Simultaneous Detection of Ozone and Nitrogen Dioxide by Oxygen Anion Chemical Ionization Mass Spectrometry: A Fast Time Response Sensor Suitable for Eddy Covariance Measurements
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Abstract. We report on the development, characterization, and field deployment of a fast time response sensor for measuring ozone (O$_3$) and nitrogen dioxide (NO$_2$) concentrations utilizing chemical ionization time-of-flight mass spectrometry (CI-ToFMS) with oxygen anion (O$_2^-$) reagent ion chemistry. We demonstrate that the oxygen anion chemical ionization mass spectrometer (Ox-CIMS) is highly sensitive to both O$_3$ ($180 \text{ ions counts s}^{-1} \text{ pptv}^{-1}$) and NO$_2$ ($97 \text{ ions counts s}^{-1} \text{ pptv}^{-1}$), corresponding to detection limits (3σ, 1 s averages) of 13 and 9.9 pptv, respectively. In both cases, the detection threshold is limited by the magnitude and variability in the background determination. The short-term precision (1 s averages) is better than 0.3% at 10 ppbv O$_3$ and 4% at 10 pptv NO$_2$. We demonstrate that the sensitivity of the O$_3$ measurement to fluctuations in ambient water vapor and carbon dioxide is negligible for typical conditions encountered in the troposphere. The application of the Ox-CIMS to the measurement of O$_3$ vertical fluxes over the coastal ocean, via eddy covariance (EC), was tested during summer 2018 at Scripps Pier, La Jolla CA. The observed mean ozone deposition velocity ($v_d(O_3)$) was $0.0134 \text{ cm s}^{-1}$ with a campaign ensemble limit of detection (LOD) of $0.002742 \text{ cm s}^{-1}$ at the 95% confidence level, from each 27-minute sampling period LOD. The campaign mean and one standard deviation range of O$_3$ mixing ratios were $41.23 \pm 8.102 \text{ ppbv}$. Several fast ozone titration events from local NO emissions were sampled where unit conversion of O$_3$ to NO$_2$ was observed, highlighting instrument utility as a total odd oxygen (O$_x$ = O$_3$ + NO$_2$) sensor. The demonstrated precision, sensitivity, and time resolution of this instrument highlight its potential for direct measurements of O$_3$ ocean–atmosphere and biosphere–atmosphere exchange from both stationary and mobile sampling platforms.

1 Introduction

The deposition of O$_3$ to the ocean surface is a significant component of the tropospheric ozone budget. Global chemical transport model studies that explicitly treat O$_3$ deposition, indicate that approximately one-third of total ozone dry deposition is to water surfaces (Ganzeveld et al., 2009). However, the magnitude of total annual global ozone deposition to ocean surfaces is highly sensitive to the deposition velocity parameterization used, with model estimates ranging from 95 to 360 Tg yr$^{-1}$ (Ganzeveld et al., 2009; Luhar et al., 2017). Several common global chemical transport models including GEOS-Chem (Bey et al., 2001), MOZART-4 (Emmons et al., 2010), and CAM-chem (Lamarque et al., 2012) apply a globally uniform deposition velocity ($v_d$) that ranges between 0.01–0.05 cm s$^{-1}$ depending on the model. In comparison to terrestrial measurements, where
O$_3$ dry deposition velocities are relatively fast (>0.1 cm s$^{-1}$, (Zhang et al., 2003), there is a paucity of direct observations of ozone deposition to the ocean surface necessary to constrain atmospheric models. Previous studies of O$_3$ deposition to water surfaces have been made from coastal towers (Gallagher et al., 2001), aircraft (Falloon et al., 2005; Kawa and Pearson, 1989; Lenschow et al., 1981), underway research vessels (Helmig et al., 2012), and in the laboratory (McKay et al., 1992), with observed $v_d$(O$_3$) ranging between 0.01 and 0.15 cm s$^{-1}$. There is only one reported study of O$_3$ deposition to freshwater, which showed $v_d$(O$_3$) of 0.01 cm s$^{-1}$ (Wesely et al., 1981). Measured deposition rates to snow and ice vary widely, with most observations of $v_d$(O$_3$) from 0 to 0.2 cm s$^{-1}$, while models suggest $v_d$(O$_3$) from 0 to 0.01 cm s$^{-1}$ (Helmig et al., 2007). Reactions of O$_3$ with iodide and dissolved organic compounds (DOC) in the ocean are known to play a controlling role in setting $v_d$(O$_3$) and may explain some of the variability in observations (Chang et al., 2004; Ganzeveld et al., 2009). However, these quantities have not typically been measured during field studies of $v_d$(O$_3$). To date there is no consensus on whether measured ocean O$_3$ deposition velocities show a wind speed dependence (Fairall et al., 2007). The most comprehensive dataset is from Helmig et al., (2012), which reported a deposition velocity range of 0.009 – 0.034 cm s$^{-1}$ from 1700 hours of observation over five research cruises. This dataset showed variability of $v_d$(O$_3$) with wind speed ($U_{10}$) and sea–surface temperature (SST), highlighting the need for further field observations as constraints for model parameterizations.

The small magnitude of O$_3$ ocean–atmosphere vertical fluxes presents a significant analytical challenge for existing ozone sensors used in eddy covariance (EC) analyses. Driven in part by stringent sensor requirements for EC techniques, significant uncertainties in the magnitude and variability of ozone deposition to water surfaces remain. In contrast, O$_3$ vertical fluxes to terrestrial surfaces are 10 to 100 times faster than to water surfaces, significantly loosening sensor precision requirements. Nonetheless, significant variability in $v_d$(O$_3$) exists between surface types (e.g. soil vs. leaf) (Wesely and Hicks, 2000). Terrestrial deposition velocities also show strong diel and seasonal variability due to factors such as stomatal opening and within–canopy chemistry (Fares et al., 2010; Fowler et al., 2001; Kurpius and Goldstein, 2003). Highly accurate and precise measurements of O$_3$ are required to correctly model the response of $v_d$(O$_3$) to each of these factors. While terrestrial and ocean exchange studies have substantial differences in experimental design, a sensor suitable for ocean–atmosphere ozone deposition measurements via EC is expected to be highly capable of biosphere–atmosphere measurements due to the significantly larger deposition rates and similar accuracy requirements.

Eddy covariance measurements typically require fast (1-10 Hz), high precision sensors in order to resolve covariance on the timescales of the fastest atmospheric turbulent eddies. Due to this constraint, standard O$_3$ monitoring instruments which utilize UV-absorption detection do not have suitable time response or precision for EC measurements and ozone flux measurements have primarily utilized fast response chemiluminescence sensors. Chemiluminescence detectors can use either gas-phase, dry, or wet-, dry-, or gas-phase reagents for detection with important differences between them (Muller et al., 2010). Gas-phase chemiluminescence sensors are typically based on the reaction of O$_3$ with nitric oxide (NO) to form an excited state NO$_2^*$ which then relaxes to the ground state, emitting a photon that can be detected. This method has well understood reaction kinetics and allows for high sensitivity detection on the order of 2.8 counts s$^{-1}$ pptv$^{-1}$ (Bariteau et al., 2010; Pearson, 1990). A practical disadvantage to this technique is the necessity of a compressed cylinder of NO which is highly toxic. Wet
Chemiluminescence techniques are used less, as they exhibit generally lower sensitivity than dry chemiluminescence sensors and can be limited by issues in the liquid flow (Keronen et al., 2003).

Dry chemiluminescence sensors have the simplest operation and have seen the most regular use for EC studies (Güsten et al., 1992; Tuovinen et al., 2004). However, dry chemiluminescence sensor discs require conditioning with high ozone (up to 400 ppbv for several hours) before operation, are known to degrade over time, and have high variability in sensitivity between sensor discs (Weinheimer, 2007). These factors have led to limitations in long term stability and to uncertainty in calibration factors for dry chemiluminescence sensors, resulting in uncertainty in the accuracy of the flux measurement (Muller et al., 2010). Muller et al. (2010) also reported a comparison of two identical co-located dry chemiluminescence sensors with half-hourly flux values differing by up to a factor of two and a mean hourly flux difference ranging from 0 to 23% between sensors. Recently Zahn et al., (2012) reported the development of a commercial dry chemiluminescence ozone detector capable of fast (>10 Hz) measurements with high sensitivity (∼9 counts s⁻¹ pptv⁻¹) suitable for EC or mobile platform sampling. However, they also report issues of short- and long-term drift and variability between sensor discs. These accuracy and drift concerns have driven an interest in the development of a new, stable and fast ozone sensor suitable for EC measurements from both stationary and mobile sampling platforms.

In addition to the inherently small magnitude of \( v_d(O_3) \), the fast chemical titration of \( O_3 \) by NO (R1) often complicates the interpretation of \( v_d(O_3) \) measurements. Surface emissions of NO result in a high bias in the measured deposition velocity when the titration reaction (R1) is fast relative to the transport time to the height of the sensor.

\[
O_3 + NO \rightarrow NO_2 + O_2 \hspace{1cm} k(O_3+NO) = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \tag{R1}
\]

Surface NO emissions from both biogenic and anthropogenic sources are widespread, with ocean emissions on the order of \( 1 \times 10^8 \) molecules cm⁻² s⁻¹ (Zafiriou and McFarland, 1981) and soil emissions ranging from \( 5 \times 10^9 \) to \( 2 \times 10^{11} \) molecules cm⁻² s⁻¹ (Yienger and Levy, 2004). These emissions correspond to a positive bias in the observed \( v_d(O_3) \) dry deposition rate on the order of 5% in the marine atmosphere (discussed in section 3.7.1) and up to 50% in a forested site (Dorsey et al., 2004).

Simultaneous flux detection of \( O_3 \) with one or both of NO or NO₂ is commonly used to address this flux divergence problem (Finco et al., 2018; Stella et al., 2013). However, these studies typically require separate sensors for \( O_3 \) and NOₓ which can introduce additional sources of uncertainty. Related challenges of fast \( O_3 \) titration exists for quantification of \( O_3 \) from mobile platforms where there is dynamic sampling of different airmasses with potentially differing \( O_3-NO-NO_2 \) steady-state conditions.

In what follows, we describe the characterization and first field observations of a novel oxygen anion chemical ionization time-of-flight mass spectrometer (Ox-CIMS) sensor for \( O_3 \) and NO₂. Over the past two decades, chemical ionization mass spectrometry (CIMS) techniques have emerged as sensitive, selective, and accurate detection methods for a diverse suite of reactive trace gases (Huey, 2007). Successful application of CIMS for EC flux measurements have been demonstrated from many sampling platforms including ground sites (Kim et al., 2014; Nguyen et al., 2015), aircraft (Wolfe et al., 2015), and underway research vessels (Blomquist et al., 2010; Kim et al., 2017; Yang et al., 2013) employing a variety of reagent ion...
chemistry systems. Here we demonstrate the suitability of the Ox-CIMS for EC flux measurements and provide detailed laboratory characterization of the instrument.

2 Laboratory Characterization

2.1 Chemical-ionization time-of-flight mass spectrometer

A complete description of the CI-ToFMS instrument (Aerodyne Research Inc., TOFWERK AG) can be found in Bertram et al. (2011). In what follows we highlight significant differences in the operation of the instrument from what is discussed in Bertram et al., (2011). Oxygen anions are generated by passing an 11:1 volumetric blend of Ultrahigh Purity (UHP) N\textsubscript{2} and O\textsubscript{2} gas (both Airgas 5.0 grade) through a polonium-210 α-particle source (NRD, P-2021 Ionizer). This N\textsubscript{2}:O\textsubscript{2} volume ratio was found empirically to maximize total reagent ion signal in our instrument while minimizing background signal at the O\textsubscript{3} detection product (CO\textsubscript{3}\textsuperscript{−}, ~60 m/Q). Further discussion of the reagent ion chemistry and precursor concentration can be found in sections 2.2 and 2.8. The reagent ion stream then mixes with ambient air in an ion-molecule reaction (IMR) chamber held at 95 mbar where product ions were generated. Further discussion of the dependence of instrument sensitivity on IMR pressure can be found in section 2.6. At this pressure, the residence time in the IMR is estimated to be on the order of 100 ms. Product ions then pass into three differentially pumped chambers before reaching the ToF mass analyzer. Ions first move from the IMR to a collisional dissociation chamber (CDC) held at 2 mbar which houses a short-segmented RF-only quadrupole ion guide. Field strengths in the IMR and CDC were tuned to be as soft as possible to preserve the transmission of weakly bound clusters while still maintaining acceptable total ion signals (ion optic potentials are listed in Table S1). Ions then sequentially pass into a second RF-only quadrupole chamber held at 1.4 × 10\textsuperscript{−2} mbar and a final chamber containing focusing optics which prepare the ion beam for entry into the compact ToF mass analyzer (CToF, TOFWERK AG and Aerodyne Research Inc.). The mass resolving power (M/ΔM) of the instrument as configured for these experiments was greater than 900 at ~60 m/Q. All ion count rates reported here are for unit mass resolution integrated peak areas. In this work extraction frequencies of 75 kHz were used, resulting in mass spectra from 27-327 –m/Q. All mass spectra were saved at 10 Hz for analysis.

2.2 Oxygen Anion Chemistry

Oxygen anion (O\textsubscript{2}\textsuperscript{−}) reagent ion chemistry has been investigated previously for its use in the detection of nitric acid and more recently hydrogen peroxide (Huey, 1996; O’Sullivan et al., 2018; Vermeuel et al., 2019). Oxygen anion chemistry has also been used for chemical analysis of aerosol particles in a thermal desorption instrument, primarily for detection of particle sulfate and nitrate (Voisin et al., 2003). Oxygen anion chemistry has also been used for the detection of SO\textsubscript{2} via a multi-step ionization process where CO\textsubscript{3}\textsuperscript{−} reagent ions are first generated by the reaction of O\textsubscript{2} with added excess O\textsubscript{3} in the presence of CO\textsubscript{2}. The CO\textsubscript{3}\textsuperscript{−} reagent ion product then ligand switches with SO\textsubscript{2} to form SO\textsubscript{3}\textsuperscript{−} which then quickly reacts with ambient O\textsubscript{2} to
form the primary detected $\text{SO}_3^-$ product (Porter et al., 2018; Thornton et al., 2002a). Ionization of analytes by oxygen anion reagent ion chemistry proceeds through both charge transfer (R2) and adduct formation (R3).

\begin{align}
O_2(H_2O)_n^+ + A &\rightarrow O_2(H_2O)_n + A^- \quad \text{(R2)} \\
O_2(H_2O)_n^- + B &\rightarrow B \cdot O_2(H_2O)_n^- \quad \text{(R3)}
\end{align}

It is expected that charge transfer from oxygen will occur to any analyte with an electron affinity (E.A.) greater than $O_2$ (0.45 eV, (Ervin et al., 2003)) resulting in a relatively non-specific reagent ion chemistry (see (Rienstra-Kiracofe et al., 2002) for a compilation of molecular E.A. values), which is sensitive to a wide class of molecules. Adduct formation is observed when the binding enthalpy of the adduct is larger than that of the oxygen-water adduct and the adduct is stable enough to be preserved through the ion optics. This adduct formation framework is analogous to what has been shown for iodide reagent ion chemistry (Lee et al., 2014).

