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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Ozonesonde profiles from the West Pacific Warm Pool" *by* R. Newton et al.

Anonymous Referee #2

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General remarks:

This paper presents the results and analysis of a series of 39 ozonesonde profiles collected from Manus Island in the West Pacific in February 2014 to investigate the vertical distribution of ozone a tropical area with strong deep convective activity, high tropopause altitude with very cold temperatures and low upper tropospheric (UT) ozone volume mixing ratios (VMR). From scientific point of view very interesting and challenging study to investigate the morphology of the vertical distribution of ozone under these strong convective conditions and certainly appropriate for publication in ACP. The difficulty here is the use of electrochemical (ECC) ozone sondes in these maritime Tropics to measure the typical low ozone concentrations in the troposphere whereby the background signal is the limiting factor in detection limit and accuracy of the ozone mea-

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surements. Even low background current values of about 50 nA (O3 partial pressure equivalent is about 0.18 mPa) can already be of the same order of magnitude as the low ozone pressures with values of 0.2-0.4 mPa which typically exist in the UT in the West Pacific. It is obvious that the background current is a crucial factor in the accuracy of the here reported ozone sonde measurements and the scientific interpretation of the measured vertical ozone distribution.

The authors have this clearly recognized and the major part of the manuscript is addressing this complexity of proper determining the background current of the flown sondes before launch and the best approach to correct for this background current. In this study it got even more complicated through the contamination in the ozone free air supply during the pre-flight preparation. This contamination (origin unknown) occurred at the beginning of the campaign and affected the first 15 sondes by causing much larger background currents than the typical values of about 50 nA obtained in the second part of the campaign. After the campaign in their home laboratory the authors have attempted to solve the origin of this contamination and how to correct for by having hybrid correction of a constant background plus a pressure dependent declining background-excess which has been assumed to be caused by the contamination.

In a qualitative way the authors have certainly fulfilled most criteria of a proper presentation, analysis and discussion of the instrumental aspects of the background current, its correction for and the impact on the ozone sonde measurements. However, what is missing but finally is essential for using ECC sondes at these low UT ozone pressures is a uncertainty analysis and discussion on the quantitative impact on the measured vertical ozone distribution in quatitave terms. Further, the experiments described in appendix A which give the rational for the applied pressure dependent correction of the “contaminated part” of the background correction are not clearly to understand and should be better structerized and more clearly formulated. Therefore, I would rate the paper as being acceptable for publication but first after major revisions

Specific remarks:

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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 where made.

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 explicitely 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) - Efeect 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

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

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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 explicitely in the paper.

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.

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

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

P16661, L6: Replace “pressure” by “time”. 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. 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)

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.

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 particu-

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larly 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 contaminent (s) eg. H2O2 in the ECC-cathode sensing solution.

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 IB2 = 50 nA correction is also most convenient in case of “non-contaminated sondes”.

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.

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

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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.

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.

Appendix A

Appendix A3 is difficult to understand and should be better structurized 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?? 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?

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. Geophy. Res., 104, 22095-22101, 1999.

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 Or-

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ganization, Geneva, Switzerland, 2012.

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 solutionstrengths: The Balloon Experiment on Standards for Ozonesondes, J. Geophys. Res.-Atmos., 113, doi:10.1029/2007JD008975, http://dx.doi.org/10.1029/2007JD008975, 2008.

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