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Tides, Winds, and Reactive Halogens
A Study of Multiphase Chemistry in the Marine Boundary Layer

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Abstract

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Reactive halogens in the atmosphere (inorganic compounds containing chlorine, bromine, and/or iodine) have the ability to catalytically destroy ozone (O_3) as well as react with NO_x ($= NO + NO_2$), influencing concentrations and ratios of important tropospheric pollutants. They can also react with and change the ratio of OH and HO_2 ($= HO_x$), altering the oxidative capacity of the atmosphere. Furthermore, heterogeneous reactions involving halogenated species can change the chemical composition of particulates, especially for sea-salt aerosols (SSAs). Reactive bromine (Br_y) specifically is known to have a chemical mechanism unique from that of chlorine and iodine, and is more efficient in the catalytic destruction of ozone on a per-molecule basis compared to chlorine. There are generally fewer in-situ observations of Br_y species because they are globally expected to be present at much lower concentrations compared to reactive chlorine. In this work we present a new transverse Ion-Molecule reaction Region, the so-called "t-IMR", for use with a Time-of-Flight Chemical Ionization Mass Spectrometer (ToF-CIMS). The t-IMR samples ambient air at a laminar high volume flow (at a rate of 10 L/min), and demonstrates a reduction in artificial signals/background from wall effects by multiple orders of magnitude across compound volatilities compared to previous low-pressure designs. The t-IMR utilizes an applied electric potential to accelerate ions and subsequent clusters across the IMR cavity, the strength of which is optimized to retain both high instrument sensitivity and total ion flux to the mass spectrometer. The t-IMR CIMS is calibrated directly to obtain sensitivity values for Br_2 and (experimentally) for HOBr, the results of which confirm the use of theoretical ion cluster binding enthalpies to generate sensitivities for other Br_y components. A dynamic water-vapor-dependent sensitivity for Br_2 is also developed and applied. Five reactive bromine components are observed at the Tudor Hill Marine Atmospheric Observatory (THMAO) located in Bermuda as part of

the Bermuda boundary Layer Experiment on the Atmospheric Chemistry of Halogens (BLEACH) campaign, including Br_2 , BrCl , BrO , HOBr , and for the first time to our knowledge, BrONO_2 . Local air masses originating from over the ocean, as well as those influenced by anthropogenic activity and pollution from the island of Bermuda, provide multiple environments in which to investigate Br_y concentrations and partitioning. HOBr and BrONO_2 are observed above detection limits almost exclusively during the day, evidencing the currently understood formation mechanisms for both which require active photochemistry and the presence of BrO . BrONO_2 shows a clear dependence on NO_2 concentrations, and a diurnal profile shape that qualitatively aligns with previous modeling studies. Comparison with the GEOS-Chem model output (with reactive halogen chemistry and SSA debromination mechanisms included) shows that the detailed atmospheric chemistry model over-predicts levels of the five observed Br_y constituents, most of which by an order of magnitude or higher. The model is in much better agreement with observed bulk particulate sodium, bromine, and chlorine concentrations, suggesting that the SSA mass concentrations in the model are likely not the source of the discrepancy, but rather partitioning among reactive bromine. The relationship of total measured reactive bromine ($\text{Br}_{y*} = 2\text{Br}_2 + \text{BrCl} + \text{BrO} + \text{HOBr} + \text{BrONO}_2$) with local wind speed, tide height, and other measurements at THMAO is examined. The magnitude of the most recent low tide height and wind speed are found to be independently significant predictors of Br_{y*} concentrations. This implies a local coastal source of reactive bromine at THMAO in addition to that expected from SSAs.

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Chapter 1: Introduction

1.1 Instrument Motivation: IMR Design

The development of the Time-of-Flight Chemical Ionization Mass Spectrometer (ToF CIMS) has made possible online, continuous in-situ observations of numerous trace gases in the atmosphere. Compounds detected using this technique have wide-ranging impacts on the global climate system, air quality, and human health. Recent and ongoing innovations to this technique continue to provide improvements for both temporal and mass spectral resolution, allowing for more detailed analyses of airborne chemical processes.[1][2][3] Chemical ionization using a variety of reagent schemes allows for more sensitive measurements for certain classes of compounds, as well as "softer" ionization, meaning that sample molecules remain intact after clustering with a charged ion. This reduces interference and uncertainty in the identification of analyte molecules, increasing the assurance that what is detected by the instrument reflects ambient (or laboratory, etc) conditions.[4][5]

