REVIEW #2

This manuscript is unique and very much appreciated reporting on the comparison of three aircraft ozone eddy covariance flux measurements operated in parallel. As the authors correctly point out, few flux intercomparisons have previously been reported.

While overall this paper is well written, unfortunately, in the opinion of this reviewer, it neglects a number of important issues that factor into this monitoring and research.

Q1: Clifton et al. (2019) presented a comprehensive overview of ozone deposition monitoring and ozone flux research. Unfortunately, this paper and findings are not recognized by Chiu et al.

A1: The paper to which the reviewer refers is Clifton et al. (2020), which was already cited in the manuscript. Clifton et al. (2019) is a study on the effects of humidity on the deposition of ozone onto stomata, which is not relevant to the work under review.

Q2: It has been known for a long time that water vapor can be a severe interference in various monitoring methods for the determination of ozone. The authors pay some credit to these effects, however, do not fully recognize the severity that quenching of the fast ozone signal from fast fluctuations of water vapor can have in the determination of eddy covariance ozone flux determination.

Willson and Birks (2006) pointed out that interferences in ozone measurement can be particularly high during the fast water vapor changes that can be experienced during aircraft sampling from elevation changes and when flying through clouds for UV absorption instruments. Their recommendation was to selectively remove water vapor from the sampling stream with a Nafion dryer.

R2: We appreciate the reviewer's focus on water vapor interference, but we disagree about the overall importance. The original paper had already actively dealt with the water interference, as we elaborate below.

We also have a different perspective on the relevance of Wilson and Birks (2006) to this study. First, Wilson and Birks (2006) consider interference in UV photometers by water vapor adsorption onto UV optics. This is not a relevant effect in the coumarin chemiluminescence channel of the FAIRO instrument, which the current EC flux comparison is based on. To the extent that the Fast O3 instrument may be affected by water vapor, such interference should already be accounted for by the Ridley et al. water vapor correction, which is empirically derived. The agreement of the FAIRO instruments (to which the Wilson and Birks water vapor effect is not relevant) with the Fast O3 results (to which a water vapor correction has been applied) gives us confidence that water vapor interference is not the source of the observed ozone flux. Second, the conditions tested by Wilson and Birks (2006) involved step changes from 0-90% RH, which are not comparable to those observed during flux legs. In RF03-C and RF06-A, the maximum ΔRH was 20% over the course of several minutes; in other flux legs, e.g. RF07-A, RH varied by no more than ~5%. In all cases, the water vapor concentration changed gradually rather than in "steps". Finally, for the sake of clarity we point out that the method of Wilson and Birks (2006) does not use the Nafion semipermeable membrane to dry the sampling stream. Rather, they use the Nafion membrane to equilibrate the sampling and reference streams. While the method is elegant, we emphasize that it solves a problem that is not relevant to two of the instruments used in this work.

We did consider the effect of changes in water vapor (dH_2O/dt) on instrument agreement and find no systematic effect. We have added Figure S2 to the SI text:

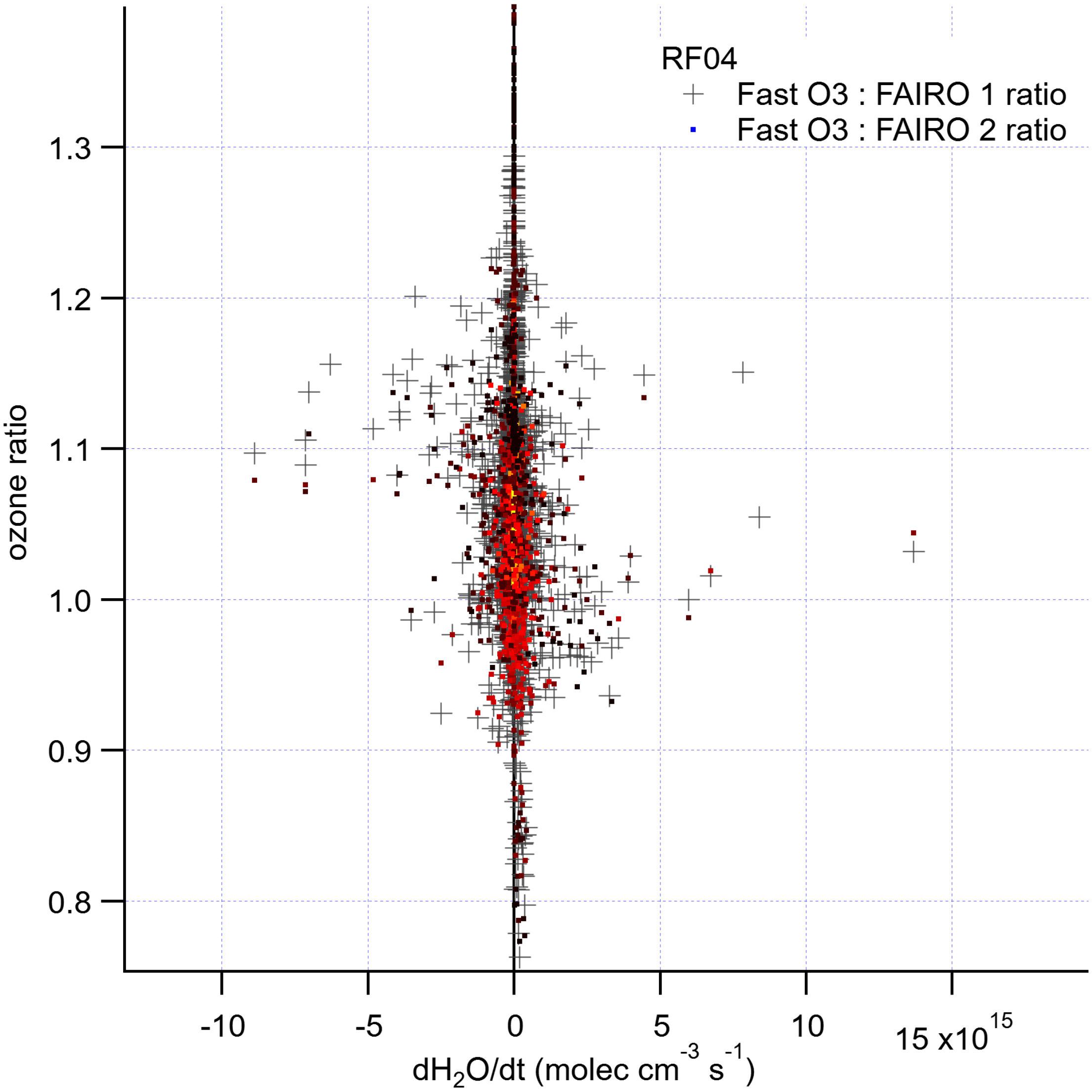


Figure S2: Effect of water vapor changes on Fast O3/FAIRO intercomparison. Ratio of Fast O3 to FAIRO 1 is shown as gray crosses. Ratio of Fast O3 to FAIRO 2 is shown as color-coded dots, with black dots indicating low ozone and hotter colors indicating higher ozone (color scale ends at 100 ppbv, yellow). Comparisons are calculated from data averaged over 10 s. No systematic behavior is observed.

Q3: Boylan et al. (2014) dedicated a full manuscript to the study of water vapor interference in eddy correlation ozone flux measurements by chemiluminescence, using an instrument similar to one of the analyzers used in this study. Importantly, they emphasize that the error from the signal quenching is not just affecting the absolute ozone mole fraction result, but that it will bias the ozone flux determination, with the relative error being dependent on the magnitude and the relative ratio of the ozone versus the water flux. These authors present a solution to this problem by drying the sample stream, similar to what Wilson and Birks (2006) proposed in their earlier work. Unfortunately, the important experiments, findings, and recommendations of Boylan et al. (2014) were not considered by Chiu et al.

R3: We respectfully disagree. The original manuscript had evaluated the water sensitivity, and states “Neglecting the water vapor correction altogether decreased the calculated exchange velocity (see Sect. 2.4) by 5%”. The reviewer must have missed this in the original manuscript.

