

# Accuracies of field CO<sub>2</sub>–H<sub>2</sub>O data from open-path eddy-covariance flux systems: Assessment based on atmospheric physics and biological environment

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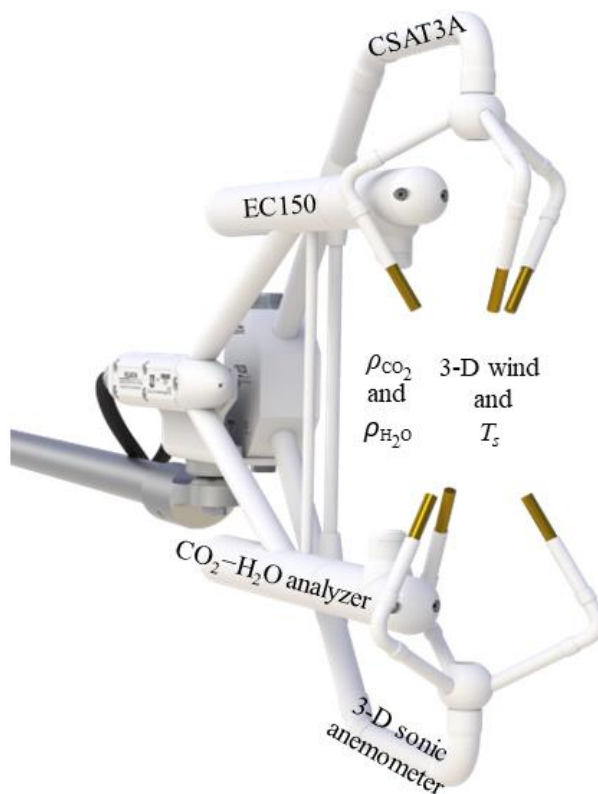
**Abstract.** Ecosystem CO<sub>2</sub>–H<sub>2</sub>O data measured ~~by infrared gas analyzers in~~ vastly from open-path eddy-covariance (OPEC) systems ~~by infrared analyzers~~ have numerous applications, such as estimations of CO<sub>2</sub> and H<sub>2</sub>O fluxes in the atmospheric boundary layer in biogeosciences. To assess the applicability of these estimations, data uncertainties from infrared gas analyzer measurements are needed. The uncertainties are sourced from infrared analyzers in zero drift, gain drift, cross-sensitivity, and precision variability. The sourced uncertainties are individually specified for analyzer performance, but no methodology exists to comprehend these individual uncertainties into a cumulative error for the specification of an overall accuracy, which is ultimately needed. Using the methodology for close-path eddy-covariance systems, this accuracy for OPEC systems is determined from all individual uncertainties via an accuracy model further formulated into CO<sub>2</sub> and H<sub>2</sub>O accuracy equations. Based on atmospheric physics and the biological environment, for EC150 infrared CO<sub>2</sub>–H<sub>2</sub>O analyzers, these equations are used to evaluate CO<sub>2</sub> accuracy ( $\pm 1.21 \text{ mgCO}_2 \text{ m}^{-3}$ , relatively  $\pm 0.19\%$ ) and H<sub>2</sub>O accuracy ( $\pm 0.10 \text{ gH}_2\text{O m}^{-3}$ , relatively  $\pm 0.18\%$  in saturated air at 35 °C and 101.325 kPa). Cross-sensitivity and precision variability are minor, although unavoidable, uncertainties. Zero drifts and gain drifts are major uncertainties but are adjustable via corresponding zero and span procedures during field maintenance. The equations provide rationales to assess and guide the procedures. For a background concentration of atmospheric CO<sub>2</sub> in an atmospheric CO<sub>2</sub> background, CO<sub>2</sub> zero and span procedures can narrow the CO<sub>2</sub> accuracy range by 40%, from  $\pm 1.21$  to  $\pm 0.72 \text{ mgCO}_2 \text{ m}^{-3}$ . In hot and humid weather, H<sub>2</sub>O gain drift potentially adds more to H<sub>2</sub>O measurement uncertainty, which requires more attention. If H<sub>2</sub>O zero and span procedures can be performed practically from 5 to 35 °C, the poorest H<sub>2</sub>O accuracy can be improved by 30%, from  $\pm 0.10$  to  $\pm 0.07 \text{ gH}_2\text{O m}^{-3}$ . Under freezing conditions, an H<sub>2</sub>O span is both impractical and unnecessary, but the zero procedure becomes imperative to minimize H<sub>2</sub>O measurement uncertainty. In cold/dry conditions, the zero procedure for H<sub>2</sub>O, along with CO<sub>2</sub>, is an operational and efficient option to ensure and improve H<sub>2</sub>O accuracy. The H<sub>2</sub>O span procedure is impractical under freezing

conditions and unnecessary under cold/dry conditions. However, the zero procedure for H<sub>2</sub>O, along with CO<sub>2</sub>, is imperative as an operational and efficient option under these conditions to minimize H<sub>2</sub>O measurement uncertainty.

## 1 Introduction

Open-path eddy-covariance (OPEC) systems are used most to measure boundary-layer CO<sub>2</sub>, H<sub>2</sub>O, heat, and momentum fluxes between ecosystems and the atmosphere (Lee and Massman, 2011). For the fluxes, an OPEC system is equipped with a fast-response three-dimensional (3-D) sonic anemometer, to measure 3-D wind and sonic temperature ( $T_s$ ), and a fast-response infrared CO<sub>2</sub>-H<sub>2</sub>O analyzer (hereafter referred to as an infrared analyzer or analyzer) to measure CO<sub>2</sub> and H<sub>2</sub>O fluctuations (Fig. 1). In this system, the analyzer is adjacent to the sonic measurement volume. Both anemometer and analyzer together provide 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). The degree of exactness for each flux from computations depends on the field measurement exactness of variables such as CO<sub>2</sub>, H<sub>2</sub>O,  $T_s$ , and 3-D wind (Foken et al., 2012). Beyond flux computations, the data for individual variables from these field measurements are important in numerous applications. Knowledge of measurement exactness is required for data analysis and applicability assessment (Csavina et al., 2017; Hill et al., 2017). 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 primarily depends on the field measurement exactness of variables, such as CO<sub>2</sub>, H<sub>2</sub>O,  $T_s$ , and 3-D wind, at the sensor sensing scales (Foken et al., 2012; Richardson et al., 2012), although this quality can also be degraded by other biases if not fully corrected. In an OPEC system, other biases are commonly sourced from the tilt of vertical axis of the sonic anemometer away from the 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 in 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 fluxes (Webb et al., 1980), and the filtering in data processing (Rannik and Vesala, 1999). These biases are correctable through coordinate rotation corrections for the tilt (Tanner and Thurtell, 1960; Wilczak, 2001), covariance maximization for the separation (Moncrieff et al., 1997; Ibrom 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 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 of 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

65 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; Anthoni et al., 2004).



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**Figure 1.** Integration of a CSAT3A sonic anemometer for three-dimensional (3-D) wind and sonic temperature ( $T_s$ ) and an EC150 infrared CO<sub>2</sub>-H<sub>2</sub>O analyzer for CO<sub>2</sub> density ( $\rho_{CO_2}$ ) and H<sub>2</sub>O density ( $\rho_{H_2O}$ ) in an open-path eddy-covariance flux system (Campbell Scientific Inc., UT, USA).

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Beyond flux computations, the data for individual variables from these field measurements have numerous applications. Knowledge of measurement exactness is also required for accurate assessment of data applicability (Csavina et al., 2017; Hill et al., 2017). The infrared analyzers in OPEC systems output CO<sub>2</sub> density ( $\rho_{CO_2}$  in mgCO<sub>2</sub> m<sup>-3</sup>) and H<sub>2</sub>O density ( $\rho_{H_2O}$  in gH<sub>2</sub>O m<sup>-3</sup>). For instance,  $\rho_{H_2O}$ , along with  $T_s$  and atmospheric pressure ( $P$ ), can be used to derive ambient air temperature ( $T_a$ ) (Swiatek, 2018). In this case, given an exact equation of  $T_a$  in terms of the three independent variables  $\rho_{H_2O}$ ,  $T_s$ , and  $P$ , the applicability of the equation to the OPEC systems for  $T_a$  depends wholly on the measurement exactness of the

80 three independent variables. The higher the degree of exactness, the less uncertain  $T_a$ . The assessment on the applicability needs the measurement exactness. In reality, to the best of our knowledge, neither the overall measurement exactness of  $\rho_{H_2O}$  from infrared analyzers nor this exactness of  $T_s$  from sonic anemometers (personal communication: Larry Jacobsen, 2022) is available. This study defines and estimates the measurement exactness of  $\rho_{H_2O}$  including  $\rho_{CO_2}$  from infrared analyzers through cumulating the measurement uncertainties, which is not mathematically correctable.

85 As comprehensively reviewed by Richardson et al. (2012), numerous previous studies including Goulden et al. (1996), Lee et al. (199), Anthoni et al. (1999, 2004), and Flanagan and Johanson (2005) have quantified various sources of flux measurement uncertainties 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)),  
90 measurement conditions (e.g., advection (Finnigan, 2008), energy closure (Foken, 2008), and sensor body heating effect (Burba et al., 2008). Instead of quantifying the flux uncertainties, Foken et al. (2004, 2012) assessed the flux data 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 less uncertainty; the higher grade, the more uncertainty. The grade matrix for flux data uncertainty (e.g., quality) has been adopted by AmeriFlux (2018). In other aspects to correct the measurement bias from infrared  
95 analyzers, Burba et al. (2008) developed the correction for a sensor body heating effect on  $CO_2$  and  $H_2O$  fluxes, whereas Fratini et al. (2014) developed a method for correcting the raw high-frequency  $CO_2$  and  $H_2O$  data using the zero and span coefficients of an infrared gas analyzer that were acquired from the same conditions, but at the beginning and ending of a time period. The corrected data were used to re-estimate the fluxes. To the best of our knowledge, no study has addressed the uncorrectable, although preventable to some degree, overall uncertainties in  $CO_2$  and  $H_2O$  data from infrared analyzers, even  
100 though both overall uncertainties are fundamental for data analysis in applications (Richardson et al., 2012).

Although the  $CO_2$  and  $H_2O$  data uncertainty sources, such as analyzer zero and gain drifts, analyzer background sensitivities, and measurement precision variability, are separately specified (LI-COR Biosciences, 2021b; Campbell Scientific Inc., 2021b), the specification for overall exactness of an individual field  $CO_2$  or  $H_2O$  measurement is unavailable due to the absence of methodology to composite all of the specified measurement uncertainties into a cumulative error. For  
105 any sensor, the measurement exactness depends on its performances as commonly specified in terms of accuracy, precision, and other uncertainty descriptors such as sensor drift. Conventionally, accuracy is defined as a systematic uncertainty, and 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 reliability in measurement performance. For example,  $CO_2$  zero drift is one of the descriptors specified for the performance of infrared analyzers in  $CO_2$  measurements  
110 (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 CO<sub>2</sub>/H<sub>2</sub>O 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 show 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 the combination of both trueness and precision. An advantage of this definition of accuracy is that it consolidates all measurement uncertainties. According to this definition, the accuracy is the range of cumulative uncertainty from all sources in field measurements. For ~~close-path eddy covariance (CPEC)~~ systems, Zhou et al. (2021) developed a method and derived a model for the assessment on this accuracy of CO<sub>2</sub>/H<sub>2</sub>O mixing ratio measurements by infrared analyzers. Their model was further formulated as equations to evaluate the defined accuracies of CO<sub>2</sub> and H<sub>2</sub>O mixing ratio data from CPEC systems. Although the CPEC systems are very different from OPEC systems in measurement designs (e.g., Measurements take place inside a closed cuvette vs. in an open space) and in computation variables (e.g., CO<sub>2</sub>/H<sub>2</sub>O mixing ratio vs. CO<sub>2</sub>/H<sub>2</sub>O density), there are similarities between CPEC and OPEC systems in measurement uncertainties as specified by their manufacturers (Campbell Scientific Inc., 2021a.; 2021b) because the infrared analyzers in both systems use the same physics theories and similar optical techniques for their measurement (LI-COR Biosciences, 2021a; 2021b). Accordingly, the method developed by Zhou et al. (2021) for CPEC systems should be reasonably applicable to their OPEC counterparts although the model needs rederivation and equations needs reformulation. 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 derive the model and formulate equations to assess the accuracies of CO<sub>2</sub> and H<sub>2</sub>O measurements from OPEC systems by infrared analyzers, discuss the uses of accuracies in data applications and analyzer field maintenance, and ultimately provide an reference for the flux measurement community to specify the overall accuracy of field CO<sub>2</sub>/H<sub>2</sub>O measurements from OPEC systems by infrared analyzers.

## 2 Specification implications

An OPEC system for this study includes, but is not limited to, a CSAT3A sonic anemometer for a fast response to 3-D wind and  $T_s$ , and an EC150 infrared analyzer for a fast response to CO<sub>2</sub> and H<sub>2</sub>O (Fig. 1). The system operates in a  $T_a$  range from -30 to 50 °C and in a  $P$  range from 70 to 106 kPa. Within both ranges, the specifications for CO<sub>2</sub> and H<sub>2</sub>O measurements (Campbell Scientific Inc., 2021b) are given in Table 1.

**Table 1.** Measurement specifications for EC150 infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers

CO <sub>2</sub>			H <sub>2</sub> O			Note
notation	value	Unit	notation	value	unit	

Calibration range		0 – 1,553	mgCO <sub>2</sub> m <sup>-3</sup>		0 – 44	gH <sub>2</sub> O m <sup>-3</sup>	For CO <sub>2</sub> up to 4,500 mgCO <sub>2</sub> m <sup>-3</sup> if specially needed. 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 $T_a$ .
Zero drift	$d_{cz}$	±0.55	mgCO <sub>2</sub> m <sup>-3</sup>	$d_{wz}$	±0.04	gH <sub>2</sub> O m <sup>-3</sup>	
Gain drift	$d_{cg}$	±0.10% <sup>a/</sup> true $\rho_{CO_2}$	mgCO <sub>2</sub> m <sup>-3</sup>	$d_{wg}$	±0.30% <sup>b/</sup> true $\rho_{H_2O}$	gH <sub>2</sub> O m <sup>-3</sup>	
Cross-sensitivity to H <sub>2</sub> O	$s_{H_2O}$	±2.69×10 <sup>-7</sup>	mgCO <sub>2</sub> m <sup>-3</sup> (gH <sub>2</sub> O m <sup>-3</sup> ) <sup>-1</sup>		N/A		
Cross-sensitivity to CO <sub>2</sub>		N/A		$s_{CO_2}$	±4.09×10 <sup>-5</sup>	gH <sub>2</sub> O m <sup>-3</sup> (mgCO <sub>2</sub> m <sup>-3</sup> ) <sup>-1</sup>	
Precision	$\sigma_{CO_2}$	0.200	mgCO <sub>2</sub> m <sup>-3</sup>	$\sigma_{H_2O}$	0.004	gH <sub>2</sub> O m <sup>-3</sup>	

<sup>a</sup> 0.10% is the CO<sub>2</sub> gain drift percentage denoted by  $\delta_{CO_2_g}$  in text, and  $\rho_{CO_2}$  is CO<sub>2</sub> density.

<sup>b</sup> 0.30% is the H<sub>2</sub>O gain drift percentage denoted by  $\delta_{H_2O_g}$  in text, and  $\rho_{H_2O}$  is H<sub>2</sub>O density.

