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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

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We agree with the reviewer that the time response of the ozone cell is an important factor in properly deriving the ozone concentration from the cell current measurement and that it should be properly treated in the data processing. However, in the equation that is currently used to convert the cell current to ozone partial pressure $P_{O3} = cTt_{100}\gamma(I(t)\text{-}I_{bg})$ *the time dependence resides in the time dependent cell current* $I(t)$*, not the assumed sensor property* I_{bg}*. It is the goal of our paper to make this distinction clear and to show that confusing this terminology in the sonde operation may*

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lead to significant errors. The "background" is currently considered a sensor property, which should be treated as a time invariant quantity. The time dependent cell current measured in flight requires a better understanding of the chemistry involved as well as of the dependency of the time constants on external parameters and of the direction of change. As pointed out in the comment by Stuebi and Levrat, the time constants for a decreasing ozone signal may not be the same as those for an increasing ozone signal. We have noticed this in our study as well, but decided to remain focused on the issue of a time invariant background. Nevertheless, the reviewer is correct that a response function correction should be applied to reduce all sources of measurement uncertainty. To that purpose, additional factors need to be considered, such as a better consideration of the stoichiometry (we have only given a glimpse that is consistent with the current understanding) as well as that of the pressure dependent pump efficiency correction. There also appears to be a difference between the cells from the two different manufacturers, which needs to be studied in greater detail and which might need to be included in the equation as cell efficiency. We would argue that the stoichiometry and the pump efficiency are the largest sources of measurement uncertainty for high ozone concentrations (stratosphere) and that the background is the largest source of measurement uncertainty at low ozone concentrations (tropical surface and upper troposphere) and that the response function is a lesser contribution to measurement uncertainty. We decided to focus on the background issue and leave the other aspects for a future study.

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

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developed) should be given.

The main results of our paper are that the treatment of the background current at present is incorrect and that this has strong implications on ozone measurements in the tropical upper troposphere. This is clearly presented in the abstract. Although, the correction factor for stoichiometry is a secondary result and we have included a statement in the abstract. We have refrained from giving the numerical values in the abstract.

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".

We have changed the sentence in the line of the reviewer's suggestion. We have retained the phrase operator dependent uncertainty, since the term "bias" implies a systematic bias, which it may not be. We do not know the statistical mean of this error. It is important to point out that it is not correct to assume a constant background after a certain time and that the human factor in this should be minimized.

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

A number of satellites give highly valuable ozone column amounts and a few give stratospheric ozone profiles, but we are not aware of a satellite instrument providing

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ozone profile observations in the upper troposphere, especially under the low ozone conditions important to this paper. Nevertheless, we have added the words 'in situ' to be more accurate.

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

We included the Smit et al. (2007) reference, since they make an explicit statement that for the tropical upper troposphere the uncertainty is larger. The BESOS results are not fully applicable here, since they refer to a mid latitude comparison.

Pg. 3155, line 12: Drop "signal"

Done

Pg. 3155, line 18: I don't think the paper gives a "detailed understanding of" the sonde background current, i.e. explain the underlying chemical reactions, stoichiometry, timescales, ... Instead it gives a "better description of" it, or proposes a "better accounting for" it.

Done

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

Changed to: "Here we investigate the ECC signal at zero ozone and at known ozone concentrations in an attempt to test the appropriateness of the background measurements in the processing of ozone sonde observations."

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

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The need for the pump efficiency is generally accepted, the magnitude is still under debate. We included the paper by Johnson et al., (2002) as reference.

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?)).

We have added a few more references, which are largely personal communications. We feel it would be the task of a more detailed paper on all of these contributions to itemize the individual points. Here it might be distracting from the focus of our paper.

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

We can't at this point. For the ECC using the V2D interface from EnSci the cell current measurement is a current to voltage op amp converter. The precision of this circuit is not know, nor the precision of the AD converter. However, indications are that these factors are small compared to the other contributions. Nevertheless, this needs to be checked in a more detailed study.

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

We added the sentence "The buffer is added to the basic KI solution to maintain a constant pH value, since the ozone reactions are considered to be pH dependent."

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.

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By significant difference we only refer to the difference in the absolute magnitude of the values during the decay, which is explained in the manuscript. The decay times for both solutions are surprisingly similar, which would indicate that the decay should be similar. This apparent contradiction can only be explained, if the terms I_0 and I_0' in our equation 4 are significantly different for the different solutions, which we have pointed out in the paper. This means that the increase during the 5 μA conditioning has to be different for the two solutions, indicating that the buffer reactions are different and non-symmetric as also pointed out in the comment by Stuebi et al. However, clarifying this point would have required additional studies that would not contribute to our main focus.

> 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?

Data are taken roughly three times per second, which avoids time step issues. The switch from high ozone to ozone free air was done manually by moving the inlet tube from one source tube to the other source tube immediately adjacent to it. This switch took certainly less than 1 s and guaranteed a clean step change in the ozone concentration, compared to simply turning off the ozone generator. Since the precise moment when the step was done was not recorded with high precision and since the flushing of the tubes also takes a small amount of time, we decided to ignore data in the initial decay phase between 5 μA and 4.5 μA and referenced all decays to the moment when the decay passed 4.5 μA. This has been described in the manuscript. We did not estimate the uncertainty of the time constants, which would have required more data and more analysis to do properly. We felt this was not needed for the focus of this paper.

> 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?

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This result is a mechanistic explanation for the differences in the solutions and we wanted to mention this already at this point. The more extensive discussions take place in section 3, where we also refer to the papers by Smit and Deshler. We have included a referral to that section.

> 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 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.

The reviewer is absolutely correct that for a proper analysis of ozone sonde data a viable de-convolution of the time dependency is important, but as discussed in the previous reply, it is also important to recognize which term is responsible for the hysteresis. To evaluate the constant "background" term in laboratory measurements, reaching steady state is essential and the reason, why we extended the measurements to that time scale.

> 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 ?

After the exposure to ozone is turned off, the reference value (I_{TEI}) would be zero and the measured cell current quickly fall off to values below 1 μA after roughly one minute and to values of less than 0.1 μA after about ten minutes. This means that the so called

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background values would be 1 μA and 0.1 μA respectively. These values clearly do not fall on the lines given by α and β. This is another indication that the instrument property called "background" cannot be measured with the current operational procedures.

> 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?

Yes, this is absolutely correct. Figure 2 clearly shows that it's a timing issue and a sensing solution issue. How much it is also a manufacturer issue remains an open question. And in operational practice it is also an issue of using a proper zero air source.

> **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 in the Antarctic ozone hole. This is clearly an improvement on the traditional method. However, as mentioned several

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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.

We have included a paragraph in our final remarks that points out the need for a time lag correction in the processing of sonde profile data. However, since the details for this correction are not well established and since the overall magnitude of the correction in the tropical upper troposphere is secondary to the use of an improperly determined background current, we have tried to stay focused on the larger source of measurement uncertainty.

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