_{a, zs} = \rho_{aT} + \Delta \rho_a^z + \Delta \rho_a^s. \]  

(A1)

where subscript z indicates zero drift uncertainty included in the measured value and subscript s indicates cross-sensitivity uncertainty included in the measured value. During the measurement process, while zero is drifting and cross-sensitivity is active, if gain also drifts, then the gain drift interacts with the zero drift and the cross-sensitivity. This is because ρa_zs is a linear factor for this gain drift (see the cells along the gain drift row in the value columns in Table 1) that is added to ρa_zs as a measured value additionally including gain drift uncertainty (ρa_zsg, where subscript g indicates gain drift uncertainty included in the measured value), given by

\[ \rho_{a, zsg} = \rho_{aT} + \delta g \rho_{a zs}. \]  

(A2)

where Δg is gain drift percentage (e.g., in the case of this study, ΔgCO2 = 0.10 % and ΔgH2O = 0.30 %, Table 1). Substituting ρa_zs, as expressed in Eq. (A1), into this equation leads to

\[ \rho_{a, zsg} = \rho_{aT} + \Delta \rho_a^z + \Delta \rho_a^s + \delta g \rho_{a zs}. \]  

(A3)

In this equation, \( \delta a, g \Delta \rho_a^g \) is the zero–gain interaction and \( \delta a, g \Delta \rho_a^s \) is the cross-sensitivity–gain interaction. In magnitude, the former is 3 orders smaller than either zero drift uncertainty (Δρa), or gain drift uncertainty (δa, g ρaT), and the latter is 3 orders smaller than either cross-sensitivity uncertainty (Δρa) or gain drift uncertainty. Therefore, both interactions are relatively small and can be reasonably dropped. As a result, Eq. (A3) can be approximated and rearranged as

\[ \rho_{a, zsg} \approx \rho_{aT} + \Delta \rho_a^z + \delta a, g \rho_{aT} + \Delta \rho_a^s + \Delta \rho_a^p. \]  

(A4)

where Δρa^p is a gain drift uncertainty. Any measured value has a random error (i.e., precision uncertainty) independent of ρaT in value (ISO, 2012). Therefore, ρa_zsg plus precision uncertainty (Δρa^p) is the measured value including all uncertainties (ρa), given by

\[ \rho_a = \rho_{a, zsg} + \Delta \rho_a^p. \]  

(A5)

The insertion of Eq. (A4) into this equation leads to

\[ \rho_a - \rho_{aT} = \Delta \rho_a^z + \Delta \rho_a^z + \Delta \rho_a^s + \Delta \rho_a^p. \]  

(A6)

This equation holds true for

\[ \Delta \rho_a \leq | \Delta \rho_a^z | + | \Delta \rho_a^s | + | \Delta \rho_a^p |. \]  

(A7)

The range of the right side of this equation is wider than the measurement uncertainty from all measurement uncertainty sources, as shown on the right side of Eq. (A6), and the difference of ρa minus ρaT (i.e., Δρa). Using this range, the measurement accuracy is defined in Model (2) in Sect. 3.

Appendix B: Water vapor density from ambient air temperature, relative humidity, and atmospheric pressure

Given ambient air temperature (Ta in °C) and atmospheric pressure (P in kPa), air has a limited capacity to hold an amount of water vapor (Wallace and Hobbs, 2006). This limited capacity is described in terms of saturation water vapor density (\( \rho_s \) in g H2O m⁻³) for moist air, given through the Clausius–Clapeyron equation (Sonntag, 1990; Wallace and Hobbs, 2006):

\[
\rho_s(T_a, P) = \begin{cases} 
    \exp\left(\frac{17.627T_a}{T_a + 243.17}\right) & T_a \geq 0 \\
    \frac{0.6112 f(P)}{Rv(273.15 + T_a)} & T_a < 0,
\end{cases}
\]

(B1)
where \( R_v \) is the gas constant for water vapor (4.61495 \( \times 10^{-4} \) kPa m\(^3\) K\(^{-1}\) gH\(_2\)O\(^{-1}\)) and \( f(P) \) is an enhancement factor for moist air, being a function of \( P \) as \( f(P) = 1.0016 + 3.15 \times 10^{-4} P - 0.0074 P^{-1} \). At relative humidity (RH in %), the water vapor density \( \rho_{H_2O}(T_a, P) \) in gH\(_2\)O m\(^{-3}\) is

\[
\rho_{H_2O}^{RH}(T_a, P) = RH \rho_a(T_a, P).
\]

This equation, along with Eq. (B1), is used to calculate \( \rho_{H_2O}^{RH} \) used in Fig. 3 in Sect. 5.4 and Figs. 4b and 5 in Sect. 6.3.

