IAE INSTITUTE OF APPLIED ECOLOGY, CHINESE ACADEMY OF SCIENCES 72 Wenhua Road, Shenyang, Liaoning, 110016, China

May 30, 2022

RE: Final author response to referees' comments on GI-2022-1

Dr. Salvatore Grimaldi Dept. for Innovation in Bio., Agro-food, & For. Systems University of Tuscia, Viterbo, Italy

Dear Dr. Grimaldi,

Thank you for allowing us to submit a revised version of our manuscript, "Accuracies of field CO₂-H₂O measurements from open-path eddy-covariance systems: Assessment based on atmospheric physics and biological environment," for further consideration of publication in *Geoscientific Instrumentation, Methods and Data Systems (GI)*. Through the interactive discussion, two journal referees reviewed our manuscript and, as indicated by the metrics on the website <u>https://gi.copernicus.org/preprints/gi-2022-1/#discussion</u>, 612 international public reviewers viewed and/or downloaded the preprinting of this manuscript.

Both referees found this manuscript to be innovative in different aspects. Referee #1 commented, "The analysis methodology based on atmospheric physics and ecosystem background is truly innovative." Referee #2 commented, "This manuscript is innovative in trying to quantify the overall uncertainties in the measurements of CO₂ and H₂O amounts by open-path eddy-covariance (OPEC) gas analysers due to their different sources." Also, as stated by Referee #1, "This manuscript along with Zhou et al. (2021) is the completion of systematic study on the overall accuracy of CO₂/H₂O measurements from eddy-covariance systems." We particularly appreciated Referee #2's strong positive general comments and detailed constructive suggestions on how to substantially improve this manuscript. We appreciate the two anonymous journal referees for their feedback, and our appreciation to both was added to the acknowledgement.

The authors carefully discussed every comment from the two journal referees for this revision. Our discussions and proposed revisions in response to the corresponding comments are given below.

The line numbers used below correlate with manuscript GI-2022-1 instead of GI-2022-1R.

We appreciate your favorable consideration for publication of this manuscript in GI.

Sincerely,

Ning Zheng, Ph.D., Application Scientist Eddy-Covariance Flux Instrumentation

Response to Referees' comments on "Accuracies of field CO₂-H₂O measurements from open-path eddy-covariance systems: Assessment based on atmospheric physics and biological environment"

X.H. Zhou, B. Yang, T. Gao, Ning Zheng, Yanlei, Li, Fengyuan Yu, T. Awada, J.J. Zhu <u>https://doi.org/10.5194/gi-2022-1</u>

Response to Referee #1

(https://doi.org/10/5194/gi-2022-1-RC1 and -RC2)

General comments

This study focuses on a practical subject needed to quantify the overall accuracy of CO₂/H₂O measurements from open-path eddy-covariance (OPEC) systems. The OPEC is more popular than CPEC because of, for example, their lower power consumption and maintain demanding, in the flux community. While I am analyzing my data, I always concern the overall accuracy in CO₂ measurements from my infrared gas analyzers in OPEC systems, but the method how to estimate the overall accuracy were unavailable from published literature. Indeed, this manuscript along with Zhou et al (2021) is the completion of systematic study on the overall accuracy of CO₂/H₂O measurements from EC systems. What is estimable is that the authors showed the accuracies of CO₂/H₂O densities based on biologically meaningful data in the field and solid physical principles. Clearly, this study provided valuable results for scientists like me to reference. The analysis methodology based on atmospheric physics and ecosystem background is truly innovative and the equation development is logical in theory and practical in applications. Although the authors only used an old version of OPEC, equations (14) and (22) were easily used to calculate the accuracies of CO₂/H₂O densities for other types of open-path analyzers, e.g., IRGASON and LI-COR 7500 series, having potentials in applications to analyzers for other gas species like CH₄ and N₂O in the areas of geosciences. Additionally, the structure was well organized and the language were also very well written. Therefore, I would highly recommend this manuscript to be accepted for publication on Geoscientific Instrumentation, Methods and Data Systems after a minor revision.

<u>Author response</u>

We sincerely thank Referee #1 for his/her recommendation for publication of this manuscript, his/her comments on our approach based on atmospheric physics and the biological environment as innovative in estimating the overall accuracies of CO_2 -H₂O measurements from open-path eddy-covariance (OPEC) gas analyzers, and his/her awareness of this manuscript as the completion of systematic studies on the overall accuracy of CO_2 -H₂O measurements from eddy-covariance gas analyzers.

Major comments

I have two open-path analyzers, i.e., EC150 and LI-COR 7500. In practice, when I perform a zero calibration, I always found a positive zero drift about 10 μ mol mol⁻¹ for LI-COR 7500 at ambient temperature, slightly higher in the unit of mg CO₂ m⁻³ and much higher than the upper of the values in the manuscript, but a much smaller accuracy due to gain drift when tubing the CO₂ span gas of 500- μ mol mol⁻¹ after a zeroing operation. I speculate that this was caused a non-negligible housing CO₂/H₂O accumulation, although the chemicals in the internal cell needs no replacement of new ones, i.e., after a zero calibration the analyzer works well for months. This is

the same for H_2O density. Therefore, in practice, I recommend the author give a short discussion of the possibility of field drift of zero and gain using the big data of analyzer-supplier, for example, that from EC150 in the lab of CSI, in the 6.3 section. These data may be helpful for providing suggestions for new users.

Author response

Yes, an individual infrared CO₂–H₂O gas analyzer may behave differently in the field than in the lab due to various reasons. As Referee #2 commented, one of the more important strengths in this study is the use of sensor specifications in determining the range of uncertainties. Instead of using field data from individual infrared analyzers, our assessment is based on official manufacturer specifications for a given model of analyzers. The validity of data from individual analyzers in the field is unsure because no benchmark data are available to assess the field data, which is why we assess the overall accuracies for field CO_2 –H₂O data using sensor specifications based on atmospheric physics and the ecological background. This approach is recognized by Referee #2 as "a valid approach to visualize the uncertainty in a straightforward way."

Minor comments

1. Title: " CO_2-H_2O " (and in the text). I understand the authors wanted to identify both gas types using "-" from one of the two gas types using "/". In my opinion, however, " CO_2/H_2O " may be better, just the same as they are in the profile system. The same for other parts of the manuscript.

<u>Author response</u>

We also preferred "CO₂/H₂O," but that designation is isolating, technically meaning "CO₂ or H₂O." Alternatively, "CO₂–H₂O" is inclusive, meaning "CO₂ and H₂O." Based on our experience, we have learned that "CO₂–H₂O" is the editorial preference of Copernicus Publications (the publisher for *GI*) for this expression.

2. Line 24: For a background concentration of atmospheric CO₂?

Author response

In our interactive discussion, we misunderstood this comment. Referee #1 clarified this comment in <u>http://doi.org.10.5194/gi-2022-1-RC2</u>. Based on that clarification, we adopted this comment.

