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Interactive comment on "Characterization and mitigation of water vapor effects in the measurement of ozone by chemiluminescence with nitric oxide" *by* P. Boylan et al.

Anonymous Referee #2

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The manuscript discusses the effect of water vapor on the determination of ozone fluxes with a chemiluminescence detector. It presents a determination of the kinetic quenching coefficient of NO_2* (already known in the literature) by water vapor, quantifies the effect on ozone flux observations, describes the setup of a drying system to remove a large part of water vapor from sample air, and characterizes its behavior. The paper gives a lot of detailed information about the experiments performed. I think the proposed modification of such an instrument and the description of the benefits justifies its publication.

A major point in the experimental description is the effect of water vapor on the be-

havior of the mass flow controllers. Two figures and more than one page are used to describe the effect. This behavior was determined by feeding air flows with different humidity through these flow controllers comparing their readout to measurements with a bubble flow meter as a reference. The raw bubble flow meter data were corrected for temperature and pressure, I presume to relate the actual air density to standard conditions. The bubble flow meter is not described in detail, but I suppose it contains a reservoir with aqueous soap solution and measures the velocity of a soap bubble in a pipe with scale divisions. In such an instrument the flow is enriched in humidity up to or close to the water vapor saturation pressure. If I assume a temperature of the soap solution which would raise humidity up to 25 mmol/mol, the results for flow meters 3 and 5 would have to be expected: the dry flow should be 2.5% larger than the flow with high humidity. There should be a (small) effect of humidity on the mass flow controllers reflecting the different heat capacities of air and water vapor but I think the major effect shown in figures A1 and A2 is caused by the bubble meter. As I said, not enough detail is given to understand these figures in detail. This paragraph has to be corrected if the assumptions made here are correct.

Eq.(2) gives the correction factor for ozone flux measurements. It has two parts: one depends on the average water concentration, one on its fluctuation. The first one is always positive, the second one can be positive or negative. The later discussion of upward and downward fluxes of ozone and water ignores this. There might be a case where the positive first part dominates a negative second part.

In section 3.2 a Nafion drying system is described. Its effect on water vapor concentration is shown in figures 5 and 7. Figure 5 shows how an incoming water concentration is reduced. The relative reduction depends on the concentration. For example, incoming concentrations of 5 and 25 mmol/mol are reduced to 2.35 and 5.75 mmol/mol. That means that a factor of 25/5=5 difference in the incoming concentration is reduced to 5.75/2.25=2.6. Is this directly transferable to figure 7, the frequency behavior of the water vapor signal with and without the dryer? If one would determine the parameters for a linear regression in fig.5 and use it to transform the time series used for figure 7A-black-line, how would that look like in relation to the red line of the same figure?

Minor points:

- Line 7 page 9264: the quenching factor α should have a unit throughout the manuscript.

- Line 14 page 9267: How large is the uncertainty of the values for the ozone flux? This relates also to figure 1. If the detection limit or precision of the ozone flux data is around 0.01 nmol mol^{-1} m s^{-1}, the larger corrections near a flux=0 are not significant.

- Line 12 page 9269: It would be nice to note here that NO chemiluminescence instruments show basically the same behavior against water vapor. Their correction factor α might be smaller and might be instrument dependent since the added reactant flow (in this case ozone diluted in air or in oxygen) is larger with respect to the ambient air flow. This should be the instrument dependency mentioned in line 10 of page 9266? Or are there other parameters which might influence the transfer of the correction factors determined here to other instruments?

- Line 13 page 9278: What is high or low frequency? Please state values like "higher than 1 Hz".

- Fig. 1: May be it is better to plot absolute instead of relative correction values.

- Fig. 1: Eq.(2) has two parts: one related to the average water concentration, one related to the water vapor flux. Is only the second part plotted here?

- Fig. 7: I guess that the two lines in panel A were measured simultaneously with two instruments, whereas the lines in panel B were measured consecutively with one instrument. Please state accordingly in the figure caption.

- Fig. 7: Is it possible to plot the correlation between O3 and water for both cases (w and w/o dryer) similar to panel C as a new panel D? That would be instructive for the

reader.

Interactive comment on Atmos. Meas. Tech. Discuss., 6, 9263, 2013.