In Table 1, the top limit of 1,553 mgCO<sub>2</sub> m<sup>-3</sup> in the calibration range for CO<sub>2</sub> density in dry air is more than double  
145 the atmospheric background CO<sub>2</sub> density of 760 mgCO<sub>2</sub> m<sup>-3</sup>, equal to 415  $\mu\text{molCO}_2 \text{ mol}^{-1}$ , where mol is for a dry air unit, reported by Global Monitoring Laboratory (2021) with a  $T_a$  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 gH<sub>2</sub>O m<sup>-3</sup> in the calibration range for H<sub>2</sub>O density is equivalent to a  
37 °C dew point, higher than the highest 35 °C dew point ever recorded under natural conditions on the Earth (National  
Weather Service, 2021).

150 The measurement uncertainties of infrared analyzers for CO<sub>2</sub> and H<sub>2</sub>O in Table 1 are specified by individual uncertainty components along with their magnitudes: zero drift, gain drift, cross-sensitivity to CO<sub>2</sub>/H<sub>2</sub>O, and precision variability. Zero drift uncertainty is an analyzer non-zero response to zero air/gas (i.e., air/gas free of CO<sub>2</sub> and H<sub>2</sub>O). Gain  
drift uncertainty is an analyzer trend-deviation response to measured gas species away from its true value in proportion (Campbell Scientific Inc., 2021b). Cross-sensitivity is an analyzer background response to either CO<sub>2</sub> if H<sub>2</sub>O is measured, or  
155 H<sub>2</sub>O if CO<sub>2</sub> is measured. Precision variability is an analyzer random response to minor unexpected factors. For CO<sub>2</sub> and H<sub>2</sub>O, respectively, these four components should be composited as a cumulative uncertainty to evaluate the accuracy that is  
ultimately needed in [practice applications](#).

Precision variability is a random error, and the other specifications can be considered as trueness. Zero drifts are  
impacted more by  $T_a$ , and so are gain drifts. Additionally, each gain drift is also positively proportional to the true magnitude  
160 of CO<sub>2</sub>/H<sub>2</sub>O density (i.e., true  $\rho_{CO_2}$  or true  $\rho_{H_2O}$ ) under measurements. Lastly, cross-sensitivity to H<sub>2</sub>O/CO<sub>2</sub> is related to the

background amount of H<sub>2</sub>O/CO<sub>2</sub> as indicated by its units, mgCO<sub>2</sub> m<sup>-3</sup> (gH<sub>2</sub>O m<sup>-3</sup>)<sup>-1</sup> for CO<sub>2</sub> measurements, and gH<sub>2</sub>O m<sup>-3</sup> (mgCO<sub>2</sub> m<sup>-3</sup>)<sup>-1</sup> for H<sub>2</sub>O measurements.

Accordingly, beyond statistical analysis, the accuracy of CO<sub>2</sub>/H<sub>2</sub>O measurements should be evaluated over a  $T_a$  range of -30 to 50 °C, a  $\rho_{H_2O}$  range of up to 44 gH<sub>2</sub>O m<sup>-3</sup>, and a  $\rho_{CO_2}$  range of up to 1,553 mgCO<sub>2</sub> m<sup>-3</sup>.

### 165 3 Accuracy model

The measurement accuracy of infrared analyzers is the maximum range of cumulative measurement uncertainty from the four components uncertainties as specified in Table 1: zero drift, gain drift, cross-sensitivity, and precision variability. The four uncertainties interactionally or independently add uncertainties to a measurement value. Given the true  $\alpha$  density ( $\rho_{\alpha T}$ , where subscript  $\alpha$  can be either CO<sub>2</sub> or H<sub>2</sub>O) and measured  $\alpha$  density ( $\rho_\alpha$ ), the difference between the true and measured  $\alpha$  densities ( $\Delta\rho_\alpha$ ) is given by

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

The analyzer overestimates the true value if  $\Delta\rho_\alpha > 0$ , exactly estimates the true value if  $\Delta\rho_\alpha = 0$ , and underestimates the true value if  $\Delta\rho_\alpha < 0$ . The measurement accuracy is the maximum range of overestimation or underestimation, being a range of  $\Delta\rho_\alpha$  (i.e., an accuracy range). According to the analyses of Zhou et al. (2021) for CPEC infrared analyzers, [as mathematically](#)

175 [shown in Appendix A](#), this range is interactionally contributed by the zero drift uncertainty ( $\Delta\rho_\alpha^z$ ), gain drift uncertainty ( $\Delta\rho_\alpha^g$ ), and cross-sensitivity uncertainty ( $\Delta\rho_\alpha^s$ ) while being independently added by the precision uncertainty ( $\Delta\rho_\alpha^p$ ).

However, any interactional contribution from a pair of uncertainties is three orders smaller in magnitude than each in the pair.

The contribution of interactions to the accuracy range can be reasonably neglected. Therefore, the accuracy range can be modeled as a simple sum of the four components uncertainties. From Eq. (A7) in Appendix A, the measurement accuracy of

180  $\alpha$  density from OPEC systems by infrared analyzers is defined in an accuracy model as

$$\Delta\rho_\alpha \equiv \pm\left(\left|\Delta\rho_\alpha^z\right| + \left|\Delta\rho_\alpha^g\right| + \left|\Delta\rho_\alpha^s\right| + \left|\Delta\rho_\alpha^p\right|\right). \quad (2)$$

Assessment on the accuracy of field CO<sub>2</sub> or H<sub>2</sub>O measurements is, [by the use of known and/or estimable variables](#), to formulate and evaluate the four terms on the right side of this accuracy model.

### 4 Accuracy of CO<sub>2</sub> density measurements

185 Accuracy Model (2) defines the accuracy of field CO<sub>2</sub> measurements from OPEC systems by infrared analyzers ( $\Delta\rho_{CO_2}$ ) as

$$\Delta\rho_{CO_2} \equiv \pm\left(\left|\Delta\rho_{CO_2}^z\right| + \left|\Delta\rho_{CO_2}^g\right| + \left|\Delta\rho_{CO_2}^s\right| + \left|\Delta\rho_{CO_2}^p\right|\right), \quad (3)$$

where  $\Delta\rho_{CO_2}^z$  is CO<sub>2</sub> zero drift uncertainty,  $\Delta\rho_{CO_2}^g$  is CO<sub>2</sub> gain drift uncertainty,  $\Delta\rho_{CO_2}^s$  is cross-sensitivity-to-H<sub>2</sub>O uncertainty, and  $\Delta\rho_{CO_2}^p$  is CO<sub>2</sub> precision uncertainty.



CO<sub>2</sub> precision ( $\sigma_{CO_2}$ ) is the standard deviation of  $\rho_{CO_2}$  random errors among repeated measurements under the same conditions (Joint Committee for Guides in Metrology, 2008). The random errors generally have a normal distribution in statistics (Hoel, 1984). Therefore, using this deviation, the precision uncertainty for an individual CO<sub>2</sub> measurement at a 95% confidence interval (P-value of 0.05) can be statistically formulated as ~~(Hoel, 1984)~~

$$\Delta\rho_{CO_2}^p = \pm 1.96 \times \sigma_{CO_2}. \quad (4)$$

The other uncertainties, due to CO<sub>2</sub> zero drift, CO<sub>2</sub> gain drift, and cross-sensitivity-to-H<sub>2</sub>O, are caused by the inability of the working equation inside an infrared analyzer to be adapted to the changes in its internal and ambient environmental conditions, such as internal housing CO<sub>2</sub> and/or H<sub>2</sub>O levels and ambient air temperature. According to From the derivations in the Theory and operation section in LI-COR Biosciences (2001, 2021a, 2021b), a general model of the working equation for  $\rho_{CO_2}$  is given by

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

where subscripts  $c$  and  $w$  indicate CO<sub>2</sub> and H<sub>2</sub>O, respectively;  $a_{ci}$  ( $i = 1, 2, 3, 4,$  or  $5$ ) is a coefficient of the five-order polynomial in the terms inside curly brackets;  $A_{cs}$  and  $A_{ws}$  are the power values of analyzer source lights in the wavelengths for CO<sub>2</sub> and H<sub>2</sub>O measurements, respectively;  $A_c$  and  $A_w$  are their respective remaining power values after the source lights pass through the measured air;  $S_w$  is cross-sensitivity of the detector to H<sub>2</sub>O, while detecting CO<sub>2</sub>, in the wavelength for CO<sub>2</sub> measurements (hereafter referred to as sensitivity-to-H<sub>2</sub>O);  $Z_c$  is the CO<sub>2</sub> zero adjustment (i.e., CO<sub>2</sub> zero coefficient); and  $G_c$  is the CO<sub>2</sub> gain adjustment (i.e., commonly known as the CO<sub>2</sub> 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<sub>2</sub> gases at different concentration levels over the ranges of  $\rho_{H_2O}$  and  $P$  (hereafter referred to as calibration). The estimated parameters are specific for the analyzer; therefore, Model (5) with these estimated parameters becomes an analyzer-specific CO<sub>2</sub> working equation. The working equation is used inside the infrared analyzer to compute  $\rho_{CO_2}$  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, 2021b). However, as used inside an optical instrument under changing environments vastly different from its manufacturing conditions, the working equation may not be fully adaptable to the changes, which might be reflected through CO<sub>2</sub> zero and/or gain drifts of the infrared analyzers in measurements. In the working equation for  $\rho_{CO_2}$  from Model (5), the parameter  $Z_c$  is related to CO<sub>2</sub> zero;  $G_c$ , to CO<sub>2</sub> gain; and  $S_w$ , to sensitivity-to-H<sub>2</sub>O. Therefore, the analyses of  $Z_c$  and  $G_c$ , along with  $S_w$ , are an approach to understand the causes of CO<sub>2</sub> zero drift, CO<sub>2</sub> gain drift, and sensitivity-to-H<sub>2</sub>O. Such understanding is necessary to formulate  $\Delta\rho_{CO_2}^z$ ,  $\Delta\rho_{CO_2}^g$ , and  $\Delta\rho_{CO_2}^s$  in Model (3).



#### 4.1 $Z_c$ and $\Delta\rho_{CO_2}^z$ (CO<sub>2</sub> zero drift uncertainty)

220 In production, An infrared analyzer was calibrated for zero air/gas to report zero  $\rho_{CO_2}$  plus an unavoidable random error. However, during use of the analyzer in measurement environments that are different from calibration conditions, the analyzer often gradually reports this zero  $\rho_{CO_2}$  value, while exposed to zero air, that is different gradually away from zero and possibly beyond  $\pm\Delta\rho_{CO_2}^p$ , which is known as CO<sub>2</sub> zero drift. This drift is primarily affected by a collection of the three factors: i) the temperature surrounding the analyzer away from the calibration temperature, and/or by ii) traceable CO<sub>2</sub> and  
225 H<sub>2</sub>O accumulations during use inside the analyzer light housing due to an inevitable, although extremely little, leaking exchange of housing air with ambient air (hereafter referred to as housing CO<sub>2</sub>-H<sub>2</sub>O accumulation), and iii) aging of analyzer components (Richardson et al., 2012)

Firstly, the dependency of analyzer CO<sub>2</sub> 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  
230 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 operating system, which is kept as proprietary by  
235 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). Secondly, the housing CO<sub>2</sub>-H<sub>2</sub>O accumulation is caused by unavoidable little leaks in the light housing of an infrared analyzer. The housing is technically sealed to keep housing air close to zero air by implementing scrubber chemicals into the housing to absorb any CO<sub>2</sub> and H<sub>2</sub>O that may sneak into the housing through an exchange with any ambient air  
240 (LI-COR Biosciences, 2021b). Over time, the scrubber chemicals may be saturated by CO<sub>2</sub> and/or H<sub>2</sub>O or lose their active absorbing effectiveness, which can result in housing CO<sub>2</sub>-H<sub>2</sub>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 in the relative long term (e.g., months or longer), whereas the dependencies of drift on ambient air temperature occur as soon as an analyzer is deployed in the field (Richardson et al., 2012). Apparently, the drift with ambient  
245 air temperature is a major concern if an analyzer is maintained as scheduled (Campbell Scientific Inc., 2021b).

Due to the CO<sub>2</sub> zero drift, the working equation needs to be adjusted through its parameter re-estimation to adapt the ambient air temperature and housing CO<sub>2</sub>-H<sub>2</sub>O accumulation near which the system is running. This adjustment technique is the zero procedure, which brings the  $\rho_{CO_2}$  and  $\rho_{H_2O}$  of zero air/gas from the working equation back to zero as closely as possible. In this section, ignoring  $\rho_{H_2O}$ , the discussion focus will be on CO<sub>2</sub>, although applicability to H<sub>2</sub>O also exists. In the  
250 field, the zero procedure must be feasibly operational simple. The simplest way is to use one air/gas benchmark to re-

estimate one parameter in the working equation. This parameter must be adjustable to output zero  $\rho_{CO_2}$  from the zero air/gas benchmark. It is  $Z_c$  indeed (see Model (5)), being adjustable to result in a zero  $\rho_{CO_2}$  value for zero air/gas, if re-estimated for the working equation from Model (5) by

$$Z_c = \left[ \frac{A_{c0}}{A_{cs}} + S_w \left( 1 - \frac{A_{w0}}{A_{ws}} \right) \right]^{-1}, \quad (6)$$

255 where  $A_{c0}$  and  $A_{w0}$  are the counterparts of  $A_c$  and  $A_w$  for zero air/gas, respectively. Inside an analyzer, the zero procedure for  $CO_2$  is to re-estimate  $Z_c$  to balance 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 calibration, an analyzer may still drift after the zero procedures due to changing ambient air temperature and/or  $CO_2$ - $H_2O$  accumulation. Nevertheless, the value of  $Z_c$ , which should be used  
260 with the ambient air temperature surrounding the infrared analyzer and particularly with housing  $CO_2$ - $H_2O$  accumulation, is unpredictable. Assuming that the scrubber chemicals inside the analyzer light housing is replaced as per the recommended maintenance schedule, the housing  $CO_2$ - $H_2O$  accumulation should not be a concern while the air temperature surrounding the infrared analyzer is not controlled. Therefore, the  $CO_2$  zero drift of analyzers is specified to be influenced more by  $T_a$  and to be  $\pm 0.55 \text{ mgCO}_2 \text{ m}^{-3}$  as its maximum range within the operational ranges in  $T_a$  and  $P$  of OPEC systems (Table 1). This  
265 specification is the maximum range of  $CO_2$  measurement uncertainty due to the  $CO_2$  zero drift.

Given that an analyzer performs best, ~~even almost~~ without zero drift, at the ambient air temperature for the calibration/zeroing procedure ( $T_c$ ), and that it possibly drifts while  $T_a$  gradually changes away from  $T_c$ , 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 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  
270 (Campbell Scientific Inc., 2021b). Accordingly,  $CO_2$  zero drift uncertainty at  $T_a$  can be formulated as

$$\Delta \rho_{CO_2}^z = \frac{d_{cz}}{T_{rh} - T_{rl}} \times \begin{cases} T_a - T_c & T_c < T_a < T_{rh} \\ T_c - T_a & T_c > T_a > T_{rl} \end{cases}, \quad (7)$$

where, over the operational range in  $T_a$  of EC150 infrared analyzers used for OPEC systems,  $T_{rh}$  is the highest-end value (50 °C) and  $T_{rl}$  is the lowest-end value (-30 °C, Table 1).  $\Delta \rho_{CO_2}^z$  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.

#### 275 4.2 $G_c$ and $\Delta \rho_{CO_2}^g$ ( $CO_2$ 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  $\rho_{CO_2}$ . As was determined with the zero drift, the analyzer, with changes in internal  $CO_2$ - $H_2O$  accumulation and ambient measurement conditions during use, could report  $CO_2$  gradually

away from the real gain trend of the change in  $\rho_{CO_2}$ , which is specifically termed CO<sub>2</sub> gain drift. This drift is affected by almost the same factors as the CO<sub>2</sub> zero drift (Richardson et al., 2012; Fratini et al., 2014; LI-COR Biosciences, 2021b).