Author proposed revision

Line 24: "In an atmospheric CO₂ background" was replaced with "For a background concentration of atmospheric CO₂."

3. Lines 27-29: I recommend deleting "Under freezing conditions, an H_2O span is both impractical and unnecessary, but the zero procedure becomes imperative to minimize H_2O measurement uncertainty.", because there was some overlap of this sentence with the next one "In cold/dry conditions, the zero procedure for H_2O , along with CO_2 , is an operational and efficient option to ensure and improve H_2O accuracy".

Author response

Reminded by comment #2 in http://doi.org.10.5194/gi-2022-1-RC2, we reread the two sentences from lines 27 to 29. Both sentences read awkwardly, in large part due to the double mentions of the role of the zero procedure. We revised the two sentences.

Author proposed revision

Lines 27–30, the two relevant sentences are revised to be:

"The H₂O span procedure is impractical under freezing conditions and unnecessary under cold/dry conditions. However, the zero procedure for H₂O, along with CO₂, is imperative as an operational and efficient option under these conditions to minimize H₂O measurement uncertainty."

4. Line 36: delete "fluctuations", for consistency with "3-D wind and sonic temperature".

<u>Author response</u> This word can be removed. It may be redundant, although the word can reflect the nature of turbulence measurements.

<u>Author proposed revision</u> Line 36: The word "fluctuations" was removed.

5. Line 75: "CO₂/H₂O molar mixing ratio" or "CO₂/H₂O dry molar fraction" is better.

Author response

If " CO_2/H_2O molar mixing ratio" is used here, then " CO_2/H_2O molar or mass density" should be used as well. That wording becomes more cumbersome than clear. For simplicity inside parentheses, " CO_2/H_2O mixing ratio vs. CO_2/H_2O density" is sufficient.

6. Line 108: "in practice"?

Author response

"In practice" can be used to replace "in applications."

Author proposed revision

Line 108:

The word "applications" was replaced with "practice."

7. Line 170: Possibly, use "the analyzer often gradually reports that this zero ρCO_2 value, when exposed to a zero gas, is different from zero".

<u>Author response</u>

This recommendation is adopted with slight revision.

Author proposed revision

Lines 169–170:

"However, during use of the analyzer in measurement environments that are different from calibration conditions, the analyzer often reports this zero ρ_{CO2} value, while exposed to zero air, gradually away from zero and possibly beyond $\pm \Delta \rho_{co_2}^p$, which is known as CO₂ zero drift."

8. Line 190: housing CO_2/H_2O accumulation.

Line 209: housing CO₂/H₂O accumulation.

9. Line 224: remove "calibration/", "span" is clear enough.

Author response

<u>Author response</u> Addressed in response to comment #1, above.

In this manuscript, "calibration" involves the full process of constructing the H_2O and CO_2 working equations in the production process; "span" means a user operation to adjust H_2O/CO_2 span coefficients. We clarified this distinction in the manuscript (see lines 160–63).

10. Lines 233-234: "that is smaller in magnitude by at least two orders" may be more concise.

<u>Author response</u> Yes, the word "reasonably" ahead of "smaller" can be removed.

Author proposed revision Line 233:

The word "reasonably" was removed.

11. Line 283: "microbial respiration" is more commonly used.

<u>Author response</u>

The word "microorganism" can be replaced with "microbial."

Author proposed revision

Line 283:

The word "microbial" replaced "microorganism."

12. Figure 2: For simplicity, I recommend using only absolute value of accuracy and relative accuracy.

Author response

Accuracy is defined as a range. The use of just one positive value to represent this range may mislead readers.

13. Table 2: These numbers are very detailed, and thus are somewhat a repeat of Figures 2 and 3. I recommend only show the temperature points in a coarse resolution, for example, -30, -20, -10, 0, 10, 20, 30, 40, 50 °C.

<u>Author response</u> We adopted this comment.

<u>Author proposed revision</u> Table 2: The rows for the ambient temperatures of -22, -18, -12, -7, -2, 2, 7, 13, 18, 22, 28, and 32 °C were removed.

Response to Referee #2

(https://doi.org/10/5194/gi-2022-1-RC3)

General comments

The manuscript is innovative in trying to quantify the overall uncertainties in the measurements of CO_2 and H_2O amounts by Open Path Eddy Covariance (OPEC) gas analysers due to their different sources. The aim is pursued by means of a Campbell Scientific IRGASON, and then generalised. A simple model is developed to combine the different sources of errors, and the resulting uncertainties are plotted under different conditions of temperature and gas concentrations. In addition, some applications of the results are reported, together with some suggestions for the users during field calibration. This preprint follows the same approach of a

paper published last year by the same main Author relative to the Closed Path Eddy Covariance (CPEC) sensors.

The study has some points of strength and some points of weakness. Among the strenghts it is the fact that the study addresses relevant scientific questions within the scope of GI, using in part novel ideas, and using a proper language. One of the more important strenghts is that it uses the specs of the sensor to define its uncertainties, and it defines the uncertainty in terms of range: the worst case scenario is depicted for each source of error as the limits of the range, and then combined with the others. This is a valid approach to visualising the uncertainty in a straightforward way.

The more important weaknesses are in my opinion: #1. the poor link with the eddy covariance method, despite this is mentioned since the beginning; #2. the generalisation from the IRGASON/EC150 to all the Open Path sensors is not robust enough; #3. Applications and calibration suggestions are only partly relevant; #4. more references are needed, as the most cited are not peer-reviewed papers but sensors manual; #5. the discussion section is more dedicated to other things (recap of what done, applications), but the real discussion is limited; #6. conclusions should be strenghten as well.

I'll recall these points in the comments below when relevant.

Author response

We sincerely appreciate Referee #2's strong positive general comments above and his/her detailed constructive suggestions below. The suggestions guided us in addressing the related issues more clearly and eventually led to a substantially improved manuscript. We also appreciate his/her high expectation.

The specific comments from Referee #2 are reorganized into two sections:

- A. Suggestions to fix the major issues pointed out in General Comments.
- B. Technical and editorial comments to improve the manuscript expressions.

Section A is organized into six sub-sections corresponding to the six major issues. In each sub-section, all comments related to this major issue are addressed and the revisons proposed.

Suggestions to fix the major issues pointed out in General Comments

#1. The EC method includes a very long chain of steps from field measurements to calculation of the fluxes. In this chain, the specs of the sensor are in general considered less important in terms of final uncertainties. Also, the uncertainty are more relevant to the EC method in terms of fluxes (as the result of covariance between sonic and IRGA signals), not concentrations: this is clearly out of the scope of the manuscript, but should be mentioned and maybe discussed a bit. Also, an OPEC system is made of two main sensors: the IRGA and the sonic. But the latter is almost not considered in the study: this could be reconsidered, or at least the reasons for excluding this sensor should be given. A possible alternative could be to reconsider the link with EC: is that really needed? The study may focus on the Open path IRGA (so the EC150, not the IRGASON), just mentioning that it is often used for eddy covariance measurements, but clearly state since the beginning that the study will not focus on EC. (please note this will clearly impact the title as well).

