



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 ($180 \text{ ions s}^{-1} \text{ pptv}^{-1}$) and NO_2 ($97 \text{ ions s}^{-1} \text{ pptv}^{-1}$), 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 0.011 cm s^{-1} with a campaign ensemble limit of detection (LOD) of 0.0042 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 $38.9 \pm 12.3 \text{ ppbv}$. 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 $Tg \text{ yr}^{-1}$ (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



O₃ dry deposition velocities are relatively fast ($>0.1 \text{ cm s}^{-1}$, (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 O₃ deposition to water surfaces have been made from coastal towers (Gallagher et al., 2001), aircraft (Faloona 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
35 observed $v_d(\text{O}_3)$ ranging between 0.01 and 0.15 cm s^{-1} . To date there is no consensus on whether measured O₃ 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 $v_d(\text{O}_3)$ with wind speed (U_{10}) and sea–surface temperature (SST), highlighting the need for further field observations as constraints for model parameterizations.

40 The small magnitude of O₃ 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, O₃ vertical fluxes to terrestrial surfaces are 10 to 100 times faster than to water surfaces, significantly loosening sensor precision requirements. Nonetheless, significant variability in $v_d(\text{O}_3)$ exists between surface types (e.g. soil vs. leaf) (Wesely and Hicks,
45 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 O₃ are required to correctly model the response of $v_d(\text{O}_3)$ 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
50 deposition rates and similar accuracy requirements.

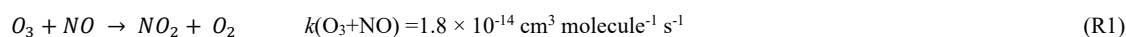
Eddy covariance measurements typically require fast (1-10 Hz), high precision sensors in order to resolve covariance on the timescales of the fastest atmospheric turbulent eddies. Due to this constraint, ozone flux measurements have primarily utilized fast response chemiluminescence sensors. Chemiluminescence detectors can use either wet, dry, or gas-phase reagents for detection with important differences between them (Muller et al., 2010). Gas-phase chemiluminescence sensors are
55 typically based on the reaction of O₃ with nitric oxide (NO) to form an excited state NO₂* 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 $\text{s}^{-1} \text{ pptv}^{-1}$ (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
60 (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



65 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
70 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
75 when the titration reaction (R1) is fast relative to the transport time to the height of the sensor.



Surface NO emissions from both biogenic and anthropogenic sources are widespread, with ocean emissions on the order of 1×10^8 molecules $\text{cm}^{-2} \text{ s}^{-1}$ (Zafiriou and McFarland, 1981) and soil emissions ranging from 5×10^9 to 2×10^{11} molecules $\text{cm}^{-2} \text{ s}^{-1}$ (Yienger and Levy, 2004). These emissions correspond to a positive bias in the observed $v_d(O_3)$ dry deposition rate on the
80 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 NO_2 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 NO_x 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
85 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 NO_2 . 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
90 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

95 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) N₂ and O₂ gas (both Airgas 5.0 grade) through a polonium-210 α -particle source (NRD, P-2021 Ionizer). This N₂:O₂ volume ratio was
100 found empirically to maximize total reagent ion signal in our instrument while minimizing background signal at the O₃ detection product (CO₃⁻, -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
105 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^{-2} mbar and a final chamber containing focusing optics which prepare
110 the ion beam for entry into the ToF mass analyzer (TOFWERK AG and Aerodyne Research Inc.). The mass resolving power ($M/\Delta M$) 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

115 Oxygen anion (O₂⁻) 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 SO₂ *via* a multi-step ionization process where CO₃⁻ reagent ions are generated by the reaction of O₂⁻ with excess O₃ in the presence of CO₂. The
120 CO₃⁻ 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). Ionization of analytes by oxygen anion reagent ion chemistry proceeds through both charge transfer (R2) and adduct formation (R3).





125 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 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).

130 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
135 water in $O_2(H_2O)_n^-$ (Bork et al., 2011) and the high field 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 (CO_3^-), which is the final detected product. First, the oxygen anion ($O_2(H_2O)_n^-$) either transfers
140 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 CO_2 molecule to form 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).



It is not clear whether it is the bare ozone anion (R4a & R5a) or the cluster (R4b & R5b) that goes on to react with 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
150 O_3^- but the magnitude of this signal is less than 1% of the signal of CO_3^- during ambient sampling. The proposed mechanism of 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_2 to form the detected product $C^{18}OO_2^-$ (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_2 proceeds directly through a charge transfer reaction with $O_2(H_2O)_n^-$ to form the detected NO_2^-
155 product (R6). This is expected based upon the high E.A. of NO_2 (2.27 eV, (Ervin et al., 1988)) compared to O_2 (E.A. 0.45 eV).
 $NO_2 + O_2(H_2O)_n^- \rightarrow NO_2^- + O_2 + nH_2O \quad (R6)$



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 O₃ and NO₂, 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 1×10^4 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 O₃ and NO₂. 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. NO₂ was delivered from a certified standard cylinder (Scott-Marrin 4.84 ± 0.1 ppmv). The primary NO₂ 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. CO₂ (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 O₃ and NO₂ are shown in Fig. 2. An overview of instrument sensitivity, limits of detection (LOD), and precision to O₃ and NO₂ 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 ($O_2^- + O_2(H_2O)_n^-$) ranged from 0.8 to 2.2×10^7 ions s⁻¹ (Fig. S1). The mean total reagent ion signal over 6 weeks of ambient sampling (Section 3.1) was 1.45×10^7 ions s⁻¹. The absolute instrument sensitivity at this reagent ion signal to O₃ and NO₂ is 180 and 97 ions s⁻¹ pptv⁻¹ respectively (at 8 g kg⁻¹ SH). 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 to a fixed reagent signal count rate (1×10^6 ions s⁻¹) to isolate the sensitivity component controlled by reagent ion chemistry, separate from total instrument count rate.