Appendix C: The relationship of measured to true covariance of vertical wind speed with \( CO_2 \), \( H_2O \), or air temperature

For open-path eddy-covariance systems, the computation of \( CO_2/H_2O \) flux between ecosystems and the atmosphere starts from covariance of an individual 3-D wind component with a \( CO_2/H_2O \) density. To express the covariance, as similarly used in Eqs. (1), \( \alpha \) is used as a subscript of \( \rho \) to represent either \( CO_2 \) or \( H_2O \) and subscript \( T \) is used to indicate a measurement free of uncertainty as if it were true. According to Eq. (1), a measured \( \alpha \) density \( (\rho_\alpha) \) with a measurement uncertainty \( (\Delta \rho_\alpha) \) can be expressed as

\[
\rho_\alpha = \rho_{\alpha T} + \Delta \rho_\alpha,
\]

where \( \rho_{\alpha T} \) is an assumed \( \alpha \) density free of measurement uncertainty as if measured by an accurate sensor with the same frequency response as the one measuring \( \rho_\alpha \). This assumed \( \alpha \) density \( (\rho_{\alpha T}) \) is also referred to as “true \( \alpha \) density” although it is not. The covariance of vertical wind speed \( (w) \) with \( \rho_\alpha \) is given by

\[
\overline{w' \rho_\alpha} = \frac{1}{n} \sum_{i=1}^{n} (w_i - \overline{w})(\rho_{\alpha i} - \overline{\rho_\alpha}),
\]

where \( n \) is the sample size or an averaging interval (e.g., 36,000 over a 1 h interval if \( w_i \) and \( \rho_{\alpha i} \) are measured at 10 Hz), subscript \( i \) indexes the sequential numbers for \( w_i \) and \( \rho_{\alpha i} \), the overbar is the Reynolds’ averaging operator, and prime denotes the fluctuation in a variable away from its mean (e.g., \( w' = w_i - \overline{w} \)). Without considering the measurement error of \( w \) for this study topic, submitting Eq. (C1) into Eq. (C2) leads to

\[
\overline{w' \rho_{\alpha T}} = \frac{1}{n} \sum_{i=1}^{n} (w_i - \overline{w}) \left[ \rho_{\alpha Ti} + \Delta \rho_{\alpha i} \right]
- \left( \rho_{\alpha Ti} + \Delta \rho_{\alpha T} \right) = \frac{1}{n} \sum_{i=1}^{n} (w_i - \overline{w}) \left( \rho_{\alpha Ti} - \overline{\rho_{\alpha T}} \right)
+ \frac{1}{n} \sum_{i=1}^{n} (w_i - \overline{w}) \left( \Delta \rho_{\alpha i} - \Delta \overline{\rho_\alpha} \right).
\]

Within an averaging interval (e.g., 1 h), the systematic error components inside terms \( \Delta \rho_{\alpha i} \) and \( \Delta \overline{\rho_\alpha} \) are not only constant but also equal. Accordingly, the systematic errors inside the term \( \Delta \rho_{\alpha i} - \Delta \overline{\rho_\alpha} \) are canceled out (Richardson et al., 2012). In essence, this term is a random error whose statistical distribution is generally assumed to be normal with a zero mean (i.e., \( \Delta \rho_{\alpha i} - \Delta \overline{\rho_\alpha} \) is expected to be zero; Hoel, 1984). The correlation of \( w \) with a random variable normally distributed with an expected zero mean tends to be zero, particularly for a large sample of 36,000 under discussion, even 18,000 for half hours (Snedecor and Cochran, 1989), which is the shortest period commonly used for flux computations. Accordingly, the term in the fourth line of Eq. (C3) can be regarded as zero. Therefore, the covariance of \( w \) with measured \( \alpha \) density is equal to the covariance of \( w \) with the true \( \alpha \) density, given by

\[
\overline{w' \rho_\alpha} = \overline{w' \rho_{\alpha T}}.
\]