Author response

The overall accuracies of CO₂ and H₂O density measurements by infrared gas analyzers (IRGAs) are often questioned by field scientists in their data observations and requested by scientists in their purchasing processes. These accuracies are also needed for field auto CO₂ and H₂O zero/span procedures to instrumentally adjust the drifts of IRGA in CO₂ and H₂O zero and/or gain drifts (e.g., EasyFlux series, Campbell Scientific Inc., UT, US). In these procedures, the overall accuracies are used to judge the degree of the drifts. Although flux uncertainties are related to several factors (Richardson et al., 2012), the measurement accuracy in CO₂/H₂O density is a fundamental question of interest to scientists (Fratini et al., 2014). Because the overall accuracy would have multiple applications, we limited our scope in this study to be within the model, estimation, and assessment of the overall accuracy of the CO₂/H₂O density measured by IRGAs and used for CO₂ and H₂O fluxes. As commented above, linking this study to the fluxes is clearly out of study scope. However, the IRGA is a major component in open-path eddy-covariance (OPEC) systems for CO₂ and H₂O fluxes. Linking the context of this manuscript to related flux topics would make this manuscript more significant. To this end, in our revision, we:

- a. Followed the comments below to link manuscript contexts to flux topics.
- b. Checked the manuscript throughout for these linking opportunities.
- c. Discussed how the overall accuracies in CO₂ and H₂O density are analytically related to the flux errors in computations (see Appendix C and section 6.2).

1.1. Lines 13-14: as the IRGAs can be used for several scopes, if the link with the EC is maintained it is preferrable to mention "fluxes" (#1).

Line 14: As the focus of the manuscript seems to be only the IRGA, and not the sonic, this should be clearly stated (#1).

Author response

Yes, this manuscript focuses on the accuracies of field CO_2 -H₂O data measured by IRGAs used in OPEC systems. The first sentence specifies this link.

Author proposed revision

Lines 14–15:

"Ecosystem CO_2 -H₂O data measured by infrared gas analyzers in open-path eddycovariance (OPEC) systems have numerous applications, such as estimations of CO_2 and H₂O fluxes in the atmospheric boundary layer. To assess the applicability of these estimations, data uncertainties from infrared gas analyzer measurements are needed."

1.2. Lines 38-39: If the link with EC is maintained, it may be relevant in my opinion to mention that the exactness of EC measurements depends also on this, but not only. There is a long way to get to the fluxes after the field measurements, and each step sources uncertainty. This should be mentioned in my opinion, also referencing the papers dealing with other sources of uncertainties. (#1).

Author response

Our dilemma has been whether to link our manuscript context either more or less to flux computations. If more, the manuscript becomes lengthy, loses focus, and dims other applications of the overall accuracies. If less, it feels misleading because the infrared gas analyzers studied are, in fact, used in OPEC systems for CO₂ and H₂O fluxes. In this revision, we adopted this comment to overcome weakness #1 while still linking the manuscript context to flux topics as much as possible.

Author proposed revision

Lines 38–42: "The degree ofHill et al., 2017)." was replaced with:

"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 CO₂, H₂O, 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), lowand 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, longterm aging of sensor detection components, and unexpected factors in field operations (Fratini et al., 2014), but they are also not mathematically correctable because their sign and magnitude are unknown (Richardson et al., 2012). The overall measurement exactness related to these uncertainties would be a valuable addition to flux data analysis (Goulden et al., 1996; Anthoni et al., 2004).

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)."

1.3. Line 473: As you are considering eddy covariance applications, mentioning only T_a is a bit reductive in my opinion (no user will buy the IRGASON to calculate T_a ...). Also, T_a is more related to sonic temperature T_s , and here you are only considering the IRGA uncertainties, not the sonic ones: ΔT_s is reported in the sensor's specs, right, as it is $\Delta \rho_{CO2}$ and $\Delta \rho_{H2O}$. T_s is probably less sensitive (e.g., not cross-sensitivity present), but still can drift with temperature for example (see for example Mauder et al. 2007 https://doi.org/10.1007/s10546-006-9139-4). (#1, #3).

<u>Author response</u>

See our response to 1.2, above. A discussion of the applications of $\Delta \rho_{CO2}$ and $\Delta \rho_{H2O}$ for flux uncertainty was added to the manuscript as section 6.2 and section 6.3. The original subsection numbers following 6.3 in section 6 were revised accordingly.

a. "A bit reductive in my opinion"

Computing T_a from T_s and a moisture-related variable (e.g., ρ_{H2O}), including atmospheric pressure (*P*), has been of interest to scientists since 1932 (Ishii, 1932; Barrett and Suomi, 1949; Kaimal and Businger, 1963; Schotanus et al., 1983; Kaimal and Gaynor, 1991; van Dijk, 2002; Swiatek, 2018; Zhou et al., 2022), although an exact equation for finding T_a from T_s , ρ_{H2O} , and *P* has not yet been reached (Zhou et al., 2022). Because this T_a is a highfrequency signal that is insensitive to the solar contamination suffered by conventional *T* sensor measurements inside a radiation shield (Lin et al., 2001; Blonquist and Bugbee, 2018) this air temperature is increasingly needed in the measurement space of flux for correction of the spectroscopic effect on CO₂ (Bogoev et al., 2015; Helbig et al., 2016; Wang et al., 2016) and on CH₄ (Burba et al., 2019). To correct a flux error due to bias in a gas concentration measurement, Fratini et al. (2014) requires the measurement of air temperature in the optical path of the infrared analyzer. T_a is the best proxy of this temperature, although Fratini et al. (2014) might not use this high-frequency T_a then.

b. "No user will buy the IRGASON to calculate T_a "

All IRGASON sensors internally calculate this T_a to correct the spectroscopic effect on CO₂ (Bogoev et al., 2015) using an approximation equation of T_a (Swiatek, 2018). The option of a corrected CO₂ was incorporated into EasyFlux-DL-CR6OP by Dr. Zhou, who is the first author of this manuscript.

c. " T_a is more related to sonic temperature T_s "

In dry air, T_a is equal to T_s ; in this case, the bias of T_a totally depends on the accuracy of T_s , although this accuracy has not been available yet (Zhou et al., 2022). In the case of moist air, if T_s is accurately measured, the bias of T_a depends on the errors in ρ_{H2O} and P. Under humid conditions at a high air temperature (e.g., 35 °C), the bias can reach a couple of Kelvins if ρ_{H2O} and P have larger errors.

d. " T_s is probably less sensitive (e.g., not cross-sensitivity present), but still can drift with temperature"

The ability to accurately measure T_s with an overall accuracy of <0.5 °C is a challenge. So far, no methodology is available to quantify the overall accuracy on a solid base (personal communications in 2022 with Larry Jacobsen [CSAT authority] and Richard McKay [Product Manager with Gill sonic anemometer for the last 10 years and now with Campbell Scientific Ltd.]). Regardless, this topic is out of the scope of this manuscript.