The $O_2^-$ reagent ions present in the IMR are expected to have a series of attached water molecules at ambient humidity and the IMR pressure (95 mbar) and electric field strengths used in this study (Bork et al., 2011). The reagent ion is therefore reported as $O_2(H_2O)_n^-$ for the remainder of this work. In the recorded mass spectra from our instrument, all reagent ion signal is observed as $n = 0$–1 (i.e., $O_2^-$ and $O_2(H_2O)^-$) as seen in Fig. 1. Oxygen anion-water clusters larger than $n = 1$ are likely present in the IMR but $H_2O$ evaporates off of the cluster in the CDC before detection due to the lower binding enthalpy of each additional water in $O_2(H_2O)_n^-$ (Bork et al., 2011) and the high filed strength at the exit of the CDC (Brophy and Farmer, 2016). Variability in the number of attached water molecules ($n$) as a function of humidity introduces the possibility of a water dependence on the ion chemistry, which is discussed further in Section 2.5.

The detection of ozone ($O_3$) by oxygen anion reagent ion chemistry proceeds via a two-step reaction leading to the formation of a carbonate anion ($\text{CO}_3^-$), which is the final detected product. First, the oxygen anion ($O_2(H_2O)_n^-$) either transfers an electron to ozone forming $O_3^-$ (R4a) or forms a stable cluster with ozone (R4b). The ozone anion (either bare or as a cluster with $O_2(H_2O)_n$) then reacts with a neutral $\text{CO}_2$ molecule to form $\text{CO}_3^-$ (R5a–5b) which is the primary, detected product in the mass spectrometer. The electron affinity of $O_3$ is 2.1 eV (Arnold et al., 1994).

\begin{align}
O_3 + O_2(H_2O)_n^- &\rightarrow O_3^- + O_2 + nH_2O \quad \text{(R4a)} \\
O_3 + O_2(H_2O)_n^- &\rightarrow O_2(O_3)(H_2O)_n^- \quad \text{(R4b)} \\
O_3^- + \text{CO}_2 &\rightarrow \text{CO}_3^- + O_2 \quad \text{(R5a)} \\
O_2(O_3)(H_2O)_n^- + \text{CO}_2 &\rightarrow \text{CO}_3^- + 2O_2 + nH_2O \quad \text{(R5b)}
\end{align}

It is not clear whether it is the bare ozone anion (R4a & R5a) or the cluster (R4b & R5b) that goes on to react with $\text{CO}_2$ to form the carbonate anion. The $O_2(O_3)(H_2O)_n$ product has not been observed in the mass spectrometer, but it may exist in the IMR and dissociate as it transfers into the CDC prior to detection. A small amount of ozone is detected directly as $O_3^-$ but the magnitude of this signal is less than 1% of the signal of $\text{CO}_3^-$ during ambient sampling. The proposed mechanism of $\text{CO}_3^-$ formation is supported by a study using isotopically labelled oxygen to form labelled ozone anions ($^{18}O_3^-$) in a corona
discharge source which then reacted with CO\textsubscript{2} to form the detected product C\textsuperscript{18}O\textsuperscript{2}\textsuperscript{-} (Ewing and Waltman, 2010). This product supports that a single oxygen is transferred from the ozone anion to carbon dioxide (as in R5a).

The detection of NO\textsubscript{2} proceeds directly through a charge transfer reaction with O\textsubscript{2}(H\textsubscript{2}O)\textsuperscript{n} to form the detected NO\textsuperscript{2-} product (R6). This is expected based upon the high E.A. of NO\textsubscript{2} (2.27 eV, (Ervin et al., 1988)) compared to O\textsubscript{2} (E.A 0.45 eV).

\[ NO_2 + O_2(H_2O)_n^- \rightarrow NO_2^- + O_2 + nH_2O \]  

(R6)

Oxygen anions are expected to be a highly general reagent ion chemistry, showing sensitivity to an array of analytes.

While the focus of this work is on detection of O\textsubscript{3} and NO\textsubscript{2}, detection of hydrogen peroxide, nitric acid, formic acid, sulfur dioxide and other species with the Ox-CIMS has demonstrated good performance (Vermeuel et al., 2019). An example ambient mass spectrum recorded at 1 Hz sampling is shown in Fig. 1, with several major peaks highlighted. Also apparent are an abundance of peaks throughout the spectra with high signal intensity. During ambient observations, over one third of masses from –m/Q 27-327 showed signal intensity greater than 1 x 10\textsuperscript{4} counts per second (cps). A larger survey and classification of oxygen anion reagent ion chemistry to utilize this versatility is underway.

2.3 Laboratory calibration

Laboratory calibrations of the Ox-CIMS were performed to determine instrument sensitivity to O\textsubscript{3} and NO\textsubscript{2}. Ozone was generated by passing UHP Zero Air (ZA, Airgas 5.0 grade) through a mercury lamp UV source (Jelight Co, Irvine CA). Outflow from the lamp source was diluted in UHP ZA and split between the Ox-CIMS and a factory calibrated 2B POM ozone monitor (2B Technologies) with an accuracy of ± 1.5 ppbv, which served as our reference standard. Ozone concentrations were varied over the range 0–80 ppbv and instrument response was determined to generate a calibration curve. NO\textsubscript{2} was delivered from a certified standard cylinder (Scott-Marrin 4.84 ± 0.1 ppmv). The primary NO\textsubscript{2} standard was diluted in UHP ZA to span the range of 0–10 ppbv. Dilutions of calibration standards were made in UHP ZA which was humidified to the desired amount by splitting a portion of the flow through a bubbler containing 18 MΩ water. CO\textsubscript{2} (Airgas Bone Dry grade) was added to the dilution flow to maintain mixing ratios of 380 ppmv for all calibrations (See Section 2.6). A Vaisala HMP 110 sensor continuously measured relative humidity and temperature inline downstream of the Ox-CIMS and POM inlets. All flows were controlled by mass flow controllers (MKS instruments, 1179C series) with an estimated total uncertainty of 10%.

Example calibration curves for O\textsubscript{3} and NO\textsubscript{2} are shown in Fig. 2. An overview of instrument sensitivity, limits of detection (LOD), and precision to O\textsubscript{3} and NO\textsubscript{2} is given in Table 1.

2.4 Absolute sensitivity

The absolute sensitivity of the Ox-CIMS for detection of analytes is controlled by the kinetics and thermodynamics of the reagent ion chemistry and the total ion generation and transmission efficiency of the instrument. Under the operational configuration described in Section 2.1, typical reagent ion signal (O\textsuperscript{2-} + O\textsubscript{2}(H\textsubscript{2}O)\textsuperscript{n} ) ranged from 0.8 to 2.2 x 10\textsuperscript{7} countsions s\textsuperscript{-1} (Fig. S1). The mean total reagent ion signal over 6 weeks of ambient sampling (Section 3.1) was 1.45 x 10\textsuperscript{7} cpsions s\textsuperscript{-1}. The absolute instrument sensitivity at this reagent ion signal to O\textsubscript{3} and NO\textsubscript{2} is 180 and 97 cpsions s\textsuperscript{-1} pptv\textsuperscript{-1} respectively (at 8 g kg\textsuperscript{-1})
Total instrument count rate is a complex function of instrument design, instrument ion optics tuning, Po-210 source decay, micro channel plate (MCP) detector decay, and ToF extraction frequency; all of which are either tunable parameters or vary in time. Conversely, the reagent ion charge transfer or adduct formation chemistry for a given analyte sets a fundamental limit on sensitivity for a given instrument configuration. Sensitivity values can be normalized by scaling all signals to a fixed total reagent ion signal count-rate of \(1 \times 10^6 \text{ cps ions s}^{-1}\) to isolate the sensitivity component controlled by reagent ion chemistry, separate from changes in instrument performance due to decay in the ion source or other factors. The total reagent ion signal is taken as the sum of the \(O_3^-\) and \(O_2(H_2O)^-\) signals. Sensitivity values through the remainder of the text are reported as either absolute sensitivities in counts per second (cps pptv\(^{-1}\)) or normalized sensitivities in normalized counts per second (ncps pptv\(^{-1}\)). Absolute sensitivity values control instrument limits of detection (LOD) and precision, while normalized sensitivities are used for comparison of calibration factors.

2.5 Dependence of instrument sensitivity on specific humidity

The dependence of instrument sensitivity on ambient water content was assessed for specific humidity (SH) ranging between 0–16 g kg\(^{-1}\) (approximately 0-80% RH at 25 °C) by triplicate calibrations as shown in Fig. 3. Sensitivity to \(O_3\) was seen to have had no significant dependence on specific humidity over the range 4-16 g kg\(^{-1}\). Sensitivity to \(NO_2\) has a specific humidity dependence over the range 4–16 g kg\(^{-1}\), decreasing from 7.9 to 4.6 ncps pptv\(^{-1}\). A 30% and 45% decline in sensitivity was observed from 0 to 4 g kg\(^{-1}\) for \(O_3\) and \(NO_2\) respectively. This low humidity range is rarely sampled in the boundary layer over water surfaces but may be significant in some terrestrial or airborne deployments and would require careful calibration. The SH range from 8 to 16 g kg\(^{-1}\) corresponds to approximately 40 to 80% RH at 25 °C which is typical of the humidity range over mid-latitude oceans (Liu et al., 1991). \textit{Ab initio} calculations of \(O_3^- (H_2O)_n\) and \(O_2^- (H_2O)_n\) clusters performed by Bork et al. (2011) showed that charge transfer from the bare \((n=0)\) \(O_3^-\) to \(O_3\) was exothermic at ca. -160 kJ/mol. At larger cluster sizes of \(n = 4–12\), charge transfer becomes less favorable and converges to ca. -110 kJ/mol. An increase in \(n\) from 0 to 4 over the SH range 0–4 g kg\(^{-1}\) is a potential explanation for the initial decline in sensitivity observed with SH before levelling off from 4–16 g kg\(^{-1}\). It is not known if the enthalpy of charge transfer from \(O_3^- (H_2O)_n\) to \(NO_2\) follows a similar trend with \(n\). Ion mobility studies to determine the \(O_3^- (H_2O)_n\) cluster size with SH and IMR pressure would provide valuable insight on the observed dependence of sensitivity on water content.

2.6 Dependence on \(CO_2\)

The ionization pathway for detection of \(O_3\) with \(O_3^- (H_2O)_n\) reagent ion chemistry differs from typical chemical ionization schemes, in that it involves a two-step reaction of charge transfer to ozone forming \(O_3^-\), which then reacts with \(CO_2\) to form the detected \(CO_3^-\) product (R4-R5). Therefore, we assessed the impact of \(CO_2\) mixing ratio in the sample flow on \(O_3\) sensitivity as shown in Fig. 4. Calibration curves were generated by diluting ozone in dry UHP \(N_2\) and mixing in a flow of variable \(CO_2\) (Airgas, Bone Dry Grade) mixing ratios before sampling. At nominally 0 ppmv \(CO_2\), the \(O_3^-\) ionization product (\(-48 \text{ m/Q}\)) was...
detected with sensitivity of $14 \pm 2$ ncps pptv$^{-1}$ and the CO$_3^-$ product ($-60 \text{ m}/Q$) at $5 \pm 1$ ncps pptv$^{-1}$. For CO$_2$ mixing ratios from 60 to 500 ppmv, the O$_3^-$ signal is less than 1% of the CO$_3^-$ product and the sensitivity at the CO$_3^-$ product is independent of CO$_2$ within the uncertainty. The presence of a significant fraction (36%) of the CO$_3^-$ product with nominally 0 ppmv CO$_2$ suggests the presence of a slight leak rate of CO$_2$ via diffusion through the perfluoralkoxy alkane (PFA) tubing, or CO$_2$ contamination in the UHP N$_2$ supply. The manufacturer stated upper limit of CO$_2$ in the UHP N$_2$ is 1 ppmv which we take to be the lower limit achievable in our system. A CO$_2$ mixing ratio of only 1 ppmv is still an order of magnitude excess relative to a high end ambient O$_3$ mixing ratio of 100 ppbv. An exponential fit of the O$_3^-$ product vs CO$_2$ indicates that O$_3^-$ makes up less than 1% of the detected ozone at CO$_2$ mixing ratios greater than 10 ppmv. This suggests ambient samples will always have a substantial excess of CO$_2$ necessary to drive the reaction completely to the CO$_3^-$ product. The measured flat response from 60–500 ppmv CO$_2$ indicates that natural variability in ambient CO$_2$ will have negligible impact on ambient measurements of ozone. No other analytes that we have calibrated for analyzed with the Ox-CIMS (HCOOH, HNO$_3$, H$_2$O$_2$) have shown a CO$_2$ mixing ratio dependence, demonstrating that CO$_2$ may be uniquely involved in the detection of O$_3$'s mechanism and is not a general feature of the oxygen-anion chemistry. All other reported laboratory calibrations reported here were performed at CO$_2$ mixing ratios of 380 ppmv and all reported sensitivities are for the CO$_3^-$ product. This CO$_2$ dependence also requires careful consideration during instrument background determinations by UHP N$_2$ overflow which is discussed in Section 2.8.

2.7 Dependence on IMR pressure

Instrument sensitivity to O$_3$ increases with increasing IMR pressure as shown in Fig. 5. The normalized signal of O$_3$ increases by 47560% at an IMR pressure of 95 mbar compared to 70 mbar over the pressure range of 70 to 95 mbar in the IMR when sampling a constant O$_3$ source of 35 ppbv. IMR pressure was increased in approximately 5 mbar steps, with CDC pressure held constant at 2 mbar, and a three-minute dwell time at each step to ensure signal and pressure were stabilized. Total reagent ion signal did not change significantly over this pressure range. Pressures above 95 mbar were not investigated due to concerns over corresponding increases in CDC pressure with the pinhole and pumping configuration used in this work. There is no evident plateauing in the signal increase over the IMR pressure range investigated here, indicating that further optimization is likely possible by operating at higher IMR pressures. The increase in sensitivity with IMR pressure could be fit well with an exponential least squares fit, which is plotted in Fig. 5. The physical meaning of the exponential relationship is not clear. The source of the response of sensitivity to pressure is not definitive but can possibly be attributed to the increase in the total number of collisions during the 100 ms residence time in the IMR and the corresponding weakening of those collisions. Higher collisional frequencies also lead to proportionally weaker collisions which could better preserve a weakly bound O$_2$(O$_3$)(H$_2$O)$_n$ cluster and allow a longer lifetime to react with CO$_2$ before dissociation. The operational IMR pressure of 95 mbar used here was empirically selected to maximize sensitivity to O$_3$ without increasing CDC pressure beyond the desired...
range. Investigation of higher IMR pressures, up to the operation of an atmospheric pressure interface, has the potential to further increase the instrument sensitivity to O$_3$.

### 2.8 Instrument background and limits of detection

Instrument backgrounds were assessed by periodically overflowing the inlet with UHP N$_2$ during field sampling. Details of the inlet and zeroing conditions used are discussed further in Section 3.1. During N$_2$ overflow, O$_3$ displayed a consistently elevated background on the order of $3.1 \times 10^5$ cps corresponding to $2.1 \times 10^4$ ncps, or approximately 1.3 ppbv O$_3$, at a typical total reagent ion signal of $1.45 \times 10^7$ cps. A representative background determination is shown in Fig. 6. The magnitude of the O$_3$ background was observed to vary with the O$_2$:N$_2$ ratio in the reagent ion precursor flow when sampling a UHP ZA overflow with 380ppm CO$_2$ as shown in Fig. S2. The background O$_3$ count rate was observed to increase from $3.0 \times 10^4$ to $6.3 \times 10^4$ ncps as the O$_2$ volume fraction in the reagent ion delivery gas flow ($f_{O_2}$) was increased from 0.05 to 0.4. The dependence of the background O$_3$ signal on $f_{O_2}$ suggests that the observed background O$_3$ is formed directly in the alpha ion source and is not from off-gassing of inlet and instrument surfaces. The magnitude of this background O$_3$ does not vary when sampling UHP zero air or N$_2$, further confirming that the background O$_3$ is formed directly in the ion source from the O$_2$ used to generate the reagent ion. An operational $f_{O_2}$ of 0.08 (actual volumetric flow ratio O$_2$:N$_2$ of 200:2200 sccm) was selected to balance maximizing the total reagent ion signal while minimizing the O$_3$ ion-source background ($3.1 \times 10^5$ cps). The magnitude of this O$_3$ background was observed to be highly consistent during field sampling at a constant $f_{O_2}$ of 0.08 and well resolved from all ambient observations (Fig. S3). The $1\sigma$ deviation of the distribution of normalized adjacent differences of O$_3$ signal during background periods gives an upper limit of variability of 9% between adjacent background periods. A variability of 9% corresponds to a difference of 70 pptv between subsequent O$_3$ background determinations. The magnitude of this O$_3$ background is a fundamental limit on the achievable limit of detection.

