

The manuscript “Characterization and Mitigation of Water Vapor Effects in the Measurement of Ozone by Chemiluminescence with Nitric Oxide” has been revised based on the reviewers’ comments. We took into consideration their comments and felt that their review helped to improve the manuscript quality. Our revised manuscript has been updated by the modification of four figures to clarify axis labels, the inclusion of more text on ozone measurement techniques in the introduction, and clarifications in the data analysis part of the text.

In the following we provide a detailed point-to-point response to the reviewers’ questions and suggestions.

Response to Reviewer #1:

Initial review:

(1) Introduction/background. An introduction on in-situ O₃ measurements and features of the gas-phase CI technique is missing, i.e. the authors blurt out with the measurement technique. Also references are missing in this context. (This was also suggested by the Editor).

The introduction has been reorganized and following the suggestions by the reviewers, this text has been added.

“The most widely used instrumental technique for the measurement of tropospheric ozone is by UV absorption (Williams et al., 2006). Ozone UV absorption monitors operate on the principle of ozone absorbing UV light at wavelengths around 254 nm. These instruments are very common because of their easy operation, they maintain a stable response for a long time, only require periodic cleaning, and do not require a reactant gas supply. Another method of measuring ozone that is gaining popularity is by Differential Optical Absorption Spectroscopy (DOAS), where average concentrations of ozone are measured within a path between the instrument telescope and a reflector array (Honninger et al., 2004). This method requires a light path of over 1 km; the measurement can be severely affected by particulates in the air (Evangelisti et al., 1995). The use of lightweight electrochemical concentration cell (ECC) ozonesondes has been the primary method for measuring vertical profiles of ozone in the atmosphere from airborne balloons due to their small size and low power consumption (Komhry et al., 1995). While ECC ozonesondes are ideal for balloon-borne measurements, their sensitivity to sulfur dioxide and the need to replace the reactant solution make them less suited for continuous and stationary measurements.

While these methods have proven to be reliable for atmospheric ozone concentration measurements, their relatively slow response to atmospheric concentration changes make them unsuitable for ozone flux measurements by the eddy-covariance technique, where time resolution at frequencies faster than ~1 Hz are desired. An ozone measurement technique with faster response, meeting the requirements for eddy covariance flux observations is by chemiluminescence, where light emitted from the reaction of ozone with a chemical reactant is used as a measure of ozone concentration. There are several options for the chemiluminescence measurements of ozone, including wet and dry techniques that use organic dyes (Guesten and Heinrich, 1996; Weinheimer, 2006; Zahn et al., 2012), and gas-phase techniques that are based on the reaction of ozone with either ethylene or nitric oxide (Kleindienst et al., 1993; Williams et al., 2006; Bariteau et al., 2010). Current gas-phase chemiluminescence ozone instruments typically use nitric oxide as the reactant gas as it provides a higher signal to noise ratio than from the reaction with ethylene (Ridley et al., 1992). This ozone measurement has also become a popular method for ozone concentration (Ridley et al., 1992;

Weinheimer et al., 1998; Slusher et al., 2010; Conley et al., 2011) and ozone flux (Lenschow et al., 1981; Lenschow et al., 1982; Kawa and Pearson, 1989) measurements from research aircraft. Recent developments in instrumentation for motion correction on moving platforms have enabled direct observations of open ocean ozone fluxes using this measurement technique (Bariteau et al., 2010; Helmig et al., 2012b).“

(2) The presence of H₂O decreases the measured signal. From the physical point of view, it is thus little conclusive to sell the story from the beginning as a positive effect (Fig. 3). Fig. 6 is fine because the signal is increasing due to the removal of H₂O. That is, first describe the signal decrease and only thereafter sell the signal increase due to the use of the Nafion dryer.

We have clarified the text to specify that the quenching effect results in a reduction of the ozone signal, as seen by a drop in the instrument response. The introduction and section 3.1 describe the quenching effect as a signal decrease. Once the Nafion dryer is introduced in section 3.2, the focus shifts to the increase of the ozone signal due to the use of the Nafion dryer.

Final Review:

The manuscript describes the H₂O cross-sensitivity of gas-phase Cl detectors measuring ozone. It is well-written and straightforward and I suggest publication in AMT after some minor revisions.

As the instrument will largely be used for fast eddy covariance measurements, which requires highly accurate determination of the exact sampling time, i.e. of the time when the sample air entered the inlet tip, a paragraph describing the sampling and the consequences by adding a Nafion dryer should be added. For instance, Zahn et al (AMT, 2012) nicely describes the effect of mixing in the sampling line which certainly increases with additional Nafion dryer and which makes the instrument slower. Thus, add information on the travel time between inlet tip and detector and on the response time, with and without dryer.

A new paragraph has been included to explain mixing in the sampling line, lag times, and reaction times.