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  $\rho_{CO_2}$  of measured air as close as possible. This is done with the CO<sub>2</sub> span procedure. This procedure can be performed through use of either one or two span gases (LI-COR Biosciences, 2021b). If two are used, one span gas is slightly below the ambient CO<sub>2</sub> density and the other is at a much higher density to fully cover the CO<sub>2</sub> density range by the working equation. However, commonly, like the zero procedure, this procedure is simplified by the use of one CO<sub>2</sub> span gas, as a benchmark, with a known CO<sub>2</sub> amount ( $\tilde{\rho}_{CO_2}$ ) around the typical CO<sub>2</sub> density values in the measurement environment. Also, because one CO<sub>2</sub> value from CO<sub>2</sub> 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<sub>2</sub> span coefficient ( $G_c$ ) (see Model (5)). The CO<sub>2</sub> span is used to re-estimate  $G_c$  to satisfy the following equation (for details, see LI-COR Biosciences, 2021b)

$$\left| \tilde{\rho}_{CO_2} - \rho_{CO_2}(G_c) \right| \leq \min \left| \tilde{\rho}_{CO_2} - \rho_{CO_2} \right|. \quad (8)$$

Similar to the zero drift, the CO<sub>2</sub> gain drift continues after the CO<sub>2</sub> span procedure. Based on a similar consideration for the specifications of CO<sub>2</sub> zero drift, the CO<sub>2</sub> gain drift is specified by the maximum CO<sub>2</sub> gain drift percentage ( $\delta_{CO_2-g} = 0.1\%$ ) associated with  $\rho_{CO_2}$  as  $\pm 0.10\% \times (\text{true } \rho_{CO_2})$  (Table 1). This specification is the maximum range of CO<sub>2</sub> measurement uncertainty due to the CO<sub>2</sub> gain drift within the operational ranges in  $T_a$  and  $P$  of OPEC systems.

Given that an analyzer performs best, almost without gain drift, at the ambient air temperature for calibration/span procedure (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 the drift has. Accordingly, the same approach to the formulation of CO<sub>2</sub> zero drift uncertainty can be applied to the formulation of approximate equation for CO<sub>2</sub> gain drift uncertainty at  $T_a$  as

$$\Delta \rho_{CO_2}^g \equiv \pm \frac{\delta_{CO_2-g} \rho_{CO_2T}}{T_{rh} - T_{rl}} \times \begin{cases} T_a - T_c & T_c < T_a < T_{rh} \\ T_c - T_a & T_c > T_a > T_{rl} \end{cases}, \quad (9)$$

where  $\rho_{CO_2T}$  is true CO<sub>2</sub> density unknown in measurement. Given that the measured value of CO<sub>2</sub> density is represented by  $\rho_{CO_2}$ , by referencing Eq. (1),  $\rho_{CO_2T}$  can be expressed as

$$\rho_{CO_2T} = \rho_{CO_2} - (\Delta \rho_{CO_2}^z + \Delta \rho_{CO_2}^g + \Delta \rho_{CO_2}^s + \Delta \rho_{CO_2}^p). \quad (10)$$

The term inside the parentheses in this equation is the measurement error for  $\rho_{CO_2T}$  that is reasonably smaller in magnitude, by at least two orders, than  $\rho_{CO_2T}$ , whose magnitude in atmospheric background under the normal temperature and pressure as used by Wright et al. (2003) is 760 mgCO<sub>2</sub> m<sup>-3</sup> (Global Monitoring Laboratory, 2021). Therefore,  $\rho_{CO_2}$  in Eq. (10) is the best alternative, with the most likelihood, to  $\rho_{CO_2T}$  for the application of Eq. (9). As such,  $\rho_{CO_2T}$  in Eq. (9) can be reasonably approximated by  $\rho_{CO_2}$  for equation applications. Using this approximation, Eq. (9) becomes

$$310 \quad \Delta\rho_{CO_2}^g = \pm \frac{\delta_{CO_2-g}\rho_{CO_2}}{T_{rh} - T_{rl}} \times \begin{cases} T_a - T_c & T_c < T_a < T_{rh} \\ T_c - T_a & T_c > T_a > T_{rl} \end{cases}. \quad (11)$$

With measured  $\rho_{CO_2}$ , this equation is applicable in estimating the CO<sub>2</sub> gain drift uncertainty. The gain drift uncertainty ( $\Delta\rho_{CO_2}^g$ ) from this equation has the maximum range of  $\pm\delta_{CO_2-g}\rho_{CO_2}$ , as if  $T_a$  and  $T_c$  were separately at the two ends of operational range in  $T_a$  of OPEC systems. With the most likelihood, this maximum range is the closest to  $\pm\delta_{CO_2-g}\times(\text{true } \rho_{CO_2})$  as specified in Table 1.

### 315 4.3 $S_w$ and $\Delta\rho_{CO_2}^s$ (sensitivity-to-H<sub>2</sub>O uncertainty)

The infrared wavelength of 4.3 $\mu\text{m}$  for CO<sub>2</sub> measurements is minorly absorbed by H<sub>2</sub>O (LI-COR Biosciences, 2021b; Campbell Scientific Inc., 2021b). This minor absorption slightly interferes with the absorption by CO<sub>2</sub> in the wavelength (McDermitt et al., 1993). The power of the same measurement light through several gas samples with the same CO<sub>2</sub> density, but different backgrounds of H<sub>2</sub>O densities, is detected with different values of  $A_c$  for the working equation from Model (5).

320 Without parameter  $S_w$  and its joined term in the working equation, different  $A_c$  values must result in significantly different  $\rho_{CO_2}$  values, although they are actually the same. To report the same  $\rho_{CO_2}$  for air flows with the same CO<sub>2</sub> density under different H<sub>2</sub>O backgrounds, the different values of  $A_c$  to report similar  $\rho_{CO_2}$  are accounted for by  $S_w$  associated with  $A_w$  and  $A_{ws}$  in the working equation from Model (5). Similar to  $Z_c$  and  $G_c$  in the 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<sub>2</sub>O

325 ( $s_{H_2O}$ ) as  $\pm 2.69 \times 10^{-7} \text{ mgCO}_2 \text{ m}^{-3} (\text{gH}_2\text{O m}^{-3})^{-1}$  (Table 1). As indicated by its unit, this uncertainty is linearly related to  $\rho_{H_2O}$ . Assuming the analyzer for CO<sub>2</sub> works best, without this uncertainty, in dry air,  $\Delta\rho_{CO_2}^s$  could be formulated as

$$\Delta\rho_{CO_2}^s \equiv s_{H_2O}\rho_{H_2O} \quad 0 \leq \rho_{H_2O} \leq 44 \text{ gH}_2\text{O m}^{-3}, \quad (12)$$

where 44 gH<sub>2</sub>O m<sup>-3</sup>, as addressed in section 2, is a threshold for H<sub>2</sub>O density measurements. Accordingly,  $\Delta\rho_{CO_2}^s$  can be in a range of

$$330 \quad \Delta\rho_{CO_2}^s \leq 44|s_{H_2O}|. \quad (13)$$

### 4.4 $\Delta\rho_{CO_2}$ (CO<sub>2</sub> measurement accuracy)

Substituting Eqs. (4), (7), (11), and (13) into Model (3),  $\Delta\rho_{CO_2}$  for an individual CO<sub>2</sub> measurement can be expressed as

$$\Delta\rho_{CO_2} = \pm \left[ 1.96\sigma_{CO_2} + 44|s_{H_2O}| + \frac{|d_{cz}| + \delta_{CO_2-g}\rho_{CO_2}}{T_{rh} - T_{rl}} \times \begin{cases} T_a - T_c & T_c < T_a < T_{rh} \\ T_c - T_a & T_c > T_a > T_{rl} \end{cases} \right]. \quad (14)$$

This is the CO<sub>2</sub> accuracy equation for the OPEC systems with infrared analyzers. It expresses the accuracy of a field CO<sub>2</sub> measurement from the OPEC systems in terms of its specifications  $\sigma_{CO_2}$ ,  $s_{H_2O}$ ,  $d_{cz}$ ,  $\delta_{CO_2-g}$ , and the OPEC system operational

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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<sub>2</sub> 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<sub>2</sub> measurements from an infrared analyzer after calibration, zero, and/or span at  $T_c$  can be evaluated using the CO<sub>2</sub> accuracy equation (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 be ranged according to its variation in ecosystems.

##### 4.5.1 $\rho_{CO_2}$ range

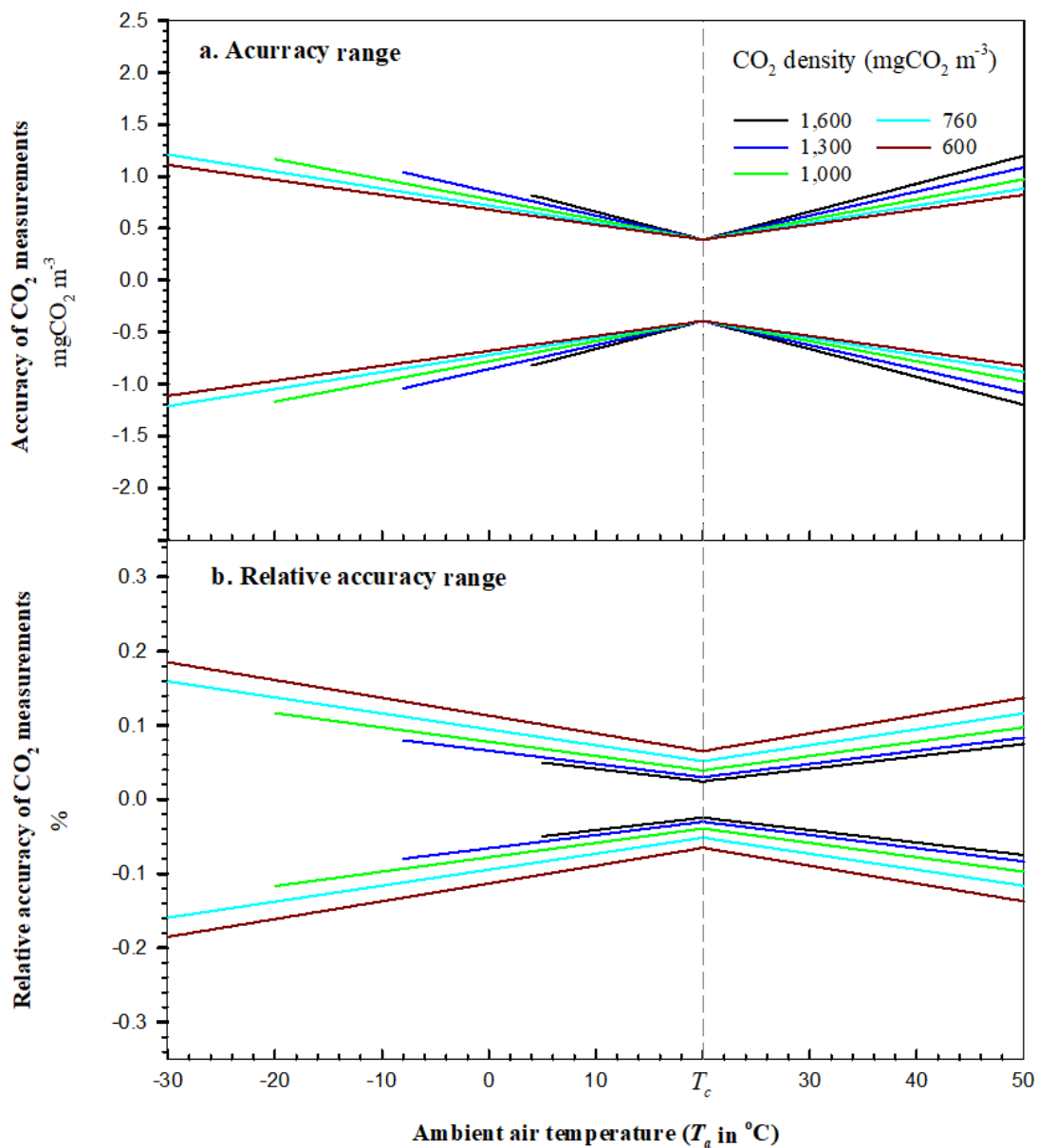
CO<sub>2</sub> density measured by the infrared analyzers ranges up to  $1,553$  mgCO<sub>2</sub> m<sup>-3</sup>. In the atmosphere, its CO<sub>2</sub> background mixing ratio currently is  $415$   $\mu\text{molCO}_2$  mol<sup>-1</sup> (Global Monitoring Laboratory, 2021). Under the normal temperature and pressure conditions (Wright et al., 2003), this background mixing ratio is equivalent to  $760$  mgCO<sub>2</sub> m<sup>-3</sup> in dry air. CO<sub>2</sub> density in ecosystems commonly ranges from  $650$  to  $1,500$  mgCO<sub>2</sub> m<sup>-3</sup> (LI-COR Biosciences, 2021b), 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  $1,600$  mgCO<sub>2</sub> m<sup>-3</sup> 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<sub>2</sub> levels, the range is further divided into five grades of  $600$ ,  $760$  (atmospheric background),  $1000$ ,  $1300$ , and  $1600$  mgCO<sub>2</sub> m<sup>-3</sup> for evaluation presentations as in Fig. 2.

According to the 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<sub>2</sub> from microorganism respiration and/or wildlife activities in terrestrial ecosystems,  $\rho_{CO_2}$  at any grade of  $1,000$ ,  $1300$ , or  $1600$  mgCO<sub>2</sub> m<sup>-3</sup> should start, at  $5$  °C, to converge asymptotically to the atmospheric CO<sub>2</sub> background ( $760$  mgCO<sub>2</sub> m<sup>-3</sup> at  $-30$  °C, Fig. 2). Without the 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<sub>2</sub> accuracy is best at its narrowest range as the sum of precision and sensitivity-to-H<sub>2</sub>O uncertainties ( $\pm 0.39$  mgCO<sub>2</sub> m<sup>-3</sup>). However, away from  $T_c$ , its range near-linearly becomes wider. The  $\Delta\rho_{CO_2}$  range can be summarized as  $\pm 0.40 - \pm 1.21$  mgCO<sub>2</sub> m<sup>-3</sup> over the domain of  $T_a$  and  $\rho_{CO_2}$  (Fig. 2a and CO<sub>2</sub> columns in Table 2). The maximum CO<sub>2</sub> relative

accuracy at the different levels of  $\rho_{CO_2}$  is in a range of  $\pm 0.07\%$  at  $1,600 \text{ mgCO}_2 \text{ m}^{-3}$  to  $0.19\%$  at  $600 \text{ mgCO}_2 \text{ m}^{-3}$  (from data for Fig. 2b).



370 **Figure 2.** Accuracy of field  $\text{CO}_2$  measurements from open-path eddy-covariance flux systems by EC150 infrared  $\text{CO}_2\text{-H}_2\text{O}$  analyzers over their operational range in  $T_a$  at atmospheric pressure of 101.325 kPa. The vertical dashed line represents

375 ambient temperature  $T_c$  at which an analyzer was calibrated, zeroed, and/or spanned. Above 5 °C, accuracy is evaluated up to the possible maximum CO<sub>2</sub> density in ecosystems (black curve). Assume this maximum starts linearly decreasing at 5 °C to the atmospheric CO<sub>2</sub> background (760 mgCO<sub>2</sub> m<sup>-3</sup>) at -30 °C. Accordingly, below 5 °C, the accuracy for CO<sub>2</sub> density at a level above the background (green, blue, or black curve) is evaluated up to this decreasing trend. Relative accuracy of CO<sub>2</sub> measurements is the ratio of CO<sub>2</sub> accuracy to CO<sub>2</sub> density.