Author proposed revision

Line 667:

After Line 667, we inserted Appendix C: Appendix C: The relationship of measured to true covariance to of vertical wind speed with CO₂, H₂O, and air temperature

Line 393:

After Line 393, we inserted section 6.1

6.1 Partial effects of $\Delta \rho_{\rm CO2}$ and $\Delta \rho_{\rm H2O}$ on uncertainty of hourly CO₂/H₂O flux

#2. It should be shown that the specs used are all necessary and sufficient, and provide guidance to the reader in case some of them are missing on a different sensor specs (better if also considering additional specs that may be found). In some occasions the authors refer to "OPEC systems" while dealing with the specs of the IRGASON - which may be not the case.

Author response

We clarified this issue in the revision in response to the following comments.

2.1 Lines 20-22: please specify that it refers to IRGASON/EC150 only: it seems to be a generic statement for OPEC systems (#2).

Author response

IRGASON and EC150 infrared CO_2 -H₂O analyzers have the same specifications. This study uses EC150 as an example.

Author proposed revision

Lines 20–22:

"Based on atmospheric physics and the biological environment, for EC150 infrared CO_2 -H₂O analyzers, these equations are used to evaluate CO_2 accuracy (±1.21 mgCO₂ m⁻³, relatively ±0.19%) and H₂O accuracy (±0.10 gH₂O m⁻³, relatively ±0.18% in saturated air at 35 °C and 101.325 kPa)."

2.2. Line 91 (tab1): if you want to make it more general, you should specify whether or not this list is sufficient and necessary: what if a different sensor is missing some info? And what if there are more sources of uncertainties listed for a sensor? This should be reported (here and/or in Appendix A) (#2)

Author response

Your comment 2.11 addresses this issue. See our response to comment 2.11 and corresponding author proposed revision.

2.3. Line 148 (eq 5): while I think this equation is general, as it is proposed in a sensor's manual (i.e., not peer-reviewed) in my opinion it is not very robust to include it in a scientific paper without an indepth analysis. As sources are present in LICOR's manual, I would prefer to see it derived from there. Otherwise, in addition to not being scientifically robust, this may also be felt as ambiguous in terms of at which sensors can be generalised: its applicability at sensors other than the one the manual is referring to should be shown (IRGASON and beyond). In alternative, if some other publications exist that already "validated" LICOR's equation, they could be referenced here. Then, the parameters in the equation can guide the reader in understanding its applicability, e.g., all the IRGAs using a 5th order polynomial for CO_2 , etc. (#2, #4).

Author response

Globally, all fast-response infrared CO₂–H₂O analyzers currently used for field OPEC and CPEC systems are made by two manufacturers: LI–COR Biosciences and Campbell Scientific. Either is trustworthy in the flux community. Their manuals and programs for release as documents and products are rigorously, but internally, reviewed within professional standards; they are not necessarily externally reviewed in the same way as journals. Particularly, all proprietary techniques related to most advanced technologies are reviewed by a small group of internal experts instead of external referees. However, these technologies in related areas are technically and commercially valuable. If journal reviews were the only data sources deemed valid, then all current CO₂ and H₂O flux data from field OPEC and CPEC systems would be invalid because many technical details inside infrared CO₂–H₂O analyzers are not published by either LI–COR Biosciences or Campbell Scientific. We believe the manuals from industry-trusted manufacturers have equal

credibility to journal publications. In fact, our first author is affiliated with Campbell Scientific; therefore, we strongly feel that citing LI–COR Biosciences documents is credible.

a. Derivation of Models (5) and (17)

Both models have been in the different versions of manuals for the LI–7500 series over last 20 years (LI–COR Biosciences 2001, 2021a, 2021b). The derivations of both models are solid in sciences and understandable. For detailed derivations, see Eqs. 2-1 to 2-17 in the Theory and operation section on pages 2-1 to 2-12 in LI–COR Biosciences (2001). In this revision, the derivations of both models are referred to in the Theory and operation section in the literature over the past 20 years.

b. Working model inside EC150, IRGASON, and EC155

The working models inside EC150, IRGASON, and EC155 infrared analyzers were not published in public domains. We are not allowed to disclose the related information, although the field auto and manual CO₂/H₂O zero/span procedures for the three models are implemented by the first author of this manuscript and are used globally. Following LI-7500, these three models of infrared analyzers were developed after 2005. There was no reason not to use Models (5) and (17) for EC150/IRGASON consistency with LI-7500 data in precision, zero drift, and gain drift uncertainties. Of the three models, EC150 was the first released, in 2011. At that time, it would have been unacceptable for EC150 data uncertainties to be inconsistent with L-I7500 uncertainties.

c. Robust of Models (5) and (17)

Figure R1 below shows two Calibration Certificates for LI–7500. One was issued in 2002 and the other in 2021. The parameters in the two certificates indicate that Models (5) and (17) have been consistently used for 20 years. Both models are robust. We are continuously looking for ways to improve the infrared CO_2/H_2O analyzers and would be glad to know of models that work better than Models (5) and (17).

LI-7500 CO2/H2O Analyzer

Calibration Certificate Serial Number <u>75H-0150</u>

LI-7500 CO2/H2O Analyzer

Calibration Certificate

Serial Number 75D-4427

Date: 23 Apr 2002	Technician	Date: <u>30 Mar 2021</u> Code:34829	Technician keep E
$CO_2 Calibration Values A = 1.3184E2 B = 1.59059E4 C = 2.21287E7 D = -5.26988E9 E = 6.28028E11 XS = 0.0075 Z = 0.0013 H_2O Calibration Values A = 5.15909E3 B = 3.44417E6 C = 2.35922E7 XS = -0.0038 C = 0.0020 C = 0.0020$	Pressure Calibration* A0 = 10.697 A1 = 26.036 * Ver 3.0.1 and above	$CO_2 Calibration Values A = 1.16284E2 B = 9.99702E3 C = 1.75717E7 D = 4.12443E9 E = 4.16348E11 XS = -0.0011 Z = 6.50000E-3 * SD1 = 0.0147 SD2 = -0.0414 SD3 = 1.9450 * Ver 6.5 and above * Ver 7.6 and above * Ver 7.6 and above$	$\begin{array}{l} H_2O\ Calibration\ Values\\ A=5.81603E3\\ B=6.55766E6\\ C=-7.08744E8\\ XS=0.0001\\ Z=-7.40000E-3\\ ^+\ SD1=0.0204\\ SD2=-0.1081\\ SD3=2.1820\\ ^*\ Signal\ Strength\\ B=1.6\\ C=3.2 \end{array}$
Z = 0.0202 Zero/Span set on 24 Apr 2 CO2 Zero = 0.8900 CO2 Spaa = 0.9980 (at 999 ppm) II20 Zero = 0.5890 H20 Span = 0.9840 (at 15 C)	002	Zero/Span set on 31 Mat CO2 Zero = 1.1271 CO2 Span = 1.0010 (at 752 ppm) CO2 Span 2= 0.0000 H2O Zero = 0.9815 H2O Span = 1.0051 (at 12 C) H2O Span = 0.0051 (at 12 C)	r 2021 Pressure Calibration A0 = 10.416 A1 = 26.036 <serial number=""></serial>

Figure R1. Two Calibration Certificates were issued in 2002 and 2021 for two LI-7500 CO_2/H_2O analyzers. For CO_2 ; see model (5); A is a_{c1} ; B, a_{c2} ; C, a_{C3} ; D, a_{C4} ; E, a_{C5} ; XS, S_w , and Z, Z_c . For H_2O ; see model (17); A is a_{w1} ; B, a_{w2} ; C, a_{w3} ; XS, S_c , and Z, Z_w .

