

Response to Reviewer 2

We thank the reviewer for their careful comments on the paper. We respond below to the specific comments made. Text added in red here and in the revised manuscript are in response to reviewers' comments. While this paper was in review, results from the CONTRAST project were published in GRL, and some additional text has been added to the manuscript (in blue) to address the CONTRAST findings.

1. The title of the paper should be more clearly express the content of the paper: (i) the focus of the paper is certainly the puzzle of what is the best approach to correct ECC sonde measurements from the background current. (ii) under which tropical conditions the measurements were made.

We have added 'measurements and validation' to the title. It is not our intention to publish a paper purely on the background current issue – the results we obtained are a contribution to the ATTREX/CONTRAST/CAST objective of better understanding TTL ozone. We have also made some changes to the Abstract to clarify the aims of the paper.

2. Decades of operation of ECC sondes have shown that even small changes in instrumentation or operating procedures can have significant effects. Therefore a proper and systematic description of the ECC-instrumental layout and the operating procedures applied are essential. When describing the operating procedures of the flown ECC sondes it should be expressed more explicitly when these deviate from the standard operating procedures (SOPs) as recommended by WMO and documented in WMO-GAW-report No.201 and what would be the impact on the ozone sonde measurements made in this study. Some deviations from SOP's here are: - ENSCI with 1% KI full buffer instead of 0.5% and half buffer - Box temperature instead of internal pump temperature - Filtered (ozone free) air instead of purified (zero air) - Effect of humidification (after passing relatively dry hair, here 50% RH) of sampled air flow on the determination of the pump flowrate during pre-flight preparation of the sonde

We have added the following text (also responding to reviewer 1's comments):

The procedures used in Manus departed, as already mentioned, from the GAW recommendations. The most important deviation (a consequence of the malfunctioning calibration unit, see below) was that the majority of sondes were not exposed to ozone during preparation. This turns out to have been advantageous, as it avoided the decay in I_{bg} reported by Vömel and Diaz (2010). Smit et al. (2007) report that the background current measured 10 minutes after exposure to ozone in the final preparation (the standard way of measuring I_{bg} , denoted IB2 in the GAW recommendations) exceeded that measured before exposure to ozone (IB0 according to GAW) by 34 nA on average for a sample of five EnSci sondes. By contrast, for the uncontaminated sondes in Manus the average difference in I_{bg} measured at the beginning and end of the final preparation was only 6 nA (Figure 2). Together with changes in solution to ensure that I_{bg} fell to around 50 nA, not exposing the cell to ozone resulted in a stable I_{bg} during preparation, lending confidence to the subsequent assumption that it remained constant during flight. We examine this assumption further in the next section.

Other departures from GAW recommendations were:

- the use of a 1% solution rather the 0.5% which leads to an oversensitivity to ozone and a bias of $\sim +5\%$ in ozone concentration (WMO, 2013)
- measurement of T_{box} rather than the pump temperature, leading to an underestimate of ozone by $\sim 3\%$ since the pump temperature is higher by around 10°C (WMO, 2013)
- use of a charcoal filter to provide ozone-free air rather than an ozone-free gas supply. The effect of this is difficult to quantify, but will be most serious in a laboratory with humid air and measurable concentrations of ozone. In this case the relative humidity of cabin air was around 50%, within the expected operational range of the filter. On occasion a sonde was allowed to sample laboratory air without the filter attached, but this made no difference to the measured current. This means either that the laboratory was essentially ozone-free or that the filter was not working. When the sonde

- was taken outside and the filter removed, an increase in signal was measured, so we conclude that the filter was working correctly and that laboratory air was essentially ozone-free.
- correction to pump flow rate measurement for humidification of air. For a laboratory at 20°C and 50% RH this correction reduces F in equation 4 by around 1.5% (WMO, 2013), increasing ozone by the same amount – in other words equation 4 underestimates ozone by ~ 1.5%.

The overall effect of departures from the GAW recommendations is therefore small – much smaller than the error due to the background current uncertainty for tropical tropospheric ozone concentrations.

3. Further, it is recommended to use same definitions of background currents as used in SOP's : IB0 = background current (after 10 minutes ozone free air) before exposure with O3 IB1 = background current (after 10 minutes ozone free air) after exposure with O3 (50 ppbv for 10 minutes) IB2 = background current measured with zero air at launch site just before launch. SOP's recommend a background correction: IB2, constant

Nowadays when using purified air: IB0 is between -10nA and +20 nA IB1 is about 40-50 nA IB2 is about 40-50 nA When using charcoal filters these usually "generate" larger IB0, IB1 and IB2.