If \( w \) from a sonic anemometer and \( \rho_\alpha \) from an infrared analyzer are not measured through spatial and temporal synchronization, the values of covariance of \( w \) with \( \rho_\alpha \) in the different lags of measurement (hereafter referred to as the lagged covariance) are computed for use in the lag maximization to find their maximum covariance as if \( w \) and \( \rho_\alpha \) were measured at the same time in the same space (Moncrieff et al., 1997; Ibrom et al., 2007). Each lagged covariance from field measurements can be expressed as \( \overline{w' \rho_{\alpha l}} \), where subscript \( l \) is the index for a lag number. If \( l = i \), \( w_i \) and \( \rho_{\alpha l} \) were measured at the same time. If \( l = i - 1 \), \( w_i \) was measured one measurement interval earlier (i.e., 100 ms for 10 Hz measurements) and \( \rho_{\alpha l} \) was measured one measurement interval earlier than \( \rho_\alpha \). The index \( l \) can be \(-k \) to \( k \) where \( k \) is a positive integer, including 0, to represent the maximum number of the lags that is optional to users. Therefore, given \( l \) from \(-k \) to \( k \), the number of \( \overline{w' \rho_{\alpha l}} \) values is \( 2k+1 \). Using the same approach to Eq. (C4), \( \overline{w' \rho_{\alpha l}} = \overline{w' \rho_{\alpha T l}} \) can be proved.

The lagged covariance values for \( \overline{w' \rho_{\alpha l}} \) and \( \overline{w' \rho_{\alpha T l}} \) (\( i = -k, -k+1, \ldots, 0, \ldots, k \)) are also computed for each lag where, in the sonic anemometer coordinate system, \( u \) is the wind speed in the \( x \) direction and \( v \) is the wind speed in the \( y \) direction. Both \( \overline{w' \rho_{\alpha l}} = \overline{w' \rho_{\alpha Ti l}} \) and \( \overline{w' \rho_{\alpha l}} = \overline{w' \rho_{\alpha Ti l}} \) can also be proved in the same way for Eq. (C4). Given the rotation angles from \( \pi, \tau, \varpi, u', v', w', \overline{u'}, \overline{v'}, \overline{w'} \) (Tanner and Thurtell, 1969), each set of \( u' \rho_{\alpha l}, \overline{v' \rho_{\alpha l}}, \text{ and } w' \rho_{\alpha l} \) is rotated to be \( \{u' \rho_{\alpha l} \}, \{v' \rho_{\alpha l} \}, \text{ and } \{w' \rho_{\alpha l} \} \), respectively, where \( u, v, \text{ and } w \) through the rotations are transformed into the natural wind coordinate system correspondingly as stream-wise, lateral, and vertical wind speeds. In the rotation process, \( \rho_\alpha \) is not additionally involved. Because \( \rho_{\alpha l} \) inside the covariance is a scalar rather than a vector variable, the rotation would not be influenced by \( \rho_{\alpha l} \) and \( \rho_{\alpha l} \) in the same way as by the three means and three variance values of 3-D wind components (Tanner and Thurtell, 1969). Because the

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same set of rotation angles also should be used for the rotations of \( w' \rho_{at} \), \( v' \rho_{at} \), and \( w' \rho_{at} \). The covariance values rotated from these three covariance values are correspondingly equal to those rotated from \( w' \rho_{at} \), \( v' \rho_{at} \), and \( w' \rho_{at} \), for the covariance values related to \( w \), given by

\[
(w' \rho_{at})_{r} = (w' \rho_{at}')_{r}. \tag{C5}
\]

Therefore, from the lag maximization (Moncrieff et al., 1997; Ibrom et al., 2007), the maximum covariance in magnitude among \( (w' \rho_{at})_{r} \) (\( l \) from \( -k \) to \( k \)) is equal to the maximum in magnitude among \( (w' \rho_{at}')_{r} \). Denoting the former maximum covariance by \( (w' \rho'_{at})_{rm} \), where subscript \( m \) indicates the lag maximization, and the latter one by \( (w' \rho'_{at})_{r} \), this equality leads to

\[
(w' \rho'_{at})_{rm} = (w' \rho'_{at})_{r}. \tag{C6}
\]