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 O₃ was seen to have no significant dependence on specific humidity over the range 4–16 g kg⁻¹. Sensitivity to NO₂ 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 O₃ and NO₂ 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). *Ab initio* calculations of O₂⁻(H₂O)_n and O₃⁻(H₂O)_n clusters performed by Bork et al. (2011) showed that charge transfer from the bare (*n*=0) O₂⁻ to O₃ 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 O₂⁻(H₂O)_n to NO₂ follows a similar trend with *n*. Ion mobility studies to determine the O₂⁻(H₂O)_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 CO₂

The ionization pathway for detection of O₃ with O₂⁻(H₂O)_n reagent ion chemistry differs from typical chemical ionization schemes, in that it involves a two-step reaction of charge transfer to ozone forming O₃⁻, which then reacts with CO₂ to form the detected CO₃⁻ product (R4-R5). Therefore, we assessed the impact of CO₂ mixing ratio in the sample flow on O₃ sensitivity as shown in Fig. 4. Calibration curves were generated by diluting ozone in dry UHP N₂ and mixing in a flow of variable CO₂ (Airgas, Bone Dry Grade) mixing ratios before sampling. At nominally 0 ppmv CO₂, the O₃⁻ ionization product (-48 m/Q) was detected with sensitivity of 14 ± 2 ncps pptv⁻¹ and the CO₃⁻ product (-60 m/Q) at 5 ± 1 ncps pptv⁻¹. For CO₂ mixing ratios from 60 to 500 ppmv, the O₃⁻ signal is less than 1% of the CO₃⁻ product and the sensitivity at the CO₃⁻ product is independent of CO₂ within the uncertainty. The presence of a significant fraction (36%) of the CO₃⁻ product with nominally 0 ppmv CO₂ suggests the presence of a slight leak rate of CO₂ via diffusion through the perfluoroalkoxy alkane (PFA) tubing, or CO₂ contamination in the UHP N₂ supply. The manufacturer stated upper limit of CO₂ in the UHP N₂ is 1 ppmv which we take to be the lower limit achievable in our system. A CO₂ mixing ratio of only 1 ppmv is still an order of magnitude excess relative to a high end ambient O₃ mixing ratio of 100 ppbv. An exponential fit of the O₃⁻ product vs CO₂ indicates that O₃⁻ makes up less than 1% of



220 the detected ozone at CO₂ mixing ratios greater than 10 ppmv. This suggests ambient samples will always have a substantial
excess of CO₂ necessary to drive the reaction completely to the CO₃⁻ product. The measured flat response from 60–500 ppmv
CO₂ indicates that natural variability in ambient CO₂ will have negligible impact on ambient measurements of ozone. No other
analytes analyzed with the Ox-CIMS show a CO₂ mixing ratio dependence, demonstrating CO₂ is uniquely involved in this
mechanism and is not a general feature of the oxygen-anion chemistry. All other reported laboratory calibrations reported here
225 were performed at CO₂ mixing ratios of 380 ppmv and all reported sensitivities are for the CO₃⁻ product. This CO₂ dependence
also requires careful consideration during instrument background determinations by UHP N₂ overflow which is discussed in
Section 2.8.

2.7 Dependence on IMR pressure

Instrument sensitivity to O₃ increases with increasing IMR pressure as shown in Fig. 5. The normalized signal of O₃ increases
230 by 175% over the pressure range of 70 to 95 mbar in the IMR when sampling a constant O₃ 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
235 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
240 collisions which could better preserve a weakly bound O₂(O₃)(H₂O)_n⁻ cluster and allow a longer lifetime to react with CO₂
before dissociation. The operational IMR pressure of 95 mbar used here was empirically selected to maximize sensitivity to
O₃ 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 O₃.

2.8 Instrument background and limits of detection

245 Instrument backgrounds were assessed by periodically overflowing the inlet with UHP N₂ during field sampling. Details of
the inlet and zeroing conditions used are discussed further in Section 3.1. During N₂ overflow, O₃ displayed a consistently
elevated background on the order of 3.1 x 10⁵ cps corresponding to 2.1 x 10⁴ ncps, or approximately 1.3 ppbv O₃, at a typical
total reagent ion signal of 1.45 x 10⁷ cps. A representative background determination is shown in Fig. 6. The magnitude of the
O₃ background was observed to vary with the O₂:N₂ ratio in the reagent ion precursor flow when sampling a UHP ZA overflow
250 with 380ppm CO₂ as shown in Fig. S2. The background O₃ count rate was observed to increase from 3.0 x 10⁴ to 6.3 x 10⁴
ncps as the O₂ volume fraction in the reagent ion delivery gas flow (*f*_{O₂}) was increased from 0.05 to 0.4. The dependence of



the background O₃ signal on f_{O_2} suggests that the observed background O₃ is formed directly in the alpha ion source and is not from off-gassing of inlet and instrument surfaces. The magnitude of this background O₃ does not vary when sampling UHP zero air or N₂, further confirming that the background O₃ is formed directly in the ion source from the O₂ used to generate the reagent ion. An operational f_{O_2} of 0.08 (actual volumetric flow ratio O₂:N₂ of 200:2200 sccm) was selected to balance maximizing the total reagent ion signal while minimizing the O₃ ion-source background (3.1×10^5 cps). The magnitude of this O₃ 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 1σ deviation of the distribution of normalized adjacent differences of O₃ 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 O₃ background determinations. The magnitude of this O₃ background is a fundamental limit on the achievable limit of detection.

Because CO₂ was not added to the UHP N₂ overflow during field sampling, the reaction was not driven fully to the CO₃⁻ product and some O₃⁻ signal at $-m/Q$ 48 was observed during UHP N₂ overflow periods as shown in Fig. S4. The magnitude of the O₃ signal observed as O₃⁻ was approximately 55% of the CO₃⁻ product (mean 1.2×10^4 and 9.6×10^3 ncps respectively) during overflow periods. The total sensitivity to O₃ as the sum of the O₃⁻ and CO₃⁻ was observed to be constant as a function of CO₂ as shown in Fig. 4. We therefore assign equal sensitivity to each O₃ detection product and took the sum of signal at O₃⁻ and CO₃⁻ in order to determine the total background O₃ concentration. This issue will be corrected in future deployments by the addition of CO₂ to the N₂ overflow used for backgrounds which will drive the product fully to CO₃⁻. The mean background of O₃ for the full field sampling period was 1.3 ± 0.3 ppbv. The 10 Hz precision of O₃ during an individual N₂ overflow period was found to be 0.75%, corresponding to 7.5 pptv as shown in Fig. S5. This suggests that variability in the O₃ 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 O₃ is 42 pptv for a S/N of 3, and a mean background O₃ signal of 2.1×10^4 ncps 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).

$$\frac{s}{N} = \frac{C_f[x]t}{\sqrt{C_f[x]t - 2Bt}} \quad \text{E1}$$

The mean background signal during field sampling for NO₂ was 3.5×10^3 ncps which corresponds to 0.28 ppbv. At this background level, the 10 Hz LOD for NO₂ is 26 pptv for a S/N of 3. The optimum LOD for NO₂ 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 NO₂ is notably above zero indicating either off gassing from inlet walls or a secondary production of NO₂ 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 NO₂ signal is not a secondary product of other species.