Because CO$_2$ was not added to the UHP N$_2$ overflow during field sampling, the reaction was not driven fully to the CO$_3^-$ product and some O$_2^-$ signal at $-m/Q$ 48 was observed during UHP N$_2$ overflow periods as shown in Fig. S4. The magnitude of the O$_3$ signal observed as O$_2^-$ was approximately 55% of the CO$_3^-$ product (mean $1.2 \times 10^4$ and $9.6 \times 10^3$ ncps respectively) during overflow periods. The total sensitivity to O$_3$ as the sum of the O$_2^-$ and CO$_3^-$ was observed to be constant as a function of CO$_2$ as shown in Fig. 4. We therefore assign equal sensitivity to each O$_3$ detection product and took the sum of signal at O$_2^-$ and CO$_3^-$ in order to determine the total background O$_3$ concentration. This issue will be corrected in future deployments by the addition of CO$_2$ to the N$_2$ overflow used for backgrounds which will drive the product fully to CO$_3^-$. The mean background of O$_3$ for the full field sampling period was $1.3 \pm 0.3$ ppbv. The 10 Hz precision of O$_3$ during an individual N$_2$ overflow period was found to be 0.75%, corresponding to 7.5 pptv as shown in Fig. S5. This suggests that variability in the O$_3$ signal from this background source is constant over short timescales and has a negligible impact on instrument precision during ambient sampling.
The 10 Hz limit of detection for $O_3$ is 42 pptv for a S/N of 3, and a mean background $O_3$ signal of $2.1 \times 10^4$ ncp/s as calculated using Eq. 1, below from Bertram et al., 2011, where $C_f$ is the calibration factor, $[x]$ is the analyte mixing ratio, $t$ is averaging time in seconds, and $B$ is the background count rate. The optimum LOD from the minimum of the Allan variance at an 11 second averaging time is 4.0 pptv (Fig. S6a).

$$\frac{s}{N} = \frac{C_f [x] t}{\sqrt{C_f [x] t - 2Bt}}$$

The mean background signal during field sampling for NO$_2$ was $3.5 \times 10^3$ ncp/s which corresponds to 0.28 ppbv. At this background level, the 10 Hz LOD for NO$_2$ is 26 pptv for a S/N of 3. The optimum LOD for NO$_2$ is 2.3 pptv at an averaging time of 19 seconds, determined from the minimum of the Allan variance (Fig. S6b). The background signal of NO$_2$ is notably above zero indicating either off gassing from inlet walls or a secondary production of NO$_3$ in the instrument. A possible source of this background is from degradation of other species such as nitric acid or alkyl nitrates on the inlet walls. Additional calibration would be necessary to ensure that observed NO$_2$ signal is not a secondary product of other species and we can currently quantify their potential interference on measured NO$_2$.

2.9 Reagent ion saturation and secondary ion chemistry

During ambient sampling the ozone signal (as CO$_3^-$ detected at −60 m/Q) is of comparable magnitude to the O$_3^-$ reagent ion signal as shown in Fig. 1. High analyte concentrations (> 5 ppbv) have been shown previously to result in non-linear calibration curves for unnormalized signals (Bertram et al., 2011; Veres et al., 2008). In our system we do not observe non-linearity in the normalized $O_3$ calibration for our highest concentration calibration point of 80 ppbv despite the CO$_3^-$ signal being larger than the O$_3^-$ reagent ion (9 $\times$ 10$^6$ cps and 6 $\times$ 10$^6$ cps respectively). The electron affinity (E.A.) of carbonate is from 3.26 (Hunton et al., 1985) to >3.34 eV (Snodgrass et al., 1990) and is significantly higher than that of oxygen (E.A. 0.45 eV), making it unlikely that carbonate is involved in charge transfer reactions when excess O$_3^-$ is present. At high $O_3$ concentrations, the reagent ion signal magnitude is reduced, which necessitates normalizing sensitivities to the 1 $\times$ 10$^6$ cps of reagent ion signal before quantification. For NO$_2$ (E.A. 2.27 eV), the normalized sensitivity showed no dependence on $O_3$ concentrations from 0 to 80 ppbv. Carbonate reagent ion chemistry has been utilized for detection of HNO$_3$ and H$_2$O$_2$ via adduct formation raising additional concern about potential secondary ion chemistry (Reiner et al., 1998). In laboratory calibrations, shown in Fig. S7, introduction of 0 to 40 ppb H$_2$O$_2$ resulted in the titration of the O$_3$ signal of 0.06 ppbv per ppbv H$_2$O$_2$. H$_2$O$_2$ was detected as an adduct with O$_3^-$ and not CO$_3^-$, indicating that O$_3^-$ reagent ion chemistry is more favorable despite high CO$_3^-$ signal intensity. The Ox-CIMS O$_3$ measurement also compared well (R$^2$ =0.99) against an EPA AQS O$_3$ monitor over 1 month of ambient sampling where H$_2$O$_2$ and HNO$_3$ concentrations both exceeded 5 ppbv at times (see Section 3.1 for further discussion of field intercomparison), further supporting the CO$_3^-$ detection product as a robust indicator of O$_3$ in complex sampling environments.

Ab initio calculations of the binding enthalpies of O$_3^-$ and CO$_3^-$ reagent ions with H$_2$O, HNO$_3$, H$_2$O$_2$, and CH$_3$OOH were performed with the MP2/aug-cc-pvdz-PP theory and basis set in order to assess the relative favorability of adduct
formation between $O_2^-$ and $CO_2^-$. Adduct formation with $O_2^-$ was favorable relative to $CO_2^-$ by 2.5 to 17 kcal mol$^{-1}$ for all analytes that were calculated. All calculated binding enthalpy values are listed in Table S2.

### 2.10 Reagent-ion saturation and secondary-ion chemistry

Short-term and long-term precision

Short term precision of the instrument was assessed by calculating the normalized difference between adjacent 10 Hz data points over a 27-minute sampling period of a constant ambient analyte concentration via Eq. 2.

$$\text{NAD} = \frac{|x_n - x_{n-1}|}{\sqrt{x_n x_{n-1}}}$$  \hspace{2cm} E2

The standard deviation of the Gaussian fit of the distribution of normalized adjacent differences (NAD) is a direct measure of the short-term instrument precision (Bertram et al., 2011). The 1σ precision from the NAD distribution for 10 Hz sampling of 38 ppbv ozone is 0.74% (Fig. 7). The 10 Hz precision for sampling of 2.3 ppbv NO$_2$ is 1.1%. The short-term precision for both analytes was larger than expected if the noise was driven by counting noise alone (10 Hz counting noise limit for O$_3$ and NO$_2$ at the concentrations used above are 0.12% and 0.63% respectively), indicating that other potential points of optimization in the instrument configuration are required to further improve short-term precision. Notably, the observed noise source appears to be white noise given the Gaussian distribution of the NAD (Thornton et al., 2002b).

Short term precision was assessed as a function of count rate by calculating the NAD for all masses in the spectrum over a stable 27-minute sampling period for both 1 Hz and 10 Hz data averaging. From this assessment, precision was observed to improve approximately linearly in a log-log scaling for count rates between $1 \times 10^3$ and $1 \times 10^6$ cps (Fig. S8) as expected in the case where counting noise drives instrument precision. Above $1 \times 10^6$ cps there is an apparent asymptote where precision no longer improves with count rate. For 10 Hz averaging and count rates of $1 \times 10^6$ and $1 \times 10^7$ cps, the corresponding instrument precision is 0.75 and 2% respectively, and appears independent of count rate. The counting noise limited 10 Hz precision for $10^6$ and $10^7$ cps are 0.32% and 0.1% respectively, while the measured values were 0.75 and 2%. The counting noise limited precision is calculated as $\sqrt{N}/N$ where $N$ is the number of counts during the integration time. This precision limit could be driven by an uncharacterized source of white noise in the instrument, including MFC drift, IMR turbulence, ion optic voltage drift, and pump drift. Measurement precision of O$_3$ and NO$_2$ could be improved by a factor of 5 and 2 respectively if this non-counting noise source of white noise was eliminated.

In theory, detection limits can be improved by signal averaging to a lower time resolution than the 10 Hz save rate. Signal-to-noise ratios are expected to improve with the square root of the integration time. At longer timescales, factors including instrument drift become significant, creating a limit on the upper end of averaging time which optimizes signal-to-noise. This was assessed quantitatively by calculation of the Allan variance as shown in Fig. S6 (Werle et al., 1993).
3 Field results and discussion

3.1 Ozone field calibration and intercomparison

Performance of the Ox-CIMS was compared against a co-located EPA Air Quality System (AQS) O₃ monitor (Thermo-Fisher 49i, AQS ID 17-097-1007) over one month of ambient sampling during the Lake Michigan Ozone Study 2017 (LMOS 2017) in Zion, IL (Vermeuel et al., 2019). A regression analysis between the two instruments at one-minute averaging showed strong agreement ($R^2 = 0.99$) as shown in Fig. 8. Ox-CIMS concentrations were averaged to 1 ppbv bins which was the output data resolution of the EPA logger system for the (Thermo-Fisher 49i). Error bars are the 1σ standard deviation of each Ox-CIMS bin average. Near one-to-one agreement (slope of 0.99) between instruments lends confidence to the calibration, baselining, and long-term stability of the Ox-CIMS. The Ox-CIMS was located on the roof of a trailer (approx. 5 m above ground) and sampled through a 0.7 m long, 0.925 cm i.d., PFA inlet. The inlet was pumped at flow rate of 18-20 slpm from which the Ox-CIMS subsampled at 1.5 slpm. Temperature and RH were recorded inline downstream of the subsampling point.

The Ox-CIMS sampling point was approximately 10 m horizontally from the Thermo-Fisher 49i and both instruments sampled at approximately equal heights. Instrument backgrounds of the Ox-CIMS were determined every 70 minutes by overflowing the inlet with dry UHP N₂. Calibration factors for O₃ were determined by scaling by the in-field continuous addition of a C-13 isotopically labelled formic acid standard to the tip of the inlet. Laboratory calibrations of the Ox-CIMS to formic acid and O₃ as a function of specific humidity were determined immediately pre- and post-campaign and were used to calculate a humidity dependent sensitivity of O₃ relative to formic acid. That relative sensitivity was then used to determine the in-field sensitivity to O₃ by scaling field sensitivities of formic acid from the continuous additions to humidity dependent calibration factors for O₃ and formic acid determined in lab pre- and post-campaign as. Full details of this deployment and calibration methods are described in Vermeuel et al., (2019). The EPA O₃ monitor shows a persistent high bias at low O₃ concentrations (<10 ppbv) relative to the Ox-CIMS. This discrepancy could arise from known interferences from water, mercury, and other species in 254 nm UV absorbance detection of ozone (Kleindienst et al., 1993).

3.2 Eddy covariance experiment overview

The Ox-CIMS was deployed to the 330 m long Ellen Browning Scripps Memorial Pier (hereon referred to as Scripps Pier) at the Scripps Institute of Oceanography (32° 52.0’ N, 117° 15.4’ W) during July and August 2018 for EC measurements of O₃ vertical fluxes. This site has been used regularly for EC flux observations from our group and others (Ikawa and Oechel, 2015; Kim et al., 2014; Porter et al., 2018). The Ox-CIMS was housed in a temperature-controlled trailer at the end of the pier. The Ox-CIMS sampled from a 20 m long PFA inlet manifold with the intake point co-located with a Gil-Sonic HS-50 sonic anemometer which recorded 3-dimensional winds sampling at 10 Hz. The Ox-CIMS inlet and sonic anemometer were mounted on a 6.1 m long boom that extended beyond the end of the pier to minimize flow distortions. The inlet height was 13 m above the mean lower low tide level. The Ox-CIMS inlet was located 8 cm below the sonic anemometer with a 0 cm horizontal displacement. The inlet manifold consisted of a 0.64 cm i.d. sampling line, a 0.64 cm i.d. overflow line, and a 0.47 cm i.d.
calibration line all made of PFA. The inlet sample line was pumped at 18-23 slpm (Reynolds number 3860-4940) by a dry scroll pump (SH-110, Agilent) to ensure a fast time response and maintain turbulent flow. Flow rates in the inlet sample line were recorded by a mass flow meter but were not actively controlled. The inlet manifold, including calibration and overflow lines, was held at 40 °C via a single resistively coupled circuit along the length of the manifold and controlled by a PID controller (Omega, model CNi 16). The Ox-CIMS front block and IMR were held at 35 °C. The Ox-CIMS subsampled 1.5 slpm from this inlet manifold through a critical orifice into the IMR. Ambient humidity and temperature were also recorded in-line downstream of the subsampling point.

3.2.1 Calibration

Instrument sensitivity was assessed by the standard addition of a C–13 isotopically labelled formic acid standard for 3 minutes every 35 minutes at the ambient end of the inlet manifold. Ozone mixing ratios were determined by scaling the humidity dependent sensitivity of \( \text{O}_3 \) from pre- and post-campaign calibrations to the field calibrations of C–13 formic acid. Ambient \( \text{O}_3 \) was also measured at 10 s time-resolution with a 2B technologies Personal Ozone Monitor (POM). The POM had a separate 10 m long, 0.47 cm i.d. PFA sampling line located 12 m from the Ox-CIMS inlet manifold and sonic anemometer. The POM was used as an independent verification of the Ox-CIMS measurement and was not used for calibration.

3.2.2 Backgrounds and inlet residence time

Background concentrations of \( \text{O}_3 \) and \( \text{NO}_2 \) from before and after each 30-minute ambient sampling period were interpolated over the ambient sampling period which was then subtracted from each 10 Hz concentration data point to obtain a background corrected time-series. Background concentrations of \( \text{O}_3 \) had a mean 1.5 ppbv and a drift of 1% between adjacent background periods, determined by the distribution of the NAD of the mean background concentrations.