**Table 2.** Accuracies of field CO<sub>2</sub> and H<sub>2</sub>O measurements from open-path eddy-covariance systems by EC150 infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers on the major values of background ambient air temperature, CO<sub>2</sub>, and H<sub>2</sub>O in ecosystems. (Atmospheric pressure: 101.325 kPa. Calibration ambient air temperature: 20 °C.)

Ambient air temperature °C	CO <sub>2</sub>				H <sub>2</sub> O			
	760 mgCO <sub>2</sub> m <sup>-3</sup> a/		1,600 mgCO <sub>2</sub> m <sup>-3</sup> b/		60% Relative humidity		Saturated	
	Accuracy	Relative accuracy	Accuracy	Relative accuracy	Accuracy	Relative accuracy	Accuracy	Relative accuracy
	± mgCO <sub>2</sub> m <sup>-3</sup>	± %	± mgCO <sub>2</sub> m <sup>-3</sup>	± %	± gH <sub>2</sub> O m <sup>-3</sup>	± %	± gH <sub>2</sub> O m <sup>-3</sup>	± %
-30	1.211	0.16			0.066	32.14	0.066	19.36
-25	1.129	0.15			0.063	19.01	0.064	11.47
-22	<del>1.080</del>	<del>0.14</del>			<del>0.062</del>	<del>14.00</del>	<del>0.062</del>	<del>8.46</del>
-20	1.047	0.14			0.061	11.46	0.062	6.94
-18	<del>1.014</del>	<del>0.13</del>			<del>0.060</del>	<del>9.41</del>	<del>0.061</del>	<del>5.70</del>
-15	0.965	0.13			0.059	7.04	0.060	4.28
-12	<del>0.916</del>	<del>0.12</del>		N/A <sup>c/</sup>	<del>0.058</del>	<del>5.30</del>	<del>0.058</del>	<del>3.23</del>
-10	0.883	0.12			0.057	4.40	0.058	2.68
-7	<del>0.834</del>	<del>0.11</del>			<del>0.055</del>	<del>3.34</del>	<del>0.057</del>	<del>2.05</del>
-5	0.801	0.11			0.055	2.79	0.056	1.71
-2	<del>0.752</del>	<del>0.10</del>			<del>0.053</del>	<del>2.14</del>	<del>0.055</del>	<del>1.32</del>
0	0.720	0.09			0.052	1.80	0.054	1.11
2	<del>0.687</del>	<del>0.09</del>			<del>0.052</del>	<del>1.54</del>	<del>0.053</del>	<del>0.95</del>
5	0.638	0.08	0.795	0.05	0.050	1.22	0.052	0.76
7	<del>0.605</del>	<del>0.08</del>	<del>0.741</del>	<del>0.05</del>	<del>0.049</del>	<del>1.05</del>	<del>0.051</del>	<del>0.65</del>
10	0.556	0.07	0.661	0.04	0.047	0.84	0.049	0.52
13	<del>0.507</del>	<del>0.07</del>	<del>0.580</del>	<del>0.04</del>	<del>0.046</del>	<del>0.67</del>	<del>0.047</del>	<del>0.41</del>
15	0.474	0.06	0.526	0.03	0.044	0.57	0.045	0.35
18	<del>0.425</del>	<del>0.06</del>	<del>0.446</del>	<del>0.03</del>	<del>0.042</del>	<del>0.45</del>	<del>0.042</del>	<del>0.28</del>
20	0.392	0.05	0.392	0.02	0.040	0.39	0.040	0.23
22	<del>0.425</del>	<del>0.06</del>	<del>0.446</del>	<del>0.03</del>	<del>0.042</del>	<del>0.36</del>	<del>0.043</del>	<del>0.22</del>
25	0.474	0.06	0.526	0.03	0.045	0.33	0.047	0.20
28	<del>0.523</del>	<del>0.07</del>	<del>0.607</del>	<del>0.04</del>	<del>0.049</del>	<del>0.30</del>	<del>0.052</del>	<del>0.19</del>
30	0.556	0.07	0.661	0.04	0.052	0.29	0.057	0.19
32	<del>0.589</del>	<del>0.08</del>	<del>0.715</del>	<del>0.04</del>	<del>0.055</del>	<del>0.27</del>	<del>0.062</del>	<del>0.18</del>
35	0.638	0.08	0.795	0.05	0.061	0.26	0.070	0.18
37	0.670	0.09	0.849	0.05	0.066	0.25	0.077	0.17
40	0.720	0.09	0.930	0.06	0.073	0.24	N/A <sup>d/</sup>	



45	0.801	0.11	1.064	0.07	0.090	0.23
48	0.851	0.11	1.145	0.07	0.099	0.23
50	0.883	0.12	1.198	0.07	N/A <sup>e/</sup>	

380 <sup>a</sup> 760 mgCO<sub>2</sub> m<sup>-3</sup> is the atmospheric background CO<sub>2</sub> density.

<sup>b</sup> 1,600 mgCO<sub>2</sub> m<sup>-3</sup> is assumed to be the maximum CO<sub>2</sub> density in ecosystems.

<sup>c</sup> CO<sub>2</sub> density in ecosystems is assumed to be lower than 1,600 mgCO<sub>2</sub> m<sup>-3</sup> when ambient air temperatures is below 5 °C.

<sup>d</sup> H<sub>2</sub>O density in saturated air above 37 °C is out of the measurement range of EC150 infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers (0 – 44 gH<sub>2</sub>O m<sup>-3</sup>).

385 <sup>e</sup> H<sub>2</sub>O density in air of 60% relative humidity above 48 °C is out of the measurement range of EC150 infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers (0 – 44 gH<sub>2</sub>O m<sup>-3</sup>).

## 5 Accuracy of H<sub>2</sub>O density measurements

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

$$\Delta\rho_{H_2O} \equiv \pm\left(\left|\Delta\rho_{H_2O}^z\right| + \left|\Delta\rho_{H_2O}^g\right| + \left|\Delta\rho_{H_2O}^s\right| + \left|\Delta\rho_{H_2O}^p\right|\right), \quad (15)$$

390 where  $\Delta\rho_{H_2O}^z$  is H<sub>2</sub>O zero drift uncertainty,  $\Delta\rho_{H_2O}^g$  is H<sub>2</sub>O gain drift uncertainty,  $\Delta\rho_{H_2O}^s$  is cross-sensitivity-to-CO<sub>2</sub> uncertainty, and  $\Delta\rho_{H_2O}^p$  is H<sub>2</sub>O precision uncertainty. Using the same approach for  $\Delta\rho_{CO_2}^p$ ,  $\Delta\rho_{H_2O}^p$  is formulated as

$$\Delta\rho_{H_2O}^p = \pm 1.96 \times \sigma_{H_2O}, \quad (16)$$

where  $\sigma_{H_2O}$ , as defined in Table 1, is the precision of EC150 analyzers for H<sub>2</sub>O measurements. The other uncertainty terms in Model (15) can be understood and formulated using the similar approach for their counterparts in Model (3).

### 395 5.1 $\Delta\rho_{H_2O}^z$ (H<sub>2</sub>O zero drift uncertainty) and $\Delta\rho_{H_2O}^g$ (H<sub>2</sub>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 \(2001, 2021a, 2021b\)](#)

$$\rho_{H_2O} = P \sum_{i=1}^3 a_{wi} \left\{ 1 - \left[ \frac{A_w}{A_{ws}} + S_c \left( 1 - \frac{A_c}{A_{cs}} \right) \right] Z_w \right\}^i \left\{ \frac{G_w}{P} \right\}^i, \quad (17)$$

400 where  $a_{wi}$  ( $i = 1, 2, \text{ or } 3$ ) is a coefficient of the three-order polynomial in the terms inside curly brackets;  $S_c$  is the cross-sensitivity of a detector to CO<sub>2</sub>, while detecting H<sub>2</sub>O, in the wavelength for H<sub>2</sub>O measurements (hereafter referred to as sensitivity-to-CO<sub>2</sub>);  $Z_w$  is the H<sub>2</sub>O zero adjustment (i.e., H<sub>2</sub>O zero coefficient); ~~and~~  $G_w$  is the H<sub>2</sub>O gain adjustment (i.e., commonly referred as to H<sub>2</sub>O span coefficient); ~~and~~  $A_w, A_{ws}, A_c,$  and  $A_{cs}$  represent the same as in Model (5). The parameters of  $a_{wi}, Z_w, G_w,$  and  $S_c$  in Model (17) are statistically estimated to establish an H<sub>2</sub>O working equation in production calibration

405 against a series of air standards with different H<sub>2</sub>O contents under ranges of  $\rho_{CO_2}$  and  $P$  (i.e., calibration). The H<sub>2</sub>O working equation (i.e., Model 17 with estimated parameters) is used inside the analyzer to compute  $\rho_{H_2O}$  as the closest proxy for true  $\rho_{H_2O}$  from field measurements of  $A_w$ ,  $A_{ws}$ ,  $A_c$ ,  $A_{cs}$ , and  $P$ .

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

$$\Delta\rho_{H_2O}^z = \frac{d_{wz}}{T_{rh} - T_{rl}} \times \begin{cases} T_a - T_c & T_c < T_a < T_{rh} \\ T_c - T_a & T_c > T_a > T_{rl} \end{cases}, \quad (18)$$

410 and  $\Delta\rho_{H_2O}^g$  is formulated as

$$\Delta\rho_{H_2O}^g = \pm \frac{\delta_{H_2O-g} \rho_{H_2O}}{T_{rh} - T_{rl}} \times \begin{cases} T_a - T_c & T_c < T_a < T_{rh} \\ T_c - T_a & T_c > T_a > T_{rl} \end{cases}. \quad (19)$$

## 5.2 $\Delta\rho_{H_2O}^s$ (sensitivity-to-CO<sub>2</sub> uncertainty)

The infrared light at wavelength of 2.7  $\mu\text{m}$  for H<sub>2</sub>O measurement is traceably absorbed by CO<sub>2</sub> (see Fig. 4.7 in Wallace and Hobbs, 2006). This absorption interferes slightly with the absorption by H<sub>2</sub>O in the wavelength (McDermitt et al., 1993). As  
 415 such, the power of identical measurement lights through several air standards with the same H<sub>2</sub>O density but different backgrounds of CO<sub>2</sub> amounts would result in different values of  $A_w$  into the H<sub>2</sub>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  $\rho_{H_2O}$  values, although  $\rho_{H_2O}$  is essentially the same. To report the same  $\rho_{H_2O}$  for air flows with the same H<sub>2</sub>O amount under different CO<sub>2</sub> backgrounds, different values of  $A_w$  to report the same  $\rho_{H_2O}$  are accounted for by  $S_c$  associated with  $A_c$  and  $A_{cs}$  in the H<sub>2</sub>O  
 420 working equation (see 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<sub>2</sub> ( $s_{CO_2}$ ) value as the maximum range of  $\pm 4.09 \times 10^{-5}$  gH<sub>2</sub>O m<sup>-3</sup> (mgCO<sub>2</sub> m<sup>-3</sup>)<sup>-1</sup> (Table 1). Assuming the infrared analyzers for H<sub>2</sub>O have the lowest sensitivity-to-CO<sub>2</sub> uncertainty for air flow with an atmospheric background CO<sub>2</sub> amount (i.e., 760 mgCO<sub>2</sub> m<sup>-3</sup>),  $\Delta\rho_{H_2O}^s$  could be formulated as

$$425 \quad \Delta\rho_{H_2O}^s = s_{CO_2} (\rho_{CO_2} - 760) \quad \rho_{CO_2} \leq 1,553 \text{ mgCO}_2 \text{ m}^{-3}. \quad (20)$$

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

$$|\Delta\rho_{H_2O}^s| \leq 793 s_{CO_2}. \quad (21)$$

### 5.3 $\Delta\rho_{H_2O}$ (H<sub>2</sub>O measurement accuracy)

430 Substituting Eqs. (16), (18), (19) and (21) into Model (15),  $\Delta\rho_{H_2O}$  for an individual H<sub>2</sub>O measurement from OPEC systems can be expressed as

$$\Delta\rho_{H_2O} = \pm \left[ 1.96\sigma_{H_2O} + 793|s_{CO_2}| + \frac{|d_{wz}| + \delta_{H_2O-g}\rho_{H_2O}}{T_{rh} - T_{rl}} \times \begin{cases} T_a - T_c & T_c < T_a < T_{rh} \\ T_c - T_a & T_c > T_a > T_{rl} \end{cases} \right]. \quad (22)$$

This equation is the H<sub>2</sub>O accuracy equation for the OPEC systems with infrared analyzers. It expresses the accuracy of H<sub>2</sub>O measurements from the OPEC systems in terms of the specifications  $\sigma_{H_2O}$ ,  $s_{CO_2}$ ,  $d_{wz}$ ,  $\delta_{H_2O-g}$ ,  $T_{rh}$ , and  $T_{rl}$ ; measured variables  $\rho_{H_2O}$  and  $T_a$ ; and a known variable  $T_c$ . Using this equation and the system specification values in Table 1, the accuracy of field H<sub>2</sub>O measurements can be evaluated as a range. Using this equation and the specification values as in Table 1 for EC150 infrared analyzers, the accuracy of field H<sub>2</sub>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 $\Delta\rho_{H_2O}$

440 H<sub>2</sub>O accuracy ( $\Delta\rho_{H_2O}$ ) can be evaluated using the H<sub>2</sub>O accuracy equation over a domain of  $T_a$  and  $\rho_{H_2O}$ . Similar to the CO<sub>2</sub> accuracy equation in Fig. 2,  $\Delta\rho_{H_2O}$  is presented as the ordinate along the abscissa of  $T_a$  at different  $\rho_{H_2O}$  levels within the ranges of  $T_a$  and  $\rho_{H_2O}$  in ecosystems (Fig. 3). As with the evaluation of  $\Delta\rho_{CO_2}$ ,  $T_a$  is limited from -30 to 50 °C and  $T_c$  can be assumed to be 20 °C. The range of  $\rho_{H_2O}$  at  $T_a$  needs to be determined using atmospheric physics (Buck, 1981).