“In typical field deployments, the measurement of surface ozone fluxes is accomplished by the use of the FROI and a sonic anemometer. The sampling inlet for the FROI is located a few centimeters behind the head of the sonic anemometer, minimizing disturbances due to the sampling line. Sample air was pulled through a 30 m Teflon-PFA line from the inlet to the instrument. There is a delay in the acquisition of the ozone signal in the FROI due to the transport time between the inlet and the reaction chamber. The lag time is regularly determined by using a “puff-system”, where a small quantity of NO is injected at the tubing inlet, causing the removal of ozone by reaction with NO during the transport to the reaction chamber (Bariteau et al., 2010). The time when the electronically actuated valve is opened is recorded in the data acquisition system. The delay between the electrical pulse and the drop in the ozone signal recorded with the instrument allows for the determination of the lag time. Flow rates are set to keep a turbulent flow regime in the sampling tubing. The addition of the Nafion dryer (and its bends and curves) enhances mixing within the tubing (Lenschow and Raupach, 1991). Prior experiments with a tubing length of 30 m and a flow rate of 12.5 l min⁻¹ gave a mean lag time of 4.76 s. Lag time standard deviations were ~0.12 s during repeated puff tests and less than 0.2 s during 2 - 4 week long

campaigns. The addition of the Nafion dryer increased the mean lag time to 5.14 s and the standard deviation to ~ 0.13 s. The time required for the ozone signal to drop to $1/e$ of its initial value is defined as the instrument response time. This response time is based on a number of instrumental operating variables, including the reaction chamber volume and pressure, purge rate, PMT response, and the electronic processing of the signal. Zahn et al. (2012) calculated a reaction time as the time required for the ozone signal to drop 90% and showed that increasing the sample tubing length increased the response time for a fixed flow rate. In our instrument, the response time without the Nafion dryer installed was 0.31 ± 0.03 s. With the addition of the Nafion dryer, the response time was 0.32 ± 0.03 s. Consequently, under the experimental conditions applied here, the addition of the Nafion dryer did not have a statistically significant effect on the response time. ”

p.9264, l.3 “gas-phase” before chemiluminescence

This wording has been added in the text.

p.9264, l.9 “flushed with ???” after Nafion dryer

The text has been modified to say that “a Nafion dryer with a counterflow of dry air from a compressed gas cylinder”

p.9264, l.20 References are missing

The sentence that the reviewer mentions has been modified along with the rest of the introduction and appropriate references have been included.

p.9266, l.16 Shift the following sentence to the beginning of the introduction. “A benefit of the fast response time and high sampling frequency of a chemiluminescence ozone instrument is the ability to define surface fluxes in combination with a sonic anemometer by the eddy covariance technique.”

The sentence that the reviewer is referring to has been reorganized and the information suggested by the reviewer was added.

p.9266, l.20 Delete “total”

The word “total” did not strengthen the point we are trying to make and was removed based on the reviewers comment.

p.9266, l.24 Give references that explain “reynolds averaging”

Two references have been added and cited that explain Reynolds Averaging:

Muller, P.: The equations of oceanic motions, Cambridge University Press, Cambridge, UK, 2006.

Stull, R. B.: An introduction to boundary layer meteorology, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1988.

p.9267, l.4 The claim “(1) no water vapor flux, no correction for the ozone flux is needed” is not entirely true (due to the term α^*r), i.e. FO_3 is still not equal to FO_{3m}

The reviewer is correct in this statement. The text for case 1 has been modified to say “no water vapor flux – Eq. (2) is reduced to only correcting for the total atmospheric water vapor mole fraction”

p.9269, I.7 Give explanation where the background comes from

The background noise of 900 counts per second is based on the dark current of the PMT. This is the number of counts per second the PMT detected with zero ozone in the reaction chamber. Cooling the PMT dramatically reduces the background noise. The text has been modified to say: “The FROI had a sensitivity of $\sim 2000 \text{ counts s}^{-1} \text{ ppbv}^{-1}$ and a background noise of $900 \text{ counts s}^{-1}$, which is based on the dark current of the PMT. The dark current decreases with decreasing PMT temperature. The background noise was $3500 \text{ counts s}^{-1}$ at -20°C , $900 \text{ counts s}^{-1}$ at -30°C , and $400 \text{ counts s}^{-1}$ at -35°C . The PMT cooler could not keep the temperature stable at -35°C , so -30°C was used throughout the experiments.”

p.9269, I.20 Give type of PMT

The PMT model is R2257P from Hamamatsu Photonics, Japan. This has been included in the text.

p.9270, I.2 Delete “high precision”

Corrected as suggested.

