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Atmospheric Measurement Techniques Discussions

Interactive comment on "Ozone sonde cell current measurements and implications for observations of near-zero ozone concentrations in the tropical upper troposphere" *by* H. Vömel and K. Diaz

Anonymous Referee #1

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1 General comments

The paper by Vömel and Diaz presents laboratory experiments that strongly suggest a modification of the usual background estimation procedure used for ECC sonde measurements of the atmospheric ozone profile. For a large number of actual ozone soundings, their modified background subtraction gives more realistic and plausible ozone profiles. The paper summarizes a lot of known and semi-known facts about ECC soundings and puts them in a new perspective. Previous work is well represented, the new results are well put into the context of existing research. Reasoning

and logical flow of the paper is generally good. The presented facts largely support the conclusions. Overall this is a good paper, with important implications.

There is, however, one important aspect, that, in my opinion, is not addressed well. This is the question of hysteresis. It is quite clear, also from the presented time series in Figs. 2 and 3, that the current $I(t)$ recorded by the ECC sonde at time t is the convolution of the previously encountered ozone levels $O_3(t')$ with some response function $f(t-t')$:

$$I(t) = \int_{-\infty}^{t} O_3(t') f(t-t') dt' \quad (1)$$

The response function describes the exponentially decaying "memory" of the ECC sonde for encountered ozone levels. This decay can be seen e.g. in Figs. 2 and 3.

Unfortunately, the authors have largely chosen to ignore this time dependent hysteresis effect in the paper. Instead they use time-constant background currents, obtained by time-constant ozone over fairly long time scales of $t > 30$ min to hours). They then assume that the obtained constant backgrounds are a linear function of the constant ozone levels (Fig. 4). This approach has the advantage of resulting in a very simple modification of the ozone vs. current relation (in their Eq. 3 I_{bg} is simply replaced by $\alpha I + \beta$), but it ignores the hysteresis effects present in real ozone soundings. This hysteresis is relevant on the time scales on which ozone varies during a sounding. In fact, the authors state themselves (pg. 3167, lines 17 to 25, Fig. 6), that these hysteresis effects may be important for low ozone values in real ozone soundings, e.g. in the polar vortex.

I think it would be important to discuss these hysteresis effects, develop a mathematical description, and estimate their magnitude. In the year 2010, a paper which deconvolves the measured current time series $I(t)$ and gives the true ozone profile $O_3(t')$

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would be much preferable to the simpler approximation of the authors' Eq. 6 (essentially from 1969). Clearly such an algorithm requires the response function, which can be constructed from the exponential decays observed in the authors' laboratory experiments.

2 Minor comments

The abstract does not really give the main results of the paper. I think the abstract should state that, according to the authors finding, ECC background current can be represented by a linear function of the ozone level, or by a modified ozone to electrons yield > 2, plus a constant generic background (with constants depending on solution buffer concentration). Numerical values for the constants (or the results of a better formulation to be developed) should be given.

Pg 3154, lines 4 and 7: I had to read this several times. Why not say that "background currents . . . vary over time, even if ozone is constant, and also depend on the encountered ozone level". Then continue "Using a fixed background current, measured e.g. 10 min after exposure to high ozone, in the standard processing of ECC data may often overestimate the real background and may frequently lead . . . ". I think this would be clearer. Pg. 3154, line 9: State what is proposed, and give values for the constants α and β. Also: replace "operator dependent variability" by "preparation dependent bias".

Pg. 3155, line 2: "The largest set"? "A large set" . Satellite people would probably claim that they have the largest set.

Pg. 3155, line 10: Add the Smit et al. 2007 Reference? Any results from BESOS (Deshler et al., 2008)?

Pg. 3155, line 12: Drop "signal"

Pg. 3155, line 18: I don't think the paper gives a "detailed understanding of" the sonde

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background current, i.e. explain the underlying chemical reactions, stochiometry, time-scales, ... Instead it gives a "better description of" it, or proposes a "better accounting for" it.

Pg. 3155, line 21: Replace "of background measurements" by "of possible background corrections"?

Pg. 3157, line 1: Add references for pump efficiency corrections here?

Pg. 3157, lines 5 to 29: I think it would be better to "itemize" this list of contributions to the accuracy. Have one bullet or paragraph for each factor. Also: Add references for each factor (e.g. deviations from yield ratio 2, pump temperature, current measurement accuracy (manufacturer?)).

Pg. 3157, line 26: Give numbers for the accuracy.

Pg. 3158, around line 10: What does the buffer achieve? Explain briefly.

Pg. 3160, after line 18: What is meant by "significant difference"? I understand that there was not much difference between the different sondes, but there was significant difference between the solutions. Was this difference significant for the absolute magnitudes (Fig. 2 looks like that), and/or for the decay time constants (Fig. 2 does not look like that). Please clarify.

Pg. 3160, lines 23 to 29: The first few data points may critically influence the result for the 19 sec decay time constants. Which data points were included/ selected? How does this affect the error estimates? What is the precision of the estimated time constants?

Pg. 3161, lines 14 to 16: Please put this into the context of the results of Smit et al. 2007 and Deshler et al. 2008. Also in the conclusions/ abstract?

Pg. 3162, around line 10: Fig. 3b clearly shows that $I_{Cell} - I_{TEI}$ is not a constant, but varies over time, especially during the 1st half hour of each step. This is the time-scale

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on which ozone varies during a real sounding! Averaging over 1 hour time-scales will give a wrong $I_{Cell} - I_{TEI}$. So the data points in Fig. 4 are not really fixed, but depend on the considered time scale. I would urge the authors to consider these obvious hysteresis effects, and come up with a viable de-convolution that calculates the true ozone profile from the history of measured currents.

Pg. 3162, Eq. 5: Again, this is a steady state approximation and does not solve for hysteresis effects.

Pg. 3164, lines 20 to 25, also pg. 3165 around line 15: Where would the cell currents measured after exposure to 5 μA ozone fall compared to the data points in Fig. 4? Would they fall on the lines given by α and β ?

Pg. 3169, around line 10: This brings up the question where the different background readings 10 min after exposure to high ozone come from. Are they resulting from different preparation procedures? Different timing? Or do they come from "manufacturing" differences between individual sondes? Right now it seems that there is no point in measuring background readings 10 min after exposure to high ozone at all. Instead the generic α and β should be used. Do I understand that correctly?

3 Summary

The paper clearly indicates that the standard ECC preparation procedure of taking a background reading some minutes after exposure to high ozone results in background values that are usually too high. Instead the authors propose a linear relation between measured cell current and "true" ozone current, that approximately accounts both for the overestimation of ozone by the measured cell current, and the background. The two parameters of the linear relation depend on solution concentration and buffer, but are otherwise assumed to be very generic. These assumptions help to resolve problems with too low or even negative ozone observations in the tropical upper troposphere and

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in the Antarctic ozone hole. This is clearly an improvement on the traditional method. However, as mentioned several times, I would feel much more comfortable, if the authors would account for the clearly apparent temporal response and hysteresis effects. They should attempt to remove those effects in their new treatment of ECC ozone observations. In several figures they have shown that a steady state approximation is not appropriate. Yet this is precisely what they use in their proposed new treatment.

4 References

Deshler, T., et al. (2008), 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., 113, D04307, doi:10.1029/2007JD008975.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 3153, 2009.