2.9 Reagent ion saturation and secondary ion chemistry

285 During ambient sampling the ozone signal (as CO_3^- detected at -60 m/Q) is of comparable magnitude to the O_2^- reagent ion
signal as shown in Fig. 1. High analyte concentrations ($> 5 \text{ ppbv}$) 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_2^- reagent ion ($9 \times 10^6 \text{ cps}$ and $6 \times 10^6 \text{ cps}$ respectively). The electron affinity (E.A.) of carbonate is from 3.26 (Hunton
290 et al., 1985) to $>3.34 \text{ eV}$ (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_2^- is present. At high O_3 concentrations, the
reagent ion signal magnitude is reduced, which necessitates normalizing sensitivities to the $1 \times 10^6 \text{ cps}$ 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_2O_2 *via* adduct formation raising
295 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_2O_2 resulted in the titration of the O_3 signal of 0.06 ppbv per ppbv H_2O_2 . H_2O_2 was detected as an
adduct with O_2^- and not CO_3^- , indicating that O_2^- 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
300 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_2^- and CO_3^- reagent ions with H_2O , HNO_3 , H_2O_2 , and CH_3OOH
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_3^- . Adduct formation with O_2^- was favorable relative to CO_3^- by 2.5 to 17 kcal mol^{-1} for all analytes
that were calculated. All calculated binding enthalpy values are listed in Table S2.

305 2.10 Reagent ion saturation and secondary ion chemistry

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.

$$\text{NAD} = \frac{|X|_n - |X|_{n-1}}{\sqrt{|X|_n |X|_{n-1}}} \quad \text{E2}$$

The standard deviation of the Gaussian fit of the distribution of normalized adjacent differences (NAD) is a direct measure of
310 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
315 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 1×10^3 and 1×10^6 cps (Fig. S8). Above 1×10^6 cps there is an apparent asymptote where precision no longer improves with count rate. For 10 Hz averaging and count rates of 1×10^6 and 1×10^7 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. 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).

330 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) O_3 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 data 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. Background of the Ox-CIMS was determined every 70 minutes by overflowing the inlet with dry UHP N_2 . Calibration factors for O_3 were determined by scaling in-field continuous addition of a C-13 isotopically labelled formic acid standard to humidity dependent calibration factors for O_3 and formic acid determined in lab pre- and post-campaign as described in Vermeuel et al., (2019). The EPA O_3 monitor shows a persistent high bias at low O_3 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

345 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 ($32^\circ 52.0' N$, $117^\circ 15.4' W$) during July and August 2018 for EC measurements of O_3



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 O₃ from pre- and post-campaign calibrations to the field calibrations of C-13 formic acid. Ambient O₃ 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

Instrument backgrounds were determined every 35 minutes by overflowing the entire inlet manifold with dry UHP N₂. Background and ambient count rates were first converted to concentrations using the laboratory determined humidity dependent sensitivities for O₃ and NO₂ scaled to the C-13 formic acid standard addition sensitivity. Background concentrations of O₃ and NO₂ 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 O₃ 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 during dry N₂ overflows were fit to a bi-exponential decay function to characterize inlet gas evacuation time (τ_1) and wall interaction times (τ_2) (Ellis et al., 2010). Best fit estimates for τ_1 of O₃ and NO₂ across overflow periods were from 0.7 to 1.2 seconds and accounted for more than 80% of the decay. For O₃, τ_2 was found to be negligible at



less than 0.3 s indicating O₃ has minimal equilibration with the inlet walls. τ_2 for NO₂ was determined to be longer at 3.2 s.
380 This suggests a potential interference at the NO₂ peak, as NO₂ is expected to have minimal equilibration, similar to O₃. NO₂ also shows a continually elevated signal during overflow periods suggesting off gassing from inlet or instrument surfaces. The cause of this slow NO₂ 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 (τ_r) for O₃ can be calculated during zeroing periods as the time required for the signal
385 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 0.9 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 τ_r according to Eq. 3.

$$f_{cut} = \frac{1}{2\pi\tau_r} \quad \text{E3}$$

390 The calculated f_{cut} from the measured mean response time was 0.18 Hz. This value suggests that minimal attenuation in the flux signal (cospectra) should be apparent at frequencies less than 0.18 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.

395 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
400 (C_l) concentrations and the dimensionless gas over liquid Henry's law constant (K_H), 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.

$$F = -K_t(C_g - K_H C_l) \quad \text{E4}$$

Trace gas flux (F) can be measured with the well-established eddy covariance (EC) technique where flux is defined
405 as the time average of the instantaneous covariances from the mean of vertical wind (w) and the scalar magnitude (here O₃) 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.

$$F = \frac{1}{N} \sum_{i=1}^N (w_i - \bar{w}) (O_{3,i} - \bar{O}_3) = \langle w' O_3' \rangle \quad \text{E5}$$

$$v_d = \frac{F}{C_g} \quad \text{E6}$$



410 For purely depositing species where the water side concentration is negligible, C_l and K_H can be neglected in Eq. 4 and K_t can be reformulated into a deposition velocity (v_d) calculated according to Eq. 6, where $\overline{C_g}$ 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

415 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).
- 3.) Stationarity: Each 27-minute flux period was divided into five even non-overlapping subperiods. Flux periods were

420 rejected if any of the subperiods differed by more than 40% (Foken and Wichura, 1996).

The selected U_* threshold of 0.1 m s⁻¹ is lower than the 0.2 m s⁻¹ used frequently as a default but is 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

425 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 results in 57% of the wind direction filtered flux periods being rejected. 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 11 data points. After all quality control filters were applied, 84% of flux periods were rejected leaving 157 quality-controlled flux periods.

430 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

435 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 $\bar{v} = 0$. Vertical wind velocity (\bar{w}) in any individual rotation period may be non-zero due to mesoscale motions but \bar{w} for the full campaign is



440 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
445 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.
450 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 O_3 flux period determined by the MAX and a 10 point AVG method showed reasonable agreement, with a
455 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 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
 $v_d(O_3)$ values. A prescribed lag time has the least bias to extreme values caused by noise, provided that the true lag time is
460 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 $v_d(O_3)$ using the prescribed, MAX, and AVG lag times were 0.011, 0.010, and 0.010
 $cm\ s^{-1}$ respectively, suggesting the campaign mean value was relatively insensitive to the lag time method.