#### 5.4.1 $\rho_{H_2O}$ range

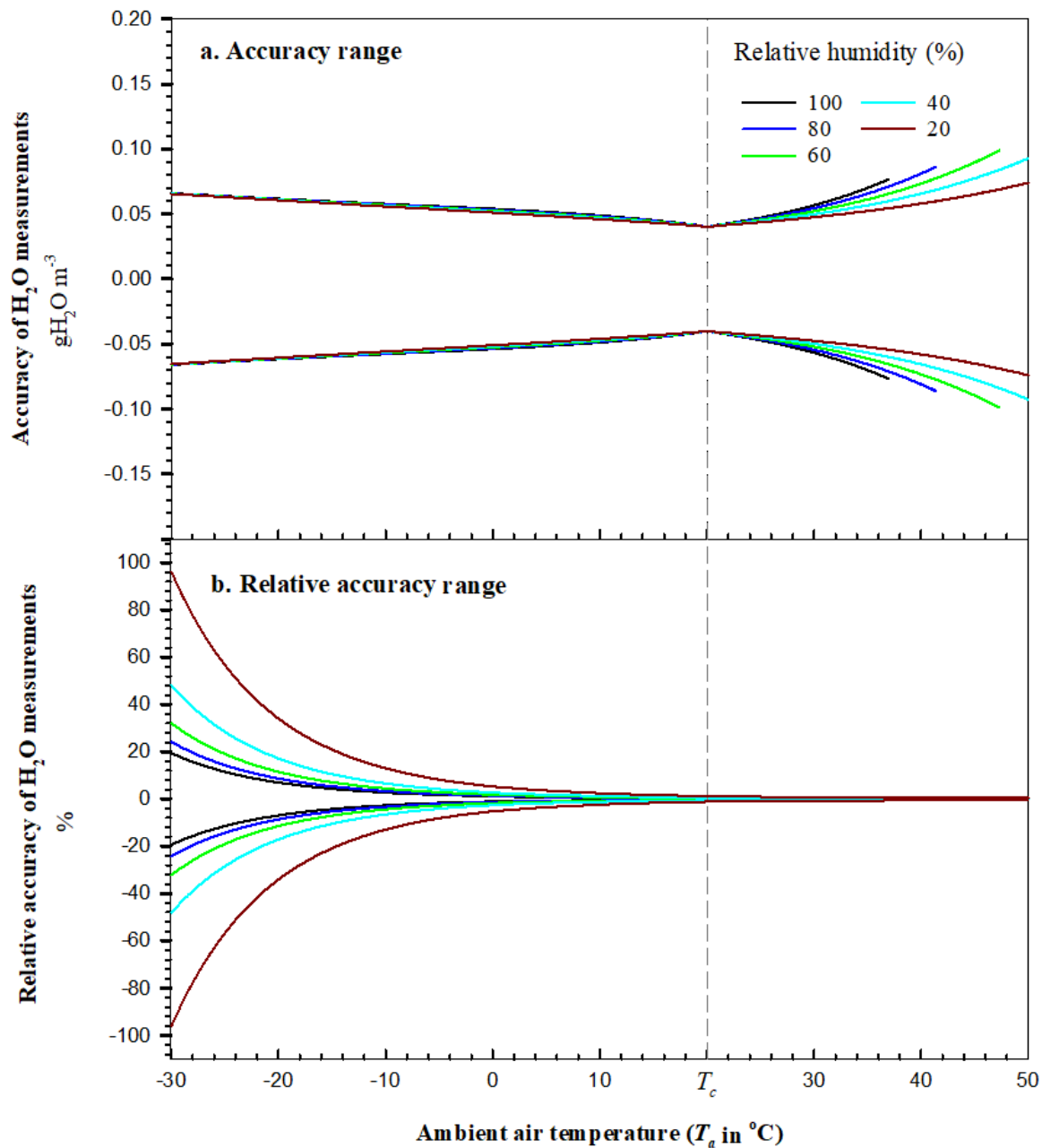
445 The EC150 analyzers were calibrated for H<sub>2</sub>O density from 0 to 44 gH<sub>2</sub>O m<sup>-3</sup> due to the reason addressed in Sect. 2. The highest limit of measurement range for H<sub>2</sub>O density by other models of analyzers also should be near 44 gH<sub>2</sub>O m<sup>-3</sup>. The analyzers measure H<sub>2</sub>O density from 0 to 44 gH<sub>2</sub>O m<sup>-3</sup>. However, due to the positive exponential dependence of air water vapor saturation on  $T_a$  (Wallace and Hobbs, 2006),  $\rho_{H_2O}$  has a range that is wider at higher  $T_a$  and narrower at lower  $T_a$ . Below 37 °C at 101.325 kPa,  $\rho_{H_2O}$  is lower than 44 gH<sub>2</sub>O m<sup>-3</sup>, and its range becomes narrower and narrower, reaching 0.34 gH<sub>2</sub>O m<sup>-3</sup> at -30 °C. To determine the H<sub>2</sub>O accuracy over the same relative range of air moisture, even at different  $T_a$ , the water vapor saturation 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,  $\rho_{H_2O}$  can be calculated at different  $T_a$  and  $P$  (Appendix B) for use in the H<sub>2</sub>O accuracy equation. In this way, over the range of  $T_a$ , H<sub>2</sub>O accuracy can be shown as curves with equal RH (Fig. 3).

#### 5.4.2 $\Delta\rho_{H_2O}$ range

455 In the same way as with CO<sub>2</sub> accuracy, the H<sub>2</sub>O accuracy at  $T_a = T_c$  is best at its narrowest as the sum of precision and sensitivity-to-CO<sub>2</sub> uncertainties (<0.040 gH<sub>2</sub>O m<sup>-3</sup> in magnitude). However, away from  $T_c$ , its non-linear range becomes

wider, very gradually below this  $T_c$  value but more abruptly above, because, as  $T_a$  increases,  $\rho_{H_2O}$  at the same RH increases exponentially (Eqs. B1 and B2 in Appendix B) while  $\Delta\rho_{H_2O}$  increases linearly with  $\rho_{H_2O}$  in the H<sub>2</sub>O accuracy equation (22). This non-linear range can be summarized as the widest at 48 °C to be  $\pm 0.099$  gH<sub>2</sub>O m<sup>-3</sup> for air with 60% RH (Fig. 3a and  
460 H<sub>2</sub>O columns in Table 2). The number can be rounded up to  $\pm 0.10$  gH<sub>2</sub>O m<sup>-3</sup> for the overall accuracy of field H<sub>2</sub>O measurements from OPEC systems by the EC150 infrared analyzers.

Fig. 3b shows an interesting trend of H<sub>2</sub>O relative accuracy with  $T_a$ . Given the RH range shown in Fig. 3b, the relative accuracy diverges with a  $T_a$  decrease and converges with a  $T_a$  increase. The H<sub>2</sub>O relative accuracy varies from 0.17% for saturated air at 37 °C to 96% for 20% RH air at -30 °C (data for Fig. 3b) and, at this low  $T_a$ , can be much greater if RH  
465 goes further lower. The H<sub>2</sub>O relative accuracy in magnitude is < 1% while  $\rho_{H_2O} > 5.00$  gH<sub>2</sub>O m<sup>-3</sup>, < 5% while  $\rho_{H_2O} > 1.20$  gH<sub>2</sub>O m<sup>-3</sup>, and >10% while  $\rho_{H_2O} < 0.60$  gH<sub>2</sub>O m<sup>-3</sup>.



470 **Figure 3.** Accuracy of field H<sub>2</sub>O measurements from open-path eddy-covariance systems by EC150 infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers over their operational range in  $T_a$  under atmospheric pressure of 101.325 kPa. The vertical dashed line represents the ambient air temperature ( $T_c$ ) at which an analyzer was calibrated, zeroed, and/or spanned. Relative accuracy of H<sub>2</sub>O measurements is the ratio of H<sub>2</sub>O accuracy to H<sub>2</sub>O density.

## 6 Application

The primary objective of this study is to develop an assessment methodology to evaluate the overall accuracies of field CO<sub>2</sub> and H<sub>2</sub>O measurements from OPEC systems by the infrared analyzers from their individual measurement uncertainties as specified using four uncertainty descriptors: zero drift, gain drift, sensitivity-to-CO<sub>2</sub>/H<sub>2</sub>O, and precision variability (Table 1). The evaluated accuracy can be used to estimate the uncertainties of CO<sub>2</sub> and H<sub>2</sub>O fluxes due to the overall accuracy uncertainties, assess CO<sub>2</sub> and H<sub>2</sub>O data applications, and the formulated accuracy equations further provide rationales to assess and guide field maintenance on the infrared analyzers.

### 6.1 Partial effects of $\Delta\rho_{CO_2}$ and $\Delta\rho_{H_2O}$ on uncertainty of hourly CO<sub>2</sub>/H<sub>2</sub>O flux

As discussed in Introduction, the uncertainty of each flux is contributed by numerous sub-uncertainties in the processes of measurements and computations, among which  $\Delta\rho_{CO_2}$  and  $\Delta\rho_{H_2O}$  are two fundamental uncertainties from infrared analyzers. Assume 3-D wind speeds are accurately measured, Appendix C demonstrates no effects of  $\Delta\rho_{CO_2}$  and  $\Delta\rho_{H_2O}$  on the uncertainty of the covariance of vertical wind speed ( $w$ ) with  $\rho_{CO_2}$ ,  $\rho_{H_2O}$ , or  $T_a$  until the covariance underwent through coordinate rotations ( $r$ ), lag maximization ( $m$ ), and low- and high-frequency ( $f$ ) are finished. Equations (C8 and C9) give:

$$\begin{aligned}\overline{(w'\rho'_{CO_2})}_{rmf} &= \overline{(w'\rho'_{CO_2T})}_{rmf} \\ \overline{(w'\rho'_{H_2O})}_{rmf} &= \overline{(w'\rho'_{H_2OT})}_{rmf} \\ \overline{(w'T'_a)}_{rmf} &= \overline{(w'T'_{aT})}_{rmf}\end{aligned}\quad (23)$$

where the overbar is an averaging operator, prime denotes the fluctuations of a variable away from its mean (e.g.,  $w'_i = w_i - \bar{w}$ ), subscript  $T$  indicates true value, and subscript  $rmf$  indicates the covariance was corrected through coordinate rotations ( $r$ ), lag maximization ( $m$ ), and low- and high-frequency ( $f$ ) corrections. Further, through WPL correction, the three terms on the left side of Eq. (23) can be used to derive an analytical equation for CO<sub>2</sub> or H<sub>2</sub>O flux from  $\rho_{CO_2}$  and/or  $\rho_{H_2O}$  with an error as ranged by its accuracy and  $T_a$  with an error whereas the three terms on the right side of this equation can be used to derive the equation from  $\rho_{CO_2T}$ ,  $\rho_{H_2OT}$  and/or  $T_{aT}$ , all of which theoretically do not include errors. The comparison of both analytical equations can demonstrate the partial effects of  $\Delta\rho_{CO_2}$  and  $\Delta\rho_{H_2O}$  on uncertainty of hourly CO<sub>2</sub> or H<sub>2</sub>O flux.

### 6.1.2 Partial effects of $\Delta\rho_{CO_2}$ and $\Delta\rho_{H_2O}$ on uncertainty of hourly CO<sub>2</sub> flux

Through WPL correction using the  $\rho_{H_2O}$  and  $T_a$  related terms for  $\rho_{CO_2}$  related term in Eq. (23), the measured CO<sub>2</sub> flux ( $F_{CO_2}$ ) is given by

$$F_{CO_2} = \overline{(w'\rho'_{CO_2})}_{rmf} + \left[ \mu \frac{\bar{\rho}_{CO_2}}{\bar{\rho}_d} \overline{(w'\rho'_{H_2O})}_{rmf} + \left( 1 + \mu \frac{\bar{\rho}_{H_2O}}{\bar{\rho}_d} \right) \frac{\bar{\rho}_{CO_2}}{\bar{T}_a} \overline{(w'T'_a)}_{rmf} \right], \quad (24)$$

where  $\mu$  is the ratio of dry air to water molecular weight and  $\rho_d$  is dry air density. Submitting Eqs. (1) and (23) leads to

$$F_{CO_2} = \overline{(w' \rho'_{CO_2T})}_{mf} + \left[ \mu \frac{\bar{\rho}_{CO_2T} + \Delta\bar{\rho}_{CO_2}}{\bar{\rho}_{dT} - \Delta\bar{\rho}_{H_2O}} \overline{(w' \rho'_{H_2OT})}_{mf} + \left( 1 + \mu \frac{\bar{\rho}_{H_2OT} + \Delta\bar{\rho}_{H_2O}}{\bar{\rho}_{dT} - \Delta\bar{\rho}_{H_2O}} \right) \frac{\bar{\rho}_{CO_2T} + \Delta\bar{\rho}_{CO_2}}{\bar{T}_{dT} + \Delta\bar{T}_a} \overline{(w' T'_{dT})}_{mf} \right], \quad (25)$$

where  $\Delta\bar{T}_a$  is the uncertainty of  $\bar{T}_a$ .  $\Delta\bar{T}_a$  commonly is  $\pm 0.20$  K in compliance with the WMO standard (WMO, 2018).

According to Eq. (24), the nominate true CO<sub>2</sub> flux ( $F_{CO_2T}$ ) is given by

$$F_{CO_2T} = \overline{(w' \rho'_{CO_2T})}_{mf} + \left[ \mu \frac{\bar{\rho}_{CO_2T}}{\bar{\rho}_{dT}} \overline{(w' \rho'_{H_2OT})}_{mf} + \left( 1 + \mu \frac{\bar{\rho}_{H_2OT}}{\bar{\rho}_{dT}} \right) \frac{\bar{\rho}_{CO_2T}}{\bar{T}_{dT}} \overline{(w' T'_{dT})}_{mf} \right]. \quad (26)$$

From Eqs (25) and (26), the uncertainty of CO<sub>2</sub> flux ( $\Delta F_{CO_2}$ ) can be expressed as

$$\begin{aligned} \Delta F_{CO_2} &= F_{CO_2} - F_{CO_2T} \\ &= \mu \left( \frac{\bar{\rho}_{CO_2T} + \Delta\bar{\rho}_{CO_2}}{\bar{\rho}_{dT} - \Delta\bar{\rho}_{H_2O}} - \frac{\bar{\rho}_{CO_2T}}{\bar{\rho}_{dT}} \right) \overline{(w' \rho'_{H_2OT})}_{mf} + \\ &\quad \left[ \left( 1 + \mu \frac{\bar{\rho}_{H_2OT} + \Delta\bar{\rho}_{H_2O}}{\bar{\rho}_{dT} - \Delta\bar{\rho}_{H_2O}} \right) \frac{\bar{\rho}_{CO_2T} + \Delta\bar{\rho}_{CO_2}}{\bar{T}_{dT} + \Delta\bar{T}_a} - \left( 1 + \mu \frac{\bar{\rho}_{H_2OT}}{\bar{\rho}_{dT}} \right) \frac{\bar{\rho}_{CO_2T}}{\bar{T}_{dT}} \right] \overline{(w' T'_{dT})}_{mf} \end{aligned} \quad (27)$$

This derivation provides a conceptual model for the partial effects of  $\Delta\rho_{CO_2}$  and  $\Delta\rho_{H_2O}$  on the uncertainty of hourly CO<sub>2</sub> flux. This uncertainty is added by  $\Delta\rho_{CO_2}$  and  $\Delta\rho_{H_2O}$  through the density effect due to H<sub>2</sub>O flux (1<sup>st</sup> term in Eq. 27) and temperature flux (2<sup>nd</sup> term in Eq. 27).

### 6.1.2 Partial effects of $\Delta\rho_{H_2O}$ on uncertainty of hourly H<sub>2</sub>O flux

Using the same approach to Eq. (27), the uncertainty of H<sub>2</sub>O flux ( $\Delta F_{H_2O}$ ) can be expressed as

$$\begin{aligned} \Delta F_{CO_2} &= \mu \left( \frac{\bar{\rho}_{H_2OT} + \Delta\bar{\rho}_{H_2O}}{\bar{\rho}_{dT} - \Delta\bar{\rho}_{H_2O}} - \frac{\bar{\rho}_{H_2OT}}{\bar{\rho}_{dT}} \right) \overline{(w' \rho'_{H_2OT})}_{mf} + \\ &\quad \left[ \left( 1 + \mu \frac{\bar{\rho}_{H_2OT} + \Delta\bar{\rho}_{H_2O}}{\bar{\rho}_{dT} - \Delta\bar{\rho}_{H_2O}} \right) \frac{\bar{\rho}_{H_2OT} + \Delta\bar{\rho}_{H_2O}}{\bar{T}_{dT} + \Delta\bar{T}_a} - \left( 1 + \mu \frac{\bar{\rho}_{H_2OT}}{\bar{\rho}_{dT}} \right) \frac{\bar{\rho}_{H_2OT}}{\bar{T}_{dT}} \right] \overline{(w' T'_{dT})}_{mf} \end{aligned} \quad (28)$$

This formulation provides a conceptual model for the partial effects of  $\Delta\rho_{H_2O}$  on the uncertainty of hourly H<sub>2</sub>O flux. This uncertainty is added only  $\Delta\rho_{H_2O}$  also through the density effect due to H<sub>2</sub>O flux (1<sup>st</sup> term in Eq. 28) and temperature flux (2<sup>nd</sup> term in Eq. 28). Further analysis and more discussion about Eqs. (27) and (28) go beyond the scope of this study.