The signal response of \( \text{O}_3 \) during dry \( \text{N}_2 \) overflows were fit to a bi-exponential decay function to characterize inlet gas response times evacuation time (\( \tau_1 \)) and wall interaction times (\( \tau_2 \)) (Ellis et al., 2010). Best fit estimates for decay time constants \( \tau_1 \) for \( \text{O}_3 \) and \( \text{NO}_2 \) across overflow periods were from 0.27 to 0.441.2 seconds and accounted for more than 80% of the decay. For \( \text{O}_3 \), \( \tau_2 \) was found to be negligible at less than 0.3 s indicating \( \text{O}_3 \) has minimal equilibration with the inlet walls. \( \text{NO}_2 \) decay responses were fit to a bi-exponential decay to characterize inlet evacuation time (\( \tau_1 \)) and wall interaction times (\( \tau_2 \)) (Ellis et al., 2010). \( \tau_2 \) for \( \text{NO}_2 \) was determined to be approximately longer at 3.2 s. This suggests a potential interference at the \( \text{NO}_2 \) peak, as \( \text{NO}_2 \) is expected to have minimal wall equilibration, similar to \( \text{O}_3 \). \( \text{NO}_2 \) also shows a continually elevated signal during overflow periods suggesting off gassing from inlet or instrument surfaces. The cause of this slow \( \text{NO}_2 \) decay and elevated background is not clear but could be from degradation of nitric acid or nitrate containing aerosol on the instrument surfaces.
The instrument response time ($\tau_r$) for O$_3$ can be calculated during zeroing periods as the time required for the signal to fall to $1/e$ of its initial value. The response time of the instrument was calculated for each overflow period during field sampling, with a mean value of 0.289 s. The cutoff frequency ($f_{cut}$) of the instrument is defined as the frequency where the signal is attenuated by a factor of $1/\sqrt{2}$ (Bariteau et al., 2010). The cutoff frequency can also be calculated from $\tau_r$ according to Eq. 3.

$$f_{cut} = \frac{1}{2\pi \tau_r}$$  

E3

The calculated $f_{cut}$ from the measured mean response time was 0.5718 Hz. This value suggests that minimal attenuation in the flux signal (cospectra) should be apparent at frequencies less than 0.5718 Hz. The instrument response time and thus cutoff frequency are function of the flow rate and sampling line volume. The flow rate of 18-23 slpm was the maximum achievable with the tubing and pumping configuration used here but could be improved in future to minimize tubing interactions and shift $f_{cut}$ towards higher frequencies.

### 3.2.3 Eddy covariance flux method

The transfer of trace gases across the air–sea interface is a complex function of both atmospheric and oceanic processes, where gas exchange is controlled by turbulence in the atmospheric and water boundary layers, molecular diffusion in the interfacial regions surrounding the air–water interface, and the solubility and chemical reactivity of the gas in the molecular sublayer. The flux ($F$) of trace gas across the interface is described by Eq. 4, as a function of both the gas-phase ($C_g$) and liquid phase ($C_l$) concentrations and the dimensionless gas over liquid Henry’s law constant ($HK_{liq}$), where $K_t$, the total transfer velocity for the gas (with units cm s$^{-1}$), encompasses all of the chemical and physical processes that govern air–sea gas exchange. Surface chemical reactivity terms to the gas exchange rate are incorporated into the $K_t$ term.

$$F = -K_t \left( C_g - HK_{liq} C_l \right)$$  

E4

Trace gas flux ($F$) can be measured with the well-established eddy covariance (EC) technique where flux is defined as the time average of the instantaneous covariances from the mean of vertical wind ($w$) and the scalar magnitude (here O$_3$) shown in Eq. 5. Overbars are means and primes are the instantaneous variance from the mean. Here $N$ is the total number of 10 Hz data points during the 27-minute flux averaging period.

$$F = \frac{1}{N} \sum_{i=1}^{N} \left( w_i - \bar{w} \right) \left( O_{3,i} - \bar{O}_3 \right) = \langle w' O_3' \rangle$$  

E5

$$v_d = \frac{F}{\bar{C}_g}$$  

E6

For purely depositing species where the water side concentration is negligible, $C_l$ and $HK_{liq}$ can be neglected in Eq. 4 and $K_t$ can be reformulated into a deposition velocity ($v_d$) calculated according to Eq. 6, where $\bar{C}_g$ is the mean gas phase mixing ratio during the flux averaging period. A summary of concentration and flux results for the full deployment period are given in Table 2.
3.3 General Data Corrections

Several standard eddy covariance data filters and quality control checks were applied before analysis. General filters included:

1.) **Wind sector**: Only periods of mean onshore flow (true wind direction 200-360°) were used.

2.) **Friction velocity**: A friction velocity ($U_*$) threshold of 0.1 m s$^{-1}$ was applied to reject periods of low shear driven turbulence (Barr et al., 2013) described further below.

3.) **Stationarity**: Each 27-minute flux period was divided into five even non-overlapping subperiods. Flux periods were rejected if any of the subperiods differed by more than 40% (Foken and Wichura, 1996). The applied selected $U_*$ threshold filter was determined by comparing the observed $U_*$ values to $U_*$ calculated with the NOAA COARE bulk flux v 3.6 algorithm (Fairall et al., 2011). COARE $U_*$ were calculated using measured meteorology including wind speed, sea-surface temperature, air temperature, and relative humidity. Flux periods were rejected if the observed $U_*$ differed from the calculated $U_*$ by more than 50%. The stress relationship of wind-speed to $U_*$ is well understood over the ocean. Fixed $U_*$ filters of ca. 0.1 m s$^{-1}$ is lower than the 0.2 m s$^{-1}$ are used frequently as a default in terrestrial flux studies but would reject nearly all observation periods in this study but is The observed friction velocities are consistent with other marine flux studies where surface roughness lengths are significantly smaller than over terrestrial surfaces (Porter et al., 2018). Methods of determining site specific $U_*$ thresholds typically require long-term data series which were not available here (Papale et al., 2006). Papale et al., (2006), applied a minimum $U_*$ threshold of 0.1 m s$^{-1}$ for forest sites and 0.01 m s$^{-1}$ for short vegetation sites where typical $U_*$ values are lower. A default $U_*$ of 0.2 m s$^{-1}$ which is a common value selected for terrestrial environments would reject over 80% of flux periods from our data set. The selected $U_*$ filter rejects an additional 46% of the flux periods remaining after the wind direction filter, ed flux periods being rejected. The stationarity criteria rejected a further 100 flux periods, potentially driven by periods of activity on the pier driving changes in the sampled O$_3$. 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. This outlier filter removed an additional 164 data points. After the wind direction filter and all quality control filters were applied, 7384% of flux periods were rejected leaving 457-246 quality-controlled flux periods. Eddy covariance flux values were calculated using 27-minute time windows. The O$_3$ timeseries was detrended with a linear function prior to the flux calculation. The O$_3$ and vertical wind data were despiked using a mean absolute deviation filter before the eddy covariance flux calculation following Mauder et al., (2013).

3.3.1 Planar Fit Wind Coordinate Rotation

Coordinate rotation of the $u$, $v$, and $w$ wind components was performed by the planar fit method to remove unintentional tilts in the sonic mounting and account for local flow distortions (Wilczak et al., 2001). Briefly, the mean $u$, $v$, and $w$ wind components and the stress tensor were determined for each 15-minute onshore flow period during the full campaign. A linear
regression was used to find the best fit of a plane with a coordinate system where the z-axis is perpendicular to the mean streamline. Individual 27-minute flux periods are then rotated such that the x-axis is along the mean wind and \( \vec{v} = 0 \). Vertical wind velocity (\( \vec{w} \)) in any individual rotation period may be non-zero due to mesoscale motions but \( \vec{w} \) for the full campaign is zero. The residual mean vertical velocity in any individual rotation period is subtracted out, so it does not impact the Reynolds averaging.

### 3.3.2 Lag time shift

The Ox-CIMS signal is delayed relative to the sonic anemometer due to transit time in the inlet line which must be accounted for before calculating the covariance between the vertical wind and analyte concentration. The cross-covariance of the two timeseries were first calculated within a ± 5 s window to determine the lag time of the Ox-CIMS and synchronize with the anemometer. The volumetric evacuation time of the inlet is 1.65 to 2.1 s for the inlet volume and flow rates of 18 to 23 slpm used in this study. Following the method and terminology outlined in Langford et al., (2015), the position of the maximum (MAX) of the cross-covariance is taken as the lag time needed to align the vertical wind and analyte concentration for that flux period. A representative lag time determination with a larger lag window (± 10 s) using the MAX method is shown in Fig. 10. In low signal-to-noise (SNR) data, the use of the MAX leads to high variability in the determined lag time caused by uncertainty in the position of the peak in the cross-covariance. This results in a systematic high bias on the absolute magnitude of the resulting flux. The position of the maximum of a centered running median (AVG) function of the cross-covariance is an alternative method to determine lag time with less expected bias for low SNR data (Langford et al., 2015; Taipale et al., 2010). Lag times for each \( \text{O}_3 \) flux period determined by the MAX and a 10 point AVG method showed reasonable agreement, with a campaign average lag time from the MAX with a mean of 1.0 seconds and the AVG at 0.7 seconds (Fig. S9). This agreement suggests that a clear peak in the cross-covariance was present for most flux periods leading to a convergence of the two methods. This lag time also shows agreement with the inlet response time of 0.9 s determined during dry \( \text{N}_2 \) overflows. Due to the convergence of the determined lag times around a central value, a prescribed lag time of 0.9 s was used for all reported \( v_d(\text{O}_3) \) values. A prescribed lag time has the least bias to extreme values caused by noise, provided that the true lag time is known well (Langford et al., 2015). Deposition velocities were then recalculated with the prescribed lag time of 0.9 s and with the MAX and AVG method over a narrower lag window of ± 3 which is expected to be physically reasonable range for the flow rate and inlet line volume. The mean \( v_d(\text{O}_3) \) using the prescribed, MAX, and AVG lag times were 0.01 \( \text{cm s}^{-1} \), 0.01 \( \text{cm s}^{-1} \), and 0.01 \( \text{cm s}^{-1} \) respectively, suggesting the campaign mean value was relatively insensitive to the lag time method.

### 3.4 Cospectra and Ogives

The frequency weighted cospectrum of \( \text{O}_3' \) with \( w' \) has a well characterized form with exhibited dependence on wind-speed and measuring height (Kaimal et al., 1972). Comparison of observed cospectra shape against the idealized Kaimal cospectra is useful to validate that the observed signal was not significantly attenuated at low or high frequencies. Cospectral averaging is performed by binning frequency into 50 evenly log spaced bins and normalizing the integrated cospectra to 1. The integral
of the unnormalized cospectra is the flux for that observation period. The mean wind-speed binned cospectra of sensible heat and O$_3$ appear to match well with the idealized Kaimal cospectra for an unstable boundary layer at sampling height $z = 13$ m (Fig. 11).

The ogive is the normalized cumulative distribution of the cospectra, which is used to validate both that no high-frequency attenuation is present and that the flux averaging time is sufficiently long that all frequencies contributing for the flux is captured. Figure 11 shows the averaged cospectra and ogives for O$_3$ and sensible heat flux from the average of two flux averaging periods 14:10 – 15:20 on July 20th. The asymptote to 1 at low frequencies validates that the 27-minute flux averaging time was sufficiently long for this site to capture the largest flux carrying eddies. High pumping rates in sampling line ensured that turbulent flow was always maintained in the line (Reynolds number 3860-4940). Higher Reynolds numbers in the turbulent regime lead to smaller high frequency attenuation (Massman, 1991). The overlap of the idealized Kaimal curve and the observed sensible heat and O$_3$ ogives suggest that high frequency attenuation in the sampling line is minimal above approximately 0.42 Hz, consistent with our calculated $f_{cut}$ of $0.5718$ Hz. Due to the small magnitude of the O$_3$ EC flux there is low signal to noise in the cospectra at high frequency for many of the flux averaging periods. This makes application of cospectra based correction factors challenging and likely to introduce added variance on the signal. We calculate the high frequency correction transfer function for turbulent attenuation in a tube from Massman, (1991) as a constraint, which is shown in Fig. 11b. This transfer function shows attenuation primarily above 1 Hz and is not sufficient to describe the observed attenuation above 0.24 Hz. This implies that the attenuation observed cannot be explained only as turbulent smearing in the inlet and that other wall interactions are likely present.

Due to the small magnitude of the O$_3$ EC flux there is low signal to noise in the cospectra at high frequency for many of the flux averaging periods. This makes application of cospectra based correction factors challenging and likely to introduce added variance on the signal. We therefore apply an attenuation correction factor following (Bariteau et al., 2010). First we calculate the idealized unattenuated Kaimal cospectra ($C_{wx,k}$) (Eq. 7) for each flux period, and then apply frequency attenuation to that cospectra by applying a low-pass filter function ($H(f)$) characterized by $\tau_c$ (Eq. 8). The ratio of the flux of the unattenuated ($F_{raw}$) and attenuated ($F_{att}$) cospectra is then taken as the correction factor ($A_f$, Eq. 9) to apply to the observed O$_3$ flux (Eq. 10).

Where $n$ is the surface layer normalized frequency defined as $n = f z/U$, where $z$ is the measurement height and $U$ is the horizontal wind speed. $F_{O_3,corr}$ is the attenuation corrected O$_3$ flux and $F_{O_3,obs}$ is the original measured flux. This approach has the benefit of applying a single correction factor to the total flux, rather than frequency dependent corrections which might serve to amplify noise at high frequencies. The net impact of this correction factor was an increase of campaign mean $v_d(O_3)$ of 4%.

$$C_{wx,k} = \frac{11n}{(1+11.3n)^{7/4}}$$

(E7)

$$H(f) = \left[1 + (2\pi f \tau_c)^2\right]^{-1}$$

(E8)
\[ A_f = \frac{F_{\text{raw}}}{F_{\text{att}}} \frac{\int_0^{\frac{m}{n}} c_{w_{xy}}(f) \, df}{\int_0^{\frac{m}{n}} c_{w_{xy}}(f) \, |H(f)|^{1/2} \, df} \]  
\[ F_{O_3, \text{corr}} = A_f F_{O_3, \text{obs}} \]

We also calculate the attenuated flux from the model of Horst, (1997) shown in Eq. 211, for a response time \((\tau_c)\) of 0.9–0.28 s, and a wind speed of 3 m s\(^{-1}\) to be 643%. The general agreement of the Horst and Bariteau attenuation correction factors indicate that the applied correction is reasonable.

\[ F_m / F_x = \frac{1}{1 + (2\pi n_m \tau_c U/\alpha)^\alpha} \]

Where \(F_m / F_x\) is the ratio of the measured flux to the unattenuated flux, \(U\) is wind speed, \(z\) is measurement height, and \(n_m\) and \(\alpha\) are scaling factors for an unstable boundary layer taken as 0.085 and 7/8 respectively. This flux attenuation of 13% is in reasonable agreement with the attenuation visible in the ogives shown. Given the uncertainty in the cospectra at high frequencies it is difficult to make a quantitative statement as to whether the observed attenuation is consistent throughout the measurement period. We therefore elect to report the uncorrected flux value here while acknowledging they are potentially a lower estimate with reasonable correction factors on the order of 15%.

3.5 Uncertainty and flux limit of detection

Variance in the atmospheric \(O_3\) signal was estimated by calculating the autocovariance of the signal during a 27-minute flux averaging period (Fig. S11). Uncorrelated white noise only contributes to the first point in the autocovariance spectrum, while autocovariance at longer time shifts represents real atmospheric variance or correlated instrument drift (Blomquist et al., 2010; Langford et al., 2015). For the analysed period, white noise is typically 45 to 65% of the total variance and atmospheric variance is 35 to 55%. This corresponds to a standard deviation from white noise \(\sigma_{O_3, \text{noise}}\) of 0.4 ppbv.

