## REVIEW #1

**Overview:**

Chiu et al. present a comparison of airborne measurements of ozone mixing ratios and vertical fluxes in the marine boundary layer from three different fast ozone sensors recently deployed on a GV aircraft. Measurements from the three instruments were shown to compare well and overall flux uncertainty was assessed from mean and deviation of the three flux measurements which is a useful addition to understanding of ozone flux uncertainties. The authors also present a modified flux limit-of-detection method building on the cross-covariance method of Langford et al. (2015) but with refinement of the time scales which is a nice addition. Finally the authors present some case studies to demonstrate the utility of the observed ozone exchange velocities which potentially imply reactions on cloud droplets as a sink of ozone and spatial variability in ozone deposition to the ozone surface on small spatial scales. My two broad comments are 1.) that while the measurements seem to be of a high quality, some relevant details of the flight campaign and data processing are lacking in places (see specific comments below), and 2.) that the analysis of the case studies are underdeveloped and conclusions of cloud loss and spatial heterogeneity need more support if they are to be included. I appreciate that these case study results are not the primary focus of this methods paper, but the authors are still making conclusions about ozone loss to clouds that I believe need more support. Some specific comments on this are included in the major comments below. Overall the comparison of the airborne ozone measurements is novel and valuable and is suitable for AMT with some revision. The interpretation of the case studies seem reasonable but require additional information in order to support the conclusions of the authors. If the above points are addressed then this work will likely be a useful contribution to AMT.

**Major Comments:**

Q1: Line 96: Some additional discussion of the EC flux leg design is needed in the main text, not just table S1. What were the lengths of these flux legs? What is the airspeed of the aircraft? Were stacked legs flown at multiple altitudes in the same location? Were vertical profiles out of the boundary layer performed to constrain the potential entrainment term?

A1: Regarding the flights, the following text has been added to the revised manuscript:

Flux legs were typically 5-10 minutes long. At airspeeds of ~110 m $s^{-1}$, flux legs covered 30-70 km. A typical flight module consisted of three legs flown in a stacked manner (RF03-B, RF03-C, and RF07-A). However, in the case of RF03-B, fluxes were below detection. Hence, other flight legs were opportunistically used for flux calculations on level legs in the marine boundary layer (MBL). Dedicated flux segments were accompanied by profile descents and ascents.
A discussion of entrainment has been added and is addressed elsewhere (see our response to the comment on section 3.5).

Q2: Relatedly, basic details of the eddy covariance data processing and quality control are missing. For example, was there a stationarity criteria applied to the flux data, what is the impact of high pass attenuation for the closed path sensors and was a correction applied. What are the random and systematic turbulent sampling errors (Lenschow et al. 1994, https://doi.org/10.1175/1520-0426(1994)011%3C0661:HLILEW%3E2.0.CO;2) ? These types of details are needed for a proper evaluation of the methods and results presented.

A2: Regarding stationarity, we have added the following text to the revised manuscript:

Stationarity is not required for wavelet analysis (WA) because WA decomposes the total flux into component fluxes at different frequencies.

Regarding the frequency response of closed path sensors, the following text along with two new SI Figures have been added to the revised manuscript:

The cospectra in Fig. 5 peak from 0.1-0.2 Hz, indicating that the bulk of the fluxes occur at 5-10 s time scales. These timescales are typical for fluxes in the MBL, and an order of magnitude larger than the mixing time for the Fast $O_3$ instrument, which for background chracterization purposes had zero-air injected in from the aircraft inlet. The e-fold rise time was <0.5 s, fast enough not to introduce bias to the flux measurements (see Figure S3 in the SI). Indeed, the cumulative frequency graph (ogive) shows that in the case of RF03-C-2, less than 10% of the total flux is carried on <1 s timescales. Ogives are shown in Figure S4. The residence time in the fast ozone instrument detection volume implied a maximum frequency response of 9 Hz. However, high pass attenuation in the inlet manifold limited the frequency response of the fast O3 instrument to 3 Hz (Lenschow & Raupach, JGR 96(D8), 15,259-15,268, 1991). The FAIRO instruments were not equipped with zero-air injection at the inlet. However, the residence time in the FAIRO flow is shorter than that in Fast O3. A calculation of FAIRO inlet manifold attenuation of high frequency signals above 20 Hz, and therefore was not the limiting factor in the FAIRO instrument frequency response, Thus the FAIRO was more sensitive to high-frequency fluxes than the Fast O3 instrument.

