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Atmospheric Measurement Techniques Discussions

Interactive comment on "A new method to correct the ECC ozone sonde time response and its implications for "background current" and pump efficiency" *by* Holger Vömel et al.

Anonymous Referee #2

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1 Overall remarks

This is an important paper, providing background on long-standing issues with electrochemical ozone sondes, offering a viable solution for correcting known problems, and improving the accuracy of ozone profiles measured by these ozone sondes. The paper is generally sound and reasonably well written. It fits well into the scope of AMT. However, because it is a very important paper, I think more effort should be put into clarifying the underlying equations and into presenting the results in a more logical and suggestive flow, and with fewer repetitions and duplications in the text. See my recommendations below. Once these issues are addressed, I think the paper will be a major

contribution to the ozone sounding field. Because it is such an important paper, I hope the authors will put in the additional effort, and will try to streamline their final text.

2 Major suggestions

Abstract: It would be more logical to first present the main reaction, which generates 2 electrons per ozone molecule with the fast 20 sec time constant (and has been known forever). Then present the slow reaction with 25 min time constant, that produces between 0.05 to 0.2 electrons per ozone molecule (2 electrons $\times\alpha$, from the numbers given near Equation 6). The major innovation of the paper is the characterization of this slow reaction, but overall it is still a secondary reaction. So I suggest to switch the order in which the reactions are presented, and also mention how many electrons the slow reaction generates (compared to 2 electrons from the fast main reaction).

Summary: The summary is very well written!! Could the person writing the summary please try to remove duplications and repetitions in the main text, and make the main text more logically flowing and succinct?

Equation 1 and following discussion: I am not happy about Equation 1. Pump correction, ozone to electrons conversion efficiency, hysteresis and background current effects are all lumped together in this empirical γ correction (or fudge factor). Later in the text (lines 114 to 138) the authors bend over backwards, explaining that use of the correct Johnson et al. 2002 pump corrections (not the fudged Khomhyr et al. ones) and proper accounting for secondary slow reactions are the correct way to go. To me, it would make a lot of sense to separate the different "γs" here, and to properly introduce and explain them, γ_{pump}, $\gamma_{conversion}$, ... The text from lines 114 to 138 should be moved here as well. In the end, according to the paper, the fudged γs can be unfudged and only the correct γ_{pump} is required. Accounting for the slow secondary reaction takes care of the rest / the background.

After properly introducing and explaining the different "γs" near Equation 1 already, the rest of the discussion would then focus on background alone, with less jumping forth and back between background, and conversion efficiency / solutions. After moving the text parts on solutions and γs, as suggested above and also further below, the authors should then revisit their discussion of background currents, background subtraction practices, and background experiments (lines 70 to 123). Make it more concise and more logically flowing. Right now, it is a lot of forth and back. E.g. the paragraph around line 110 seems out of place where it is, and should probably come earlier.

3 Mathematics

Just like reviewer 1, I cannot follow the mathematical reasoning from Equation 3 to 6. I find Equation 4 plausible, although it is not really clear what I_{ss} and I'_{ss} are. They seem to drop from the sky. I assume they are something like the real I_{O3} and I'_{O3} that would be measured, if the time constants of the fast and slow reactions were infinitely small. I do not understand how the authors get from Equation 4 to Equation 5. Taking the derivative of Equation 5, I get something very different from Equation 4 (even when I only take the slow reaction part of Equation 4 ($\frac{dI'_0}{dt} = -\frac{1}{\tau'}(I'_0 - I'_{ss})$).

What I could understand, is using the slow part of Equation 4 to numerically calculate I'_0 from one time step to the next:

$$I'_0(t) = I'_0(t_0) - \frac{t - t_0}{\tau'} \left(I'_0(t_0) - I'_{ss}(t_0)\right) \tag{1}$$

This can be re-arranged to

$$I'_0(t) = \frac{t - t_0}{\tau'} I'_{ss}(t_0) + \left(1 - \frac{t - t_0}{\tau'}\right) I'_0(t_0) \tag{2}$$

which is the first order term of a Taylor series expansion of the authors' Equation 5, and is probably the numerical solution the authors are using anyway. Assuming $I'_{ss} = \alpha I_{ss} = \alpha I_{O3} \approx \alpha I_m$ we would then arrive at the first order term of the Taylor series expansion of the authors' Equation 6.

$$I'_0(t) = \frac{t - t_0}{\tau'} \alpha I_m(t_0) + \left(1 - \frac{t - t_0}{\tau'}\right) I'_0(t_0) \tag{3}$$

To me this seems a more logical and mathematically stringent way. For small time steps (seconds, compared to the 25 minute time constant), this Equation 3 will give very similar results to the authors Equation 6. However, both reviewer 1 and I were not able to understand how the authors' Equations 5 and 6 were derived, and we both are wondering if they are correct. Given all this, I suggest that the authors check their mathematical reasoning, consider using the simpler linear equations above, and re-think and simplify the accompanying text.