p.9272, I.2 “At all tested water vapor levels at and above $0.4 \text{ mmol mol}^{-1}$, while the MFC reported that the flow remained constant at 7.98 L min^{-1} , the flow rate determined with the bubble meter was 7.93 L min^{-1} , a drop of 2.3 %.” Hard to believe that with dry air the bubble meter showed 8.12 and suddenly a higher and constant value of 7.93 L min^{-1} is seen with continuously wetter air

The text was clarified to say “the **average** flow rate determined with the bubble meter was 7.93 L min^{-1} ”. Figure A1, which is mentioned in the previous sentence, shows that at water vapor mixing ratios above 0.04 (the 5 right-most points) the flow varied between 7.90 and 7.96 with a mean value of 7.93.

p.9273, I.22 Why again a new parameter? Please further use O_3m or even O_3r .

At the suggestion of the reviewer, we removed equation 3 and included text to explain the relationship between the measured ozone in wet and dry air and the correction factor, alpha.

“Despite their reaction chamber being half the size of ours at 17 cm^3 with a sensitivity of $2000 \text{ counts s}^{-1} \text{ ppbv}^{-1}$ it yielded a similar response to our instrument”. Where shown or based on what figure..., this conclusion was derived?

Lenschow et al., 1981 and Ridley et al., 1992 stated their reaction chamber size was 17 cm^3 , yielding a sensitivity of 2000 counts per s per ppbv under their operating conditions. The text was modified to “Despite their reaction chamber being half the size of ours at 17 cm^3 , it yielded a similar signal response under their operating conditions as our instrument, with a sensitivity of $2000 \text{ counts s}^{-1} \text{ ppbv}^{-1}$.”

p.9274, I.28f I don’t see the values given in the text (12.2 , <5 , $4.6 \text{ mmol mol}^{-1}$)

The text was corrected to state “In Fig. 4 the flow bypassed the Nafion dryer for the first 2 minutes; during that time the LI-COR recorded $25.4 \text{ mmol mol}^{-1}$. After two minutes the flow was switched to the Nafion dryer and the water vapor mole fraction dropped below $6.0 \text{ mmol mol}^{-1}$. It took between 6 and 10 minutes for the water vapor to slightly increase again and then equilibrate at $6.1 \text{ mmol mol}^{-1}$.”

Response to Reviewer #2:

Initial Review:

No comments

Final Review:

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 NO₂* (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 behavior 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.

The reviewer is correct in pointing out the omission of this detail in the description of the flow rate determination using the bubble meter. As a matter of fact, the correction for water vapor was included in our initial analysis. The bubble meter flows were first corrected for the water vapor in the sample air. The actual water vapor mixing ratio of the sample air was measured before the flow reached the bubble meter. The measured bubble meter flow was then corrected by the ratio of the measured water vapor pressure over the saturated water vapor pressure at the measured temperature. Then the flow was corrected for temperature and pressure to allow for a direct comparison with the flow readings from a MFC that was calibrated at STP. The text was modified to say "Reference flow rates were determined with a bubble meter. Flow rates determined with the bubble meter were first corrected for the increase in the flow reading due to the moisturizing of the air flow in the bubble meter, then corrected for temperature and pressure to yield mass flow rates at standard conditions, and then compared with the set point flow rates of the mass flow controller."

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.

The text was modified after the description of Figure 1 to say: “There is a small subset of the data where there is a relatively small upward water vapor flux compared to the downward ozone flux, which results in the uncorrected measured ozone fluxes being greater than the actual ozone fluxes. This is seen in Fig. 1 as the area between where the water vapor flux is equal to zero and the dashed line for a zero % correction, showing a slight negative slope. This is due to the fact that the correction of the ozone flux depends on both the water vapor concentration and water vapor flux. “

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?

The reviewer is correct that the amount of water vapor removed by the Nafion dryer asymptotically approaches a limit that the Nafion manufacturer reports as ~90%. The removal of water vapor is not linear with water vapor mole fraction; therefore a linear regression would not be appropriate. The integral of the power spectra in Figure 7a gives the total amount of water vapor. In the example given in Figure 7a, the area under the black curve is the amount of water vapor without the Nafion dryer installed and the area under the red curve is the amount with the Nafion dryer. The ratio of the integrals shows a 56% reduction of water vapor mole fraction (this is discussed in the second paragraph of section 3.4). This is consistent with the ~54% water vapor removed at water vapor mixing ratios around 6 mmol mol⁻¹ seen in Figure 5. We left out the operating conditions for the data in Figure 7: The sample air contained ~40 nmol mol⁻¹ of ozone and 6.0 mmol mol⁻¹ of water vapor. What is shown in Figure 7 is essentially the “spectral view” of a single data point from Figure 5. Text in the manuscript body and in the figure 7 caption was modified to include the operating conditions.