Figures S3 and S4, which have been added to the revised SI, appear below:

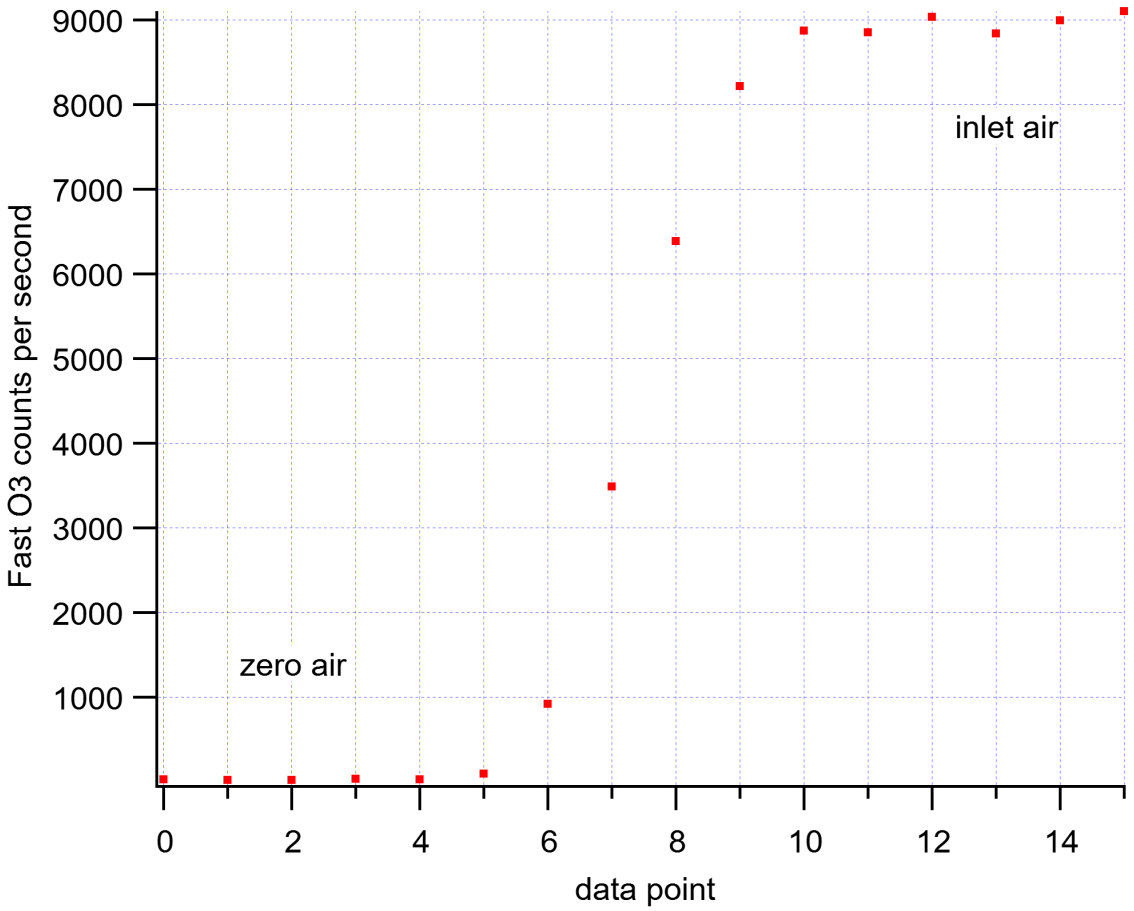


Figure S3: Fast O3 photon counts during valve-switching from zero air back to sampling outside air from the inlet. Data points are collected at 10 Hz.