The error in each flux averaging period (LOD\(\sigma\)) can be determined by taking the standard deviation of the cross-covariance between vertical wind speed and mass spectrometer signal at lag times significantly longer than the calculated true lag time (Spirig et al., 2005; Wienhold et al., 1995). The random flux error is determined using lag windows of -150 to -180 and 150 to 180 s, which are significantly larger than the true lag time from sensor separation of 0.9 s as shown in Figure S12. The selection of the -150 to -180 and 150 to 180 s lag windows is somewhat arbitrary and may still capture organized atmospheric structure that persists over long time periods. We also calculate the root mean squared deviation (LOD\(\text{RMSE}\)) of the cross-covariance over the same lag windows as proposed by Langford et al., (2015), which captures the variance in the cross-covariance in those regions but also accounts for long term offsets from zero in the cross-covariance. The resulting error from the LOD\(\sigma\) and LOD\(\text{RMSE}\) methods showed good correlation (Fig S13), with periods where the LOD\(\text{RMSE}\) error is larger. We apply the RMSE method for our reported flux error determination. The final deposition velocity limit of detection was determined for each 27-minute flux averaging period by multiplying the LOD\(\text{RMSE}\) error by 1.96 to give the flux limit-of-
detection at the 95% confidence level. The flux error was then divided by the mean \( O_3 \) concentration for that averaging period to convert from flux to deposition velocity units. The campaign ensemble flux LOD_{RMSE} was 0.002742 cm s\(^{-1}\), calculated using Eq. 128 following Langford et al.,(2015). A total of 5962 out of 246452 (2439\%) flux periods had deposition velocities below the campaign ensemble LOD. These values are still included in the reported mean \( v_d(O_3) \).

\[
\text{LOD} = \frac{1}{N} \sum_{i=1}^{N} \text{LOD}^2
\]

3.6 Density fluctuation corrections

The Ox-CIMS measures \( O_3 \) as the apparent mixing ratio relative to moist air, as is true of all CIMS based measurements, which means fluctuations in the density of air due to changes in temperature, pressure, and humidity could introduce a bias in the EC flux measurement (Webb et al., 1980). The temperature and pressure in the Ox-CIMS and sampling lines were both actively controlled during sampling, making density fluctuations from those sources negligible. The long (20 m) inlet sampling line used likely also dampened a substantial portion of the water vapor flux. This has been demonstrated in an EC study utilizing a closed path H\(_2\)O sensor for EC flux measurements (through an 18 m long, 0.635 cm i.d. inlet, pumped at 18 slpm, comparable to the inlet used in this study) which showed complete attenuation above 0.1 Hz and overall attenuation of ~80% of the H\(_2\)O (latent heat) flux (Yang et al., 2016). However, without a direct measure of water vapor fluctuations collocated with the Ox-CIMS this is difficult to assess directly definitively rule out in our measurement. We therefore calculate a conservative estimate of this correction factor from Eq 45b. in Webb et al., (1980), assuming a latent heat flux of 50 W m\(^{-2}\) and neglecting the sensible heat term which is removed by active heating of the inlet. For a specific humidity of 12 g kg\(^{-1}\), a temperature of 293 K, a pressure of 1 atm, and an \( O_3 \) mixing ratio of 40 ppbv, we calculate a flux correction term of 2.6 x 10\(^9\) molecules cm\(^{-2}\) s\(^{-1}\), which is 2024\% of our mean measured flux of -1.34 x 10\(^{10}\) molecules cm\(^{-2}\) s\(^{-1}\). We expect that the actual density correction for our instrument much smaller given that water vapor fluctuations were likely dampened in the inlet line, and the high latent heat flux used in the calculation (50 W m\(^{-2}\)). Due to the uncertainty in this correction term for our instrument, we do not add it to our measured flux values and instead use the calculated value above as a conservative constraint on the magnitude. The addition of a Nafion drier on the inlet has been successfully implemented in other \( O_3 \) flux instruments to fully remove water fluctuations and will be used in future deployments of the Ox-CIMS (Bariteau et al., 2010).

3.7 Flux divergence

3.7.1 Surface NO emissions

The observed dry deposition velocity of ozone is potentially biased by simultaneous air-sea exchange of nitric oxide (NO). NO is expected to be emitted from the ocean on the order of 1 x 10\(^8\) molecules cm\(^{-2}\) s\(^{-1}\) with dependence on dissolved surface nitrate and solar irradiance (Zafiriou and McFarland, 1981). This NO source near the surface will cause titration of \( O_3 \) to NO\(_2\) resulting in a positive bias for the observed \( v_d(O_3) \). Assuming a maximum NO emission flux of 5 x 10\(^8\) molecules cm\(^{-2}\) s\(^{-1}\) and
that all NO reacts with O₃ before being advected to the sensor height, the resulting O₃ flux bias would be \(-5 \times 10^8\) molecules \(\text{cm}^{-2} \text{s}^{-1}\). Our mean case of 40 ppbv O₃ and \(v_d\) (O₃) of 0.0134 cm s\(^{-1}\) corresponds to a flux of \(-1.31 \times 10^{10}\) molecules \(\text{cm}^{-2} \text{s}^{-1}\). Therefore, the resulting bias in observed \(v_d\) (O₃) from NO emissions is 34.85% or \(4.94 \times 10^4\) cm s\(^{-1}\). This value is an upper limit for expected ocean NO emissions and is well within the uncertainty of the observed \(v_d\) (O₃). There is also potential for short term anthropogenic emissions of NO (such as from a boat engine passing by the sensor) to create a flux divergence term. We expect that the combination of signal despiking and the flux stationarity criteria described in Section 3.3 will minimize the impact of this potential divergence term. Despiking will remove most short term (<1 s) emission events and the stationarity criteria will filter out any period where longer term titration events cause large changes in the observed flux within a flux measurement period.

3.7.2 Free troposphere entrainment

The entrainment of O₃ enhanced or depleted air in the free troposphere to the marine boundary layer (MBL) creates a potential flux gradient that will contribute to the measured flux values at the near surface measurement height \((z_o)\) of 13 m. (Lenschow et al., 1982) presented aircraft observations of O₃ deposition over the Gulf of Mexico at heights of 15, 60, and 325 m which showed a strong flux gradient term driven by entrainment from the free troposphere. The boundary layer height \((z_i)\) during those flights was approximately 1.2 km, suggests a strong flux gradient was present even within the surface layer (approximated as the lowest 10% of the boundary layer). The magnitude of this flux gradient depends on the magnitude of the O₃ concentration gradient \((\Delta C)\) and the entrainment velocity \(w_e\) of air from free troposphere into the MBL. Faloona et al., (2005), reported entrainment velocities from 0.12 to 0.72 cm s\(^{-1}\) and an enhancement in O₃ \((\Delta C)\) of 20 ppbv in the free troposphere relative to the boundary layer in the summertime eastern subtropical pacific. Using those values and Equations 9 and 10 below we calculate the percent fractional error from entrainment on the observed flux for a range of reasonable \(\Delta C\) and \(w_e\) as shown in Fig. 12 (Blomquist et al., 2010).

\[
\frac{\Delta F_{\text{est}}}{F_0} = \frac{z_i}{z_i} \left( \frac{F_i}{F_0} - 1 \right)
\]

\[
F_i = w_e \Delta C
\]

Where \(z_i\) is the boundary layer height, \(z_o\) is the measurement height, and \(F_i\) and \(F_0\) are the entrainment flux and surface flux respectively. We use the SIO measurement height \((z_o)\) = 13 m and mean surface flux \((F_0)\) = \(-5.24 x 10^3\) ppbv m s\(^{-1}\) (from \(v_d\) = 0.0134 cm s\(^{-1}\) and [O₃] = 40 ppbv ), and an O₃ mixing ratio gradient \((\Delta C)\) from -20 to +20 ppbv in the free troposphere relative to the boundary layer. The resulting fractional error in our observed mean surface flux from Scripps Pier using the values from Faloona et al, 2005 \((\Delta C)\) of +20 ppbv, MBL height of 800m) is \(4.46\%\) for \(w_e\) of 0.12 and \(3344\%\) for 0.72 cm s\(^{-1}\). This entrainment flux error is clearly significant for marine O₃ flux measurements assuming there is a gradient of O₃ in the free troposphere relative to boundary layer. This entrainment flux error is independent of the surface flux instrument measurement error and adds a systematic bias on the surface flux measurement. This calculation also makes clear that marine O₃ measurements should be made as close to the surface as possible, and that the O₃ concentration gradient and entrainment...
rate should be explicitly measured if possible. We do not have an explicit measure of \( \Delta C \), \( w_* \), or the MBL height so we tentatively assign entrainment error of up to 3344\% from the maximum values of those parameters reported in Faloona et al. (2005). We emphasize this source of uncertainty is independent of the \( O_3 \) sensor and is a systematic bias that should be considered in all \( O_3 \) air-sea exchange determinations.

4 Fast NO\(_2\) measurements, eddy covariance and \( O_3 \) titration

Discussion of EC flux results have been limited to \( O_3 \) because ocean—atmosphere exchange of NO\(_2\) is expected to be small and below the limit of detection of our instrument. The potential flux divergence from the reaction of \( O_3 \) with NO is also below the instrument flux limit of detection as discussed in section 3.6. However, over terrestrial surfaces where NO\(_2\) emissions can be large, we expect this instrument would be well suited for measuring NO\(_2\) flux. Following Equations 15 and 16, we calculate the expected flux LOD for the case where counting noise is the controlling term in the flux error. The calculated flux LOD is of 4.3 × 10\(^9\) molecules cm\(^2\) s\(^{-1}\) (1.6 pptv m s\(^{-1}\)) for an NO\(_2\) mixing ratio of 1 ppbv and a friction velocity of 0.2 m s\(^{-1}\).

\[
F = C_a \sqrt{\frac{0.06 u_*^2}{C_a E}} \tag{E15}
\]
\[
\Gamma = \frac{a z}{U} \tag{E16}
\]

Where \( u_* \) is the friction velocity (m s\(^{-1}\)), \( C_a \) is the gas phase concentration (ppbv), \( E \) is the instrument sensitivity (cps ppbv\(^{-1}\)), and \( \Gamma \) is the integral time scale (s). \( \Gamma \) can be further expressed following Eq. 12 where \( a \) is constant taken as 0.3 for neutral conditions (Lenschow and Kristensen, 1985), \( z \) is the measurement height (here 10 m), and \( U \) is the horizontal wind speed at that measurement height (taken as 5 m s\(^{-1}\)).

Observations of a short duration NO plume from a boat motor starting near our inlet at Scripps Pier highlights the utility of the simultaneous \( O_3 \) and NO\(_2\) detection from this instrument (Fig. 13). Highly localized NO emissions were observed as the titration of \( O_3 \) and prompt production of NO\(_2\). Observed total odd oxygen (\( O_x = O_3 + NO_2 \)) was conserved during this titration event, where NO\(_2\) and \( O_3 \) concentrations were determined from independent calibration factors and backgrounds. The 1:1 conversion of \( O_x \) from \( O_3 \) to NO\(_2\) shown in Fig. 13b, validates the laboratory generated instrument calibration factors for \( O_3 \) and NO\(_2\). The temporal agreement of the \( O_3 \) and NO\(_2\) signals also demonstrates that both \( O_3 \) and NO\(_2\) are transmitted through the inlet and detected with nearly identical instrument response times. This analysis assumes that there were no direct NO\(_2\) emissions during the titration event. A NO\(_2\) to NO\(_x\) emission ratio of 0.08 was observed for ship emissions from diesel motors on inland shipping vessels (Kurtenbach et al., 2016). Without additional knowledge amount the NO\(_x\) emission source during this event, the observed conservation of total \( O_x \) could be partially driven by compensating errors within 10\%. This simultaneous detection of both \( O_x \) species is likely also well suited for mobile sampling in the presence of dynamic NO
emission sources, which challenge other fast ozone measurements. This method would also be well suited for direct measurement of flux divergence in the presence of strong surface NO emission sources.

5 Conclusions and Outlook

This study demonstrated the utility of oxygen anion chemical ionization mass spectrometry for the fast and sensitive detection of O3 and NO2. Field measurements of O3 dry deposition to the ocean surface from Scripps Pier, La Jolla CA demonstrate that this method has suitable time response, precision, and stability for successful EC measurements. The mean measured $v_d(O_3)$ with the Ox-CIMS is in range of good agreement with prior studies of O3 ocean-atmosphere exchange. Further optimization and characterization of the Ox-CIMS is ongoing, including efforts to validate the specificity of the NO2 detection, addition of a Nafion drier system, and better background determination methods. While this work has focused primarily on the deposition of O3 to the ocean surface, the demonstrated instrument performance suggests the Ox-CIMS to be highly capable of O3 and NO2 flux measurements in the terrestrial biosphere and urban environments and from mobile platforms.

Author Contributions

GAN, MPV, and THB designed the lab and field experiments and GAN and MPV collected all data. GAN lead the data processing, interpretation and analysis with MPV contributing. GAN prepared the manuscript with contributions from all co-authors. THB supervised all work and contributed to data analysis, writing and editing of the manuscript.

Acknowledgments

This work was supported by National Science Foundation (NSF) Grant GEO AGS 1829667. The authors thank the staff at Scripps Pier, Scripps Institute of Oceanography and at the UW—Madison Department of Limnology for support in instrument deployments.

Glenn M. Wolfe is gratefully acknowledged for publicly providing a Matlab based “FluxToolbox” of analysis scripts, portions of which were altered for use in this analysis. Code is archived at https://github.com/AirChem

This research was performed using the computing resources and assistance of the UW-Madison Center for High Throughput Computing (CHTC) in the Department of Computer Sciences. The CHTC is supported by UW-Madison, the Advanced Computing Initiative, the Wisconsin Alumni Research Foundation, the Wisconsin Institutes for Discovery, and the National Science Foundation, and is an active member of the Open Science Grid, which is supported by the National Science Foundation and the U.S. Department of Energy's Office of Science.
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Table 1. Summary of instrument sensitivity, precision, and accuracy for detection of O$_3$ and NO$_2$ from laboratory calibrations. Sensitivity is reported at a specific humidity (SH) of 8 g kg$^{-1}$ which corresponds to 40% RH at 25 °C. All limits of detection (LOD) are for a $S/N = 3$. The optimum LOD is reported as the LOD at the optimum averaging time determined by the minimum of the Allan variance spectrum. Optimum averaging times were determined to be 11 s for O$_3$ and 19 s for NO$_2$. The reported field comparison ($R^2$) is from a regression of 1-minute bin averaged ozone concentration from the Ox-CIMS with an EPA (Thermo-Fisher 49i) monitor in Zion, Il during four weeks of ambient observation shown in Fig. 7.

| Species | Normalized Sensitivity (8 g kg$^{-1}$ SH, 1σ) | Absolute Sensitivity (8 g kg$^{-1}$ SH) | LOD optimum | LOD (1 Hz) | LOD (10 Hz) | Background (cps, 1σ) | Precision (10 Hz) | Field Calibration $R^2$ |
|---------|---------------------------------|---------------------------------|-------------|-----------|-----------|--------------------|-----------------|---------------------|
| O$_3$   | $12.4 \pm 1.2$ ncps pptv$^{-1}$ | 180 cps pptv$^{-1}$ | 4.0 pptv (11s) | 13 pptv | 42 pptv | $3.1 \times 10^5$ ± $5.0 \times 10^4$ | 0.74% | 0.99 |
| NO$_2$  | $6.7 \pm 1.0$ ncps pptv$^{-1}$ | 97 cps pptv$^{-1}$ | 2.3 pptv (19s) | 9.9 pptv | 32 pptv | $5.1 \times 10^4$ ± $1 \times 10^4$ | 1.1% | — — — |
Table 2. Overview of flux and concentration measurements of O$_3$ and NO$_2$ from Scripps Pier. Concentration ranges are reported for all periods of onshore winds. Flux results are reported only for final quality-controlled flux periods. Ozone mean deposition velocity ($v_d$) was well resolved from the campaign ensemble average LOD of 0.0042 cm s$^{-1}$. Reported $v_d$ LOD is the ensemble mean of the LOD determined by the RMSE method at long lag times for each 27-minute flux period. 39% of quality-controlled flux periods fell below the campaign ensemble LOD. Deposition velocity of NO$_2$ across the air-sea interface is expected to be small (<0.002 cm s$^{-1}$) and was consistently below the LOD of our instrument so no values are reported here.