3.4 Cospectra and Ogives

465 The frequency weighted cospectrum of 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
470 and O_3 appear to match well with the idealized Kaimal cospectra for an unstable boundary layer at sampling height $z = 13m$
(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 O₃ 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 O₃ ogives suggest that high frequency attenuation in the sampling line is minimal above 0.2 Hz, consistent with our calculated f_{cut} of 0.18 Hz. Due to the small magnitude of the O₃ 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 0.2 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. We also calculate the attenuated flux from the model of Horst, (1997) shown in Eq. 7, for a response time (τ_c) of 0.9 s, and a wind speed of 3 m s⁻¹ to be 13%.

$$\frac{F_m}{F_x} = \frac{1}{1+(2\pi n_m \tau_c U/z)^\alpha} \quad \text{E7}$$

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 α 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 O₃ 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_{σ}) 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_{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_{σ} and LOD_{RMSE} methods showed good correlation (Fig S13), with periods where the LOD_{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_{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 0.0042 cm s^{-1} , calculated using Eq. 8 following Langford et al.,(2015). A total of 62 out of 157 (39%) flux periods had deposition velocities below the campaign ensemble LOD. These values are still included in the reported mean $v_d(O_3)$.

$$\overline{LOD} = \frac{1}{N} \sum_{i=1}^N LOD^2 \quad E8$$

3.6 Density fluctuation corrections

The Ox-CIMS measures O_3 as the apparent mixing ratio relative to moist air, 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. However, without a direct measure of water vapor fluctuations collocated with the Ox-CIMS this is difficult to assess directly. 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 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 $2.6 \times 10^9 \text{ molecules cm}^{-2} \text{ s}^{-1}$, which is 24% of our mean measured flux of $-1.1 \times 10^{10} \text{ molecules cm}^{-2} \text{ s}^{-1}$. 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).



535 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 1×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ 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 $v_d(\text{O}_3)$. Assuming a maximum NO emission flux of 5×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$ and that all NO reacts with O_3 before being advected to the sensor height, the resulting O_3 flux bias would be -5×10^8 molecules $\text{cm}^{-2} \text{s}^{-1}$. Our mean case of 40 ppbv O_3 and $v_d(\text{O}_3)$ of 0.011 cm s^{-1} corresponds to a flux of -1.1×10^{10} molecules $\text{cm}^{-2} \text{s}^{-1}$. Therefore, the resulting bias in observed $v_d(\text{O}_3)$ from NO emissions is 4.5% or $4.9 \times 10^{-4} \text{ cm s}^{-1}$. This value is an upper limit for expected ocean NO emissions and is well within the uncertainty of the observed $v_d(\text{O}_3)$.

545 3.7.2 Free troposphere entrainment

The entrainment of O_3 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. The magnitude of this flux gradient depends on the magnitude of the O_3 concentration gradient (ΔC) and the entrainment velocity (w_e) of air from free troposphere into the MBL. Faloon et al. (2005), reported entrainment velocities from 0.12 to 0.72 cm s^{-1} and an enhancement in O_3 (ΔC) 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 ΔC and w_e as shown in Fig. 12 (Blomquist et al., 2010).

$$\frac{\Delta F_{0,est}}{F_0} = \frac{z}{z_i} \left(\frac{F_i}{F_0} - 1 \right) \quad \text{E9}$$

$$F_i = w_e \Delta C \quad \text{E10}$$

555 Where z is the boundary layer height, z_i 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) = -4.4×10^{-3} ppbv m s^{-1} (from $v_d = 0.011 \text{ cm s}^{-1}$ and $[\text{O}_3] = 40$ ppbv), and an O_3 mixing ratio gradient (ΔC) 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 Faloon et al, 2005 (ΔC of +20 ppbv, MBL height of 800m) is 6.25% for w_e of 0.12 and 44% for 0.72 cm s^{-1} . This entrainment flux error is clearly significant for marine O_3 flux measurements assuming there is a gradient of O_3 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 O_3 measurements should be made as close to the surface as possible, and that the O_3 concentration gradient and entrainment rate should be explicitly measured if possible. We do not have an explicit measure of ΔC , w_e , or the MBL height so we tentatively assign entrainment error of up to 44% from the maximum values of those parameters reported in Faloon et al. (2005). We emphasize this source



of uncertainty is independent of the O₃ sensor and is a systematic bias that should be considered in all O₃ air-sea exchange determinations.

4 Fast NO₂ measurements, eddy covariance and O₃ titration

Discussion of EC flux results have been limited to O₃ because ocean—atmosphere exchange of NO₂ is expected to be small and below the limit of detection of our instrument. The potential flux divergence from the reaction of O₃ with NO is also below the instrument flux limit of detection as discussed in section 3.6. However, over terrestrial surfaces where NO₂ emissions can be large, we expect this instrument would be well suited for measuring NO₂ flux. Following Equation 1 in Bariteau et al., (2010), we calculate an expected flux LOD of 4.3×10^9 molecules cm s⁻² s⁻¹ (1.6 pptv m s⁻¹) for an NO₂ mixing ratio of 1 ppbv and a friction velocity of 0.2 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 O₃ and NO₂ detection from this instrument (Fig. 13). Highly localized NO emissions were observed as the titration of O₃ and prompt production of NO₂. Observed total odd oxygen (O_x = O₃ + NO₂) was conserved during this titration event, where NO₂ and O₃ concentrations were determined from independent calibration factors and backgrounds. The 1:1 conversion of O_x from O₃ to NO₂ shown in Fig. 13b, validates the laboratory generated instrument calibration factors for O₃ and NO₂. The temporal agreement of the O₃ and NO₂ signals also demonstrates that both O₃ and NO₂ are transmitted through the inlet and detected with nearly identical instrument response times. 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.

585 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 $v_d(\text{O}_3)$ with the Ox-CIMS is in good agreement with prior studies of O₃ ocean-atmosphere exchange. Further optimization and characterization of the Ox-CIMS is ongoing, including efforts to validation 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

595 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.

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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 ± 1.2 ncps pptv ⁻¹	180 cps pptv ⁻¹	4.0 pptv (11s)	13 pptv	42 pptv	3.1 × 10 ⁵ ± 5.0 × 10 ⁴	0.74%	0.99
NO ₂	6.7 ± 1.0 ncps pptv ⁻¹	97 cps pptv ⁻¹	2.3 pptv (19s)	9.9 pptv	32 pptv	5.1 × 10 ⁴ ± 1 × 10 ⁴	1.1%	— — —

825 **Table 1. Summary of instrument sensitivity, precision, and accuracy for detection of O₃ and NO₂ 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 O₃ and 19 s for NO₂. The reported field comparison (R²) 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.**