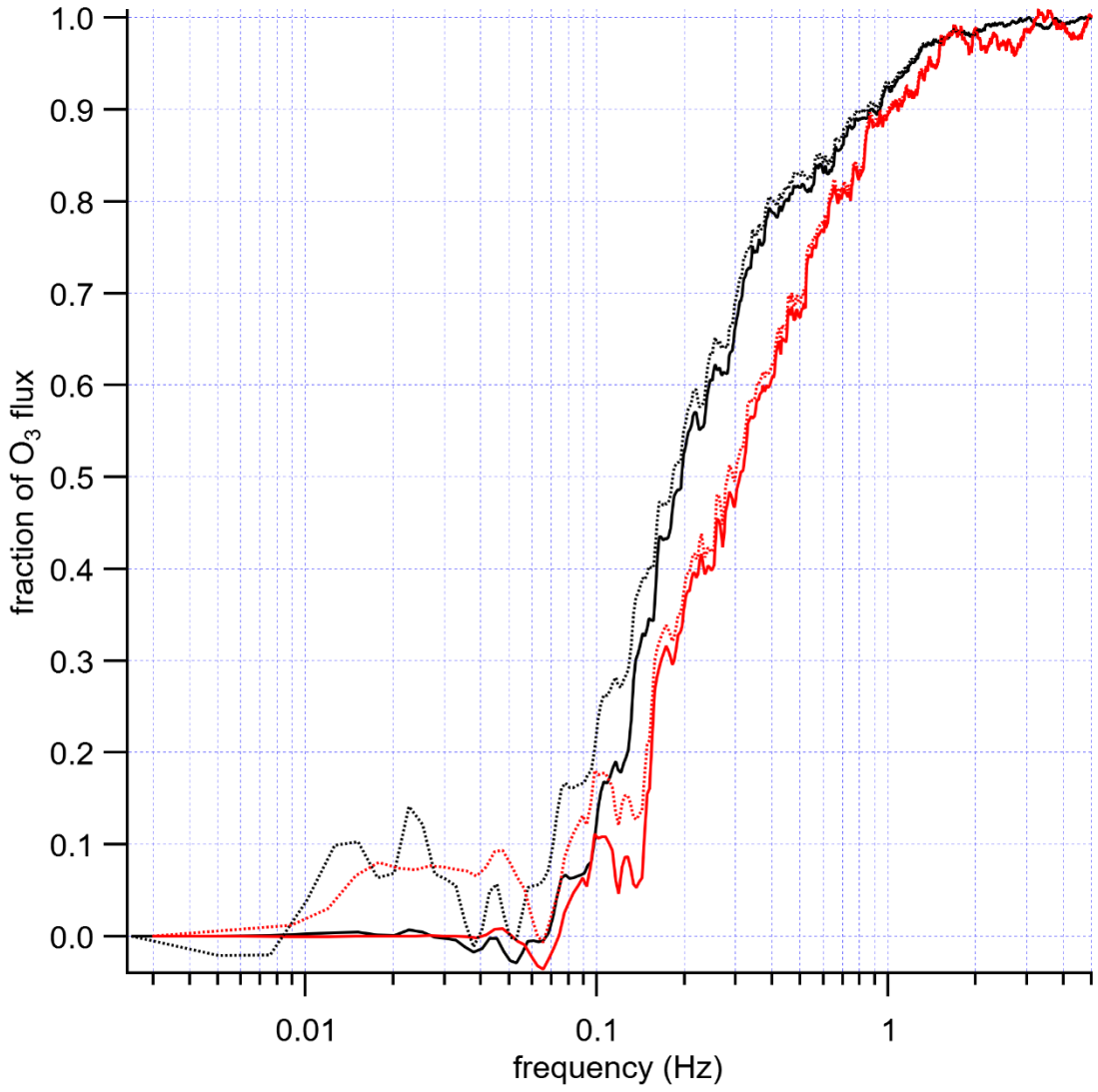


Figure S4: Cumulative frequency graphs (ogives) for RF03-C-2 (black) and RF04-A-1 (red) of the ozone fluxes from the Fast O3 instrument. Solid lines: detrended to 10 s; dotted lines: no detrending. Detrending eliminates fluxes over >10s time frames. Fluxes at frequencies >1 Hz account for ~10% of total flux.

Q3: Line 255: The large time desynchronization mid-flight mentioned around line 255 even after applying the manual synchronization method is concerning. Inlet flow would have to vary strongly as a function with altitude or clock drift would seemingly have to be non-linear to describe this behavior. Were either of the inlets for the ozone instruments pressure and or mass flow controlled? What implications are there for systematic flux uncertainty if flow rate changed significantly as a function of altitude?

A3: The text has been revised to clarify what appears to be a misunderstanding here. The 5 s time offset is from before manual synchronization of computer clocks; this is an artifact which occurred on an

individual flight when the instrument computer's clock was not being synchronized with the time server. We mention this because the ability of the method for manual time synchronization based on O3 and H2O is found to be capable of capturing even such large artificial delays; this should thus be reassuring rather than worrisome. After time synchronization, delays typically less than 0.5 s, consistent with internal flow differences between closed path sensors. We have clarified this in the revised manuscript:

Because the Fast O3 instrument computer was not synchronized with the time server, there was an artificial delay of 5 s between it and VCSEL. After the time synchronization procedure, even artificial clock delays are resolved to within ±0.1 s.

The flow through both instruments is described in the manuscript:

"The total mass flow in the inlet was 2370 sccm." for Fast O3 and "Outside air was pulled at 11 vol.-L $min^{-1}$ at ambient pressure" for FAIRO.