For flux computations, both covariance values in this equation need further corrections for their low- and high-frequency loss (Moore, 1986). The correction factor for \( (w' \rho'_{at})_{rm} \) can be denoted by \( f_{ca} \) and for \( (w' \rho'_{at})_{r} \), can be denoted by \( f_{ca}T \). Both \( f_{ca} \) and \( f_{ca}T \) are integrated in the same way as from the cospectrogram of \( w \) with a scalar as represented by \( T_{a} \) (air temperature) and the transfer functions of high-frequency loss separately for \( w \) and \( \alpha \) density (Moore, 1986; van Dijk, 2002) and low-frequency loss for Reynolds’ averaging \( w' \rho'_{a} \) (Massman, 2000). Although depending on the structure of boundary-layer turbulent flows (Kaimal and Finnigan, 1994), under the same boundary-layer turbulent flows, the cospectrum for \( w \) with \( \rho_{a} \) is the same as for \( w \) with \( \rho_{T} \). Because the sensor for \( \rho_{T} \) is assumed to have the same frequency response as the sensor for \( \rho_{a} \), both sensors have the same high-frequency loss, sharing the same transfer function (Moore, 1986). The transfer function for low-frequency loss due to Reynolds’ averaging either side of Eq. (C6) is also used for its other side (Massman, 2000). Therefore, \( f_{ca} \) is equal to \( f_{ca}T \), which, from Eq. (C6), leads to

\[
f_{caT}(w' \rho'_{at})_{rm} = f_{caT}(w' \rho'_{at})_{r}. \tag{C7}
\]

In this equation, the left term is the frequency-corrected \( (w' \rho'_{at})_{rm} \), which can be denoted by \( (w' \rho'_{at})_{r} \), where subscript \( f \) indicates this covariance to be corrected for frequency loss, and the right term is the frequency-corrected \( (w' \rho'_{at})_{r} \), which can be denoted by \( (w' \rho'_{at})_{rm} \) (Moore, 1986; Massman, 2000; van Dijk, 2002). Accordingly, Eq. (C7) becomes

\[
(w' \rho'_{at})_{rm} = (w' \rho'_{at})_{r}. \tag{C8}
\]

where subscript \( rmf \) indicates the covariance was corrected through coordinate rotations (\( r \)), lag maximization (\( m \)), and low- and high-frequency corrections (\( f \)). Equation (C8) shows the covariance of \( w \) with measured \( \rho_{a} \) is equal to its counterpart of \( w \) with true \( \rho_{a} \) even after a series of corrections before being used to calculate \( \alpha \) flux through Webb–Pearman–Leuning (WPL) corrections (Webb et al., 1980).

For the covariance of \( w \) with \( T_{a} \), the same conclusion can be derived, given by

\[
(w' T'_{at})_{rmf} = (w' T'_{at})_{r}. \tag{C9}
\]

Assuming \( w \) to be an accurate value for this study topic, through WPL corrections, \( (w' \rho'_{at})_{rmf} \) and \( (w' T'_{at})_{rmf} \) can be used to derive an analytical equation for a measured \( \alpha \) flux from \( \rho_{a} \) and \( T_{a} \), each of which includes a measurement error, whereas \( (w' \rho'_{at})_{r} \) and \( (w' T'_{at})_{r} \) can be used to derive an analytical equation for a true \( \alpha \) flux from \( \rho_{T} \) and \( T_{T} \), each of which is assumed not to include an error. The comparison of both analytical equations can demonstrate the partial effects of \( \Delta \rho_{a} \) on the uncertainty in \( \alpha \) flux data (see Sect. 6.1).

Data availability. Figure data files (Data_Fig2a, _Fig2b, _Fig3a, _Fig3b, _Fig4a, _Fig4b, and _Fig5_Zhou et al.xlsx) were deposited in https://datadryad.org/stash/share/7MEws8ABU6Gla8Bhcrji4zNGVFw1ueWcZRAItpoTSTs (Zheng and Gao, 2022).

Author contributions. XZ, TG, and NZ developed models, derived equations, analyzed data, and drafted the manuscript; BY revised manuscript; YL, FY, and TA discussed the points of this study topic and made comments on the paper; and JZ led the team.

Competing interests. Xinhua Zhou, Bai Yang, and Yanlei Li are affiliated with Campbell Scientific Incorporation, which is the manufacturer of the example model EC150 of infrared CO$_{2}$–H$_{2}$O analyzers. The other authors declare that they have no conflict of interest.

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