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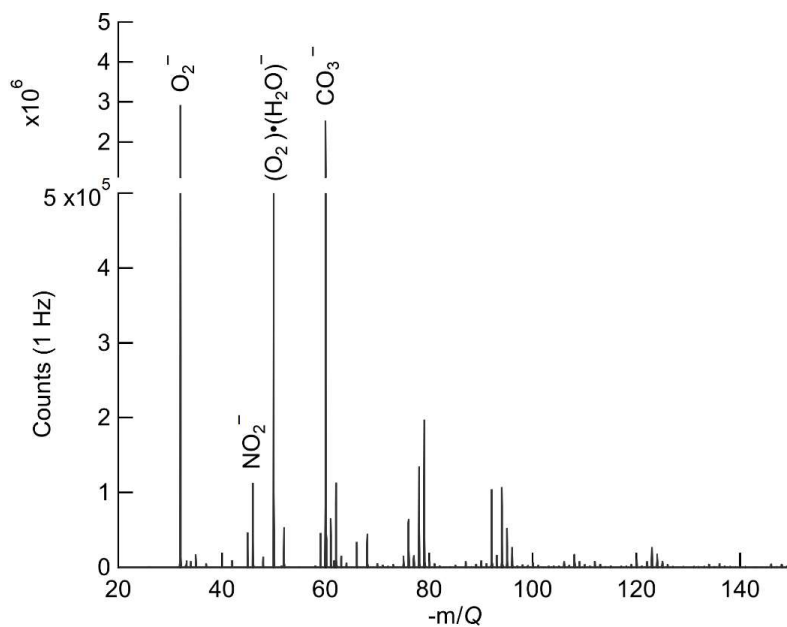


Species	Concentration Mean (ppb) & 1 σ range	5 th to 95 th percentile Concentration Range (ppbv)	v_d mean (cm s ⁻¹)	v_d 20-80% range (cm s ⁻¹)	v_d LOD 1.96 σ (cm s ⁻¹)
O ₃	38.9 ± 12.3	16.9 – 56.9	0.011	-0.0048 – 0.0249	0.0042
NO ₂	4.7 ± 5.5	0.45-16.9	-----	-----	-----

850 **Table 2. Overview of flux and concentration measurements of O₃ and NO₂ 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 NO₂ 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.**

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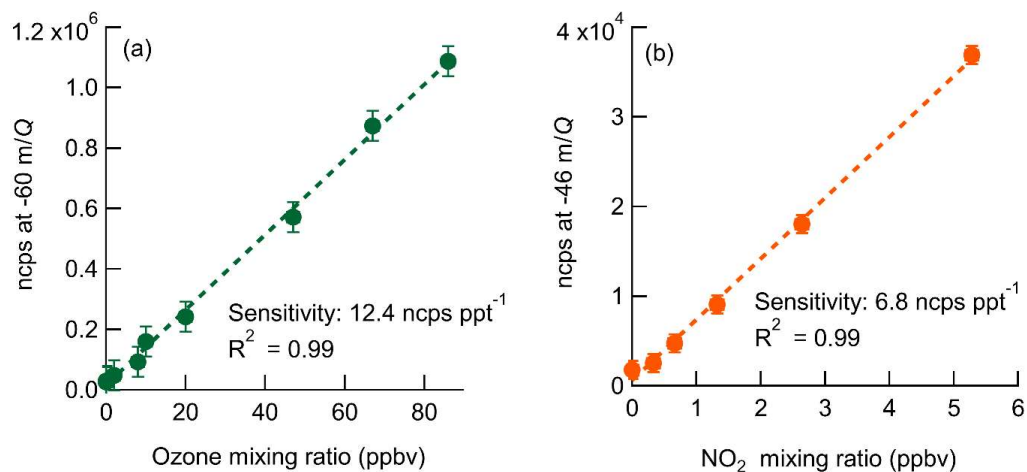
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865 **Figure 1: Ox-CIMS mass spectra collected at 1 Hz and mass resolution of 950 $M/\Delta M$ (at $-60 m/Q$), with major peaks highlighted. O_2^- and $O_2(H_2O)^-$ at $-32 m/Q$ and $-50 m/Q$ respectively are the two observed forms of the reagent ion. The detected ozone product (CO_3^- , $-60 m/Q$) is of comparable magnitude to the O_2^- reagent ion during ambient sampling. NO_2 is detected as the charge transfer product NO_2^- at $-46 m/Q$. Masses greater than $-150 m/Q$ contribute less than 2% to the total signal and are not plotted.**

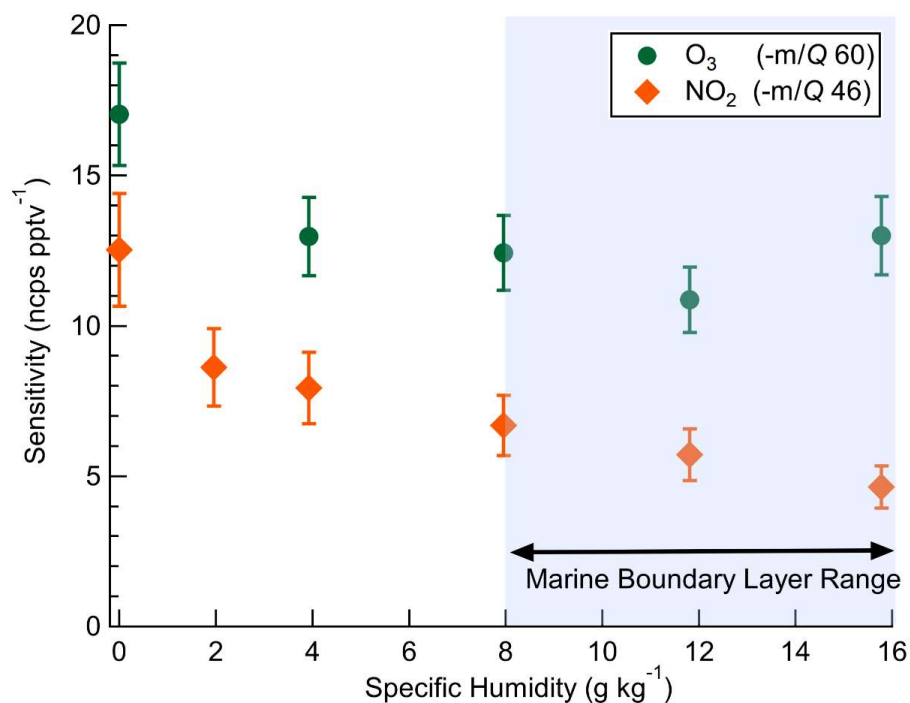
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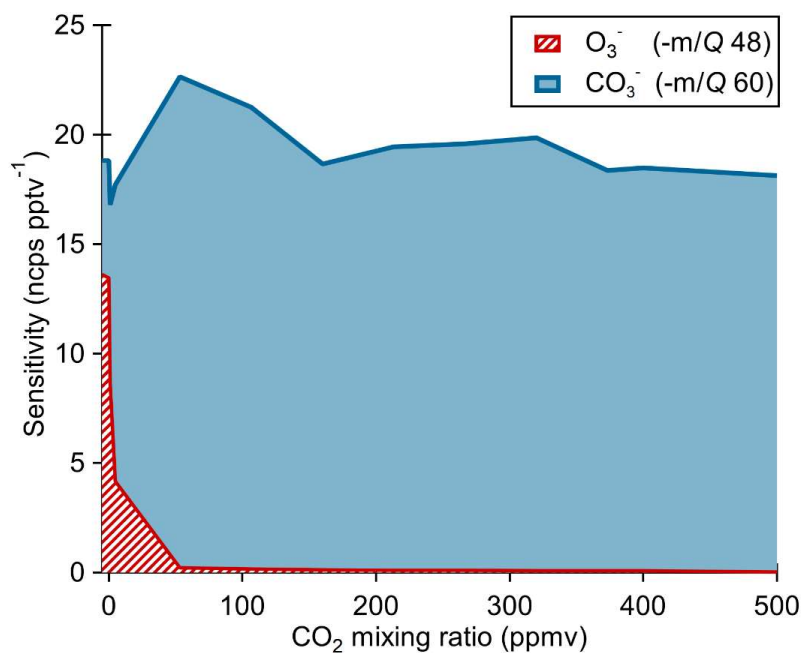
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Figure 2: Normalized calibration curves of O₃ (a) and NO₂ (right) at 8 g kg⁻¹ specific humidity (approximately 40% RH at 25 °C). Ozone is detected as CO₃⁻ at -60 m/Q. NO₂ is detected as the charge transfer product (NO₂⁻) at -46 m/Q. Error bars are the standard deviation in normalized count rate for each measurement point.