The implications for systematic error in the fluxes is addressed in this new text in the revised manuscript:

Whereas the Fast $O_3$ instrument used constant mass flow at constant pressure, the FAIRO instruments used constant volume flow at ambient pressure. In principle, the flow rates in the two instrument designs could differ between the high altitude/low pressure legs typically used for time synchronization and the low altitude/high pressure legs used for flux measurements. Although the different flow rates can create time lag between wind and ozone data, no systematic error is introduced to the ozone flux because we empirically determine the time offset, and do not prescribe a constant offset in the MATLAB flux toolkit. Rather, the time synchronization is used in conjunction with water vapor fluxes calculated from VCSEL data to find the true ozone time offset.

Q4: Figure 5. Some additional analysis of the spectral response would be appreciated in the SI. Generally it would be useful to validate that there is no significant high-frequency attenuation for the ozone instruments and comment on any attenuation corrections applied.

A4: We address this along with the previous comment regarding volumetric flow rates and stationarity with the addition of the following text (see A2).

Q5: Section 3.5: My primary comment on the manuscript relates to this section as a whole. There are limited conclusions that you can draw from an eddy covariance flux measurement at a specific altitude in isolation. Interpreting the measured flux values to infer source or sink terms requires some knowledge of the vertical profile of (here) ozone mixing ratios and fluxes. The magnitude of the surface deposition and the entrainment flux at the top of the boundary layer influence what the measured flux magnitude (and direction) will be at some altitude in the boundary layer in addition to chemical source and sink terms at the measurement altitude. The O3 vertical profile shown in Figure 6 shows lower O3 mixing ratios aloft then a weak turnover at ~1200 m, however it is not clear what the boundary layer top is and what the profile is above that. While the measured ozone flux could be indicative of loss on evaporating cloud droplets, there may be contributions from entrainment of ozone depleted air from the free troposphere into the boundary layer. At a minimum some marking of the boundary layer height, ozone mixing ratios above the boundary layer, and the cloud depth would be quite useful on this figure. More generally I encourage you to present these results as vertical flux divergence figures ( see Wolfe et. al. (2015) () and Conley et. al. (2011) for examples). Some estimate of entrainment velocities in the clear sky case could also be useful both as a valuable result in their own

right, but also to aid in interpretation of the cloud loss argument (see Faloona et al., https://doi.org/10.1175/JAS3541.1)

A5: We agree, and are providing more context to our observations based on this feedback:

The entrainment velocity as defined by (Deardorff, 1976) is modified here, as in exchange velocity, such that upward is positive:

$$w_e = \frac{flux(ppbms^{-1})}{\Delta{-}concentration(ppb)} \times \frac{100cm}{1m} \quad (9)$$

In Equation 9, Δ-concentration is the difference in the concentration of a species across a boundary to the mixed layer. In previous work, the flux at the transition layer (TL) was extrapolated from the measured fluxes in stacked legs within the MBL and used to estimate the entrainment velocity (Faloona et al., 2005; Wolfe et al., 2015). This method is not applicable to the RF03-C legs because the conditions are not mixed to the surface, and because RF03-C-2 is flown en route to the airport in a decoupled TL characterized by minimum $O_3$ concentrations and a partial cloud layer near the top (visually estimated from flight videos as ~1 km). The MBL below extends to ~500m, and the entrainment velocity measured during RF03-C-3 at this altitude (Figure 6, Panel A, shaded) is 6.3 times smaller than the exchange velocity based on the observed $\Delta O_3$ of 5.2 ppb and Eq. (9) (existence of a concentration change is not necessarily indicative of a flux); the lower $O_3$ in the decoupled TL is hence curious. Contributions due to entrainment of ozone from the free troposphere would result in a negative exchange velocity during RF03-C-2 (the $O_3$ profile increases with altitude in the free troposphere) and cannot explain the positive $O_3$ exchange velocity observed. If there were a significant $O_3$ entrainment from aloft, the observed positive $O_3$ exchange velocity would be a lower limit.
Furthermore, the temporal correlation between the $O_3$ and $H_2O$ fluxes along RF03-C-2 are neither consistent with entrainment from above, nor detrainment from below as a driver of the observed exchange velocities, since the $H_2O$ profile is continuously decreasing with altitude. The negative $H_2O$ flux during RF03-C-2 cannot be explained by entrainment from above or from below. Overhead cloud cover can be qualitatively estimated from $NO_2$ photolysis frequency ($J_{NO2}$) measured by the HIAPER Airborne Radiation Package (HARP) actinic flux instrument (Figure 6, Panel B). During cloud-free portions of RF03-C-2 the exchange velocity approaches zero for both $H_2O$ and $O_3$, indicating that the observed exchange velocities are cloud related. There are only two possible explanations: (1) the cloud induces dynamical change to increase $O_3$ entrainment from the MBL into the decoupled TL (in which case the $H_2O$ source above the aircraft is a lower limit); or (2) the cloud above is a sink of $O_3$ and a source of $H_2O$ (evaporating cloud). Notably, the WA time series in Fig. 6 reveals a pronounced maximum $O_3$ exchange velocity of +1.8 cm $s^{-1}$ at the edge of a cloud. Such a large $O_3$ exchange velocity would require a 5 times larger $\Delta O_3$ towards the MBL than is compatible with the observed $O_3$ profile, and would require $O_3$ concentrations in the MBL well in excess of 50 ppbv. No such elevated $O_3$ concentrations were observed anywhere near this case study, nor during landing (the $O_3$ concentration two minutes before landing was 32 ppbv, compatible with the profile shown in Fig. 6). Detrainment of $O_3$ from below, and entrainment of $O_3$ from the free troposphere hence cannot explain the observed positive $O_3$ exchange velocity during portions of RF03-C-2. We conclude that a chemical $O_3$ sink related to an evaporating cloud is the most likely explanation for our observations.