Author proposed revision

Lines 146–147:

"According to LI-COR Biosciences (2021b)" was revised to be:

"From the derivations in the Theory and operation section in LI–COR Biosciences (2001, 2021a, 2021b)."

2.4. Line 195: For EC150, not for OPEC in general (#2).

<u>Author proposed revision</u> Line 195:

Between "of" and "OPEC," we inserted the words "EC150 infrared analyzers used for."

2.5. Lines 203-204: These values are again for the EC150 only. (#2) Please also note that "rh" may be misunderstood for relative humidity.

<u>Author response</u>

Revised in the same way as above. The subscript "rh" written in lowercase should be fine. To avoid the risk of introducing errors with revision, we decided to keep this subscript in its current form.

<u>Author proposed revision</u> Line 203:

Between "of" and "OPEC," we inserted the words "EC150 infrared analyzers used for."

2.6. Line 211: Again, if it has to be generic, sentences from LICOR manuals shouldn't be used

alone, as 1. they are not peer-reviewed and 2. things could be different for different models (#2, #4).

<u>Author response</u> Richardson et al. (2012) and Fratini et al. (2014) also support this statement. Both references were added.

<u>Author proposed revision</u> Line 211:

Between "(" and "LI–COR," we inserted "Richardson et al., 2012; Fratini et al., 2014;" 2.7. Line 271: Again, it should be noted that these specs, and then the results below, are relative to the EC150, including the operational range: are you sure you can generalise to all the OPEC systems? (e.g., LICOR LI7500DS has a range of -25 to 50°C) (#2)

Author response

Yes, both LI-COR Biosciences and Campbell Scientific used the same specification term, although the specification values in some terms are slightly different (e.g., measurement range for CO₂). Because some authors of this manuscript have an affiliation with Campbell Scientific, it seems appropriate to give more credit to LI-COR and less generalization about LI-COR products.

Author proposed revision Line 270:

Between "which" and "OPEC," we inserted the words "EC150 infrared analyzers used for."

2.8. Line 323: see the comments in section 4, in particular at line 148 (#2, #4).

<u>Author response</u> See response to comment 2.3.

Author proposed revision Lines 322–323:

The words "by (LI–COR Biosciences 2001b)" was revised to be "also by the derivations in the Theory and operation section in LI–COR Biosciences (2001, 2021a, 2021b)"

2.9. Line 360: Here could be a good candidate to mention the generalisation point (#2).

Author response

For the generalization, it is better to be specific in the last sentence in this paragraph and then mention the application of Eq. (12) for other models of infrared analyzers. We sincerely appreciate Referee's thinking.

Author proposed revision

Lines 359–360:

The last sentence in these two lines was replaced with:

"Using this equation and the specification values as in Table 1 for EC150 infrared analyzers, the accuracy of field H_2O measurements can be evaluated as a range for OPEC systems with such anlyzers. For an OPEC system with another model of open-path infrared anlyzer, such as the LI-7500 series (LI-COR Biosciences, NE, USA) or IRGASON (Campbell Scientific Inc., UT, USA), its corresponding specification values are used."

2.10. Line 367: please consider rephrasing: this is a plausibility range, and the calibration range

of both EC150 and LI7500. It is likely the same for most analysers, but again I think it can't be generalised in absolute terms. (#2).

Author response

Yes, any manufacturer should calibrate their gas analyzers for H_2O measurement for H_2O density around or below the highest dew point temperature of 35 °C ever recorded under natural conditions on the earth (National Weather Service, 2021). The top limit of 44 gH₂O m⁻³ is equivalent to 37 °C at dew point in EC150 production conditions. This dew point is 2 °C higher than the highest one under natural conditions. Accordingly, this sentence can be rephrased.

Author proposed revision Line 367:

The first sentence was replaced with the two sentences below:

"The EC150 analyzers were calibrated for H_2O density from 0 to 44 gH₂O m⁻³ due to the reason addressed in Sect. 2. The highest limit of measurement range for H₂O density by other models of analyzers also should be near 44 gH₂O m⁻³."

2.11. Line 407: Here it is a good candidate to discuss the fact that any other uncertainties are lacking in the model (#2).

Author response

Over last 20 years, the measurement uncertainties of infrared CO_2 -H₂O analyzers for OPEC systems have been defined consistently using precision, cross-sensitivities, zero drifts, and gain drifts for both H₂O and CO₂ (LI-COR Biosciences, 2001, 2021a, 2021b; Campbell Scientific Inc., 2021). With the development of optical technologies, more measurement uncertainties are not expected to be added to analyzer specifications, and current measurement uncertainties could be removed from the current specification list. However, this removal would not happen in the near future unless low-cost laser heads for such measurements become available for field applications in performance stability and power saving. As you suggested, we added more discussion in the Discussion section.

Author proposed revision Line 413:

After Line 413, the following paragraph was added.

"Additionally, included in the accuracy model, the four types of measurement uncertainties (zero drift, gain drift, sensitivity-to- CO_2/H_2O , and precision variability) to specify the performance of infrared CO_2-H_2O 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_2-H_2O analyzers."

#3. The suggestion of calibrating on an "average" temperature (Ta) to basically avoid to be in the worst case scenario (Ta and Tc at the extremes) is not robust as this is what normally happens, also because the range of Ta between two calibrations can be very large. In addition, it is based

on the assumption of linear relationship between the difference Ta-Tc and the drift magnitude, which derives from a simplification not so deeply documented. Also the applications proposed are not very impactful: if the EC method is kept (see #1) many more interesting applications could be thought of (but again, probably out of the scope). Even without that, I would use this idea of "applications" to improve the point above: the first and more relevant application should be "how to calculate the uncertainty for a generic IRGA".