In the paper it is not always clear which IB the authors mean. For example when changing solutions in the laboratory and flushing the sonde with ozone free air then IB should be very low , having values close to IB0. The need to change sensing solution of the ECC-cells is not the usual SOP-case and indicates that there are problems with the EEC-sonde or zero air supply. The authors should discuss this more explicitly in the paper.

We do not agree with this comment for the following reason. The GAW SOPs are designed for a procedure whereby the sonde is exposed to ozone during preparation. We did not do this due to the malfunction of the TSC01, and argue in the paper that this was, in fact, an advantage since the background current remained more stable during preparation than it would if the sonde were exposed to ozone. Thus, adopting the GAW conventions would be misleading: the value of I_{bg} we used does not correspond to any of them. We do however follow the GAW practice of using I_{bg} measured just before launch.

P16656, L26: Add reference Folkins et al, 1999 because he was the first investigator who identified the mixing barrier at 14 km altitude and the TTL region above by ozone measurements.

Done

P 16660, L7: Better reference Komhyr, 1969 instead of Komhyr 1972

Done

P16660, L16: Better reference Komhyr, 1969 instead of Voemel and Diaz, 2010

Done

P16661, L6: Replace "pressure" by "time".

Done

From several laboratory investigations it is known that there is no pressure, or significant oxygen dependence. However, there are indications that the origin of the background current is caused by a small second chemical path way of O3 + KI producing a chemical intermediant followed by a slow decaying chemical reaction producing Iodine molecule. This second chemical pathway is strongly dependent on the strength of the phosphate buffer concentrations. This should be pointed out more clearly in the paper.

This is now pointed out in the text, section 2.1

Further this second chemical pathway have a typical decay time of 20-30 minutes (Voemel and Diaz). Contaminants favourizing this second slow decaying chemical pathway can explain the excess, slowly decaying background contribution in the hybrid background correction derived by the authors from their post-campaign laboratory experiments (Appendix A)

We have included at the end of the appendix:

This decay in I_{bg} is consistent with the slow timescale for the reaction of KI with peroxide identified by Cohen et al. (1967).

P16663, L4-5: The repeated changes of the sensing solutions needed to reduce the background current is a serious point of concern: this not normal practice. Either sondes or gas flow is contaminated.

No, it is not normal practice, and the reason we discuss it in the paper is that we found that doing so ensured a stable and repeatable background current during preparation. As a result we managed to get excellent agreement with the aircraft measurements.

P 16663, L10-20 Point to consider: Air conditioned laboratories with much colder temperatures than the outside ambient air as in the Tropics can be a source of problems of condensation of water vapor when moving instruments (e.g. gas filters or TSC01) between laboratory and ambient air (much warmer and wetter) conditions. Or particularly when sucking ambient (moist) air through a tube into the relative colder TSC01- preparatory instrument in the laboratory. For example: when once traces of liquid (condensed) water “stick” in the TSC01-quartz glas cuvette and being irradiated with UV-light this can produce not only O3 but also significant amounts of H2O2 (resolved in the liquid water). Evaporated gaseous H2O2, even present when UV is turned off and flushed with zero air, will react also with KI in cathode cell but its response time in ECC-sonde is very slow and typical of the order of 20-30 minutes. This might be the origin of the contamination that occur at the beginning of the campaign and explain the large background currents and the pressure dependence but which is actually a time dependent declining of contaminant (s) eg. H2O2 in the ECC-cathode sensing solution.

We thank the reviewer for this suggestion. This does seem consistent with the problem we encountered and although we have no record of condensation problems in the laboratory we can't rule out the possibility either. We will add the following text to Appendix A2:

A plausible explanation for the contamination, pointed out by one of the reviewers, is that condensation of water occurred inside the tube at some point, which, when irradiated by ultraviolet light, led to the production of hydrogen peroxide. H2O2 is known to react with KI in the cathode cell with a very slow response time, consistent with the behaviour of the contaminant, and to stick to surfaces for a long time. The contaminant appeared first thing in the morning when the equipment had been enclosed in the air-conditioned laboratory overnight.

Chapter 3 Validation

The intercomparisons with aircraft gives some experimental evidence that the hybrid correction method is a good approach to overcome the specific difficulties caused by the contamination and that a constant $I_{B2} = 50$ nA correction is also most convenient in case of “non-contaminated sondes”.

The text discussing Fig. 4 now ends:

We conclude that the hybrid correction provides a satisfactory estimate of I_{bg} but reiterate the point made in the previous section that a quantitative error estimate in TTL ozone for the contaminated sondes is not possible.