The revised version of Figure 6 appears below:

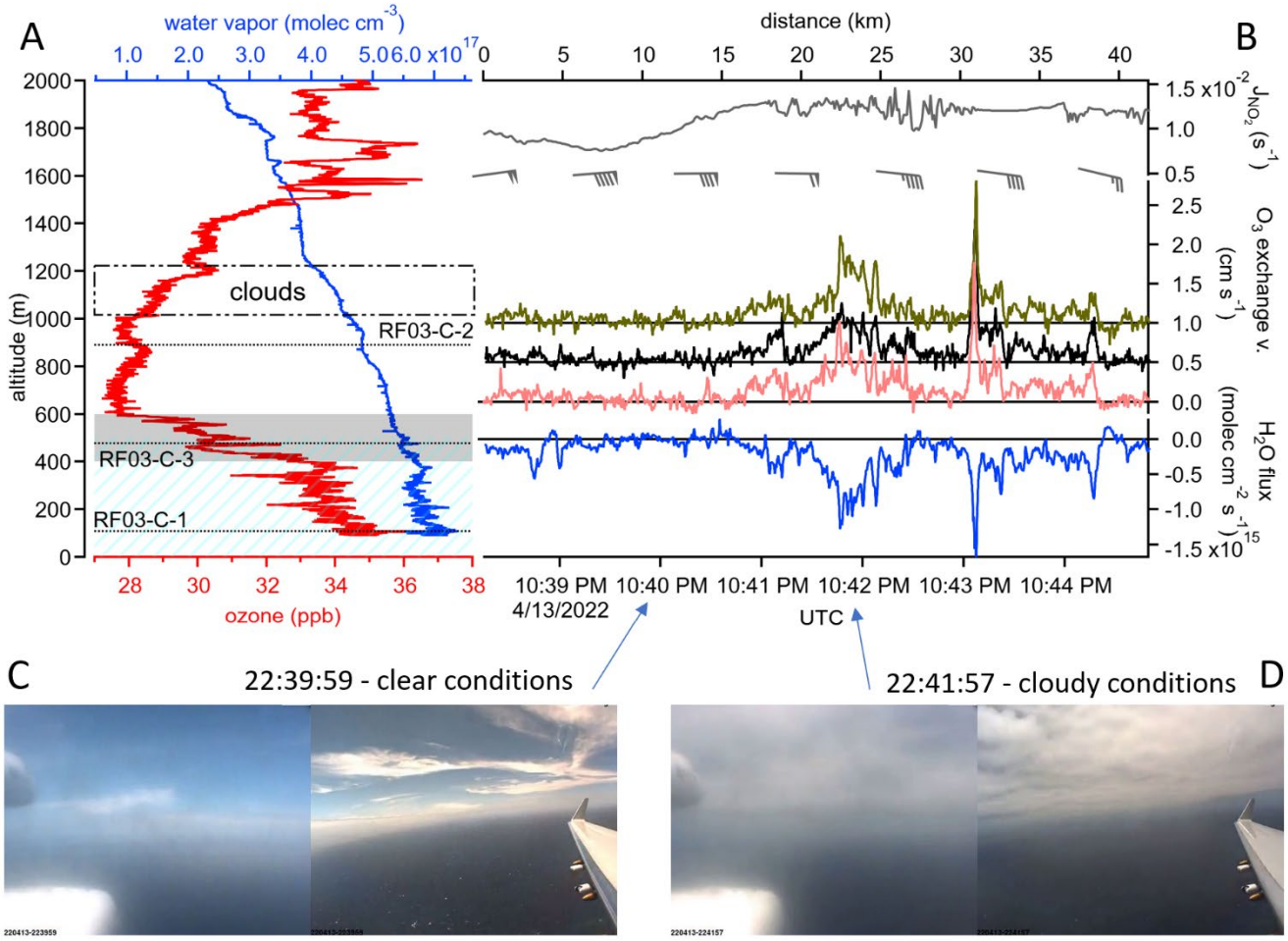


Figure 1. Ozone and water vapor vertical profiles and time series for EC fluxes from the RF03-C leg. Ozone profile is the average of all three instruments. Dashed lines indicate flight altitudes; dashed rectangle represents visually estimated cloud layer. Right: $J_{NO2}$ in gray, fluxes from Fast O3 (salmon), FAIRO 1 (black), FAIRO 2 (olive), and VCSEL (blue). Vertical offsets of 0.5 cm s$^{-1}$ and 1 cm s$^{-1}$ have been added to FAIRO 1 and 2 to better illustrate the close agreement between the three $O_3$ instruments. Images of the webcams from RF03 flight movies illustrate cloud cover conditions.

Q6: Similarly for Fig 7 and the related discussion, I agree that the observed variability in measured O3 exchange velocity is not due to turbulence and reflects some variability in the oceanic or atmospheric chemical state. However you do have at least some additional information that can be used to constrain this observed behavior. Are O3 mixing ratios changing significantly across the flux segments? How do the vertical profiles and the beginning and end of this segment compare?

A6: Because the RF03-C flux legs were performed on approach to the airport for landing, only a descent profile is available. Ozone profiles have also been added to Fig. 4, included below:

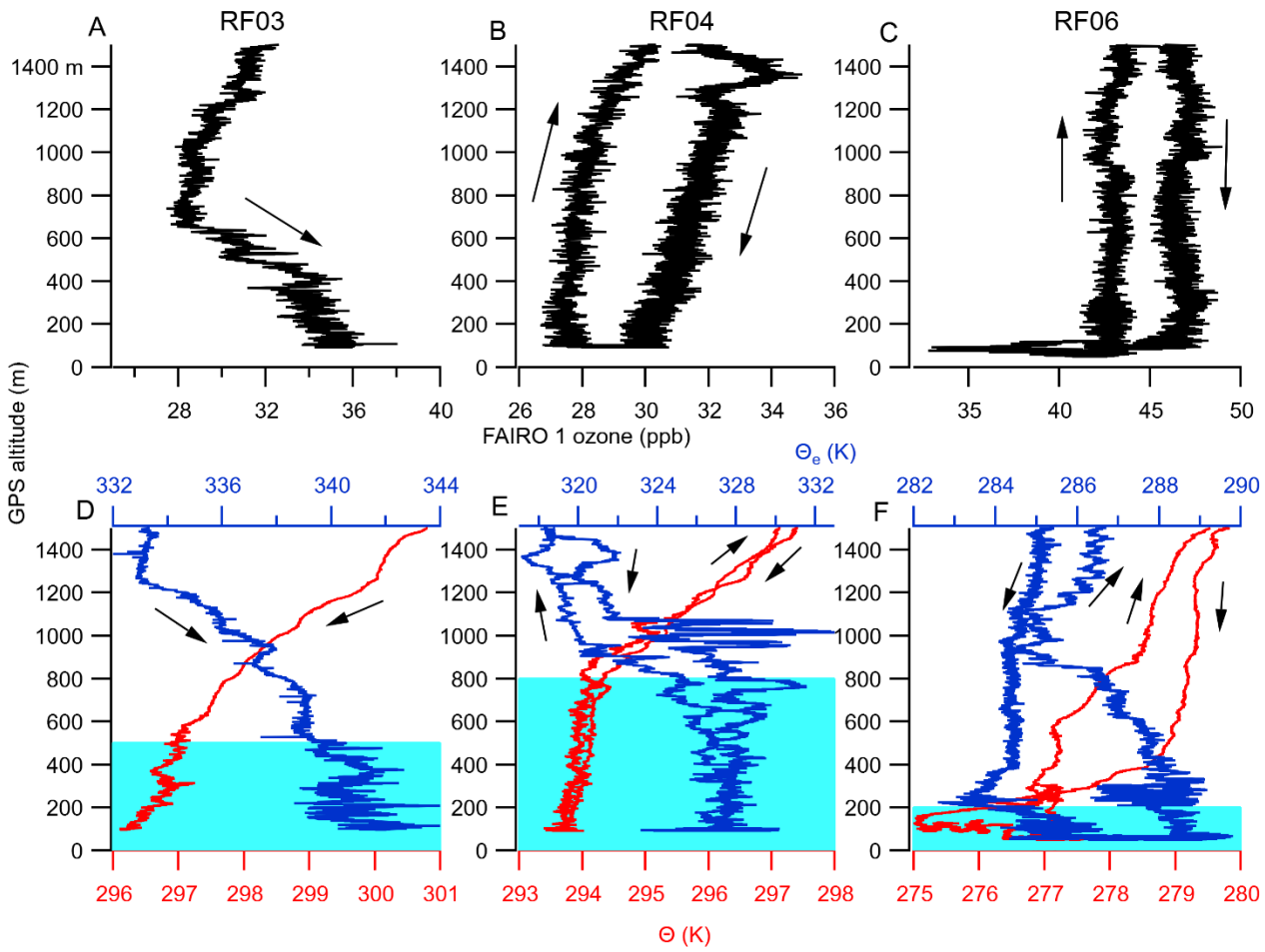


Figure 2. A-C: Profiles of ozone during RF03-C, RF04-A, and RF06-A, respectively. D-F: Corresponding potential temperature and equivalent potential temperature profiles for RF03-C, RF04-A, and RF06-A, respectively. MBL height is shown as light blue shading. Arrows indicate profile ascents and descents.

Overall, I don't think the interpretations suggested by the authors are unreasonable, however they should be presented in a more comprehensive way with more relevant constraints.

**Minor Comments:**

Q7: Line 36: The implications of the observed high variability of v(O3) should be made more explicit in the abstract.

A7: The revised abstract now reads:

Additionally, we present two case studies. In one, the direction of ozone and water vapor fluxes were reversed (vO3 = +0.134 ± 0.005 cm s-1), suggesting that overhead evaporating clouds could be a strong ozone sink. Further work is needed to better understand the role of clouds as a possibly widespread sink of ozone in the remote marine boundary layer. In the second case study, ozone fluxes vO3 are negative (varying by a factor of 6-10 from -0.036 ± 0.006 to -0.003 ± 0.004 cm s-1), while the water vapor

fluxes are consistently positive due to evaporation from the ocean surface and spatially homogeneous. This case study demonstrates that the processes governing ozone and water vapor fluxes can become decoupled, and illustrates the need to elucidate possible drivers (physical, chemical, or biological) of the variability in ozone exchange velocities on fine spatial scales (~20 km) over remote oceans.

Q8: Line 61: Much is made of the rarity of comparison studies of ozone flux but there is no motivation for specific knowledge gaps that such comparisons can provide. To my knowledge there has not been much suggestion in the literature that instrument uncertainty is a major driver of overall uncertainty in parameterizing ozone deposition. Some synthesis of the literature and implications from previous comparison studies would be welcome here to motivate this study.

A8: We appreciate this comment, and agree with the reviewer.

We also note, that for example reviewer #2 suggests instrument uncertainties are caused by water sensitivities as major uncertainties in ozone fluxes. This is also a view in the community. Our responses below makes it clear that these water sensitivities are indeed small. We thus agree with reviewer #1. However, there is no previous intercomparison of different instruments that rely on different measurement concepts and respond differently to water sensitivities on research aircraft. We have clarified this in the revised manuscript, along with other reasons that motivate this work.

Q9: Line 70: Hannun et al. (https://doi.org/10.5194/amt-13-6877-2020) presented airborne EC flux results over the ocean and a comparison of mixing ratio measurements from a new broadband cavity-enhanced UV absorption instrument with an NO chemiluminescence instrument on the NASA DC-8 aircraft during the FIREX-AQ campaign.

A9: Thank you for this helpful comment. We have made significant revisions to that introductory paragraph:

Whereas EC flux measurements of ozone are numerous, comparison studies are fewer. Ozone fluxes from EC methods have been compared to those from gradient measurements (Muller et al., 2009; Zhu et al., 2020; Loubet et al., 2013) and dynamic chamber methods (Plake et al., 2015). Over grassland, Plake et al., (2015) report that dynamic chamber methods agree "well" with EC flux methods (within 11-26%). Over maize fields, Zhu et al., (2020) describe the discrepancy between EC flux and gradient methods as "not very good," with gradient methods measuring ozone fluxes 11.7 – 45.6% higher than those measured by EC flux methods. Furthermore, comparisons of co-located EC flux measurements are uncommon, and complicated due to vertical gradients in the measured fluxes that may explain differences of 10% between measurements on towers (measured by chemiluminescence) and aircraft (measured by a TECO-49) (Massman et al., 1995). To our knowledge, the only aircraft instrument intercomparison for ozone EC flux was performed by Muller et al., (2010), who compared two identical dry chemiluminescence instrumental clones over grassland, and found differences up to 12% due to differing sensitivities of chemiluminescent discs. Furthermore, a water sensitivity for chemiluminescent measurement techniques (Ridley et al., 1992) has been suggested to propagate onto EC ozone flux measurements (Boylan et al., 2014), and methods for water correction differ between different methods for measuring ozone. More commonly, a fast ozone instrument is compared to other ozone instruments only in terms of concentrations (Conley et al., 2011; Hannun et al., 2020). There is currently no intercomparison of different fast ozone instruments that rely on different measurement concepts and respond differently to water sensitivities on research aircraft. Furthermore, the error analysis to estimate EC flux uncertainties is not well developed and is not always treated consistently. This leaves room for instrument and method uncertainty as drivers for overall uncertainty in parameterizing ozone exchange velocities and deposition. Here we eliminate spatial gradients as a source of uncertainty in ozone EC flux intercomparisons by deploying three ozone instruments of two different designs on research aircraft in remote marine air. We further use the agreement found among

the three sensors to evaluate and refine the EC flux error analysis and define better criteria of use to estimate detection limits.

Q10: Line 109: An estimate of the total volumetric inlet residence time would be useful. Same for the FAIRO instruments.

A10: The following text has been added to the revised manuscript. For Fast O3: Total residence time is ~2.5 s. For FAIRO: Residence time in the line is approximately 0.3 s.

Q11: Line 170: How many of these anticorrelation synchronization anchors do you generally get in a flight? Do you use events at all altitudes or only ones at low altitudes relevant for the flux sampling conditions.

A11: The following text has been added to the revised manuscript:

Anticorrelation events are not uncommon. For instrument intercomparison, anticorrelation events from the start and end of the entire flight are used to synchronize data; averaging the synchronized data over 10 s is sufficient to resolve any residual (<100 ms) synchronization uncertainty. For flux sampling, anticorrelation events were found before and after each flux leg.

Q12: Figure 5: What is driving the shift in the cospectra toward higher frequencies on RF6 and the rapid fall off in spectral power at frequencies below 0.1 Hz? Could be due to the detrending method or due to real atmospheric turbulent structure. Analysis of the vertical wind power spectra would help clarify.

A12: The following text has been added to the revised manuscript:

Detrending the data at 10 s removes spectral power and frequencies below 0.1 Hz.

Please also see A2, where ogives have been added to the SI.

Q13: Relatedly at Line 226, it is not clear that a fixed detrending window of 10 s is appropriate when boundary layer height and cloudiness and thus convective strength are varying between flux legs. Some additional justification would be useful.

A13: The following text has been added to the revised manuscript:

For all flux legs, various detrending times were tested to see whether visually identifiable structures could be observed in the cross-covariance. A uniform 10 s detrending time was found to remove systematic structures from all flux legs. To minimize the number of subjective inputs, we did not attempt to customize the detrending time for each flux leg. Because detrending accounts for meteorological conditions rather than instrument response, meaningful intercomparisons could be performed using uniform conditions and consistent detrending times.

Q14: Line 318: Filtering out low signal to noise flux measurements does not seem totally appropriate. These measurements provide real information on the flux magnitude (e.g. that they are below the LOD). Excluding those values from an average of the ozone flux would artificially bias the magnitude low, much like excluding below LOD gas phase mixing ratio measurements would add a high bias to the mean. This is of minor importance in this paper since flux results are mostly considered in the

context of case studies from single flux legs, but I want to raise this as a general point in the data interpretation.

A14: We do not report a global average of fluxes due to the technical nature of this campaign. We only summarize cases where fluxes are above detection.

Q15: Line 363: How are the "relatively smooth areas of cross-correlation near the candidate peak" identified?

A15: The following text has been added to the revised manuscript:

Identifying "smooth" areas was necessarily subjective as the cross-correlation behavior is unique to each leg.

**Technical Comments:**

Q16: Line 143: Give inlet diameter in cm or mm instead of inches.

A16: The revised manuscript reads:

The FAIROs sampled from a separate HIMIL (aft-facing inlet line) through a PFA line with a length of 4.3 m and a 0.42 cm (1/6 in.) inner diameter.

**Citation**: https://doi.org/10.5194/amt-2023-198-RC1