The Ion-Molecule reaction Region (IMR) is where neutral analytes receive a charge from charge transfer, ion-neutral adduct formation, etc. The design and sampling regime of an IMR has a large impact on the sensitivity and ability of the CIMS technique to measure specific classes of chemicals, as well as the total ion-flux to the mass spectrometer and limits of detection (LOD).[6][7][8] IMR setups used in previous studies typically operate at pressures lower than that of the atmosphere, allowing for larger apertures for ion flows into the MS, lower collision frequency between sample molecules, and lower water vapor concentrations in the instrument. Instrument sensitivities to many compounds are known to be heavily dependent on the amount of water vapor in the instrument/IMR, especially for iodide reagent ion (I^-) chemistry, used for all studies reported herein.[9][10] However, reducing the pressure from ambient dilutes sample molecules by orders of magnitude, reducing the collision frequency between analytes and ions as well.[11][12] This reduces sensitivity in addition to reducing the likelihood of detecting very low concentration species, i.e. less than 1 part per trillion (ppt).

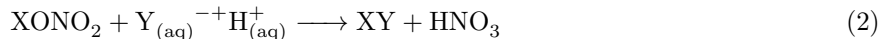
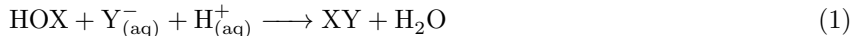
Low pressure designs can also introduce turbulent mixing and increased instrument surface interactions

by way of air mass expansion through an orifice. Sample molecules interacting with instrument surfaces create artificial signals by reacting with other species potentially present, e.g. particles settled onto the walls of the IMR, creating products that are not present in the actual sample (ambient or otherwise). Molecules can also deposit onto surfaces without reacting, and be re-emitted and detected at a later time, creating or adding to a signal of a compound sampled earlier but not present at the time of detection. Wall effects therefore have the potential to create artificial signals both in molecular composition and in time.[13][14][15] A large goal of IMR innovation is to reduce this effect. Operating an IMR with laminar sample flow can reduce turbulent mixing and likelihood of surface interactions.

1.2 Reactive Bromine Importance

Reactive halogens, referring to molecules containing chlorine (Cl), bromine (Br) and/or iodine (I) are known to play an important role in atmospheric chemistry through many channels. They can substantially affect the oxidation capacity of the atmosphere by way of catalytic ozone destruction cycles, in addition to reacting with HO_x ($= \text{OH} + \text{HO}_2$), changing concentrations and the ratio of its constituents.[16][17][18][19] Halogens can also react with NO_x ($= \text{NO} + \text{NO}_2$), NO_3 , and N_2O_5 , impacting reactive nitrogen concentrations and influencing their potential long-range transport.[20][21][22] Reactive halogens also influence the composition and even formation of atmospheric aerosols, an important yet uncertain climate forcer. Inorganic reactive bromine, Br_y ($= \text{Br} + 2\text{Br}_2 + \text{HOBr} + \text{BrO} + \text{HBr} + \text{BrONO}_2 + \text{BrNO}_2 + \text{BrCl} + \text{IBr}$), is particularly important among halogen species. Bromine species exist globally at lower concentrations than reactive chlorine, making them more difficult to detect in-situ, yet bromine is more efficient at depleting ozone on a per-molecule basis compared to chlorine and has been observed to coincide with ozone depletion events in the arctic. Br_y not only has a unique chemical mechanism compared to chlorine and iodine, but has also been reported to react with and influence the cycles of both mercury (Hg) and dimethyl-sulfide (DMS).[23][24]

The largest source of reactive bromine globally is sea-salt aerosols (SSAs), while the largest sink is also uptake onto aerosol surfaces.[25][26] Br_y species are liberated from halogen-containing particles by way of heterogeneous reactions involving other gas-phase reactive halogens, producing bromine containing gaseous products. Examples of such reaction include the uptake of hypohalous acids and halogen nitrates:



where $\text{X}_Y = \text{Cl}, \text{Br}, \text{I}$. If X and/or Y are Br, then the product of either reaction is a reactive bromine