Minor points:

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

The quenching factor alpha was intentionally left without units in the manuscript. The unit is a derived quantity, not a measured quantity, and is dimensionless. When the quenching factor is introduced in the abstract and in the introduction, it is referred to as a “dimensionless quenching factor”.

- 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.

The uncertainty in the ozone measurement (and then also the ozone flux) is primarily due to statistical fluctuations in the detected number of photons and background noise. The counting noise due to the statistical fluctuations is proportional to the square root of the total number of photons. The background noise is ~900 counts per second. Consequently, at lower ozone levels the signal to noise ratio will be reduced. Over the open ocean, ozone mole fractions are typically over 20 ppbv which results in a signal to noise ratio of ~45. It is important to note that the detection limit of $-0.020 \mu\text{g m}^{-2} \text{s}^{-1}$ is based on the average of 15 minute periods over the course of several hours. In Helmig et al., 2012 individual 15 minute fluxes were seen on the scale of $0.002 \mu\text{g m}^{-2} \text{s}^{-1}$.

- 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 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?

Yes, NO chemiluminescence instruments would be expected to show similar behavior with water vapor. Unfortunately, we do not have direct experimental results to prove this as we did not have an instrument for the detection of NO to examine this effect. This probably was not that clear before this study, but our findings underscore this effect. We contacted several researchers that operate NO chemiluminescence instruments and found that they often apply the correction factor determined by Ridley et al. (1992) but have not performed any specific tests to address this issue. A paragraph was added to the summary and conclusions section that explains the relevance of these findings on NO chemiluminescence instruments and NO fluxes calculated by the eddy-covariance technique. "The same detection principle is used for atmospheric measurements of NO. In those chemiluminescence instruments, the air sample is mixed with a flow of ozone in air or ozone in oxygen as the reactant gas. While the ratio of reactant gas flow to the sample flow is higher (than in instruments for measurement of ozone, i.e. on the order of 1:10 compared to 1:100 for the measurement of ozone), the humidity content in the reaction chamber is still primarily determined by the sample flow. Consequently, these NO detection instruments suffer from a similar interference. To the best of our knowledge, researchers apply the same quenching correction coefficient in this instrument configuration, and we are not aware of targeted tests that have examined the quenching behavior in the NO measurement. In the NO measurement, calibrations can be performed by standard addition of a small flow of a NO calibration gas standard, which allows determining the actual instrument sensitivity at varying humidity for measurements of the NO mole fraction in ambient air. However, this approach does not compensate for the quenching interference of the fast water signal in the eddy covariance flux measurement of NO fluxes. Consequently, our study should be of interest for NO flux research as well. In particular, our findings suggest that consideration of a Nafion dryer in the sample flow path will likely mitigate the fast quenching interference on the NO signal, and should likely yield an improvement in the determination of the NO flux by the eddy covariance technique. "

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

When data are averaged over a timescale of 15 to 30 minutes, high frequency eddies are on the order of 1 to 100 s while lower frequencies are greater than 100 s. For this manuscript we define high frequencies as greater than 10^{-2} Hz. The text has been modified to reflect this.

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

We felt that relative corrections helped exemplify the point we are trying to make, which is that when ozone and water vapor fluxes are in the same direction, the measured ozone flux has a positive error and requires a negative correction. The opposite is true when the fluxes are in opposing directions. This is mentioned in the text page 9267 line 20.

- 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?

This builds on what was mentioned in the previous comment. Equation 2 has 4 variables. Two of the variables, ozone flux and water vapor flux, are varied in the figure. In this example, ozone and water vapor mole fractions were set constant to show the percent correction required based on the fluxes. We chose typical values for ambient air ozone mole fraction (40 nmol mol^{-1}) and ambient water vapor (18 mmol mol^{-1}). Results in the figure reflect both parts of the equation; however, two of the variables were held constant.

- 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.

For these experiments we only used one hydrometer and one ozone instrument to eliminate any discrepancies due to offsets or sensitivities of multiple instruments. The details of the hydrometer are on page 9270 line 2. The figure caption has been modified to say "Spectral distribution plots using two consecutive two-hour periods of data from the same hydrometer and ozone instrument, with and without the Nafion dryer."

- 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.

We examined this relationship during our initial exploratory analysis of the data in hopes to include such a plot but found low spectral correlation for both cases with and without the Nafion dryer. Looking further into this, we found that the covariance between the ozone and water vapor fluctuated around zero, leading to a low and noisy cross-spectrum. This cross-spectrum is the numerator in the calculation of the spectral correlation. This result is not surprising as the cross-spectrum describes the distribution of the ozone-water vapor flux at each frequency. Typically, fluxes are determined from the vertical wind component and a chemical species, not two chemical species. The noisy cross-spectrum can be attributed to the lack of a clear peak in the ozone and water vapor power spectra.