Author response

We adopted this idea to revise our manuscript. We offer the following discussion in response to several points in this comment:

a. "on an "average" temperature"

Our first author, Dr. Zhou, was trained to use LI–7500 series for eight OPEC stations at University of Nebraska–Lincoln for over the course of 10 years. Now, Dr. Zhou advises global Campbell Scientific users daily. It is a popular recommendation to zero and/or span infrared CO_2 –H₂O analyzers around the average air temperature for analyzer operations rather than perform the zero and/or span procedure at extreme conditions or lab conditions. Fratini et al. (2014) recommended the zero and/or span procedure "at the temperature that minimizes the temperature departure, on average, during the period of interest." This recommendation is better in wording, but it is hard for users to digest. We adopt this wording in our revision.

b. "on the assumption of linear relationship"

This assumption is not the first principle, but it is a way to describe the behavior of zero and gain drifts with ambient air temperature (T_a). As seen in Figure 4b, the H₂O accuracy as influenced by the linear trend of zero and gain drifts with T_a is more shadowed by the exponential trend of saturated H₂O density with T_a . In Figure 2a, the CO₂ accuracy as influenced by the linear trend of zero and gain drifts with T_a is dominated by the CO₂ density of the ecosystem background with T_a . The merits of our methodology are the uses of atmospheric physics and biological environment principles for field data.

c. "not very impactful"

According to the metric of interactive discussion (<u>https://gi.copernicus.org/preprints/gi-2022-1/#discussion</u>), so far, 612 viewers have viewed and/or downloaded this manuscript. This high number of viewers indicates that this manuscript is already impactful.

Our finding, based on atmospheric physics, that H_2O gain drift insignificantly contributes the accuracy range for H_2O measurement at low temperatures (e.g., <5 °C) and/or under dry conditions, has been successfully applied to the field auto adjustment of H_2O zero coefficient instrumentally for IRGASON and EC150 + CSAT3A OPEC systems. This technique has been used in remote areas in Tibet and Qinghai in China and Logan in the US, although it has not been published yet. When published, this technique will benefit a large number of users who operate OPEC system in cold and/or dry regions.

Our finding, based on atmospheric physics, that the trend of H₂O relative accuracy can answer the question of the H₂O relative accuracy of infrared analyzers. This question is often asked by scientists worldwide for their selection in purchase processes.

3.1. Line 335: I think an important point should be taken into consideration here: Tc must be significantly lower than Ta at the moment of field calibration for H₂O span to avoid condensation

(3-5°C, as reported in the LICOR manual) (#3).

Author response

 T_c is the environmental temperature at which an infrared analyzer is zeroed or spanned. What Referee #2 talked about is the dew point temperature set for an LI–610 Dew Point Generator to perform an H₂O span for an infrared analyzer (LI–COR Biosciences, 2004). A common recommendation is to set the dew point temperature for LI–610 at 5 °C, at least, below T_c . The correct use of LI-610 also needs the consideration of the difference between the pressures inside and outside the compressor. In our opinion, this manuscript does not have room to train users on such details (LI–COR Biosciences, 2004).

<u>Author proposed revision</u> N/A

3.2. Line 439: Applications should probably go in a dedicated section. However, the first two suggested applications of relative accuracy is just a way to define sensors' specs, then in my opinion they should be just mentioned, not reported in such details. (#3, #5).

Author response

The H_2O relative accuracy of infrared analyzers has not been clearly addressed before this study, even though many users do care about the relative accuracy in their instrument selection processes. We are often asked this question by scientists, which is the motivation for us to write this paragraph. The CO_2 relative accuracy of infrared analyzers is not an issue; however, if we only address the H_2O relative accuracy, the question of why the CO_2 relative accuracy is not discussed will ultimately arise. We prefer to detail the use of relative accuracies here.

<u>Author proposed revision</u> N/A

3.3. Lines 512-513: it is also true that the widest possible range would apply only if calibrating in extreme conditions far from the daily average (#3, #5).

Author response

We do not suggest that users zero and/or span the infrared analyzers under extreme conditions (e.g., T_c below -15 °C or above 30 °C), although it is possible for analyzers to run in extreme conditions. Therefore, our discussion gives the H₂O limit T_c within a range of 5 to 20 °C (see Figure 5) for analyzer use in a range of T_a from -30 to 50 °C (see Figure 5), over which the EC150/IRGASON infrared analyzers can run.

<u>Author proposed revision</u> N/A

3.4. Line 524: See comment at line 335: the span procedure with a dew point generator MUST be performed at a much lower temperature than ambient to avoid condensation in the tubes and a bad calibration. This should be mentioned (also, does it worth it to "risk" to perform a bad calibration for correcting this? This is probably out of topic for the manuscript, but a short note could be beneficial to the reader). This risk is also reported in the LICOR manual (a note on "Checking the span" section) (#3, #5).

Line 568: again, the worst case scenario is also less likely... (#3, #5)

Author response

See our author response to comment 3.1.

<u>Author proposed revision</u> N/A

3.5. Lines 617-618: this suggestion is mostly for sensors producers (#3, #6)

Author response

Not necessarily, because producers and users should share an understanding of instrument specifications. Producers need the knowledge gained from research community feedback, including demands and desires. To be clear, the developers and manufacturers of infrared CO_2 -H₂O analyzers, including sonic anemometers that are used for OPEC systems, are scientists, and users who use the OPEC systems are mostly for scientific projects.

<u>Author proposed revision</u> N/A

#4. I think the paper from Fratini et al. 2014 (Fratini, G., McDermitt, D. K., and Papale, D.: Eddy-covariance flux errors due to biases in gas concentration measurements: origins, quantification and correction, Biogeosciences, 11, 1037–1051, https://doi.org/10.5194/bg-11-1037-2014, 2014) should definitely be included in the discussion, as it develops a correction of EC fluxes based on the drift of the IRGA as measured during field calibrations. It is different from what presented in this preprint, strongly bounded to the EC method; however it cannot be omitted in a paper dealing with the drift of the IRGA. Some publications on the theory beyond the IRGA working principles, from which the working equations presented are derived, should also be included, in addition (and in support) to the ones in the LICOR manual (not peer-reviewed). Also, publications dealing with uncertainties in EC method should be present, if the link with EC (#1) is maintained.

Author response

We regret missing this publication for our discussion in our study. Following Referee #2's advice, we thoroughly reviewed Fratini et al. (2014) and Richardson et al. (2012). Both studies supported our understanding of drifts of infrared analyzers with ambient air temperature for measurements. Both were valuable additions to our discussion in this manuscript and were cited several times in our revision.

4.1. Line 55-56: This is likely the case. However, several publications exist trying to quantify the uncertainties of EC measurements: this should be mentioned and the difference between this study discussed (here we are dealing with the exactness of the measurements of the IRGA only, there they are considering the EC flux. In some work the instrumentation uncertainty is included in the overall uncertainty). (#4).

Author response

The topic of flux uncertainties is broad. Additional information may make readers feel the introduction is too lengthy. To follow this comment, we added one paragraph to mention related studies.

Author proposed revision

Line 52:

After Line 52, we inserted the following:

"As comprehensively reviewed by Richardson et al. (2012), numerous previous studies including Goulden et al. (1996), Lee et al. (1999), Anthoni et al. (1999, 2004), and Flanagan

and Johonson (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)), 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 the 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 analyzers, Burba et al. (2008) developed the correction for a sensor body heating effect on CO₂ and H₂O fluxes, wheras Fratini et al. (2014) developed a method for correcting the raw high-frequency CO₂ and H₂O data using the zero and span coeffcients 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 CO₂ and H₂O data from infrared anlyzers, even though both overall uncertainties are fundamental for data analysis in applications (Richardson et al., 2012)."