By the way: Reviewer 1 was wondering why in Equation 6 $I'_0(t)$ only depends on the instantaneous $I_m(t)$, and does not integrate $I_m(t)$ over time. The iterative process described by Equation 3 above clearly shows that $I'_0(t)$ integrates over I_m from all previous time-steps.

Since the authors' Equation 3 only seems to inspire Equation 4, but is not really mathematically connected here, I sugggest to drop it completely. It seems more confusing then helpful here. Just introduce the two time constants, and start with Equation 4.

4 Minor suggestions

Line 22: insert "secondary" before "slow reaction". Switch order of the two reactions, as mentioned above.

Line 25: "remaining" -> "main".

Line 37: A pump correction cannot improve the time response. In fact no post-processing can change the time response, which is defined by hardware and chemistry. Instead of "which . . . ", start a new sentence. "This improves the accuracy of ECC sonde ozone profiles, especially for very low ozone cooncentrations or large ozone gradients, and removes systematic biases . . . "

Lines 39 to 41: I don't get this entire sentence. 1.) ECC measurements are influenced, no matter how you correct for it. So this is really a NULL statement. 2.) You already said in the previous paragraph that, due to correcting for the fast response time, gradients are reported more accurately. So what is NEW here? I would suggest dropping the entire sentence, or really making clearer what is NEW and IMPORTANT here.

Line 59: As mentioned above, most operationally used γs are more than a pump correction. So I think this text should be corrected here, and clarified.

Lines 68-72: It would be good to give some numbers / ranges for typical background currents here.

Lines 91 to 102: I think the introduction of the different solutions here interrupts the logical flow of the background discussion. Therefore, I suggest to move this paragraph right after line 50, before Equation 1.

Lines 105/106: Fix "assumption" . . . "assumed"

Line 107: "zero" missing before "ozone"?

Lines 123 to 138: As already mentioned, I think this should be disussed earlier, right after Equation 1 when γ is discussed.

Line 133: "currently recognized as properly describing" -> "properly describes . . . and is consistent . . . "?

Equations 10 and 11: Minus sign is missing in the exponents.

Figure 1: Maybe also show the difference between ECC raw and TEI49C in the bottom panel. That would show the improvement by the new processing even better.

Figure 2: It would be good to also show the derived slow reaction current, on a log-scale, or in a separate panel.

Line 256: I do not understand how 6 step changes can represent a total of 60 step changes. Do you mean average of 60 step changes? Or just 6 (typical) examples? Please reword / clarify.

Figure 3 / Line 291: "follow slightly better". Line 319: "dramatically" improved. I don't know. To me it rather looks like the yellow (raw ECC) curves in the bottom panels are overall closer to the zero lines than the red (ECC corrected) curves. I certainly do not see a "dramatic" improvement. The wording should be more neutral / conservative here.

Figure 4: Can you please also show the correction for the fast (25 sec) response time? It seems to be much smaller than the pink correction for the slow (25 min) reaction.

Lines 294 to 303, Figs. 3 and 4: So the pump corrections were also changed. Now things get really confusing. Can you please dis-entangle the pump correction effect? Show with an additional separate line? Do not change the pump correction here?

Figure 5: OK, here I can see an improvement. Most of it seems to come from the "fast response" correction.

Figure 6: Several additional things would be good here. a.) standard deviations for the red and blue difference profiles. b.) the average ozone profiles (original, corrected and OPM reference. c.) the average fast and slow response corrections.

Lines 354 to 356: This has already been said many times. Delete the sentence.

Figure 7: I assume there was no change in the pump correction - different from Figs. 3 and 4.

Line 362: Delete "what was assumed with"?

Line 366: Replace "smoothing and correcting for time lag" by "fast response correction"?

Line 374: Replace "The" by "This"?

Line 392: "rapidly decays"? Should it not decay with a time constant of 25 minutes? Maybe reword "is about 10% at launch, but soon becomes insignificant, as ozone is increasing rapidly with altitude."

Figure 11: Should "fast reaction" in the legend in the plot not be "slow reaction"? Figure caption and legend in the plot seem to be inconsistent.

Line 437: Add "much" after "affected"? There is an effect, up to about 1% in Fig. 12.

Line 439, Figure 13: How many ozone sondes during CEPEX? Maybe add the number. Rightmost panel: Maybe add standard deviations, or thin lines of individual profiles? Why is the peak change so much larger ($\approx$80%) than in Fig. 11 (8%)?

Lines 467 to 477: Has that not been said several times by now? Maybe drop these two paragraphs?

Line 483, see also line 392: Well, the effect should be there for 10 to 20 minutes. However, if ozone becomes large enough it will be very small. Reword?

Line 517: "justify" seems the wrong word. "quantify"?

Lines 516 to 524: There is a lot hedging, ifs, and maybes here. Can this not be worded shorter and more succinct? E.g. The two sentences in lines 521 to 524 are saying alsmost the same thing.

Lines 544 to 548: This has been known and sometimes corrected since the 1980s. Maybe add one or two of these old references?

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