## 515 6.2 Application of H<sub>2</sub>O accuracy in data use

The measured variables  $\rho_{H_2O}$ ,  $T_s$  and  $P$  can be used to compute  $T_a$  (Swiatek, 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<sub>2</sub>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 measurement 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 its 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

$$\Delta T_a = \pm \left( \frac{\partial T_a}{\partial \rho_{H_2O}} \Delta \rho_{H_2O} + \frac{\partial T_a}{\partial T_s} \Delta T_s + \frac{\partial T_a}{\partial P} \Delta P \right). \quad (23)$$

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 while  $T_a$  is, the better analyzers perform. However, the analyzers are mostly used in OPEC systems 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<sub>2</sub>/H<sub>2</sub>O uncertainty and precision variability, but both are minor (their sum < 0.392 mgCO<sub>2</sub> m<sup>-3</sup> for CO<sub>2</sub>, Eqs. 4 and 13; < 0.045 gH<sub>2</sub>O m<sup>-3</sup> for H<sub>2</sub>O, Eqs. 16 and 21) as compared to the zero or gain drift uncertainties. However, the zero and gain drift uncertainties are major in determination of field CO<sub>2</sub>/H<sub>2</sub>O measurement accuracy (Figs. 2 to 4 and Eqs. 14 and 22), but adjustable, through the zero and/or span procedures, to 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, 2021b). [Fratini et al.](#)

(2014) provided a technique implemented into the EddyPro program to correct the drift bias from a raw time series of CO<sub>2</sub> and H<sub>2</sub>O data through post-processing. This study provides rationales how to assess, schedule, and perform the procedures (Figs. 2a, 3a, and 4).

### 6.3.1 CO<sub>2</sub> zero and span procedures

Figure 4a shows that the CO<sub>2</sub> 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<sub>2</sub> gain drift uncertainty increase for a given CO<sub>2</sub> 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  $\pm 20$  of  $T_c$  if the procedures are performed at a right moment of  $T_a$ . For our study case on atmospheric CO<sub>2</sub> background (left CO<sub>2</sub> column in Table 2), the procedures can narrow the widest possible range of  $\pm 1.21$  mgCO<sub>2</sub> m<sup>-3</sup> for field CO<sub>2</sub> measurement at least 40% to  $\pm 0.72$  mgCO<sub>2</sub> m<sup>-3</sup> (i.e., accuracy at 0 or 40 °C when  $T_c = 20$  °C), which would be a significant improvement to ensure field CO<sub>2</sub> measurement accuracy through CO<sub>2</sub> zero and span procedures.

### 6.3.2 H<sub>2</sub>O zero and span procedures

Figure 4b shows that the H<sub>2</sub>O zero drift uncertainty increases as  $T_a$  moves away from  $T_c$  in the same trend as CO<sub>2</sub> zero drift uncertainty. Therefore, an H<sub>2</sub>O zero procedure can be performed in the same technique as for CO<sub>2</sub> zero procedure. H<sub>2</sub>O gain drift uncertainty has a different trend. It exponentially diverges, as  $T_a$  increases away from  $T_c$ , to  $\pm 5.0 \times 10^{-2}$  gH<sub>2</sub>O m<sup>-3</sup> near 50 °C, and gradually converges by two orders smaller, as  $T_a$  decreases away from  $T_c$ , to  $\pm 6.38 \times 10^{-4}$  gH<sub>2</sub>O m<sup>-3</sup> at -30 °C (data for Fig. 4b). The exponential divergence results from the linear relationship of H<sub>2</sub>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<sub>2</sub>O gain drift uncertainty with  $T_a$  is a rationale to guide the H<sub>2</sub>O span procedure, which adjusts the H<sub>2</sub>O gain drift.

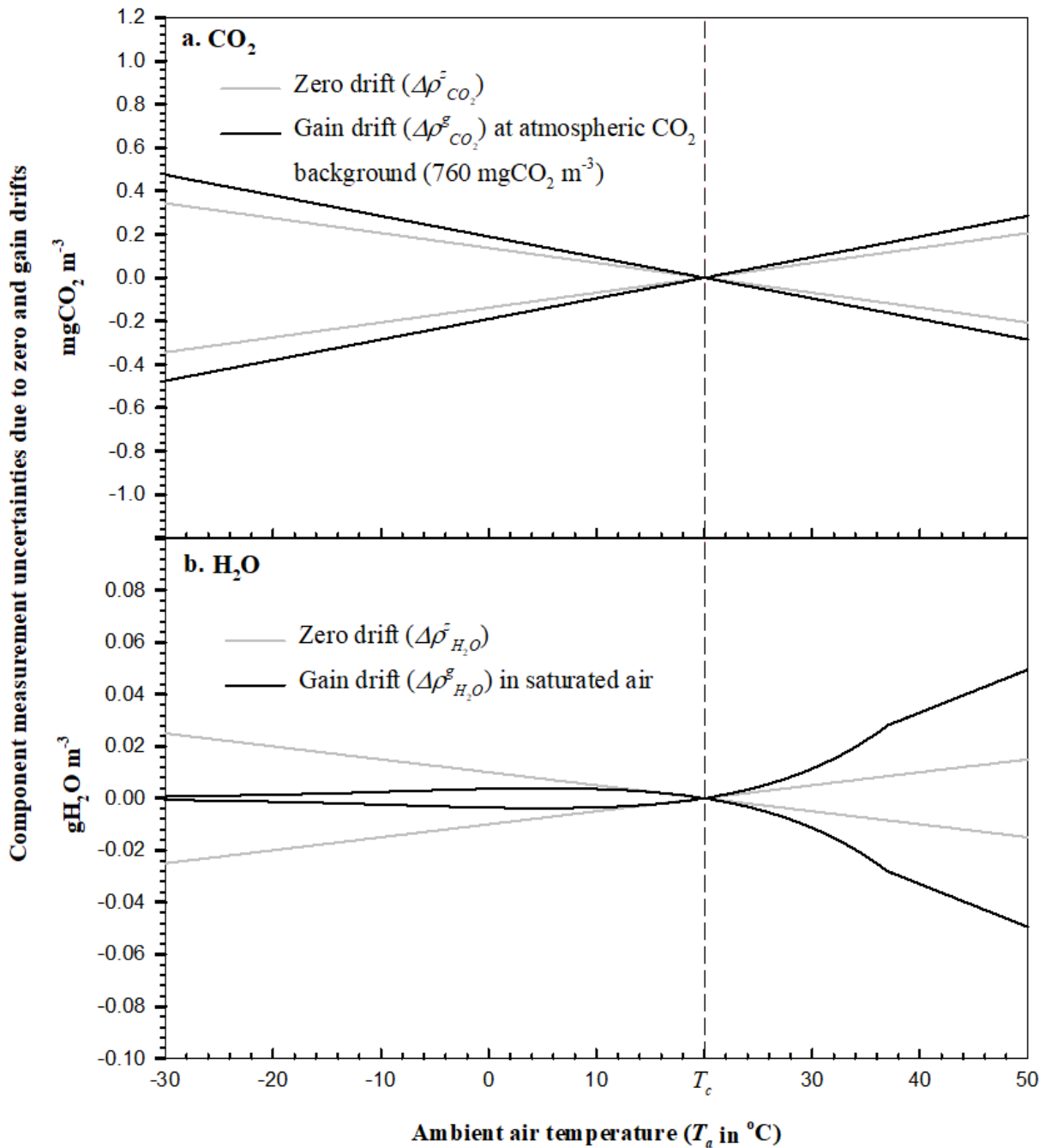
The H<sub>2</sub>O span procedure needs standard moist air with known H<sub>2</sub>O density from a dew point generator. The generator is not operational near or below freezing conditions (LI-COR Biosciences, 2004), which limits the span procedure to be performed only under non-freezing conditions. This condition, from 5 to 35 °C, may be considered for the generator to be conveniently operational in the field. Accordingly, the H<sub>2</sub>O zero and span procedures should be discussed separately for a  $T_a$  above and below 5 °C.

### 6.3.2.1 $T_a$ above 5 °C

575 Looking at the right portion with  $T_a$  above 5 °C in Fig. 4b, H<sub>2</sub>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<sub>2</sub>O span procedure is most needed. In this range, the maximum accuracy range of  $\pm 0.10$  gH<sub>2</sub>O m<sup>-3</sup> can be narrowed by 30% to  $\pm 0.07$  (assessed from data for Fig 3a) if H<sub>2</sub>O zero and span procedures can be sequentially performed as necessary in a  $T_a$  range from 5 to 35 °C.

### 6.3.2.2 $T_a$ below 5 °C

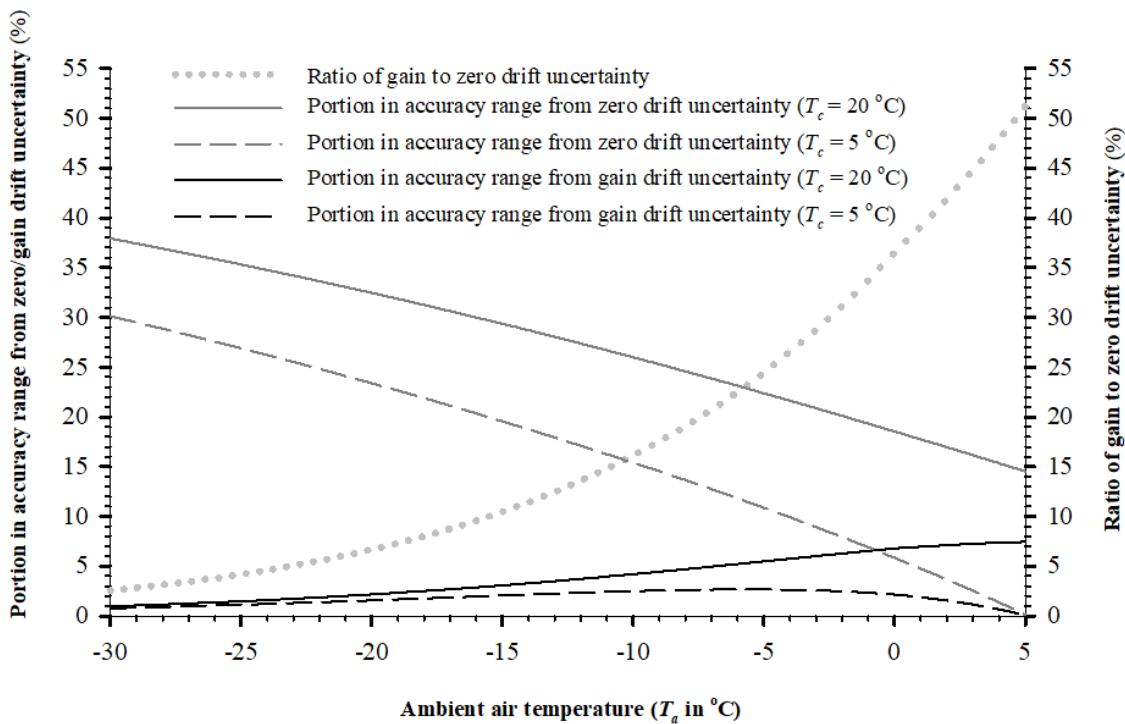
580 Looking at the left portion with  $T_a$  below 5 °C in Fig 4b, H<sub>2</sub>O gain drift has a less obvious contribution to the measurement uncertainty in a lower  $T_a$  range (e.g., below 5 °C), within which the H<sub>2</sub>O span procedure may be unnecessary. An H<sub>2</sub>O gain drift uncertainty at 5 °C is 50% of the H<sub>2</sub>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 dotted curve in Fig. 5). Thus, for H<sub>2</sub>O measurements over the lower  $T_a$  range, it can be concluded that H<sub>2</sub>O zero drift is a major uncertainty source, and H<sub>2</sub>O gain drift is a minor uncertainty source.



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**Figure 4.** Component measurement uncertainties due to the zero and gain drifts of EC150 infrared CO<sub>2</sub>–H<sub>2</sub>O analyzers in open-path eddy-covariance flux systems over their operational range in  $T_a$  under an atmospheric pressure of 101.325 kPa. The vertical dashed line represents the ambient temperature ( $T_c$ ) at which an analyzer was calibrated, zeroed, and/or spanned.

A close examination of the other curves in Fig. 5 for the portion in the accuracy range from H<sub>2</sub>O zero/gain drift makes this conclusion more convincing. Given  $T_c = 20$ , in accuracy range, the portion from H<sub>2</sub>O zero drift uncertainty is much greater (maximum 38% at  $-30$  °C) than that from H<sub>2</sub>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<sub>2</sub>O gain drift uncertainty is even smaller (maximum only 3% at  $-5$  °C); in contrast, the portion from zero drift uncertainty is more major (one 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<sub>2</sub>O span procedure is reasonably unnecessary under cold/dry conditions, and, under such conditions, the H<sub>2</sub>O zero procedure is the only necessary option to efficiently minimize H<sub>2</sub>O measurement uncertainty in OPEC systems. This finding gives confidence in H<sub>2</sub>O measurement accuracy to users who are worried about H<sub>2</sub>O span procedures for infrared analyzers in the cold seasons when a dew point generator is not operational in the field (LI-COR Biosciences, 2004).



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**Figure 5.** For a range of low  $T_a$ , the portion in the accuracy range from zero/gain drift uncertainty (left ordinate) and the ratio of gain to zero drift uncertainty (right ordinate). The curves are evaluated by Eqs. (18), (19), and (22) from measurement specifications for EC150 infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers in open-path eddy-covariance flux systems over the  $T_a$  range from  $-30$  to  $5$  °C under atmospheric pressure of 101.325 kPa.  $T_c$  is the ambient air temperature at which an analyzer was calibrated, zeroed, and/or spanned.

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### 6.3.3 H<sub>2</sub>O zero procedure in cold and/or dry environments

In cold environments, although the non-operational H<sub>2</sub>O span procedure is unnecessary, the H<sub>2</sub>O zero procedure is asserted to be a prominently important option for minimizing the H<sub>2</sub>O measurement uncertainty in OPEC systems. This procedure, although operational under freezing conditions, is still inconvenient for users when weather is very cold (e.g., when  $T_a$  is below  $-15\text{ }^\circ\text{C}$ ). If the field H<sub>2</sub>O zero procedure is performed as needed above this  $T_a$  value, an OPEC system can be assumed to run at  $T_a$  with  $\pm 20\text{ }^\circ\text{C}$  of  $T_c$ . Under this assumption, the poorest H<sub>2</sub>O accuracy of  $\pm 0.066\text{ gH}_2\text{O m}^{-3}$  below  $5\text{ }^\circ\text{C}$  in Table 2 can be narrowed, through the H<sub>2</sub>O zero procedure, by at least 22% to  $0.051\text{ gH}_2\text{O m}^{-3}$  (assessed from data for Fig. 3a). Correspondingly, the relative accuracy range can be narrowed by the same percentage. The H<sub>2</sub>O zero procedure can ensure both accuracy and relative accuracy of H<sub>2</sub>O measurements in a cold environment ([Fratini et al., 2014](#)). In a dry environment, it plays the same role as in a cold environment, but it would be more convenient for users if warmer.