4.2. Line 173: ref needed. Indeed, other reasons for the drifts are: dirt contamination, ageing of the IRGA's components, errors in pressure correction (absorptances are normalised to P), and errors in field calibration. If only Ta has to be considered, all of the other sources should be assumed to be zero - which should be at least mentioned. See also Fratini et al. 2014 (#4)

Author response

Dirt contaminations in the field and field zero/span errors from users cannot be considered by any manufacturer while specifying the drifts. No open-path analyzers for eddycovariance measurements can perform reasonably well under heavy pollution, fog, rain, snow, ice, and/or sandstorm conditions. The measurement uncertainties from these events are unpredictable, which is out of the scope of the manufacturer specifications. The drifts as influenced by the aging of infrared analyzers within some age range (e.g., 10 years), a little CO₂/H₂O accumulation inside a light house under normal maintenance, and thermal expansion/contraction of instrument components are in the scope of manufacturer specifications. Fratini et al. (2014) had the most excellent analysis for the dependence of drift on ambient air temperature, which we included to revise Lines 173 to 176.

Author proposed revision

Lines 171–176:

We revised Lines 171 to 176 to connect the context to the following inserted paragraph:

"Firstly, the dependency of analyzer CO_2 zero drift on ambient air temperature arises due to a thermal expansion/contraction of analyzer components that slightly changes the analyzer geometry (Fratini et al., 2014). This change in geometry can deviate the light path length for measurement a little away from the length under manufacturer calibration, contributing to the drift. Additionally, inside an analyzer, the performance of the light source and absorption detector for measurement, as well as the electronic components for measurement control,

can vary slightly with temperature. In production, an analyzer is calibrated to compensate for the ensemble of such dependencies as assessed in a calibration chamber. The compensation algorithms are implemented in the analyzer operating system, which is kept as proprietary by the analyzer manufacturer. However, the response of an analyzer to a temperature varies as conditions change over time (Fratini et al., 2014). Therefore, manufacturers typically specify an expected range of typical or maximal drift per °C (see Table 1). Secondly, the housing CO₂-H₂O 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 CO₂ and H₂O that may sneak into the housing through an exchange with any ambient air (LI-COR Biosciences, 2021b). Over time, the scrubber chemicals may be saturated by CO₂ and/or H₂O or lose their active absorbing effectiveness, which can result in housing CO₂-H₂O 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 air temperature is a major concern if an analyzer is maintained as scheduled (Campbell Scientific Inc., 2021b)."

4.3. Line 347-348: I understand the logic behind this, however some evidence should be provided that this is the case, against the case, for example, that the lowest cross sensitivity to CO_2 unc. is with CO_2 -free air - or vice versa in the CO_2 case, that the lowest cross sensitivity to H_2O is with dry air and not with a "standard" water vapour concentration (somehow related to #4, and to #5 as it could be matter of discussion).

Author response

We appreciate Referee #2's understanding of the rationale behind Eqs. (13) and (20). It is our innovation to use atmospheric physics and the biological environment as a base to assess the overall accuracies of CO₂ and H₂O data from infrared analyzers deployed in ecosystems for flux measurement. In ecosystems, the minimum H₂O density is close to zero (e.g., cold and/or dry), and the minimum CO₂ density is close to 760 mgCO₂ m⁻³, which is the atmospheric background CO₂ density. This represents a conservative way to estimate sensitivity-to-CO₂/H₂O uncertainty. Additionally, the magnitude of this term is small (see Table 1).

<u>Author proposed revision</u> N/A

4.4. Lines 500-502: this is also a good place to discuss Fratini paper, which is based on field calibration data (#4, #5).

Author response

We added an extensive discussion about Fratini et al. (2014) in response to comments 4.1 and 4.2. Here, their work should be mentioned.

<u>Author proposed revision</u> Line 501:

Before the word "this," we inserted:

"Fratini et al. (2014) provided a technique implemented into the EddyPro program to correct

the drift bias from a raw time series of CO₂ and H₂O data through post-processing."

4.5. Lines 571-572: Ref. needed (#4, #5)

<u>Author response</u> Fratini et al. (2014) supports this statement.

<u>Author proposed revision</u> Line 571:

After the word "environment," we inserted the citation "Fratini et al. (2014)."

#5. if some more applications are described, I would opt for a separate section of the paper, and for enriching the discussion section with discussion, citing different papers and going more details on what the results suggest.

Author response

We appreciate this idea from Referee #2. Separation of Discussion into Application and Discussion will improve the structure of manuscript.

Author proposed revision

The discussion section was separated section 6 into Application and Discussion. The section number for Conclusion was revised from 7 to 8.

5.1. Line 393: In general, this section is often more a (even useful) recap of what has been done and an application study (also useful) than a discussion of what done, also against other studies (#5).

<u>Author response</u> See author response to comment #5.

5.2. Line 424-426: This is quite a critical point: I agree that such a relationship is not modeled yet, and that considering the maximum range is what the users may want and understand; however, I think assuming a linear scaling of the uncertainty and including it in the computation is a bit risky. At least, how far from the actual uncertainty is that one? Some more discussion needed, also checking Fratini et al. 2014 (#5, #4).

<u>Author response</u>

See Author response b. to comment #3; the discussion can be enhanced here. For comparison of this study to Fratini et al. (2014), due to the distinction between the two studies (see Author proposed revision in response to comment #4.1 and Author response b. to comment #4), the authors decided not to compare.

Author proposed revision

Line 427:

After this line, we added:

"In fact, the H₂O 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 H₂O density with T_a (Fig. 4b). Similarly, the CO₂ accuracy as influenced by the linear trend of zero and gain drifts with this difference is dominated by the CO₂ 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 CO₂ and H₂O, which

shows the merits of our methodology in the uses of atmospheric physics and biological environment principles for the field data."

5.3. Lines 490-491: this is correct and probably the most relevant part of this section. However, this is strongly related to the drift uncertainty that is re-scalded to the difference Tc-Ta, and this is said above to be not exact (@425), and is also based on the assumptions that only the Ta dependency impacts the drifts. As no other demonstrations are given, this is also not very robust in my understanding (#5).

Author response

According to the definition of analyzer drifts by unit (see the first paragraph in section 3.3.1 of Fratini et al. (2014) and Table 1 in this manuscript), it is robust. As both Referee #2 and authors agree, it is not. This term would not be considered an uncertainty if any mathematical description could describe this trend exactly based on the first principles of physics. We believe, based on the best of our knowledge, we adequately addressed this issue in discussion and in Author proposed revision in response to comment 5.2.

#6. With the improvements above, the conclusion section will become more robust.

6.1 Line 577: Some of the comments above clearly applies to this section as well (all the points, #6).

Author response

See author response to comment #5. Based on revisions suggested by both referees, the conclusion was revised.

<u>Author proposed revision</u> See conclusion section.