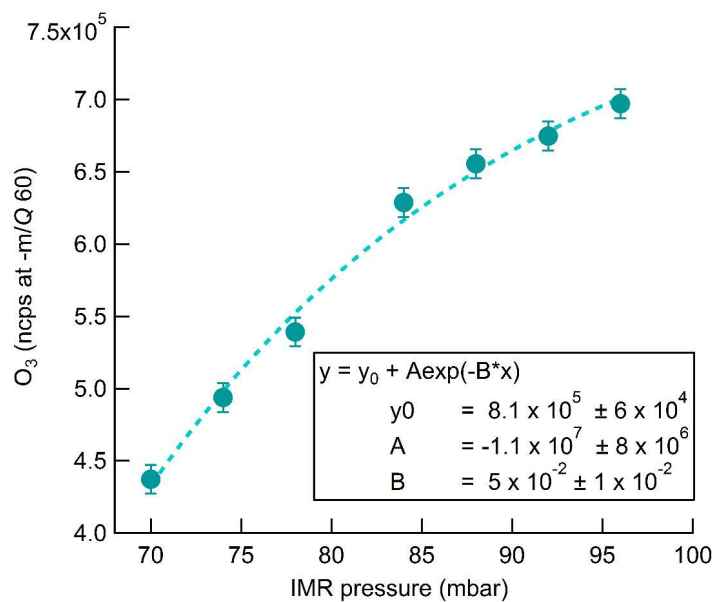
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Figure 3: Dependence of O₃ and NO₂ sensitivities on specific humidity. Error bars indicate standard deviation of triplicate calibration curves. The blue shaded region from SH 8–16 g kg⁻¹ is the approximate typical range of specific humidity in the mid-latitude marine boundary layer.

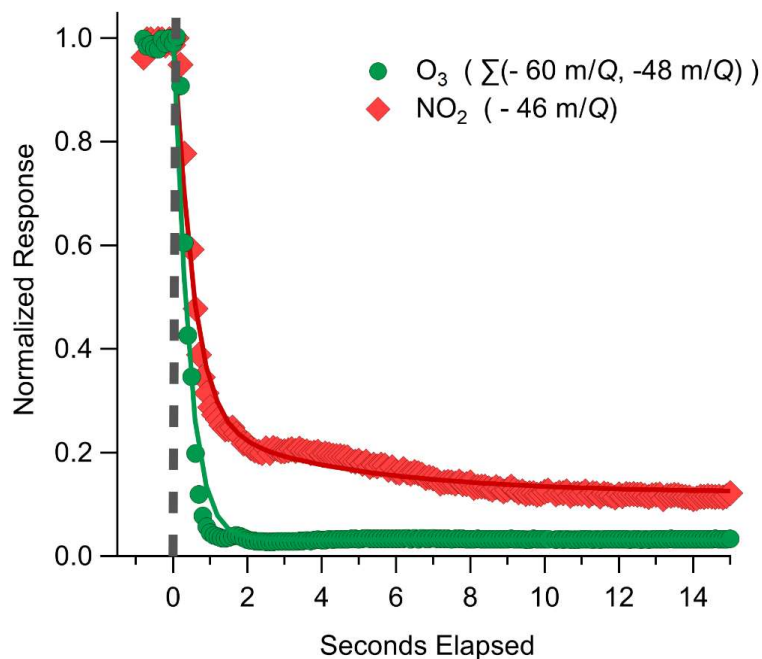


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Figure 4: Ox-CIMS cumulative sensitivity to O₃ detected either directly as O₃⁻ or as CO₃⁻ as a function of CO₂ mixing ratio. The sum of sensitivity as O₃⁻ and CO₃⁻ shows that total sensitivity to O₃ is conserved as the product distribution shifts with CO₂ mixing ratio. Greater than 99% of O₃ is observed as CO₃⁻ at CO₂ mixing ratios greater than 60 ppmv.