In a cold and/or dry environment, H<sub>2</sub>O zero procedures that are undergone on a regular schedule would best minimize the impact of zero drifts on measurements. Under such an environment, the automatic zero procedure for CO<sub>2</sub> and H<sub>2</sub>O together in CPEC systems is an operational and efficient option to ensure and improve field CO<sub>2</sub> and H<sub>2</sub>O measurement accuracies (Campbell Scientific Inc., 2021a; Zhou et al., 2021).

## 7 Discussion

The primary objective of this study is to develop an assessment methodology to evaluate the overall accuracies of field CO<sub>2</sub> and H<sub>2</sub>O measurements from OPEC systems by the infrared analyzers from their individual measurement uncertainties as specified using four uncertainty descriptors: zero drift, gain drift, sensitivity-to-CO<sub>2</sub>/H<sub>2</sub>O, and precision variability (Table 1). For the evaluation, these uncertainty descriptors are comprehensively composited into the accuracy model (2) formulated as a CO<sub>2</sub> accuracy equation (14) and an H<sub>2</sub>O accuracy equation (22) (Sects. 3 to 5 and Appendix A). The assessment methodology, along with the model and the equations, is our development for the objective (Sects. 4.5 and 5.4). The evaluated accuracy can be used to assess CO<sub>2</sub> and H<sub>2</sub>O data applications, and the formulated accuracy equations further provide rationales to assess and guide field maintenance on the infrared analyzers.

### 7.1 Methodology development

The methodology is developed from the derivation of accuracy model for the formulation of CO<sub>2</sub> and H<sub>2</sub>O accuracy equations applicable in ecosystems to the evaluation of field CO<sub>2</sub> and H<sub>2</sub>O measurement accuracies.

#### 7.1.1 Accuracy model

Accuracy model (2) composites the four measurement uncertainties (zero drift, gain drift, sensitivity-to-CO<sub>2</sub>/H<sub>2</sub>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 contribution from the interaction inside any pair of uncertainties is negligible because the interaction is three orders smaller in magnitude than an individual uncertainty in the pair (Appendix A). This derived model is simple and applicable, opening an approach to the formulation of accuracy equations that are computable to evaluate the overall accuracies of field CO<sub>2</sub> and H<sub>2</sub>O measurements from OPEC systems by infrared analyzers.

Additionally, included in the accuracy model, the four types of measurement uncertainties (zero drift, gain drift, sensitivity-to-CO<sub>2</sub>/H<sub>2</sub>O, and precision variability) to specify the performance of infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers for OPEC systems have been consistently used over last 20 years (LI-COR Biosciences, 2001, 2021a, 2021b; Campbell Scientific Inc., 2021). With the advancement of optical technologies, the measurement uncertainties for analyzer specifications are not expected to increase rather some current measurement uncertainties could be removed from the current specification list, even if not in the near future. If removed, the corresponding terms in the model could be easily removed, at which point, this model would be adapted to the new set of specifications for infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers.

### 7.1.2 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<sub>2</sub> and H<sub>2</sub>O, respectively (Eqs. 4, 7, 11, 13, 16, 18, 19, or 21). The accuracy model, whose terms are replaced with the formulated sub-equations for CO<sub>2</sub>, becomes a CO<sub>2</sub> accuracy equation and, for H<sub>2</sub>O, becomes an H<sub>2</sub>O accuracy equation. In the formulation, approximation is used for zero drift, gain drift, and sensitivity-to-CO<sub>2</sub>/H<sub>2</sub>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<sub>2</sub>-H<sub>2</sub>O accumulation is assumed to be minimized as insignificant under normal field maintenance (LI-COR Biosciences, 2021b; 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  $T_c$  linearly in proportion to the difference between  $T_a$  and  $T_c$  but 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 most likelihood estimation, is most needed by users.

In fact, the H<sub>2</sub>O accuracy as influenced by the linear trend of zero and gain drifts with the difference between  $T_a$  and  $T_c$  is more shadowed by the exponential trend of saturated H<sub>2</sub>O density with  $T_a$  (Fig. 4b). Similarly, the CO<sub>2</sub> accuracy as influenced by the linear trend of zero and gain drifts with this difference is dominated by the CO<sub>2</sub> density of the ecosystem background with  $T_a$ , particularly in the low temperature range. Ultimately, the assumed linear trend does not play a dominant role in the accuracy trends of CO<sub>2</sub> and H<sub>2</sub>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<sub>2</sub>/H<sub>2</sub>O uncertainty can be formally formulated as Eq. (20) or (12), but, if directly used, this  
670 formulation would add an additional variable to the CO<sub>2</sub>/H<sub>2</sub>O accuracy equation. Equation (12) would add H<sub>2</sub>O density ( $\rho_{H_2O}$ )  
to the CO<sub>2</sub> accuracy equation, and Eq. (20) would add CO<sub>2</sub> density ( $\rho_{CO_2}$ ) to the H<sub>2</sub>O accuracy equation. 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<sub>2</sub>/H<sub>2</sub>O uncertainty is known and, compared to the zero/gain drift as a  
major uncertainty (Table 1), this range is narrow (Table 1 and Eqs. 13 and 21). Therefore, the sensitivity-to-CO<sub>2</sub>/H<sub>2</sub>O  
675 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 at least in one order; however, it eliminates the need for  $\rho_{H_2O}$  in the  
CO<sub>2</sub> accuracy equation and for  $\rho_{CO_2}$  in the H<sub>2</sub>O accuracy equation, which makes the equations easily applicable.

Precision uncertainty is statistically formulated as Eq. (4) for CO<sub>2</sub> and Eq. (16) for H<sub>2</sub>O. This formulation is a  
common practice based on statistical methods (Hoel, 1984).

### 680 **7.1.3 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<sub>2</sub> accuracy magnitude is small in a range within one order (0.39 ~ 1.21  
mgCO<sub>2</sub> m<sup>-3</sup>, data for Fig. 2a), and so is H<sub>2</sub>O accuracy (0.04 ~ 0.10 gH<sub>2</sub>O m<sup>-3</sup>, data for Fig. 3a). In ecosystems, CO<sub>2</sub> is  
685 naturally high, as compared to its accuracy magnitude, and does not change much in terms of a magnitude order (e.g., no  
more than one order from 600 to 1,600 gH<sub>2</sub>O m<sup>-3</sup>, assumed in this study). However, unlike CO<sub>2</sub>, H<sub>2</sub>O naturally changes in its  
amount dramatically across at least three orders in magnitude (e.g., at 101.325 kPa, from 0.03 gH<sub>2</sub>O m<sup>-3</sup> when RH is 10% at  
-30 °C to 40 gH<sub>2</sub>O m<sup>-3</sup> when dew point temperature is 35 °C at the highest as reported by National Weather Service (2021);  
under drier conditions, the H<sub>2</sub>O amount could be even lower). Because, in ecosystems, CO<sub>2</sub> changes differently than H<sub>2</sub>O in  
690 amount across magnitude orders, the relative accuracy behaviors in CO<sub>2</sub> differ from H<sub>2</sub>O (Figs. 2b and 3b).

#### **7.1.3.1 CO<sub>2</sub> relative accuracy**

Because of the small CO<sub>2</sub> accuracy magnitude relative to the natural CO<sub>2</sub> amount in ecosystems, the CO<sub>2</sub> 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  
– 0.19% or an inequality of  $\leq 0.19\%$  can be specified as the CO<sub>2</sub> relative accuracy magnitude for field CO<sub>2</sub> measurements.  
695 Both range and inequality would be equivalently perceived by users to be a fair performance of OPEC systems. For  
simplicity, our study with the OPEC systems can be specified for their CO<sub>2</sub> relative accuracy to be  $\pm 0.19\%$ .

### 7.1.3.2 H<sub>2</sub>O relative accuracy

Although the H<sub>2</sub>O accuracy magnitude is also small, the “relatively” great change in natural air H<sub>2</sub>O across several magnitude orders in ecosystems results in a much wider range of the H<sub>2</sub>O relative accuracy magnitude, from 0.23% at maximum air moisture to 96% when RH is 20% at –30 °C (Fig. 3b and Sect. 5.4.2). H<sub>2</sub>O relative accuracy can be much greater under dry conditions at low  $T_a$  (e.g., 192% for air when RH is 10% at –30 °C). Accordingly, if the relative accuracy is used, either a range of 0.23 – 192% or an inequality of  $\leq 192\%$  can be specified as the H<sub>2</sub>O relative accuracy magnitude for field H<sub>2</sub>O measurements. Either 0.23 – 192% or  $\leq 192\%$  could be perceived by users intrinsically as poor measurement performance of the infrared analyzers, although either specification is conditionally right for fair H<sub>2</sub>O measurement.

Apparently, the relative accuracy for H<sub>2</sub>O measurements in ecosystems is not intrinsically interpretable by users to correctly perceive the performance of OPEC systems. Instead, if H<sub>2</sub>O relative accuracy is unconditionally specified just in an inequality of  $\leq 192\%$ , it could easily mislead users to wrongly assess the performance of OPEC systems as unacceptable for H<sub>2</sub>O measurements, although this performance of OPEC systems is fair for air when RH is 10% at –30 °C. Therefore, H<sub>2</sub>O relative accuracy is not recommended to be used for specification of infrared analyzers for H<sub>2</sub>O measurement performance. If this descriptor is used, the H<sub>2</sub>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, 2021)) under normal  $P$  of 101.325 kPa (Wright et al., 2003). For our study case, under such a standard condition, the H<sub>2</sub>O relative accuracy can be specified within  $\pm 0.18\%$  after manufacturing calibration (data for Fig. 3b).

## 8 Conclusions

The accuracy of field CO<sub>2</sub>/H<sub>2</sub>O measurements from OPEC systems by the infrared analyzers can be defined as a maximum range of composite measurement uncertainty sourced from component uncertainties: zero drift, gain drift, sensitivity-to-CO<sub>2</sub>/H<sub>2</sub>O, and precision variability, all of which are included in the system specifications (Table 1). The specified uncertainties interactionally or independently contribute to the overall uncertainty. Fortunately, the interactions between component uncertainties in each pair is three orders smaller than either component individually (Appendix A). Therefore, these specified uncertainties can be simply added as the accuracy range in a general CO<sub>2</sub>/H<sub>2</sub>O accuracy model for 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<sub>2</sub> accuracy equation (14) and the H<sub>2</sub>O accuracy equation (22), both of which are computable to evaluate corresponding CO<sub>2</sub> and H<sub>2</sub>O accuracies. For the OPEC systems in this study over their operational range in  $T_a$  at the standard  $P$  of 101.325 kPa (Figs. 2 and 3 and Table 2), the CO<sub>2</sub> accuracy can be specified as  $\pm 1.21 \text{ mgCO}_2 \text{ m}^{-3}$  (relatively within  $\pm 0.19\%$ , Fig. 2) and H<sub>2</sub>O accuracy as  $\pm 0.10 \text{ gH}_2\text{O m}^{-3}$  (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 error/uncertainty analyses in CO<sub>2</sub> and H<sub>2</sub>O data applications (see Sect. 6.1), but they also may be used as a rationale to assess and guide field maintenance on infrared

analyzers. Combining Eq. (14) as shown in Fig. 2a with Eqs. (7) and (11) as shown in Fig. 4a guides users to adjust the CO<sub>2</sub> zero and gain drifts, through the corresponding zero and span procedures, near the middle of the  $T_a$  range within which the analyzer runs. As assessed on atmospheric background, the procedures can narrow the maximum CO<sub>2</sub> accuracy range by 40%, from  $\pm 1.21$  to  $\pm 0.72$  mgCO<sub>2</sub> m<sup>-3</sup>, and thereby greatly improve the CO<sub>2</sub> measurement accuracies with these regular CO<sub>2</sub> zero and span procedures.

Equation (22) as shown in Fig. 3a, plus Eqs. (18) and (19) as shown in Fig. 4b, present users with a rationale to adjust the H<sub>2</sub>O zero drift of analyzers in the same technique as for CO<sub>2</sub>, but the H<sub>2</sub>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 needs no further concern (see the left portion below 0 °C in Fig. 4b). In a  $T_a$  range above 5 °C, the maximum H<sub>2</sub>O accuracy range of  $\pm 0.10$  gH<sub>2</sub>O m<sup>-3</sup> can be narrowed by 30% to  $\pm 0.07$  gH<sub>2</sub>O m<sup>-3</sup> if both H<sub>2</sub>O zero and span procedures are performed as necessary. In a  $T_a$  range below 5 °C, the H<sub>2</sub>O zero procedure alone can narrow the maximum H<sub>2</sub>O accuracy range of  $\pm 0.076$  gH<sub>2</sub>O m<sup>-3</sup> by 22%, to  $\pm 0.051$  gH<sub>2</sub>O m<sup>-3</sup>. Under cold environmental conditions, the H<sub>2</sub>O span procedure is found to be unnecessary (Fig. 5), and the H<sub>2</sub>O zero procedure is proposed as the only, and prominently efficient, option to minimize H<sub>2</sub>O measurement uncertainty in OPEC systems. This procedure plays the same role under dry conditions. Under cold and/or dry environments, the zero procedure for CO<sub>2</sub> and H<sub>2</sub>O together would be a practical and efficient option to not only warrant, but also to improve, measurement accuracy. In a cold environment, adjusting the H<sub>2</sub>O gain drift is impractical because of a dew point generator that fails to generate standard H<sub>2</sub>O gas near freezing conditions. This lack of necessity relieves user worry with regard to H<sub>2</sub>O measurement uncertainty from the H<sub>2</sub>O gain drift under such environments where the H<sub>2</sub>O span procedure is not operational.

Additionally, as a specification descriptor for OPEC systems used in ecosystems, relative accuracy is applicable for CO<sub>2</sub> instead of H<sub>2</sub>O measurements because, in ecosystems, the CO<sub>2</sub> relative accuracy varies slightly within a magnitude order, and the H<sub>2</sub>O relative accuracy varies dramatically across several magnitude orders. A small range in the CO<sub>2</sub> relative accuracy can be perceived intuitively by users as normal. In contrast, without specifying the condition of air moisture, a large range in H<sub>2</sub>O relative accuracy under cold and/or dry conditions (e.g., 100%) can easily mislead users to automatically transfer this relative accuracy onto very poor H<sub>2</sub>O measurements, although, under such conditions, it is the best that modern technology can do in the field. The authors suggest to conditionally define H<sub>2</sub>O relative accuracy at 35 °C dew point (i.e., 39.66 gH<sub>2</sub>O m<sup>-3</sup> at 101.352 kPa). Ultimately, this study provides our logic to the flux community in specifying the accuracy of CO<sub>2</sub>-H<sub>2</sub>O measurement from OPEC systems by infrared analyzers.

## Appendix A: Derivation of accuracy model for infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers

As defined in the Introduction, the measurement accuracy of infrared CO<sub>2</sub>-H<sub>2</sub>O analyzers is a range of the difference between the true  $\alpha$  density ( $\rho_{\alpha T}$ , where  $\alpha$  can be either H<sub>2</sub>O or CO<sub>2</sub>) and measured  $\alpha$  density ( $\rho_a$ ) by the analyzer. The difference is denoted by  $\Delta\rho_a$ , given by Eq. (1) in Sect. 3. Analyzer performance uncertainties contribute to this range, as

specified in the four descriptors: zero drift, gain drift, cross-sensitivity, and precision (LI-COR Biosciences, 2021b; Campbell Scientific Inc., 2021b).