Technical and editorial comments to improve the manuscript expressions

1. Line 25: "narrow the accuracy" is improving it? Please consider rephrasing.

<u>Author proposed revision</u> Line 25:

"CO2 accuracy" was revised to be "CO2 accuracy range."

2. Line 48-49: Such an example at the beginning of the intro is misplaced in my opinion. Also, Ts accuracy is not under discussion. I would keep it for later.

Author response

Following to other comments, the introduction section was revised.

<u>Author proposed revision</u> N/A

3. Line 64: Also CPEC.

Author response

"CPEC" was added, and the context related to this abbreviation was also revised.

Author proposed revision Line 64:

"... in OPEC systems" was revised to be "... in OPEC and CPEC systems, where CPEC is an

acronym for closed-path eddy-covariance."

Line 71:

"For closed-path eddy-covariance (CPEC) systems" was revised to be "For CPEC systems."

4. Line 72: To be more clear: density measurements. It is probably worth it to state that in the manuscript CO_2/H_2O measurements always refer to density, not flux (as EC technique estimates CO_2/H_2O fluxes).

Author response

Yes, the wording needed precision. We clarified the same expression throughout the manuscript.

Author proposed revision

Line 72:

"CO₂/H₂O measurements" was specified to be "CO₂/H₂O mixing ratio measurements."

Line 73:

"CO2 and H2O data" was specified to be "CO2 and H2O mixing ratio data."

5. Line 83: a (typo)

<u>Author proposed revision</u> Line 83:

The word "an" was revised to be "a."

6. Line 88: amount.

Author proposed revision Line 88:

We inserted "amounts" between "H₂O" and "(Fig. 1)."

7. Line 128: This is mathematically shown in Appendix A: Please clearly refer to it (not only later).

Author response

A reader would benefit from an early reference to the mathematical derivations in Appendix A.

<u>Author proposed revision</u> Line 125: We inserted "as mathematically shown in Appendix A" between "analyzers" and "this."

8. Lines 133-134: Not clear: please consider rephrasing.

Author proposed revision Lines 133–134:

We inserted ", by the use of known and/or estimable variables," between "is" and "to."

9. Line 143 (eq 4): Under the assumption that the errors are normally distributed? Please also specify that σ_{CO_2} is the std. dev of...

Author response

 σ_{CO_2} was specified again.

<u>Author proposed revision</u> Line 140: The term " (σ_{co_2}) " was inserted between "CO₂ precision" and "is." Line 14:

Behind "... 2008)", we inserted "The random errors generally have a normal distribution in statistics (Hoel, 1984)."

10. Line 166: Please consider expliciting here which parameters of eq. 5 are defined at the factory, and which ones can be corrected by field (or lab) calibration, even if reported in details later.

<u>Author proposed revision</u> Line 160: The first sentence was revised to be: "The analyzer-specific working equation is deemed to be accurate immediately after calibration through the estimation 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)."

11. Line 168: is that part of the experiment? not very clear how it relates to the rest

Author proposed revision Line 168:

"In production" was added at the beginning of this line.

12. Lines 170-171: bad wording

<u>Author response</u> This was revised as Referee #1 suggested. See our response to comment #7 by Referee #1.

14. Line 180-182: I feel it as a "manual-like" text. I suggest avoiding expressions like "must be simple", "indeed", and be more descriptive.

<u>Author proposed revision</u> Lines 180–182:

Two sentences were combined to be:

"In the field, the zero procedure must be feasibly operational, using one air/gas benchmark to re-estimate one parameter in the working equation."

15. Line 197: What do you mean? Almost?

<u>Author response</u> "Even without zero drift" was not an appropriate phrase.

<u>Author proposed revision</u> Line 197: "even without zero drift," was revised to be "almost without zero drift."

16. Line 199: Respect to ...?

<u>Author response</u> Respect to CO₂ zero. *Author proposed revision* Line 199:

After "... drifts." we inserted "the CO2 zero."

17. Line 207: See comment at line 168. I think you are referring here to what is done at the factory during production and/or recalibration. If so, please explain better.

<u>Author response</u> The term "calibration" in this manuscript was defined particularly as the production calibration (see lines 154–156).

18. Lines 214-215: This is correct, this is what is done in 80-90% of the cases. However, there exist the possibility to perform more than one span calibration, e.g., one slightly below the ambient CO2 concentration and one at a much higher value, to have a better reconstruction of the sensor behaviour: this should be mentioned in my opinion.

<u>Author response</u> All options available should be mentioned to readers.

Author proposed revision

Line 214:

The following text was inserted:

"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_2 density and the other is at a much higher density to fully cover the CO_2 density range by the working equation. However, commonly..."

19. Line 216: Yes, but you can adjust it twice in the case of two span calibration (in LICOR IRGA, actually this parameter is a linear function relating absorptance to density, and what is set by the software is the offset, as the slope is fix and determined at the factory).

<u>Author response</u> We perform the zero and span procedures iteratively two or three times.

20. Line 255 (eq. 12): Please recall to the reader that 44 gH₂O m⁻³ is a threshold for H₂O concentration in air based on dew point values.

Author proposed revision Line 256:

Ahead of "Accordingly ...", we inserted "where 44 $gH_2O m^{-3}$, as addressed in section 2, is a threshold for H_2O density measurements."

21. Line 318 (eq. 16): Where $\sigma_{H,O}$ is the standard deviation of the random errors...

Author proposed revision Line 319:

Ahead of "The other ...", we inserted "where σ_{H_2O} , as defined in Table 1, is the precision of EC150 analyzers for H₂O measurements."

22. Line 324 (eq. 17): Even if defined earlier in the CO₂ section, it is probably worth it to report again what A_c , A_w etc are. Probably a symbols list would help the reader.

Author response

It would be lengthy to redefine A_w , A_{ws} , A_c , and A_{cs} . Alternatively, we decided to direct readers to revisit the definitions for these parameters in Model (5).

Author proposed revision Line 328:

After "... coefficient)" we inserted "; and A_w , A_{ws} , A_c , and A_{cs} represent the same as in Model (5)."

23. Line 333: I would also mention the same assumptions as above (i.e., $\rho_{H,O}$ is the closer proxy

for true ρ_{H_2O}).

Author proposed revision Line 331:

After "... $\rho_{H,o}$ ", we inserted "as the closest proxy for true $\rho_{H,o}$ "

24. Line 348: Typo, subscript should be H₂O. Line 351: Typo: $\Delta \rho_{H,o}^s$ range.

<u>Author response</u> Both are the same typos.

<u>Author proposed revision</u> Lines 348 and 351:

" $\Delta \rho_{CO_2}^s$ " was corrected to be " $\Delta \rho_{H_2O}^s$."

25. Lines 385-386: At which Ta?

Author response

The relative accuracy of infrared analyzers for H₂O density measurements relies on the base amount of air moisture. When a temperature is high but dry (e.g., $\rho_{H,O}$ is close to zero), the

relative accuracy would be very poor.

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