| Species | Concentration Mean (ppb) & 1σ range | 5th to 95th percentile Concentration Range (ppbv) | $v_d$ mean (cm s$^{-1}$) | $v_d$ 20-80% range (cm s$^{-1}$) | $v_d$ LOD 1.96σ (cm s$^{-1}$) |
|---------|-------------------------------------|-----------------------------------------------|------------------------|---------------------------------|-------------------------------|
| O$_3$   | 38.9 ± 12.3                         | 16.9 – 56.9                                    | 0.011                  | -0.0048 – 0.0249                | 0.0042                        |
| NO$_2$  | 4.7 ± 5.5                           | 0.45-16.9                                      |           |                                |                               |
|         |                                     |                                               |           |                                |                               |
| Species | Concentration Mean (ppb) & 1σ range | 5th to 95th percentile Concentration Range (ppbv) | $v_d$ mean (cm s$^{-1}$) | $v_d$ 20-80% range (cm s$^{-1}$) | $v_d$ LOD 1.96σ (cm s$^{-1}$) |
|---------|-------------------------------------|-----------------------------------------------|------------------------|---------------------------------|-------------------------------|
| O$_3$   | 41.2± 10.1                          | 28.9 – 67.1                                    | 0.013                  | -0.0011 – 0.027                 | 0.0027                        |
| NO$_2$  | 4.7 ± 5.5                           | 0.45-16.9                                      |           |                                |                               |
Figure 1: Ox-CIMS mass spectra collected at 1 Hz and mass resolution of 950 $M/\Delta M$ (at $-60 \text{ m/Q}$), with major peaks highlighted. $O_2^-$ and $O_2(H_2O)^-$ at $-32 \text{ m/Q}$ and $-50 \text{ m/Q}$ respectively are the two observed forms of the reagent ion. The detected ozone product ($CO_3^-$, $-60 \text{ m/Q}$) is of comparable magnitude to the $O_2^-$ reagent ion during ambient sampling. NO$_2$ is detected as the charge transfer product at $-46 \text{ m/Q}$. Masses greater than $-150 \text{ m/Q}$ contribute less than 2% to the total signal and are not plotted.
Figure 2: Normalized calibration curves of O₃ (a) and NO₂ (right) at 8 g kg⁻¹ specific humidity (approximately 40% RH at 25 °C). Ozone is detected as CO₃⁻ at –60 m/Q. NO₂ is detected as the charge transfer product (NO₂⁻) at –46 m/Q. Error bars are the standard deviation in normalized count rate for each measurement point.
Figure 3: Dependence of $O_3$ and $NO_2$ sensitivities on specific humidity. Error bars indicate standard deviation of triplicate calibration curves. The blue shaded region from SH 8–16 g kg$^{-1}$ is the approximate typical range of specific humidity in the mid-latitude marine boundary layer.
Figure 4: Ox-CIMS cumulative sensitivity to O$_3$ detected either directly as O$_3^-$ or as CO$_3^-$ as a function of CO$_2$ mixing ratio. The sum of sensitivity as O$_3^-$ and CO$_3^-$ shows that total sensitivity to O$_3$ is conserved as the product distribution shifts with CO$_2$ mixing ratio. Greater than 99% of O$_3$ is observed as CO$_3^-$ at CO$_2$ mixing ratios greater than 60 ppmv.
Figure 5. Normalized count rate of CO$_3^-$ (~60 m/Q) ozone detection product as a function of pressure in the IMR during sampling of a constant 35 ppbv O$_3$ source. The exponential fit of the data is shown by the dashed line. Fit parameters are included to allow for calculation of potential sensitivity improvements with further increase in IMR pressure.
Figure 6: Representative instrument backgrounding determination for O$_3$ and NO$_2$ where the inlet was rapidly switched from ambient sampling to an overflow with dry UHP N$_2$ indicated by the grey dashed line. O$_3$ response is fit to a bi-exponential decay, plotted as solid lines with a mean response time of 0.28 s. NO$_2$ is fit to a bi-exponential decay where the initial rapid decay ($\tau_1$) is attributed to gas evacuation of the inlet line and the second slower decay ($\tau_2$) is attributed to equilibration with the inlet walls. Best fit estimates for $\tau_1$ of O$_3$ and NO$_2$ were from 0.7 to 1.2 seconds. $\tau_2$ for O$_3$ was negligible at 0.3 s indicating O$_3$ has minimal interactions with the walls. $\tau_2$ for NO$_2$ was determined to be 3.2 s for this decay period.
Figure 7: Distribution of normalized adjacent differences measured at 10 Hz during a stable 27-minute ambient sampling period of 38 ppbv O₃ from Scripps Pier. The 1σ value of the distribution gives an upper limit of instrument precision of 0.74%.
Figure 8: Regression of 1-minute average $O_3$ mixing ratios from the Ox-CIMS against an EPA $O_3$ monitor (Thermo-Fisher 49i) binned to 1 ppbv over four weeks of ambient sampling in Zion, Illinois in May-June 2017. The solid black line is the linear least-squares regression. Error bars represent the standard deviation of each bin. Instrument agreement is strong for $O_3$ greater than 10 ppbv, with an apparent bias in one or both instruments below 10 ppbv.
Figure 9: Observed meteorology and O$_3$ mixing ratio and deposition velocities for DOY 194-199 from Scripps Pier (a) Horizontal wind speed ($U_{10}$) and sea-surface temperature (SST). (b) O$_3$ mixing ratios and $v_d$(O$_3$).
Figure 10: Lag time determination for an individual 27-minute O$_3$ flux averaging period. The lag time for this flux period determined from the maximum of the covariance to be 0.9 seconds which compares reasonably with the volumetric evacuation time of the inlet of 1.7 to 2.1 seconds.
Figure 11. (a) Mean binned frequency weighted cospectra $O_3$ and sensible heat flux with vertical wind from the average of two consecutive flux periods from 14:10 – 15:20 local time on July 20th. The Kaimal trace is the idealized cospectra Kaimal et al. (1972) for mean windspeed of 4.4 m s$^{-1}$ and an unstable atmosphere. The sensible heat trace is inverted, and the observed net sensible heat flux was positive for this period (b) Corresponding ogives for cospectra shown in (a). The M91 Transfer trace is the calculated transfer function for turbulent attenuation in a tube from (Massman, 1991).
Figure 12. Calculated percent error in the measured O₃ surface flux due to entrainment from the free troposphere as a function of the MBL height and the entrainment flux ($F_e$). Entrainment flux is the product of the free troposphere to boundary layer concentration gradient ($ΔC$), and the entrainment velocity ($w_e$). Calculation of percent error used the Scripps Pier measuring height of 13 m, and mean surface flux of $-54.6 x 10^{-3}$ ppbv m s$^{-1}$. 

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Figure 13: Observations of ozone titration by NO emissions from a boat engine near the SIO pier. (a) 10 Hz timeseries of O₃, NO₂, and Oₓ (O₃ + NO₂) demonstrating ability to capture transient titration events. (b) Regression of O₃ and NO₂ plotted with a reference line of slope -1, showing conservation of total Oₓ at 10 Hz during a NO titration event.
Response to Reviewers

Comments for all Reviewers: We thank all reviewers for their time and thoughtful comments which have substantially improved the quality and clarity of our manuscript! Below we highlight three alterations to the manuscript, based on reviewer comments, which we believe are relevant for all reviewers. These changes have not necessitated changes to any of the conclusions of this work but have meaningfully improved the quality of our data treatment.

1) Based on very helpful comments from Reviewer 1, several portions of the eddy covariance data processing and quality control have been altered. In particular, we have devised a friction velocity filter based on agreement between our measured values and calculated values using the NOAA COARE v3.6 bulk flux algorithms, rather than a fixed friction velocity threshold. This has increased the number of valid quality controlled flux periods and improved our ensemble flux LOD. We have also applied a frequency attenuation correction to our flux values which resulted in a mean increase in \( v_{d(O_3)} \) of 4.5%. These changes necessitated updating all reported EC flux values in the text and in Table 2, and Figures 6, 9, 12, S9, and S12. The updated mean campaign \( v_{d(O_3)} \) is 0.013 (changed from 0.011 cm s\(^{-1}\) in the original manuscript) and the ensemble LOD is 0.0027 cm s\(^{-1}\) (changed from 0.0042 cm s\(^{-1}\)). The total number of valid quality-controlled flux observations is now 246 (changed from 151). Further details on each of these corrections are described in specific responses to Reviewer 1. We believe these changes, made directly following recommendations of the reviewer, have significantly enhanced the quality of our manuscript.

2) Also based on helpful comments from Reviewer 1 who noted that our determined response time of 0.9 s seemed longer than expected, we have revisited our determination of the instrument response throughout the campaign. It became apparent that infrequently the automated bi-exponential decay algorithm we applied over weighted the second exponential and gave poor fitting results. Instrument response times for \( O_3 \) have been recalculated using a single exponential decay fit which provides a better fit to the data. Calculated fits were manually verified for the full campaign. The updated response time is faster than the original reported value (0.28 s (0.25 to 0.31 s 95% confidence bounds), previously 0.9 s). Review of this response time calculation was also motivated by its direct use in the newly implemented frequency attenuation calculation described in comment number 1. This updated response time value was also used to calculate an updated value of the cutoff frequency (now 0.57 Hz, previously 0.18 Hz). This response time is more in keeping with expectations given that \( O_3 \) is a “non-sticky” gas and the high flow rates and low volumes in our instrument. The use of a single-exponential decay also follows the method of Bariteau et al. (2010) for the characterization of their fast-response chemiluminescence \( O_3 \) sensor. These values have been updated throughout the text. Additional discussion is provided in responses to Reviewer 1.

3) Based on private communications during the review process, we have included additional caveats in Section 5 regarding the conservation of total \( O_x \) observed during an \( O_3 \) titration from local NO emissions. In particular, it was noted that engine NO\(_x\) emissions cannot always be assumed to be exclusively as NO. Ship emissions have shown NO\(_x\) to NO2
emission ratios on the order of 10%. If some emissions are indeed in the form of NO$_2$, the reported conservation of total O$_x$ in section 5 would be partially spurious resulting from various compensating errors. We have added some discussion of this important point.

The manuscript has been revised to state in Section 4: “This analysis assumes that there were no direct NO$_2$ emissions during the titration event. A NO$_2$ to NO$_x$ emission ratio of 0.08 was observed for ship emissions from diesel motors on inland shipping vessels (Kurtenbach et al., 2016). Without additional knowledge amount the NO$_x$ emission source during this event, the observed conservation of total O$_x$ could be partially driven by compensating errors within 10%.”

Responses to individual reviewer comments follow. Reviewer comments are reproduced in italic black font. Author responses are shown in regular blue font. Text added to the manuscript is underlined and text removed from the manuscript has a strikethrough.
Response to Reviewer 1:

This paper describes the use of the oxygen anion chemical ionization mass spectrometer for simultaneous measurements of N2O and O3, 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.

We are very grateful to the reviewer for their thorough review and numerous suggestions which have improved the quality of our data treatment and our manuscript as a whole. Below we address specific reviewer comments.

Abstract: Counts /s/ppt instead of ions/s/ppt
All instances of ions s\(^{-1}\) pptv\(^{-1}\) have been changed to counts s\(^{-1}\) pptv\(^{-1}\) or cps pptv\(^{-1}\) (or ncps pptv\(^{-1}\), etc.) as appropriate in the abstract and throughout the text to maintain consistency. We had used these terms interchangeably which was not made clear.

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

This point is well taken and the text has been rearranged as suggested but the content is unchanged.

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.

We thank the reviewer for catching this arithmetic error. The increase in absolute numbers was from 4.37E5 to 6.97E5 ncps. This corresponds to a 60% increase, or a signal at 95 mbar that is ~160% of the signal at 70 mbar. This value has been corrected and the text slightly clarified.

So far we have focused on ground based deployments at fixed sampling sites for the Ox-CIMS and so have not made significant efforts to ensure highly accurate pressures. The standard deviation of IMR pressure during individual flux sampling periods were typically from 0.1-0.3 mbar which would have a negligible impact on our observations. Methods for accurate and constant pressure control for CIMS instruments have been developed for airborne studies (i.e Lee et al. (2014)) and should be directly translatable to this instrument. This type of pressure control would be a useful addition before any airborne or ship-based deployments of the Ox-CIMS.

The manuscript has been revised to state: The normalized signal of O\(_3\) increases by 175% 60% at an IMR pressure of 95 mbar compared to 70 mbar over the pressure range pf 70 to 95 mbar in the IMR when sampling a constant O\(_3\) source of 35 ppbv.
Line 245. Have the authors compared this N2 background vs. simply scrubbing the measured air (e.g. with activated charcoal)? The differences in H2O and CO2 between ambient air and scrubbed air are much smaller than those between ambient air and N2. This should make the background measurements easier to interpret.

The used of a scrubber will absolutely be explored before any future deployments. We also intend to explore the development of catalytic zero air generator to overflow the inlet which would maintain near ambient CO2 and H2O. In this initial deployment we had also aimed to measure a variety of other trace gases detectable with the Ox-CIMS not discussed in this manuscript. It was decided that the N2 background was the most versatile method for zeroing all species of interest even if it necessitated additional considerations for O3. Future deployments could implement a combination of scrubber-based zeros for O3 and N2 overflow zeros for other species to remove this issue.

Section 2.9. authors have shown that O3 normalized sensitivity is linear (up to 80 ppbv), despite the fact that CO3- signal and O2- signal being comparable in magnitude. They have also shown that NO2 normalized sensitivity doesn’t depend on O3 level. Does the O3 normalized sensitivity depend on the NO2 concentration?

We have not directly assessed the dependence of O3 normalized sensitivity on NO2 but this will be a valuable future laboratory experiment, especially if we intend to sample in an urban high NOx environment. We can note that the ambient normalized O3 signal was insensitive to the high concentration formic acid standard additions described in this deployment which we expect to behave similarly to NO2.

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.

We agree this section was confusing as written and have improve phrasing to clarify this discussion. The quoted sentence was primarily intended to show that from 1E6 to 1E7 cps instrument precision did not continue to improve with count rate. Instrument precision below 1E6 cps did improve with count rate as expected when precision is controlled by counting noise. The meaning of the observed precision at 1E6 and 1E7 cps being specifically 0.75 and 2% is not clear and is again only meant to highlight that precision is no longer improving with count rate as expected for counting noise. The equation for counting noise has been added which is $\sqrt{\frac{N}{N}}$ where N is the number of counts during the observation period.

The manuscript has been revised to state: “From this assessment, precision was observed to improve approximately linearly in a log-log scaling for count rates between 1 x 10^3 and 1 x 10^6 cps (Fig. S8) as expected in the case where counting noise drives instrument precision. Above 1
x 10^6 cps there is an apparent asymptote where precision no longer improves with count rate. For 10 Hz averaging and count rates of 1 x 10^6 and 1 x 10^7 cps, the corresponding instrument precision is 0.75 and 2% respectively, and appears independent of count rate. The counting noise limited 10 Hz precision for 10^6 and 10^7 cps is 0.32% and 0.1% respectively, while the measured values were 0.75 and 2%. The counting noise limited precision is calculated as \( \sqrt{\frac{N}{N}} \) where \( N \) is the number of counts during the integration time.”