Expanding on this, the method of Boylan et al. (2014) decreases the magnitude of the Ridley et al. (1992) water vapor correction but does not obviate the need for such a correction in the first place. Indeed, Boylan et al. state that their work "confirms the correctness of… developed correction algorithms." They calculate a water vapor correction factor $\alpha = 4.15 \times 10^{-3}$, which is within the Ridley et al. (1992) error bars. The original manuscript had also varied the water vapor correction to the full Ridely et al. (1992) range ($4.0\text{-}4.6 \times 10^{-3}$). This changes the ozone flux by only 0.7%. Thus, the Boylan et al. (2014) water vapor correction is already considered in the original manuscript.

Moreover, we point out that Boylan et al. (2014) themselves, referring to the ozone frequency response, state that while the Nafion dryer reduces the water vapor flux by 97%, "the spectral components of the ozone signal remained unchanged." They also conclude, "The ozone mean concentration and ozone fast fluctuations were not affected by the Nafion dryer." Rather, the primary benefit of the Boylan et al. (2014) method is that it simplifies the ozone volume mixing ratio calculation. Thus, we consider the Boylan et al. (2014) method "nice to have," but not critical.

Q4: It is striking that ozone exchange velocities showed a high response to water vapor fluxes. This is exactly the interference that the Boylan et al. paper focuses on. While the three instruments response in a similar direction, this may well be from a similar response to the water vapor interference. Unfortunately, Chiu et al. do not present a convincing case that these ozone fluxes are real and not an interference effect.

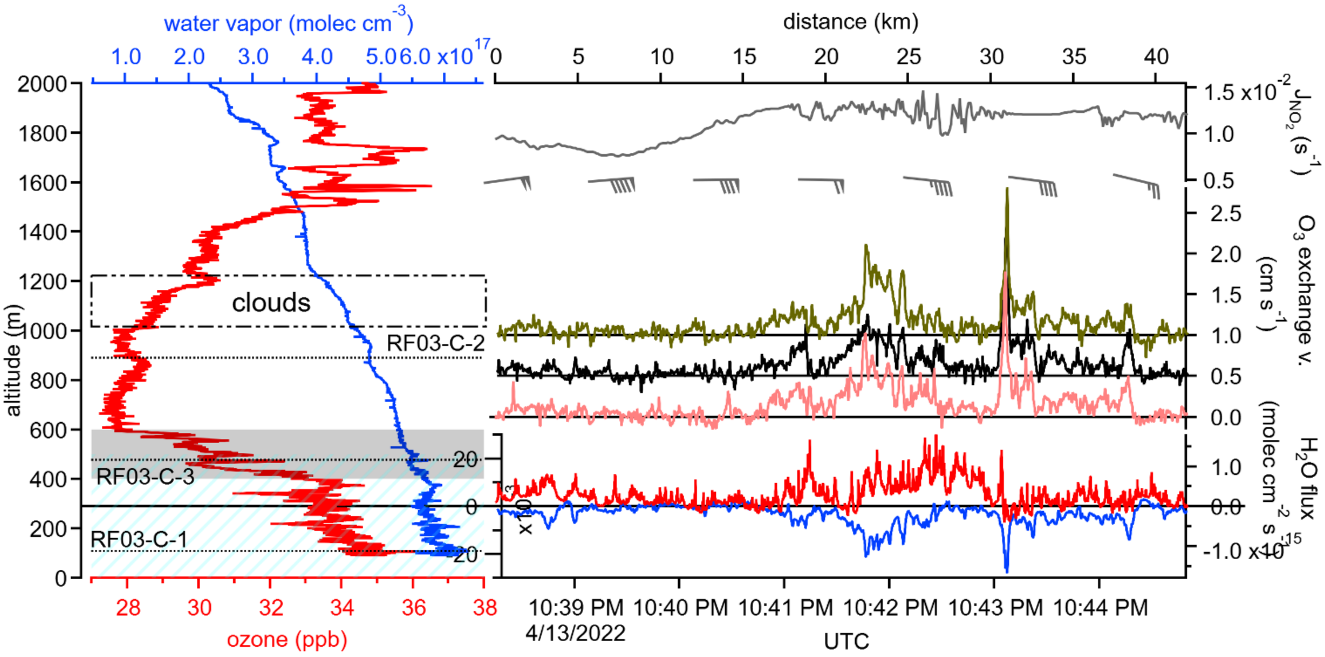
A4: We respectfully disagree. First and foremost, we added the following text to the revised manuscript:

The water vapor interference for the coumarin instruments goes in the opposite direction than for the UV instruments, i.e. water vapor makes Fast O3 less sensitive to ozone, but FAIRO more sensitive (Güsten et al., 1992; Schurath et al., 1991; Zahn et al., 2012). The fact that all three instruments agree after water vapor correction gives us confidence that water vapor bias is removed.

Second, RF06-A-1 shows a case in which ozone fluxes are below detection even when water vapor flux is observed, and the fastest ozone exchange velocities do not coincide with the greatest water vapor fluxes. These observations are not consistent with ozone flux being an artifact of water vapor interference.

Third, the water vapor fluxes in RF04-A-1, RF07-A-4, and RF03-A-1 are 1.65, 1.32, and 1.25×10^{15} molec cm^2 s^{-1}, respectively. The corresponding ozone exchange velocities in these legs are 0.036 ± 0.006, -0.033 ± 0.004, and 0.024 ± 0.012 cm s^{-1}, respectively. If ozone flux is purely a water vapor interference artifact, decreasing the water vapor flux from 1.65×10^{15} molec cm^2 s^{-1} to 1.32×10^{15} molec cm^2 s^{-1} first changes the direction of the ozone flux from +0.036 cm s^{-1} to -0.033 cm s^{-1}, and further decreasing the water vapor flux from 1.32×10^{15} molec cm^2 s^{-1} to 1.25×10^{15} molec cm^2 s^{-1} changes the direction of the ozone flux *again* to +0.024 cm s^{-1}. This trend is implausible and refutes the hypothesis that ozone flux is a water vapor artifact, especially since the water vapor corrections for the Fast O3 and FAIRO instruments operate in opposite directions.

Finally, as a check, we calculated the temperature flux (which is correlated with the sensible heat flux) as measured by the fast ambient temperature probe, which operates completely independently of water vapor measurements. Below we show Figure 6 with the temperature flux added to the lower right panel as the red trace. The temperature flux shows similar temporal behavior as do the water vapor and ozone fluxes, giving us confidence that we are measuring true atmospheric dynamics, not just water vapor interference.



On the magnitude of possible water vapor interference, we have added the following text to the revised manuscript:

Using the average water vapor concentration during the entire leg for the water vapor correction increases the calculated exchange velocity 2% to 0.134 cm s^{-1}; this case represents the extreme case in which water vapor reaching the ozone instruments is completely smeared out by longitudinal diffusion. We conclude that water vapor interference in the Fast O3 instrument contributes at most 5% to the ozone flux uncertainty, and likely less than 2%.

Q5: While this manuscript claims to present an evaluation of three ozone flux techniques, it does not really present a statistical quantitative comparisons and methods evaluation of the ozone fluxes that were determined by the three measurements.

A5: We respectfully disagree, for reasons described above. We refer the reviewer to section 3.4 of the original manuscript.

Minor issues

Q6: It is acknowledged that one of the authors is on the editorial board of ATM. For full transparency, the name of the author should be provided.

A6: The phrasing of the COI statement is as prescribed by the AMT submission guidelines. Other papers published in AMT do not single out individuals in similar situations.

References

Wilson, K. L. and Birks, J. W.: Mechanism and elimination of a water vapor interference in the measurement of ozone by UV absorbance. Environ. Sci. Technol., 40, 6361–6367, 2006.

Boylan, P. et al.: Characterization and mitigation of water vapor effects in the measurement of ozone by chemiluminescence with nitric oxide. Atmos. Meas. Tech., 7, 1231–1244, 2014.

Clifton, O. et al: Dry Deposition of Ozone Over Land: Processes, measurement, and modeling. Reviews of Geophysics, https://doi.org/10.1029/2019RG000670, 2019.

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