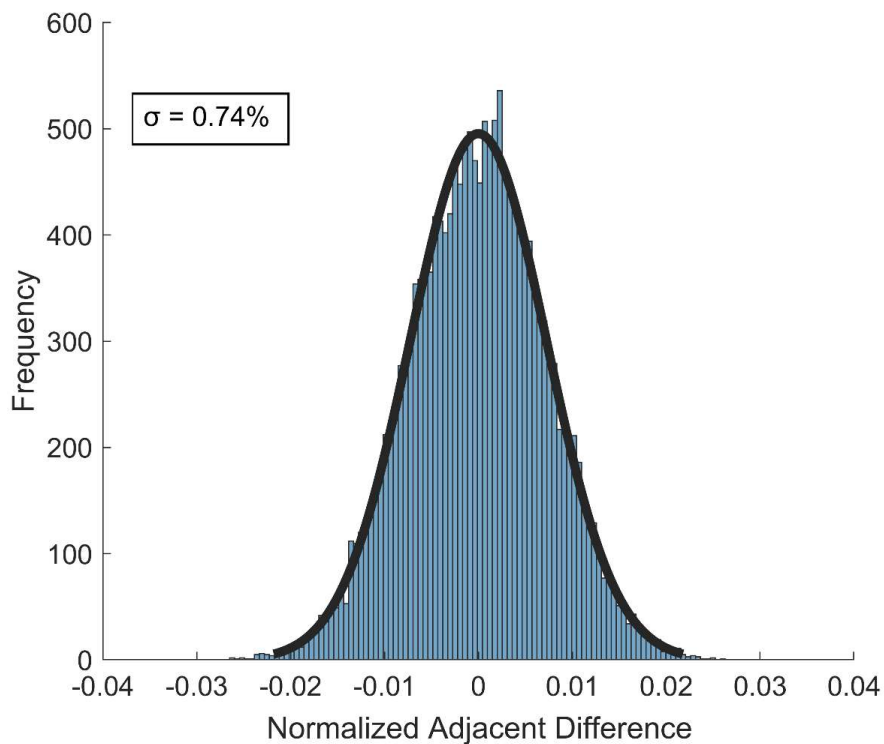


895 Figure 5. Normalized count rate of CO_3^- (-60 m/Q) ozone detection product as a function of pressure in the IMR during sampling of a constant 35 ppbv O_3 source. The exponential fit of the data is shown by the dashed line. Fit parameters are included to allow for calculation of potential sensitivity improvements with further increase in IMR pressure.

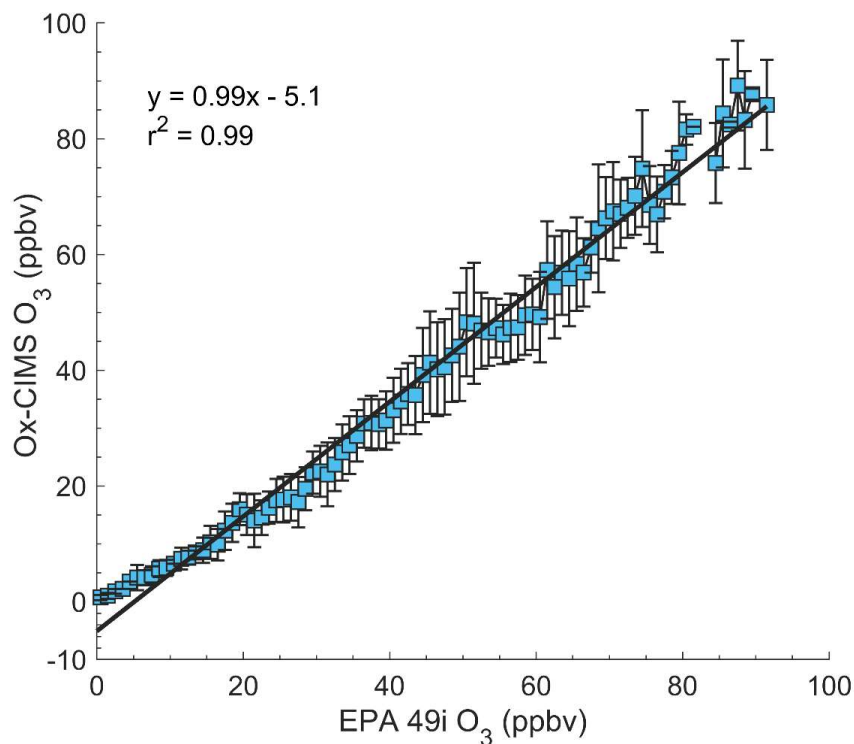


900 Figure 6: Representative instrument backgrounding determination for O₃ and NO₂ where the inlet was rapidly switched from ambient sampling to an overflow with dry UHP N₂ indicated by the grey dashed line. Response is fit to a bi-exponential decay, plotted as solid lines, where the initial rapid decay (τ_1) is attributed to gas evacuation of the inlet line and the second slower decay (τ_2) is attributed to equilibration with the inlet walls. Best fit estimates for τ_1 of O₃ and NO₂ were from 0.7 to 1.2 seconds. τ_2 for O₃ was negligible at 0.3 s indicating O₃ has minimal interactions with the walls. τ_2 for NO₂ was determined to be 3.2 s.

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910 **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 1 σ value of the distribution gives an upper limit of instrument precision of 0.74%.



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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.

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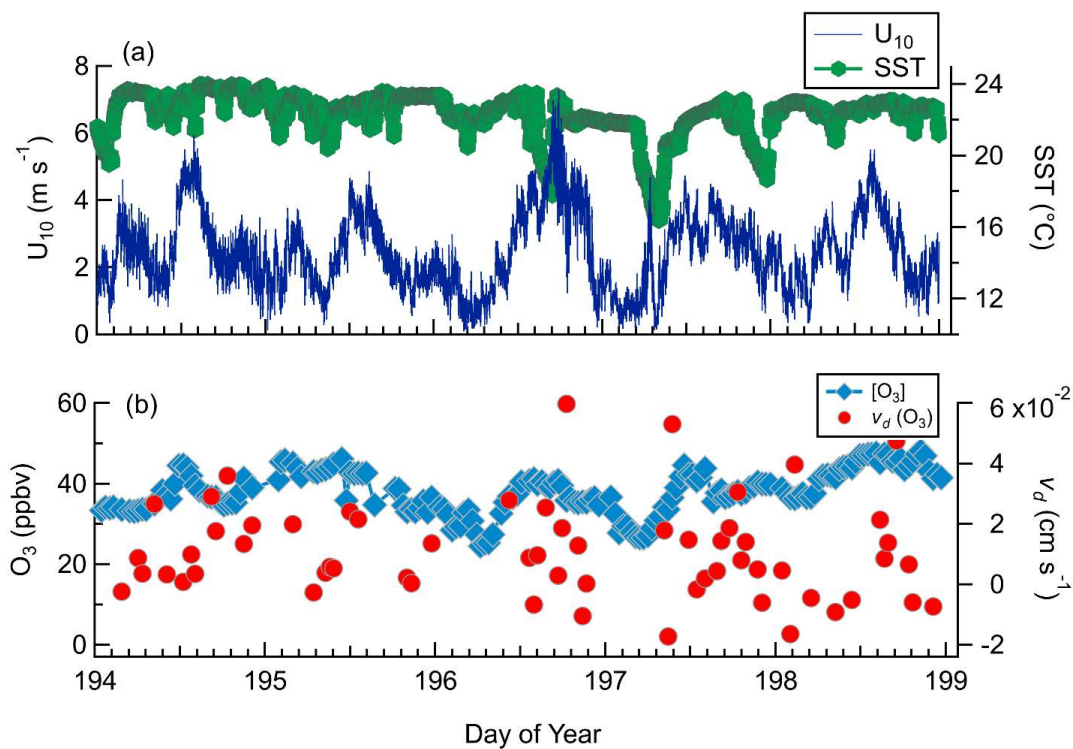
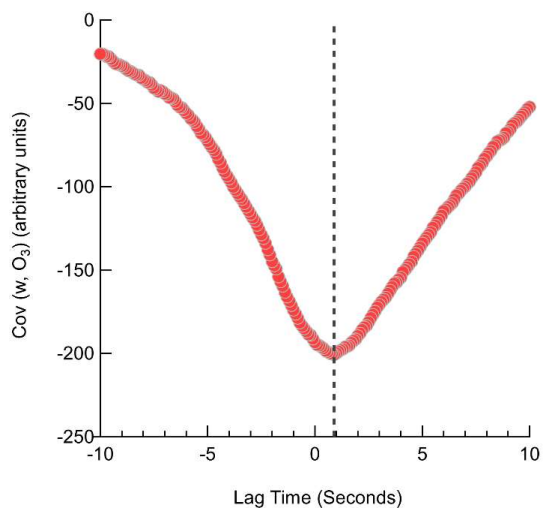