According to the definitions in Sect. 2, zero drift uncertainty ( $\Delta\rho_\alpha^z$ ) is independent of  $\rho_{aT}$  value and gain trend related to analyzer response; so, too, is cross-sensitivity uncertainty ( $\Delta\rho_\alpha^s$ ), which depends upon the amount of background H<sub>2</sub>O in the measured air if  $\alpha$  is CO<sub>2</sub>, and upon the amount of background CO<sub>2</sub> in the measured air if  $\alpha$  is H<sub>2</sub>O. In the case that both gain drift and precision uncertainties are zero,  $\Delta\rho_\alpha^z$  and  $\Delta\rho_\alpha^s$  are simply additive to any true value as a measured value, including zero drift and cross-sensitivity uncertainties ( $\rho_{\alpha-zs}$ )

$$\rho_{\alpha-zs} = \rho_{aT} + \Delta\rho_\alpha^z + \Delta\rho_\alpha^s, \quad (\text{A1})$$

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  $\rho_{\alpha-zs}$  is a linear factor for this gain drift (see the cells in gain-drift row and value columns in Table 1) that is added to  $\rho_{\alpha-zs}$  as a measured value additionally including gain drift uncertainty ( $\rho_{\alpha-zsg}$ , where subscript  $g$  indicates gain drift uncertainty included in the measured value), given by

$$\rho_{\alpha-zsg} = \rho_{\alpha-zs} + \delta_{\alpha-g}\rho_{\alpha-zs}, \quad (\text{A2})$$

where  $\delta_{\alpha-g}$  is gain drift percentage ( $\delta_{CO_2-g} = 0.10\%$  and  $\delta_{H_2O-g} = 0.30\%$ , Table 1). Substituting  $\rho_{\alpha-zs}$  in this equation with Eq. (A1) leads to

$$\rho_{\alpha-zsg} = \rho_{aT} + \Delta\rho_\alpha^z + \Delta\rho_\alpha^s + \delta_{\alpha-g}\rho_{aT} + \delta_{\alpha-g}\Delta\rho_\alpha^z + \delta_{\alpha-g}\Delta\rho_\alpha^s. \quad (\text{A3})$$

In this equation,  $\delta_{\alpha-g}\Delta\rho_\alpha^z$  is the zero-gain interaction, and  $\delta_{\alpha-g}\Delta\rho_\alpha^s$  is the sensitivity-gain interaction. In magnitude, the former is three orders smaller than either zero drift uncertainty ( $\Delta\rho_\alpha^z$ ) or gain drift uncertainty ( $\delta_{\alpha-g}\rho_{aT}$ ). The sensitivity-gain interaction is three orders smaller than either cross-sensitivity uncertainty ( $\Delta\rho_\alpha^s$ ) 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:

$$\begin{aligned} \rho_{\alpha-zsg} &\approx \rho_{aT} + \Delta\rho_\alpha^z + \delta_{\alpha-g}\rho_{aT} + \Delta\rho_\alpha^s \\ &= \rho_{aT} + \Delta\rho_\alpha^z + \Delta\rho_\alpha^g + \Delta\rho_\alpha^s, \end{aligned} \quad (\text{A4})$$

where  $\Delta\rho_\alpha^g$  is gain drift uncertainty. Any measured value has random error (i.e., precision uncertainty) independent of  $\rho_{aT}$  in value (ISO, 2012). Therefore,  $\rho_{\alpha-zsg}$  plus precision uncertainty ( $\Delta\rho_\alpha^p$ ) is the measured value including all uncertainties ( $\rho_a$ ), given by

$$\rho_a = \rho_{\alpha-zsg} + \Delta\rho_\alpha^p. \quad (\text{A5})$$

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

$$\rho_a - \rho_{aT} = \Delta\rho_a^z + \Delta\rho_a^g + \Delta\rho_a^s + \Delta\rho_a^p. \quad (\text{A6})$$

790 This equation holds

$$\Delta\rho_a \leq |\Delta\rho_a^z| + |\Delta\rho_a^g| + |\Delta\rho_a^s| + |\Delta\rho_a^p|. \quad (\text{A7})$$

The range of the right side of this equation is wider than the measurement uncertainty from all measurement uncertainty sources and the difference of  $\rho_a$  minus  $\rho_{aT}$  (i.e.,  $\Delta\rho_a$ ). Using this range, the measurement accuracy is defined in Model (2) in Sect. 3.

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

Given ambient air temperature ( $T_a$  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  $\text{gH}_2\text{O m}^{-3}$ ) for moist air, given through the Clausius–Clapeyron equation (Sonntag, 1990; Wallace and Hobbs, 2006)

$$\rho_s(T_a, P) = \frac{0.6112f(P)}{R_v(273.15 + T_a)} \begin{cases} \exp\left(\frac{17.62T_a}{T_a + 243.12}\right) & T_a \geq 0 \\ \exp\left(\frac{22.46T_a}{T_a + 272.62}\right) & T_a < 0 \end{cases}, \quad (\text{B1})$$

800 where  $R_v$  is the gas constant for water vapor ( $4.61495 \times 10^{-4} \text{ kPa m}^3 \text{ K}^{-1} \text{ gH}_2\text{O}^{-1}$ ), and  $f(P)$  is an enhancement factor for moist air, being a function of  $P$ :  $f(P) = 1.0016 + 3.15 \times 10^{-5} P - 0.0074 P^{-1}$ . At relative humidity (RH in %), the water vapor density [ $\rho_{\text{H}_2\text{O}}^{\text{RH}}(T_a, P)$  in  $\text{gH}_2\text{O m}^{-3}$ ] is

$$\rho_{\text{H}_2\text{O}}^{\text{RH}}(T_a, P) = \text{RH} \rho_s(T_a, P). \quad (\text{B2})$$

This equation, along with Eq. (B1), is used to calculate  $\rho_{\text{H}_2\text{O}}^{\text{RH}}$  used in Fig. 3 in Sect. 5 and Figs. 4b and 5 in Sect. 6.3.

## 805 **Appendix C: The relationship of measured to true covariance to of vertical wind speed with CO<sub>2</sub>, H<sub>2</sub>O, and air temperature**

For open-path eddy-covariance systems, the computation of CO<sub>2</sub>/H<sub>2</sub>O flux between ecosystems and the atmosphere starts from covariance of 3-D wind with a CO<sub>2</sub>/H<sub>2</sub>O density. Same as in Eqs. (1) and (2),  $\alpha$  is used as a subscript of  $\rho$  to represent either CO<sub>2</sub> or H<sub>2</sub>O and subscript  $T$  is used to indicates “true”. According to Eq. (1), a measured  $\alpha$  density ( $\rho_a$ ) can be

810 expressed as

$$\rho_a = \rho_{aT} + \Delta\rho_a, \quad (\text{C1})$$

where  $\rho_{aT}$  denotes true  $\alpha$  density and  $\Delta\rho_a$  is measurement uncertainty of  $\rho_a$ . The covariance of vertical wind speed ( $w$ ) with measured  $\alpha$  density is given by:

$$\overline{w' \rho'_\alpha} = \frac{1}{n} \sum_{i=1}^n (w_i - \bar{w})(\rho_\alpha - \bar{\rho}_\alpha), \quad (\text{C2})$$

815 where  $n$  is the sample number over an averaging interval (e.g., 36,000 over an hour interval if  $w$  and  $\rho_\alpha$  are measured at 10 Hz), the overbar is an averaging operator, and prime denotes the fluctuation of a variable away from its mean (e.g.,  $w'_i = w_i - \bar{w}$ ). Without considering the measurement error of  $w$  for this study topic, submitting Eq. (C1) into (C2) leads to

$$\begin{aligned} \overline{w' \rho'_\alpha} &= \frac{1}{n} \sum_{i=1}^n (w_i - \bar{w}) \left[ \rho_{\alpha Ti} + \Delta \rho_{\alpha i} - \overline{(\rho_{\alpha Ti} + \Delta \rho_{\alpha i})} \right] \\ &= \frac{1}{n} \sum_{i=1}^n (w_i - \bar{w})(\rho_{\alpha Ti} - \bar{\rho}_{\alpha T}) + \frac{1}{n} \sum_{i=1}^n (w_i - \bar{w})(\Delta \rho_{\alpha i} - \Delta \bar{\rho}_\alpha) \end{aligned} \quad (\text{C3})$$

Over an hour interval, the systematic error components inside terms  $\Delta \rho_{\alpha i}$  and  $\Delta \bar{\rho}_\alpha$  are not only constant, but also equal. Accordingly, the systematic errors inside the term  $\Delta \rho_{\alpha i} - \Delta \bar{\rho}_\alpha$  are cancelled out (Richardson et al., 2012). In essence, this term is a random error whose distribution generally is assumed to be normal. As such, the expected mean of  $\Delta \rho_{\alpha i} - \Delta \bar{\rho}_\alpha$  is zero (Hoel, 1984). The correlation of  $w$  with a random variable with an expected zero mean tends to be zero, particularly for a large sample number of 36,000 under discussion (Snedecor and Cochran, 1989). Accordingly, the second term in the second line of Eq. (C3) is zero. Therefore, the covariance of  $w$  with measured  $\alpha$  density is equal to the covariance of  $w$  with true  $\alpha$  density, given by

$$\overline{w' \rho'_\alpha} = \overline{w' \rho'_{\alpha T}}. \quad (\text{C4})$$

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 to find the 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 can be expressed as  $\overline{w' \rho'_{\alpha l}}$ , where subscript  $l$  is the index for a lag number. If  $l = 0$ ,  $w_i$  and  $\rho_{\alpha 0i}$  were measured at the same time. If  $l = -1$ ,  $w_i$  was measured one measurement interval (i.e., 100 ms for 10-Hz measurements) later than  $\rho_{\alpha(-1)i}$  whereas  $w_i$  was measured one measurement interval earlier than  $\rho_{\alpha 1i}$  if  $l = 1$ . 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 values for  $\overline{w' \rho'_{\alpha l}}$  is  $2k+1$ . Using the same approach to Eq. (C4),  $\overline{w' \rho'_{\alpha l}} = \overline{w' \rho'_{\alpha T}}$  can be proved.

The lagged covariance values for  $\overline{u' \rho'_{\alpha l}}$  and  $\overline{v' \rho'_{\alpha l}}$  ( $l$  is  $-k, -k+1, \dots, 0, \dots, k$ ) 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  $\overline{u' \rho_{\alpha l}} = \overline{u' \rho_{\alpha T l}}$  and are also can be proved in the same way for Eq. (C4). Given the rotation angles from  $\overline{u}, \overline{v}, \overline{w}, \overline{u^2}, \overline{v^2}, \overline{v^2}, \overline{u'v}, \overline{u'w}$ , and  $\overline{v'w}$  (Tanner and Thurtell, 1960), each set of  $\overline{u' \rho_{\alpha l}}, \overline{v' \rho_{\alpha l}}$ , and  $\overline{w' \rho_{\alpha l}}$  are rotated to be

840  $\overline{(u' \rho_{\alpha l})_r}, \overline{(v' \rho_{\alpha l})_r}$ , and  $\overline{(w' \rho_{\alpha l})_r}$ , respectively. In the rotation process,  $\rho_{\alpha}$  is not additionally involved. Because  $\rho_{\alpha}$  inside the covariance is a scalar rather than vector variable, the rotation would not be influenced by  $\overline{\rho_{\alpha l}}$  and  $\overline{\rho_{\alpha l}^2}$  as by the three means and three variance values of 3-D wind components (Tanner and Thurtell, 1960). Therefore, the covariance values rotated from  $\overline{u' \rho_{\alpha l}}, \overline{v' \rho_{\alpha l}}$ , and  $\overline{w' \rho_{\alpha l}}$  are correspondingly equal to those rotated from  $\overline{u' \rho_{\alpha T l}}, \overline{v' \rho_{\alpha T l}}$ , and  $\overline{w' \rho_{\alpha T l}}$ . Accordingly,

$$\overline{(w' \rho_{\alpha l})_r} = \overline{(w' \rho_{\alpha T l})_r}. \quad (\text{C5})$$

845 Therefore, the maximum covariance in magnitude among  $\overline{(w' \rho_{\alpha l})_r}$  ( $l$  from  $-k$  to  $k$ ) [ $\overline{(w' \rho_{\alpha})_{mm}}$ ] is equal to the maximum in magnitude among  $\overline{(w' \rho_{\alpha T l})_r}$  [ $\overline{(w' \rho_{\alpha T})_{mm}}$ ] (Moncrieff et al., 1997; Ibrom et al., 2007), given by

$$\overline{(w' \rho_{\alpha})_{mm}} = \overline{(w' \rho_{\alpha T})_{mm}} \quad (\text{C6})$$

Multiplying the frequency correction factor ( $f_c$ ) on the both sides of this equation to correct the low- and high-frequency loss (Moore, 1986; Massman, 2000; van Dijk, 2002) leads to

850  $f_c \overline{(w' \rho_{\alpha})_{mm}} = f_c \overline{(w' \rho_{\alpha T})_{mm}}. \quad (\text{C7})$

$f_c$  is integrated from the cospectrum of  $w$  with  $T_a$  (air temperature, as a proxy of  $\rho_{\alpha T}$  for spectrum representation) and the transfer functions of high-frequency loss for  $w, \rho_{\alpha}$  (Moore, 1986; van Dijk, 2002), and low-frequency loss for averaging  $w' \rho_{\alpha}$  (Massman, 2000). Over the integration,  $\rho_{\alpha}$  is not involved through cospectrum and transfer functions, either. If the left-side term of Eq. (C7) is expressed as  $\overline{(w' \rho_{\alpha})_{rmf}}$  and the right-side one as  $\overline{(w' \rho_{\alpha T})_{rmf}}$ , Eq. (C7) leads to

855  $\overline{(w' \rho_{\alpha})_{rmf}} = \overline{(w' \rho_{\alpha T})_{rmf}}, \quad (\text{C8})$

where subscript  $rmf$  indicates the covariance was corrected through coordinate rotations ( $r$ ), lag maximization ( $m$ ), and low- and high-frequency ( $f$ ) corrections. Equation (C8) shows the covariance of  $w$  with measured  $\rho_{\alpha}$  is equal to its counterpart with true  $\rho_{\alpha}$  even after these corrections before used to calculate the  $\alpha$  flux through WPL correction (Webb et al., 1982).

For the covariance of  $w$  with  $T_a$ , the same conclusion can be derived, given by

860  $\overline{(w' T_a)_{rmf}} = \overline{(w' T_{aT})_{rmf}} \quad (\text{C9})$



Assume  $w$  to be true value for this study topic, through WPL correction,  $\overline{(w'\rho_\alpha)_{mf}}$  and  $\overline{(w'T_\alpha)_{mf}}$  can be used to derive an analytical equation for  $\alpha$  flux from  $\rho_\alpha$  with an error as ranged by its accuracy and  $T_\alpha$  with an errors whereas  $\overline{(w'\rho_{\alpha T})_{mf}}$  and  $\overline{(w'T_{\alpha T})_{mf}}$  can be used to derive an analytical equation for  $\alpha$  flux from  $\rho_{\alpha T}$  and  $T_{\alpha T}$ , both of which theoretically do not include errors. The comparison of both analytical equations can demonstrate the partial effects of  $\Delta\rho_\alpha$  on uncertainty of hourly  $\alpha$  flux (see Sect. 6.2).

### Author Contributions

XZ, BY, TG, and NZ contributed equally to this this work; YL, FY, and YA discussed the points of this study topic and made comments on the manuscript; JZ led the team.

### Competing interest

XZ, BY, and YL have affiliation with Campbell Scientific Incorporation, which is the manufacturer of the example model EC150 of infrared CO<sub>2</sub>–H<sub>2</sub>O analyzers. The authors declare that they have no conflict of interest.

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