*P16666, L2426: It is to be noted that the Voemel & Diaz (V&D) correction is directly linked to the “stationair” value of the stoichiometry of the reaction of KI + O₃ > I₂ which can be larger than 1 (generates more than 2 electrons) depending on the strength of the phosphate buffer concentrations (Johnson et al, 2002). However, the V&D method will usually overestimate the background effect when cell currents are larger than 1000 nA. The hybrid method used in this study have nothing in common with V&D background correction of a constant and time dependent part. Also clearly express that the here used V&D correction is for sondes with 1%KI full buffer. For sondes with 0.5%KI, half buffer the stoichiometric factor 0.09*I is much smaller.*

We agree, we should not refer to V+D here, and have removed this sentence. Also we have added ‘1% KI full-buffer’ where suggested.

The experimental evidence as presented in Appendix A1-A4 is rather limited and certainly not sufficient or robust enough to generalize the here applied hybrid correction formula for more broader application. It might be a good starting point for further investigation in order to overcome the often enhanced background currents measured when using charcoal filters in general. However, then better and more precise laboratory experiments are needed.

We completely agree – we only consider in the paper what would happen if you applied this correction to other cases. Our aim was simply to understand the present data set. Our bell jar experiments were only intended to investigate the nature of the contamination in our system.

Chapter 4 Results

Interesting chapter but the presented results more or less confirm the results obtained in earlier studies. Nevertheless, the data have certainly much more potential for further scientific investigations. I hope the authors will do that in future work.

That is the plan

Appendix A3 is difficult to understand and should be better structured in order to distinguish better between experimental design/set up, results and implications for background current and the derived hybrid correction formula derived. Even when this part is moved into the appendix, it is still essential for the paper in order to justify the use of the hybrid correction formula developed from these experments , and particularly to overcome the contamination occurring for the sondes #3-15.

P16674, L1-2 Obviously the source of contamination has been identified but how and what kind of contamination??

We identified the source by dismantling the TSC01 and working back to the point where contamination was found – inside the tube which was irradiated by the UV light. Interestingly, we found contaminant not only in this tube but also on the PTFE manifold at the outlet of the TSC01, suggesting that the substance, whatever it was, could stick to surfaces very well. This does seem consistent with the reviewer’s earlier suggestion of hydrogen peroxide (See above).

P16674, L6-9 How did you contaminated the ozone sondes and how you can distinguish but heavily and moderately contaminated?? How bel-jar experiment works?

The TSC01 unit retained the contamination when returned to the UK. We used it as a source of contamination, with the exposure time determining the degree of contamination. We will make this point more clearly in the paper. Section A3 now starts

The effect of lowering the ambient pressure on the contamination was then investigated by placing the ozonesonde in a bell jar and lowering the pressure as the sonde continually sampled the air inside the bell jar. The bell jar was too small to admit the ozone destruction filter but ozone measurements inside the jar

at ambient pressure were the same as in the laboratory with the filter attached; thus air in the bell jar was ozone-free. Three ozonesondes were exposed to different amounts of contaminant by drawing air through the TSC01 unit for different times: the first was heavily contaminated, the second slightly contaminated, and the third not contaminated at all.

Additional references:

Folkins, I., M. Loewenstein, J. Podolske, S. Oltmans, and M. Proffitt, A barrier to vertical mixing at 14 km in the tropics: Evidence from ozonesondes and aircraft measurements, J. Geophys. Res., 104, 22095-22101, 1999.

included

SOP's: Smit, H. G. J. and the Panel for the Assessment of Standard Operation Procedures for Ozonesondes (ASOPOS): Quality Assurance and Quality Control for Ozonesonde Measurements in GAW, GAW Report No. 201, World Meteorological Organization, Geneva, Switzerland, 2012.

included

Typical low backgrounds when using purified air instead of filtered air: Deshler, T., Mercer, J. L., Smit, H. G. J., Stubi, R., Levrat, G., Johnson, B. J., Oltmans, S. J., Kivi, R., Thompson, A. M., Witte, J., Davies, J., Schmidlin, F. J., Brothers, G., and Sasaki, T.: Atmospheric comparison of electrochemical cell ozonesondes from different manufacturers, and with different cathode solution strengths: The Balloon Experiment on Standards for Ozonesondes, J. Geophys. Res.-Atmos., 113, doi:10.1029/2007JD008975, <http://dx.doi.org/10.1029/2007JD008975>, 2008.

This paper shows background currents just prior to flight of 50-60 nA for 1% KI EnSci sondes and 40-80 nA for 0.5% KI EnSci sondes. These values are consistent with ours.