Figure 9: Observed meteorology and O_3 mixing ratio and deposition velocities for DOY 194-199 from Scripps Pier (a) Horizontal wind speed (U_{10}) and sea-surface temperature (SST). (b) O_3 mixing ratios and $v_d(\text{O}_3)$.

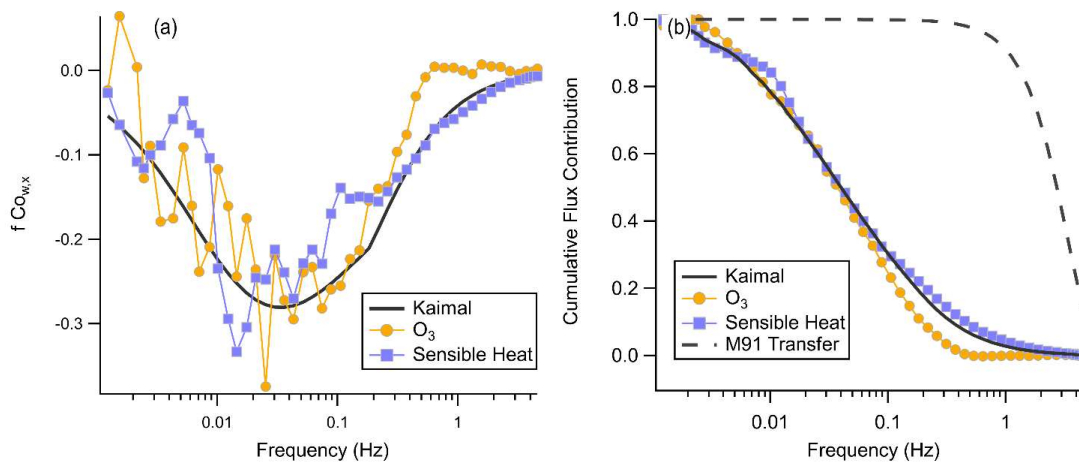


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Figure 10: Lag time determination for an individual 27-minute O₃ flux averaging period. The lag time for this flux period determined from the maximum of the covariance to be 0.9 seconds which compares reasonably with the volumetric evacuation time of the inlet of 1.7 to 2.1 seconds.

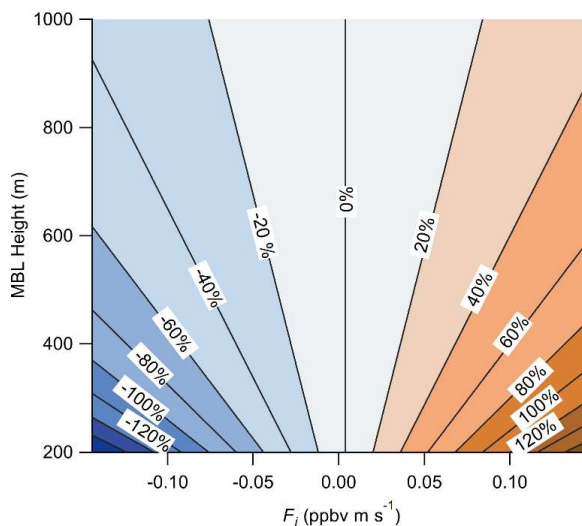
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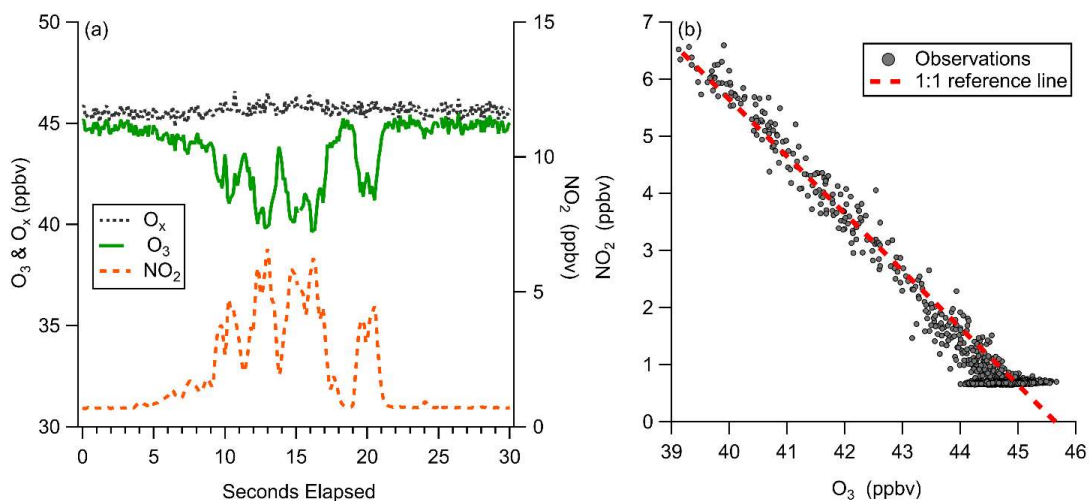
940 **Figure 11.** (a) Mean binned frequency weighted cospectra O_3 and sensible heat flux with vertical wind from the average of two consecutive flux periods from 14:10 – 15:20 local time on July 20th. The Kaimal trace is the idealized cospectra Kaimal et al. (1972) for mean windspeed of 4.4 m s^{-1} 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).

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950 **Figure 12.** Calculated percent error in the measured O_3 surface flux due to entrainment from the free troposphere as a function of the MBL height and the entrainment flux (F_i). 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 $-4.4 \times 10^{-3} \text{ ppbv m s}^{-1}$.

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960 **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 O_x (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 O_x at 10 Hz during a NO titration event.**

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