Line 339. Without being familiar with these TOFMS or exploring the Vermeuel et al. reference, it’s unclear how this O3 calibration factor is applied. You could refer readers to section 3.2.1 here.

and

Section 3.1 suggest adding 1-2 sentences describing how the CIMS was deployed. Was it subsampling from a inlet manifold like on Scripps pier? Length of inlet? Instrument temperatures?

Based on discussion from Reviewers 1 and 2, significant details have been added back to this section rather than requiring the reader to refer to Vermeuel et al. (2019).

The manuscript has been revised to state: Section 3.1: “The Ox-CIMS was located on the roof of a trailer (approx. 5 m above ground) and sampled through a 0.7 m long, 0.925 cm i.d., PFA inlet. The inlet was pumped at flow rate of 18-20 slpm from which the Ox-CIMS subsampled at 1.5 slpm. Temperature and RH were recorded inline downstream of the subsampling point. The Ox-CIMS sampling point was approximately 10 m horizontally from the Thermo-Fisher 49i and sampled at approximately equal heights. Instrument backgrounds of the Ox-CIMS were determined every 70 minutes by overflowing the inlet with dry UHP N_2. Calibration factors for O_3 were determined by scaling the in-field continuous addition of a C-13 isotopically labelled formic acid standard to the tip of the inlet. Laboratory calibrations of the Ox-CIMS to formic acid and O_3 as a function of specific humidity were determined immediately pre- and post-campaign and were used to calculate a humidity dependent sensitivity of O_3 relative to formic acid. That relative sensitivity was then used to determine the in-field sensitivity to O_3 by scaling field sensitivities of formic acid from the continuous additions. Full details of this deployment and calibration methods are described in Vermeuel et al., (2019).”

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 O3 titration event due to NO the CIMS would initially see lower O3 than the EPA monitor at 1-minute resolution.

We agree that there remain open questions in this instrument comparison which are difficult to assess with the data available. While agreement between the two instruments is not perfect, we believe they show strong agreement for field sampling in a complex environment, especially as we are comparing to a monitoring grade instrument. The Thermo Fischer 49i (EPA O3 monitor) was not equipped with a Nafion drier and the manufacturer quoted response time for the instrument alone is 20 seconds. An additional unquantified response time of similar magnitude was likely present due to the instrument sampling from a long, wide diameter inlet at a low flow rate. Unfortunately, specific details of EPA O3 monitor inlet configuration were not recorded.
during this deployment, as it was not originally devised as an O\textsubscript{3} intercomparison study. Taken together, the EPA O\textsubscript{3} monitor was likely subject to interferences from water vapor and other species and had a slower response to titration events and changes in air masses. We also note that O\textsubscript{3} mixing ratios exceeding 80 ppbv were only sampled on three afternoons during the study, which were driven by highly polluted urban airmasses from Chicago, making robust comparison between the instruments at high mixing ratios a challenge. An instrument intercomparison study with a research grade O\textsubscript{3} instrument, such as an NO chemiluminescence sensor, rather than a monitoring grade instrument like the Thermo Fischer 49i will be valuable in further characterizing the Ox-CIMS.

**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. nlet line have any affect on O\textsubscript{3}/heterogenous chemistry within the inlet?

The inlet temperature of 40°C was primarily selected to ensure that the inlet line was always held above ambient temperatures to prevent any potential condensation of water vapor in the line and to ensure consistent sampling conditions. Additional impacts on heterogeneous chemistry or ion-adduct stability were not quantitatively assessed. We speculate that these effects would be minor due to being only slightly above ambient temperatures (ca 25°C).

**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 N2 overflow tube consisted of N2 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 N2 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 N2 puff multiple times in succession. 2. Alternatively, could the fairly low response time be due to the multi-stage chemistry?

Based on the reviewer’s comments we have revisited our determination of the instrument response throughout the campaign. It became apparent that the automated bi-exponential decay algorithm we applied frequently over weighted the second exponential and gave poor fitting results. Instrument response times for O\textsubscript{3} have been recalculated using a single exponential decay fit which provides a better fit to the data. Calculated fits were manually verified for the full campaign. The updated response time is faster than the original reported value (0.28 s (0.25 to 0.31 s 95% confidence bounds), previously 0.9 s). Review of this response time calculation was also motivated by its direct use in the newly implemented frequency attenuation calculation described in comment number 1. This updated response time value was also used to calculate an updated value of the cutoff frequency (now 0.57 Hz, previously 0.18 Hz). This response time is more in keeping with expectations given that O\textsubscript{3} is a “non-sticky” gas and the high flow rates and low volumes in our instrument. The use of a single-exponential decay also follows the method of Bariteau et al. (2010) for the characterization of their fast-response chemiluminescence O\textsubscript{3} sensor. These values have been updated throughout the text. See below for a plot of single-exponential decays fits determined throughout the full campaign shown as grey traces, and the binned mean decay curve shown in the red trace. The dashed horizontal line is at 1/e which corresponds to the response time.
Eq. 4. Suggest replace KH with just H, to avoid confusion with Kt. This terminology has been changed as suggested.

Line 427. 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.”

We appreciate this note and have updated the text as suggested.

Line 429. 84% flux rejection is clearly not ideal. Instead of applying a simple \(u^*\) threshold, 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 \(O_3\) flux values when the measured \(u^*\) or \(Cd\) is far from expected.

We are grateful to the reviewer for this suggestion which we have implemented as follows. We have calculated the expected \(U^*\) for each flux period using the NOAA COARE v3.6 bulk flux algorithms, using observed wind speeds, SST, air temperature, and humidity as inputs. Flux periods were rejected if the calculated \(U^*\) was within 50% of the observed value. This filter resulted in a total of \(N = 246\) valid flux points, mean \(v_d(O_3) = 0.013\) cm s\(^{-1}\) and ensemble LOD of 0.0027 cm s\(^{-1}\). We note that we are relatively insensitive to the specific threshold applied, selecting a threshold of 40% agreement yields \(N = 191\), \(v_d(O_3) = 0.0137\) cm s\(^{-1}\), and LOD = 0.0032 cm s\(^{-1}\). A threshold of 30% agreement yields \(N = 138\), \(v_d(O_3) = 0.0145\) cm s\(^{-1}\), and LOD = 0.0027 cm s\(^{-1}\). We have selected the threshold that minimizes the LOD while maintaining more valid flux points than the fixed \(U^*\) filter of 0.1 cm s\(^{-1}\). We would also like to point out that the 84% flux rejection included the wind direction filter which may not have been clear. Over 30% of flux points were immediately rejected based on winds not coming from the ocean. We also note that even in the case of the 30% agreement threshold the ensemble LOD was improved compared to our original fixed \(U^*\) threshold. This suggests that this relative threshold does a better job of filtering low quality flux periods.

The text has been updated substantially in Section 3.3 to account for these changes.
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 O3 and wind measurement, or the fact that the inlet pressure is much lower than 1 atm (such as the volumetric flow rate is _2x the mass flow rate).

The slight disagreement of these values was also notable to us. We believe the source of this is likely due to a timing error as suggested by the reviewer as the software saving the mass spectrometer and anemometer data signals were not optimized to have highly precise timing. The inlet pressure is also a likely contributing factor as suggested. A quick calculation of expected pressure drop in our inlet suggest that pressure at the Ox-CIMS subsampling point is ~150 mbar lower than ambient. As noted by the reviewer, this pressure drop will increase the volumetric at a given measured mass flow rate. Taken together we expect these factors to explain our observed lag time. We note that applying a fixed lag time corresponding to the volumetric residence time results in a calculated \( v_{\text{df}}(O_3) \) of 0.012 cm s\(^{-1}\) compared the our value of 0.013 cm s\(^{-1}\) using the fixed lag time.

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\(_2\) was injected into the inlet, the O3 signal should start to drop _1 s later, and reach 1/e of the initial value _1.9 s after \( t_0 \).

We agree that the total instrument response time should be the sum of the volumetric clearing time of the inlet and the instrument response time. In our case the determined lag time for eddy covariance also appears to be influenced by software timing consideration as noted above. In our determination of the instrument response time, we treated \( t_0 \) as the point immediately before the signal responded to the N\(_2\) overflow. This is done to separate out determinations of the inlet lag time and the instrument response time. This follows the method used by Bariteau et al (2010), which based on our determination on. Additionally, the position of the solenoid valve controlling the N\(_2\) overflow was only recorded at 1Hz which makes it difficult to resolve the lag time based on the when the solenoid was flipped. This is also why we were no able to determine the instrument lag time using the “puff method” described in Bariteau et al. Calculating the response time based on when the signal begins to respond rather when the solenoid flipped removes that imprecision.

Also, as noted in the comment we made above we have since revisited our determination of the instrument response time, with a new mean value of 0.28 s based on a single-exponential decay fit.

Line 495. One way to deal with estimation of high frequency flux loss without directly using the noisy O3 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 O3 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.
We thank the reviewer for the push to treat this attenuation correction properly. We have implemented a frequency correction following this suggestion. Briefly, we calculated the unattenuated Kaimal cospectra (assuming an unstable boundary layer) for each individual flux measurement period. We then applied the low pass filter function described by Bariteau et al. (2010) using a fixed response time of 0.28 s to determine the attenuated cospectra. The ratio of the attenuated to unattenuated cospectra was then taken and used as a correction factor. The net effect of this correction was an increase of \( \nu_d(O_3) \) of 4% (increased from 0.0127 to 0.0132 cm s\(^{-1}\)). The manuscript has been changed in many locations to account for this change.

The manuscript has been revised significantly in Section 3.4 to reflect these changes.

*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.*

We thank the reviewer for bringing this to our attention. We have added a short discussion and citation to the text.

The manuscript has been revised to state: Line 523: “This has been demonstrated in an EC study utilizing a closed path H\(_2\)O sensor for EC flux measurements (through an 18 m long, 0.635 cm i.d. inlet, pumped at 18 slpm, comparable to the inlet used in this study) which showed complete attenuation above 0.1 Hz and overall attenuation of \( \sim 80\% \) of the H\(_2\)O (latent heat) flux (Yang et al., 2016). However, without a direct measure of water vapor fluctuations collocated with the Ox-CIMS this is difficult to assess definitively rule out in our measurement.”

*Section 3.7.1 it might be worth mentioning that emission of NO from other sources (e.g. ships) could also bias the O\(_3\) flux measurement. Though the authors’ despiking of the O\(_3\) signal probably removed such short-term ship emission-related O\(_3\) titrations. We agree that this point should be stated explicitly. As stated by the reviewer we expect the combination of the despiking and stationarity criteria will do a suitable job of filtering out the very short and longer titration events respectively.*

The manuscript has been revised to state: Section 3.7.1: “There is also potential for short term anthropogenic emissions of NO (such as from a boat engine passing by the sensor) to create a flux divergence term. We expect that the combination of signal despiking and the flux stationarity criteria described in Section 3.3 will minimize the impact of this potential divergence term. Despiking will remove most short term (<1 s) emission events and the stationarity criteria will filter out any period where longer term titration events cause large changes in the observed flux within a flux measurement period.”

*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 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\(_2\)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.*
Our exploration of flux divergence was inspired by the aircraft observations of Lenschow et al. (1982) which showed a linear flux divergence with altitude for measurements at 15, 60, and 325 m over the ocean. The boundary layer height during those flights was ca. 1.2 km. The flux observations at the 15 and 60 m measurement heights showed strong divergence despite being in within the constant flux layer (based on the lowest 10% rule). Lenschow et al. (1982), argue that because the surface flux of O$_3$ is much smaller than the entrainment flux ($w_e = 0.8$ cm s$^{-1}$), it is acutely sensitive to boundary layer processes. Faloona et al. (2005) also showed a linear flux divergence in O$_3$ down to 100m with a boundary layer height of ~800 m. There it is unclear if the lowest level leg was within the constant flux layer but still suggests that entrainment driven flux divergence should be considered. We realize that not citing and discussing Lenschow et al. (1982) in this section was an oversite and have revised the text to include discussion of their observations.

We also made our calculations directly following the equations in Blomquist et al. (2010) who assessed impacts of entrainment on near surface ($z_i = 18$ m) observations of DMS flux. Blomquist et al. (2010) applied a linear extrapolation from the boundary layer height to the surface and did not invoke a constant flux layer. Based on these results we believe there is value in exploring this potential source of bias in our observations even if we do not have direct constraints on its magnitude.

The manuscript has been revised to add: “Lenschow et al., (1982) presented aircraft observations of O$_3$ deposition over the Gulf of Mexico at heights of 15, 60, and 325 m which showed a strong flux gradient term driven by entrainment from the free troposphere. The boundary layer height ($z_i$) during those flights was approximately 1.2 km, suggests a strong flux gradient was present even within the surface layer (approximated as the lowest 10% of the boundary layer).”

We also note the correction of a typo on line 571. $z_i$ is the boundary layer height and $z$ is the measurement height. These definitions were reversed in the text but were used correctly in Eq. 9 and all calculations following it.

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

This point is well taken, and the text has been updated using the reviewer’s phrasing.

References:

Bariteau, L., Helmig, D., Fairall, C. W., Hare, J. E., Hueber, J. and Lang, E. K.: Determination of oceanic ozone deposition by ship-borne eddy covariance flux measurements, Atmos. Meas. Tech., 3(2), 441–455, doi:10.5194/amt-3-441-2010, 2010.

Blomquist, B. W., Huebert, B. J., Fairall, C. W. and Faloona, I. C.: Determining the sea-air flux of dimethylsulfide by eddy correlation using mass spectrometry, Atmos. Meas. Tech., 3(1), 1–20, doi:10.5194/amt-3-1-2010, 2010.
Faloona, I., Lenschow, D. H., Campos, T., Stevens, B., van Zanten, M., Blomquist, B., Thornton, D., Bandy, A. and Gerber, H.: Observations of Entrainment in Eastern Pacific Marine Stratocumulus Using Three Conserved Scalars, J. Atmos. Sci., 62(9), 3268–3285, doi:10.1175/JAS3541.1, 2005.

Lee, B. H., Lopez-Hilfiker, F. D., Mohr, C., Kurtén, T., Worsnop, D. R. and Thornton, J. A.: An iodide-adduct high-resolution time-of-flight chemical-ionization mass spectrometer: Application to atmospheric inorganic and organic compounds, Environ. Sci. Technol., 48(11), 6309–6317, doi:10.1021/es500362a, 2014.

Lenschow, D. H., Pearson, R. and Stankov, B. B.: Estimating the ozone budget in the boundary layer by use of aircraft measurements of ozone eddy flux and mean concentration, J. Geophys. Res., 86(C8), 7291, doi:10.1029/JC086iC08p07291, 1981.
Responses to Reviewer 2:

This paper describes the development and application of an oxygen anion chemical ionization mass spectrometry approach for directly measuring the flux of ozone and nitrogen dioxide. Of particular note, is the successful application of this technique in the marine boundary layer where the magnitude of O3 and NO2 fluxes is low. The authors describe thoughtful and extensive laboratory characterization, comparison with traditional measurements in the field, initial deployment for flux measurements, and data analysis and correction. The paper is well organized and clearly written. The comments and suggestions below are meant to improve an already very good paper.

We thank the reviewer for their supportive and thoughtful comments! Replies to all specific reviewer comments are below.

Specific Comments:

L35-39: Is there any experimental evidence that vd-O3 depends on factors beyond wind speed and SST? e.g., surface ocean composition? Could such factors contribute to the order of magnitude range noted in L35? Do any measurements exist over snow ice? Or freshwater versus seawater?

