

## ***Interactive comment on “Simultaneous Detection of Ozone and Nitrogen Dioxide by Oxygen Anion Chemical Ionization Mass Spectrometry: A Fast Time Response Sensor Suitable for Eddy Covariance Measurements” by G. A. Novak et al.***

**Mingxi Yang (Referee)**

miya@pml.ac.uk

Received and published: 6 December 2019

This paper describes the use of the oxygen anion chemical ionization mass spectrometer for simultaneous measurements of N<sub>2</sub>O and O<sub>3</sub>, with the application of eddy covariance flux measurements over the sea. It's another example of the versatile utility of the time-of-flight CIMS. The paper is generally well written and the authors have carefully considered the various aspects of data processing and interpretation. I recommend publication after they address the following mostly minor comments.

C1

Abstract: Counts /s/ppt instead of ions/s/ppt

Line 53: authors introduced wet, dry, and gas-phase chemiluminescence methods here in this order, but discussed them subsequently in a different order (gas-phase, wet, dry). Suggest discussing the methods following the order of wet, dry, gas-phase

Line 230. The increase in ncps of 175% doesn't quite square up with Fig. 5 by eye. This pressure sensitivity needs to be treated with care. How precise/accurate is the pressure in the IMR controlled? On a mobile platform (e.g. ship), motion sometimes can induce a pressure fluctuation. It would be good if the instrument can keep the pressure very accurate and constant, even in the presence of motion.

Line 245. Have the authors compared this N<sub>2</sub> background vs. simply scrubbing the measured air (e.g. with activated charcoal)? The differences in H<sub>2</sub>O and CO<sub>2</sub> between ambient air and scrubbed air are much smaller than those between ambient air and N<sub>2</sub>. This should make the background measurements easier to interpret.

Section 2.9. authors have shown that O<sub>3</sub> normalized sensitivity is linear (up to 80 ppbv), despite the fact that CO<sub>3</sub><sup>-</sup> signal and O<sub>2</sub><sup>-</sup> signal being comparable in magnitude. They have also shown that NO<sub>2</sub> normalized sensitivity doesn't depend on O<sub>3</sub> level. Does the O<sub>3</sub> normalized sensitivity depend on the NO<sub>2</sub> concentration?

Paragraph beginning on line 317. This paragraph isn't very clear. How is it that above 1e6 cps, precision no longer improves with count rate, yet “For 10 Hz averaging and count rates of 1e6 and 1e7 cps, the corresponding instrument precision is 0.75 and 2% respectively, and appears independent of count rate”?

Also, it would help the readers to spell out how the counting noise is computed.

Line 339. Without being familiar with these TOFMS or exploring the Vermeuel et al. reference, it's unclear how this O<sub>3</sub> calibration factor is applied. You could refer readers to section 3.2.1 here.

Section 3.1 suggest adding 1-2 sentences describing how the CIMS was deployed.

C2

Was it subsampling from a inlet manifold like on Scripps pier? Length of inlet? Instrument temperatures?

Line 342. The difference between the two instruments warrants further investigation. Even at 80 ppb the two instruments don't perfectly agree. Did the EPA monitor have a Nafion dryer to remove water vapor? What's the response time of the EPA monitor? If fairly slow, then during an O<sub>3</sub> titration event due to NO the CIMS would initially see lower O<sub>3</sub> than the EPA monitor at 1-minute resolution. . .

Line 358. The authors have not discussed how their measurements might depend on the front block and IMR temperatures. Does temperature affect the stability of the clusters in the multi-step reactions?

Also, does the use of 40 deg. inlet line have any affect on O<sub>3</sub>/heterogenous chemistry within the inlet?

Line 392. These are pretty high flow rates. I'm not familiar with the internal volumes of the mass spec, but would've expected to see a faster response time than the 0.9 s quoted here. A couple of questions: 1. Are the authors confident that the N<sub>2</sub> overflow tube consisted of N<sub>2</sub> only (i.e. no diffusion of ambient air into that tube)? From experience, even when using a fairly thin tube (1/8" OD) to tee into the main manifold, there can be some diffusion of ambient air into the N<sub>2</sub> line if it's just an open tee. This can be overcome by either having the shut-off valve next to the tee, or by doing the N<sub>2</sub> puff multiple times in succession. 2. Alternatively, could the fairly low response time be due to the multi-stage chemistry?

Eq. 4. Suggest replace KH with just H, to avoid confusion with Kt.

This sentence very confusing. Suggest rewrite: "Outliers in  $v_d(O_3)$  and the flux limit of detection were determined and removed for points three scaled median absolute deviations from the median. "

Line 429. 84% flux rejection is clearly not ideal. Instead of applying a simple  $u^*$  thresh-

C3

old, I encourage the author to investigate the  $u^*$  and Cd vs. wind speed relationship. This stress relationship is fairly well known over the ocean, and the authors could choose to reject O<sub>3</sub> flux values when the measured  $u^*$  or Cd is far from expected.

Line 455. The lag time determined from maximum covariance is approximately half as much as those computed from the gas evacuation. I suppose this could be due to either a time error between the O<sub>3</sub> and wind measurement, or the fact that the inlet pressure is much lower than 1 atm (such as the volumetric flow rate is  $\sim 2x$  the mass flow rate).

Line 467. One wouldn't expect the lag time to be the same as the response time. If  $t_0 = 0$  represents the time when the N<sub>2</sub> was injected into the inlet, the O<sub>3</sub> signal should start to drop  $\sim 1$  s later, and reach  $1/e$  of the initial value  $\sim 1.9$  s after  $t_0$ .

Line 495. One way to deal with estimation of high frequency flux loss without directly using the noisy O<sub>3</sub> cospectra would be to take an unattenuated cospectra (could be Kaimal, or could be the less noisy measured heat cospectra), attenuated it with a filter function (e.g. Eq. 7 in Bariteau et al. 2010), and compute the ratio between unattenuated and attenuated cospectra. Finally you can apply this ratio to your measured O<sub>3</sub> flux to get the unattenuated flux. The flux loss at high frequencies is pretty obvious despite the very low wind speed. So this correction is worth characterizing well.

Line 523. This is most likely true. See [www.atmos-meas-tech.net/9/5509/2016/](http://www.atmos-meas-tech.net/9/5509/2016/) for example.

Section 3.7.1 it might be worth mentioning that emission of NO from other sources (e.g. ships) could also bias the O<sub>3</sub> flux measurement. Though the authors' despiking of the O<sub>3</sub> signal probably removed such short-term ship emission-related O<sub>3</sub> titrations.

Section 3.7.2 My understanding is that a vertical gradient in flux does occur within the MBL when there's a large entrainment flux, but this mostly applies to the region ABOVE the 'constant flux layer' (i.e. more relevant for aircraft studies). The constant flux layer

C4

latter is usually taken to be roughly the lowest 10% of the MBL. Within the constant flux layer, we typically assume that there isn't a vertical gradient in flux, and the measured flux = surface flux. I'm not aware of people making H<sub>2</sub>O flux measurements from a ship/buoy needing to worry about the entrainment flux, for example. Some more discussion/references on this topic would be welcomed.

Line 589. 'Within range' instead of 'in good agreement', since there's a lot of variability in previous measurements.

---

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2019-445, 2019.