**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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The paper presents a new analysis of the background current of the ECC sondes used for ozone profiling. The issue is important for the accuracy of ozone profiles, in particular in the tropical troposphere, where ozone concentrations are low, and has been subject to many discussions. The analysis is based on laboratory measurements and the results are used for a reanalysis of ozone soundings made over the equatorial pacific during the CEPEX campaign (Kley et al., 1996). The major outcome of the experiments is that the so-called background current of the ECC sondes

results from the treatment with high ozone concentrations. It is demonstrated that this current is not a universal constant but decreases in time. The data presented are as such convincing, although one might argue that a larger ensemble of sondes should have been investigated in order to improve the statistical basis. Therefore, some caution might be appropriate before changing the routine operation of ECC soundings. Nevertheless, the findings themselves support earlier findings about the chemistry involved.

Although we studied only three sondes, there is no doubt that the results presented here apply qualitatively to all ECC sondes. The time constants that we have derived are largely consistent with previous studies (Davis et al., 2000), but we have not tried to quantify the uncertainty of these values in an attempt to narrow these values compared to previous studies. The regression analysis may be improved and we have already pointed out that a larger data set exists, i.e. the JOSIE data set, which may be used to study this correlation in greater detail. Thus the argument of a small statistics does not raise concern. We have pointed out that the largest impact is at the tropical upper troposphere, where much lower ozone concentrations are found and that improper background measurements, which provide too large values for this term, have very significant impacts both for individual profiles (see our CEPEX results) as well as for large data sets (see the SHADOZ reanalysis). The threshold of 0.028 μA in the SHADOZ reanalysis was chosen to indicate the level of sensitivity of the reprocessed data on the value for offset parameter β. If our estimate for β ($\beta \approx 0.014 \mu$A) was off by a factor of 2, then the distribution would still look close to the corrected ozone distribution using the smaller offset parameter. The largest impact of the reanalysis is to remove all high background measurements, which brings the tropical upper troposphere ozone distribution using high background measurements into agreement with the one using smaller background measurements. This result will not change using a larger sonde statistics.

General Comments: I fully agree with anonymous referee 1, that the best explanation of the experimental results presented in figures 2-4 is a memory effect due to slow reactions in the oxidation of iodide by ozone in the solution. I would argue further that the results suggest that the overall stoichiometry of the reaction is approximately 1.1 (instead of 1, as normally assumed in ECC analysis). I disagree with the argumentation of the authors on the higher deviations after long exposure times. The effect seems to be almost proportional to the ozone concentration in the sample gas. The results in Figure should thus be plotted and analyzed in terms of relative deviation (i.e. stoichiometry).

The indication of an improper stoichiometry is a result of the data shown in Figure 4. Our goal was to test whether a constant instrument property called background could be measured under exposure of ozone as the difference between measured and expected cell current. Figure 4 was designed to show, whether this difference is constant under varying ozone concentrations or not. It clearly shows that this difference is proportional to the ozone concentration as the reviewer remarks. We therefore would not want to change this figure to show relative deviations. The slope α of this correlation is related to the stoichiometry and the offset β is related to what we defined as modified background. This analysis is only valid if the time is sufficient to avoid the memory effect. Larger deviations may or may not occur after very long exposure times, but solutions certainly do evaporate during the experiment, concentrating the solutions and introducing another variable that should be avoided. Thus the limitation to times encountered in typical ozone soundings is essential.

In order to prove or disprove the influence of exposure time, the experiments need to be repeated. Rather than terminating the individual runs at the highest concentration they should be continued with smaller concentrations of O3. This should give a clear answer if a change in stoichiometry

as a function of O3 or an effect of a slowly concentrating solution is the cause for the slight increase in the ECC equilibrium response to a given O3 concentration.

Our assumption is that the memory effect disappears given enough time, meaning several time constants determined from the data in Figure 2. If our assumption is valid, then the exact sequence of ozone plateaus does not matter. We did vary the order of ozone levels throughout the experiment and ended at either high or low values. All data are shown and the obtained correlation indicates that our assumption is valid. We felt it unnecessary to elaborate on this point.

To me, the conclusion of the paper is that the ECC chemistry has a fast and a slow component which leads, in equilibrium, to a stoichiometry of about 1.1. Therefore, the reanalysis of the CEPEX soundings, albeit intriguing in providing a much more homogeneous picture, should be made using an appropriate memory function, as detailed by referee 1, and including the appropriate stoichiometry. While it is clear that the approach suggested by the authors (with the modifications suggested above and by referee 1) is a clear improvement above the use of a constant background current, it should be pointed out more clearly that it still awaits in-situ validation before implemented in the ozone sounding network.

We included a new paragraph elaborating this point. Nevertheless, going away from (incorrectly) measured backgrounds to a fixed background will have stronger impacts on the tropical upper troposphere than including a memory correction.

The authors fall short in putting the findings into perspective. There has been a long discussion in the literature on the stoichiometry of the O3-iodide chemistry as a function of pH. The results for neutral solutions as

used in the ECC range from slightly under 1.0 to as much as 1.5 (e.g., Dietz et al., 1973 and references therein). See also the comment by Stuebi, who found a stoichiometry of 0.98 in contradiction to the results of the authors. Therefore, the conclusions may be not as universal as the authors suggest and need to be verified in intercomparison experiments involving, e.g., the JOSIE community before one could try to adopt it for general use.

We disagree with the reviewer on this point. JOSIE, numerous balloon intercomparison such as the very extensive BESOS campaign, and small scale dual sonde launches have shown that a stoichiometry factor of one may not be appropriate. Our results are consistent with their findings. Further work may be required in better quantifying this value. We have already pointed to the JOSIE data set, which could be used for this purpose. However a factor of 1.5 would appear inconsistent with the current knowledge.

I noted that some of the soundings plotted in Figure 5a appear as almost linear functions in the semi-logarithmic diagram. They are still seen in Fig. 5b. I couldn't identify such soundings in the original publication by Kley et al. This needs to be addressed or corrected if due to erratic data. It would be easier if a linear ozone scale would be used in Figure 5.

We are not completely clear to what in figure 5 the reviewer refers. We speculate that the reviewer refers to the nearly evenly spaced straight lines at low mixing ratios. This feature is a result of the Tmax-H interface with an effective ten bit resolution, which was one of the two interface types that were used in the experiment. Here the 10 bit resolution at low cell currents was insufficient to resolve more detail, leading to nearly evenly spaced stripes, corresponding to single bit changes. At higher mixing ratios the spacing becomes smaller on a semi logarithmic scale. Although this feature is quite noticeable, low ozone concentrations were also observed using the Tmax-C interface,

which used a 12 bit AD converter and provided roughly 4 times the resolution, making these stripes much less noticeable. The original publication by Kley at al.(1996), showed these profiles as a solid line on a linear mixing ratio scale, thus de-emphasizing lower mixing ratio values and hiding these features, which would otherwise have been visible.

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