Ocean surface composition is known to be a controlling factor in $v_d(O_3)$, with iodide and various dissolved organic compounds (DOCs) being the primary contributors. Parameterizations to SST are primarily made as a proxy for iodide which is globally directly correlated with SST. In nearly all field measurements of $v_d(O_3)$, DOC and iodide were not measured. Instead laboratory studies of O3 deposition to water containing DOC and iodide are used to model their role in ambient O3 deposition. To our knowledge there is one EC measurement of O3 deposition to freshwater (Weseley et al. (1980)) who reported a $v_d(O_3)$ of 0.01 cm s$^{-1}$. Incidentally we have a manuscript in progress applying the Ox-CIMS reported here for deposition measurements to lake water. Observations to snow vary widely but current best estimates suggest that deposition is slow (0-0.01 cm s$^{-1}$). Mention of these values has been added to the text. We have also added some discussion to the role of iodide and DOC in controlling O3 to the text here.

The manuscript has been revised to state: Starting at Line 35: “There is only one reported study of O3 deposition to freshwater, which showed $v_d(O_3)$ of 0.01 cm s$^{-1}$ (Wesely et al., 1981). Measured deposition rates to snow and ice vary widely, with most observations of $v_d(O_3)$ from 0 to 0.2 cm s$^{-1}$, while models suggest $v_d(O_3)$ from 0 to 0.01 cm s$^{-1}$ (Helmig et al., 2007). Reactions of O3 with iodide and dissolved organic compounds (DOC) in the ocean are known to play a controlling role in setting $v_d(O_3)$ and may explain some of the variability in observations (Chang et al., 2004; Ganzeveld et al., 2009). However, these quantities have not typically been measured during field studies of $v_d(O_3)$.”

L53: Is it worth pointing out explicitly here, for the non-expert reader, that UV photometric detection of O3 doesn’t provide fast enough time response for flux measurements?

We agree this is important to state explicitly and have added this discussion as suggested.
The manuscript has been revised to state: Starting at Line 53: “Due to this constraint, standard O\textsubscript{3} monitoring instruments which utilize UV-absorption detection do not have suitable time response or precision for EC measurements and ozone flux measurements have primarily utilized fast response chemiluminescence sensors.”

L110-111: Which type of TofWerk ToF is used here? e.g., HToF or CToF?
We use a CToF with resolution of ca. 950 at the CO\textsubscript{3}- product (-m/Q 60). We have updated the text to state this more explicitly.

The manuscript has been revised to state: Line 110: “the ion beam for entry into the compact ToF mass analyzer (CToF,…”

L126-127: Any reference for “a wide class or molecules”? Or, can the authors be slightly more specific? e.g., hydrocarbons/oxygenates/S-containing/N-containing etc
The text as written was likely too vague and we have removed the phrase “a wide class of molecules” and instead point the reader to a review paper which compiled electron affinity measurements and calculations. This reference provides the reader with a starting place to easily assess if the Ox-CIMS has potential to measure a molecule of interest.

The manuscript has been revised to state: Line 126: “…resulting in a relatively non-specific reagent ion chemistry which is sensitive to a wide class of molecules (see Rienstra-Kiracofe et al., (2002) for a compilation of molecular E.A. values).”

L181-189 (and elsewhere): Is ions/s used equivalently with counts/s? Does one quantity rely on the calibration of the single ion signal? A clear definition would be helpful.
Thank you for pointing out this ambiguity. Ions s\textsuperscript{-1} and counts s\textsuperscript{-1} are equivalent and were used interchangeably throughout the text. We have changed all instances of ion s\textsuperscript{-1} or related expressions throughout the text to counts s\textsuperscript{-1} (or cps/ncps as appropriate) for clarity.

L187: Does this mean that signals are normalized to a fixed value? Or normalized to the variable signal for a reagent ion? Or, does this refer to the signal/pptv you would obtain for a reagent ion signal of 1e6 ions/s? Clarification would be helpful.
We normalize signals by scaling to a fixed total reagent ion signal of 1E6 cps. This follows the standard approach in many CIMS applications. Based on suggestions from Reviewers 2 and 3, this section has been clarified.

The manuscript has been revised to state: Line 187: “Sensitivity values can be normalized by scaling all signals to a fixed total reagent ion signal count rate of 1 \times 10^6 cps ions s\textsuperscript{-1} to isolate the sensitivity component controlled by reagent ion chemistry, separate from total instrument count-rate changes in instrument performance due to decay in the ion source or other factors. The total reagent ion signal is taken as the sum of the $O_5^-$ and $O_5(H_2O)^-$ signals.”

L223-224: Reference or supplemental data for this statement?
This statement as written was likely an overstatement based on the amount of evidence we currently have. Laboratory calibrations of formic acid, H$_2$O$_2$, NO$_2$, and nitric acid have shown insignificant difference when performed in N$_2$ or in ambient air. Beyond that we have not performed a robust set of experiments to specifically rule out the involvement of CO$_2$ in the detection of other analytes. We have revised the text to be less definitive and acknowledge that only a small set of molecules have been specifically calibrated.

The manuscript has been revised to state: Line 223: “No other analytes that we have calibrated for analyzed with the Ox-CIMS (HCOOH, HNO$_3$, H$_2$O$_2$) have shown a CO$_2$ mixing ratio dependence, demonstrating suggesting that CO$_2$ may be is uniquely involved in the detection of O$_3$ this mechanism and is not a general feature of the oxygen-anion chemistry.”

L292-293: Are signals only normalized to the reagent ion when the reagent ion is lower than the analyte signal?

Ambient data was normalized for all analyte signal magnitudes. This is necessary for applying laboratory humidity dependent sensitivities to ambient observations despite slow drift in instrument performance.

L331 (section 3.1): The next section (3.2) contains quite a lot of detail on instrument set up in the field (temperatures, inlet etc.), but relatively little information is given here. More detail would be useful.

And

L339-341: Somewhat more detail on this scaling and how it is assessed/applied is warranted here, rather than relying heavily on the Vermeuel reference.

Based on discussion from Reviewers 1 and 2, significant details have been added back to this section rather than requiring the reader to refer to Vermeuel et al. (2019).

The manuscript has been revised to state: Section 3.1: “The Ox-CIMS was located on the roof of a trailer (approx. 5 m above ground) and sampled through a 0.7 m long, 0.925 cm i.d., PFA inlet. The inlet was pumped at flow rate of 18-20 slpm from which the Ox-CIMS subsampled at 1.5 slpm. Temperature and RH were recorded inline downstream of the subsampling point. The Ox-CIMS sampling point was approximately 10 m horizontally from the Thermo-Fisher 49i and sampled at approximately equal heights. Instrument backgrounds of the Ox-CIMS were determined every 70 minutes by overflowing the inlet with dry UHP N$_2$. Calibration factors for O$_3$ were determined by scaling the in-field continuous addition of a C-13 isotopically labelled formic acid standard to the tip of the inlet. Laboratory calibrations of the Ox-CIMS to formic acid and O$_3$ as a function of specific humidity were determined immediately pre- and post-campaign and were used to calculate a humidity dependent sensitivity of O$_3$ relative to formic acid. That relative sensitivity was then used to determine the in-field sensitivity to O$_3$ by scaling field sensitivities of formic acid from the continuous additions. Full details of this deployment and calibration methods are described in Vermeuel et al., (2019).”
L356-358: How do these temperatures impact instrument performance? Is it species dependent?

The primary motivation for these temperatures was to ensure that the inlet and instrument front end temperatures were always higher than ambient temperatures to prevent any condensation of water vapor. O₃ is typically considered a “non-sticky” molecule and is likely not significantly impacted by the selected temperature as long as it is ensured that there is no condensation of water.

L429: Does 84

It appears the Reviewers comment here was lost somewhere in the uploading process but we will provide additional detail here to hopefully answer their question. The 84% rejected flux periods refers to all ambient sampling periods, including those where winds were not from the ocean. The wind direction filter removed approximately 30% of the campaign data, followed by an additional 57% reduction due to the u* filter and further cuts due to the stationarity and outlier filters.

Additionally, please note that all values in this section have been revised as described in Comment 1 to all reviewers.

L431: How does ‘despiking’ impact the results?

The despiking algorithm as applied is intended to remove short large spikes in the data, primarily driven by electronics issues. If these short electronic spikes were left in the data they could bias the observed flux value and increase the LOD, as they would drive a strong short covariance signal. This despiking correction and our specific implementation are standard in EC data processing. Such spikes were negligible in our dataset and the correction was applied for completeness.

L520-521: For the non-expert reader it may be useful to clarify whether this bias is specific to O₃ measurement with Ox-CIMS, or to CIMS measurements of trace gases in general.

We agree that this is a useful point to clarify. This correction would impact all CIMS instruments as they also measure mixing ratios relative to moist air with variable density. Due to the high mixing ratios of O₃ and the small deposition magnitude to water, measurements of O₃ air-sea exchange are particularly sensitive to this potential bias. Still, this factor should be considered for all flux sensors that do not directly measure mole fractions or mixing ratios relative to dry air.

The manuscript has been revised to state: Line 520: “The Ox-CIMS measures O₃ as the apparent mixing ratio relative to moist air, as is true of all CIMS based measurements, which means fluctuations in the density of air due to changes in temperature, pressure, and humidity could introduce a bias in the EC flux measurement (Webb et al., 1980).”

L766-767: incomplete citation to Vermeuel 2019. doi?

Thank you, this citation has been corrected.
Technical Corrections:
L194: “was seen to have” to “had”
L223: “analytes analyzed” to “analytes detected/measured”
L305: Repeated section title? (Same as 2.9)
L527: Repeated phrase “which is removed by active heating of the inlet”
L528: semicolon use
L590: validation to validate

We thank the reviewer for their careful reading! All of the above technical corrections have been made following the suggestions of the reviewer.

The title of Section 2.10 was indeed accidental copied from the title of Section 2.9. The title of Section 2.10 has been corrected to: “Short- and long- term precision”
Responses to Reviewer 3:

General comments:
A novel method of measuring O3 and NO2 based on chemical ionization time-of-flight mass spectrometry with oxygen anion (O2-) as the reagent ion (Ox-CIMS) is developed. This new method is able to measure O3 and NO2 at fast time response and low mixing ratios, which is applicable to eddy covariance flux measurements. The authors conducted thorough characterization of the sensitivity, ion chemistry, inlet, calibration in the laboratory. They also used the instrument for the measurement of O3 vertical fluxes over the coastal ocean, via eddy covariance. Their measured flux is in good agreement with prior studies of O3 ocean-atmosphere exchange. Potentially, fluxes for multiple species can be obtained with one measurement with the Ox-CIMS. During the same campaign, they also used a 2B ozone monitor to measure ozone, which agreed well with the Ox-CIMS measurement. The paper is well written, and I suggest publishing this work after addressing the following specific comments.

We thank the reviewer for their thoughtful and supportive review. Responses to specific reviewer comments are below.

Specific comments:
1.) Around line 138 to 153 on the discussion of CO3- ion formation, do other chemicals also form CO3-? It was mentioned early on line 119 that SO2 also forms CO3-? How to rule out that CO3- detected are not from other chemicals? Similarly, on line 215, would CO3- come from other species, rather than O3+CO2+O2-chemistry?

We believe the discussion of use of CO3- reagent ions for detection of SO2 was confusingly worded. In that work, SO2 does not generate CO3-, rather CO3- reagents are used to ionize SO2 forming SO3-. We highlighted this prior work as CO3- reagent ions were made by first generating O2- ions and reacting them with intentionally added O3 in the presence of CO2. In our work the same mechanism is used, but rather than intentionally adding excess O3 to form CO3-, we detect ambient O3 in the form of the CO3- product.

We believe it is unlikely that other species significantly compete with the O3+CO2+O2-chemistry. For a species to favorably transfer an O- to CO2 it must be a strong gas phase oxidizing agent and form a more stable product following O- transfer. It is apparent what species might follow the above requirements. Those species if present are also likely highly reactive oxidized molecules which would be at low mixing ratios relative to O3.

The manuscript has been revised to state: starting at line 118 “Oxygen anion chemistry has also been used for the detection of SO2 via a multi-step ionization process where CO3- reagent ions are first generated by the reaction of O2- with added excess O3 in the presence of CO2. The CO3- reagent ion product then ligand switches with SO2 to form SO3- which then quickly reacts with ambient O2 to form the primary detected SO5- product (Porter et al., 2018; Thornton et al., 2002a).”
2.) **Line 154:** Are there other interfering species that will end up as NO2- in the CIMS? Do HNO3, HONO, PAN or Organ-NO2 form NO2- with the ion chemistry? For example, on line 282, the authors mention that “A possible source of this background is from degradation of other species such as nitric acid or alkyl nitrates on the inlet walls.” Did the authors do any test for interfering species?

We agree that this is an important consideration that should be made clear to the reader. We have not yet extensively tested for other potential interfering species at the NO2- product. Laboratory and field calibrations of HNO3 do not show contribution to the NO2- product, but a small fraction is seen as NO3-. The conservation of total odd-oxygen during an O3 titration event discussed in Section 4 gives some qualitative indication that interfering species are likely small, but more direct evidence is necessary. Further validation of the NO2 detection product is certainly warranted to characterize any interferences but we believe that to be beyond the scope of this work. The manuscript focuses primarily on the O3 measurement and we tried to be upfront that the NO2 measurement currently has less validation than the O3 measurement. We make further reference to this in section 5 (Conclusions and outlook) stating “Further optimization and characterization of the Ox-CIMS is ongoing, including efforts to validate the specificity of the NO2 detection…”

The manuscript has been revised to state: Line 282: “Additional calibration will be necessary to ensure that observed NO2 signal is not a secondary product of other species and we cannot currently quantify their potential interference on measured NO2.”

3.) **Line 189**, can the authors specify what the normalized counts are? Is it normalized to the reagent ion counts?

Based on suggestions from Reviewers 2 and 3, discussion of the normalization of the normalization process has been clarified. Generally, we use it in the same was as is common in chemical ionization mass spectrometry applications, where all signals are scaled relative to a fixed total reagent ion signal of $1 \times 10^6$ cps.

The manuscript has been revised to state: Line 188: “Sensitivity values can be normalized by scaling all signals to a fixed total reagent ion signal of $1 \times 10^6$ cps to isolate the sensitivity component controlled by reagent ion chemistry, separate from total instrument count rate changes in instrument performance due to decay in the ion source or other factors. The total reagent ion signal is taken as the sum of the $O_2^-$ and $O_2(H_2O)^-$ signals.”

4.) **Section 2.8:** The authors mentioned that background measurement influences the detection limit. Do they have any recommendation in improving the detection limit?

Because the instrument O3 background is driven by chemistry in the reagent-ion source it is not clear what best approach is for reducing this background. We speculate that use of an alternative ionization source (**i.e.** soft x-rays or a corona discharge) may reduce this background issue but that would require laboratory work beyond the scope of this work. Alternatively a mass selective filter at the interface of the ion source and the IMR could be
used to remove the larger $O_3^-$ ions (-m/Q 48) and preserve the $O_2^-$ reagent ions (-m/Q 32) which would also be a substantial undertaking.

5.) **Line 572:** It might be easier for readers to include the equation in the paper and cite Bariteau et al., so readers won’t need to download Bariteau et al.

The equations from Bariteau, 2010 have been added to the text as suggested. In the course of revising the text, we realized a citation of Lenschow and Kristensen (1985) was also warranted, which has also been added.

The manuscript has been revised in this section to list the equations and define all variables starting at Line 572.

References:

Lenschow, D. H. and Kristensen, L.: Uncorrelated Noise in Turbulence Measurements, J. Atmos. Ocean. Technol., 2, 68–81, doi:https://doi.org/10.1175/15200426(1985)002<0068:UNITM>2.0.CO;2, 1985.