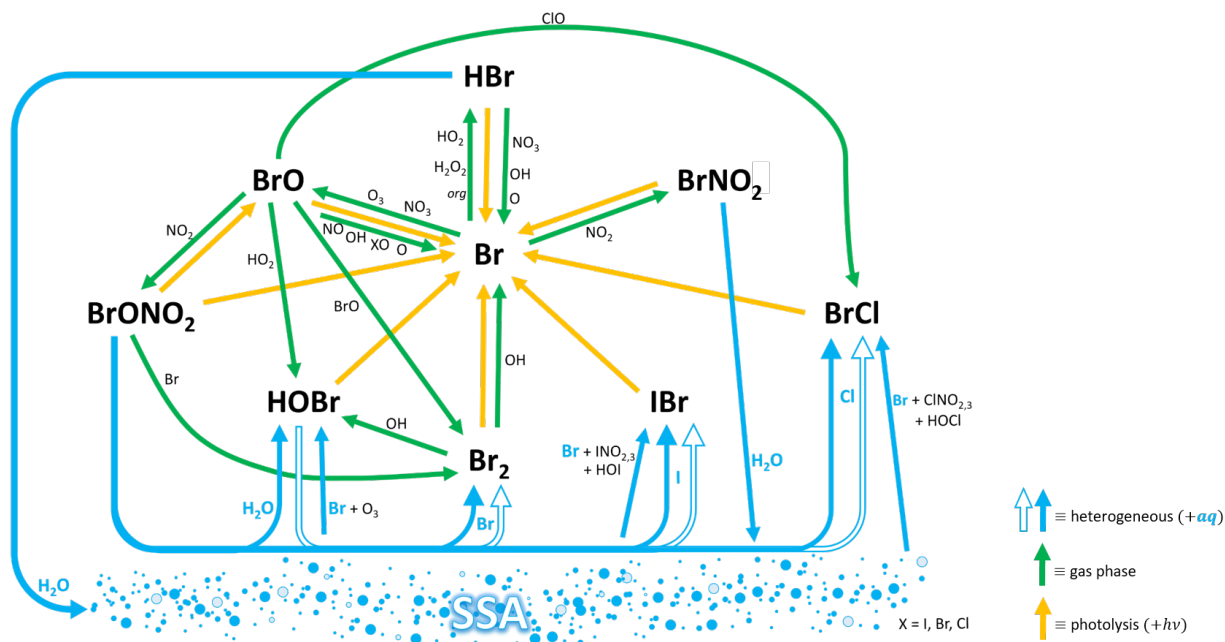


Figure 1.1: Schematic of reactive bromine chemistry. Green arrows show gas phase reactions, blue arrows heterogeneous reactions, and yellow arrows for photolysis. Open blue arrows are the same as closed, used to distinguished heterogeneous reactions with HOBr

compound. Because SSAs are the main source, sink, and provide a reactive shift for Br_y , regions with high levels of sea spray and elevated SSA concentrations, i.e. the Marine Boundary Layer (MBL), are key to conduct atmospheric measurements to improve our understanding of this important chemical mechanism.

1.3 Reactive Bromine Chemistry

Shown in figure 1.1 is a summary schematic of reactive bromine chemistry. Arrows point from reactants to products, with other reactants in smaller fonts along arrows. Green represents gas phase reactions, blue arrows denote heterogeneous reactions (with aqueous reactants highlighted in blue), and yellow shows photolysis. The open blue arrows are used to denote heterogeneous reactions with HOBr to distinguish from those with BrONO_2 and others. This figure shows the inter-dependent web of reactions dependent on multiple environmental factors, including availability of reactants such as NO_x . All other Br_y components can photolyze to form free atomic bromine, Br, a reactant in the ozone destruction mechanism:



This key step produce bromine monoxide, BrO, which has a relatively short photolifetime and can react to form multiple other Br_y components, including the immediate reformation of free atomic bromine:



The net result of some of these pathways can be the destruction of ozone and the production of atomic bromine, restarting the cycle. Though in some cases, ozone can be produced as a byproduct, making it a "null" cycle where O₃ is not consumed. These photolysis, gas-phase, and heterogeneous reactions importantly occur at different rates.[27][28] Thus, the branching of reactive bromine along different pathways dictates the rate at which Br is formed, ozone can be destroyed, HO_x ratios can be altered, etc. Pollution-driven effects on Br_y chemistry have also been observed.[29][30][31][32] It is therefore critical to obtain observations in multiple environments within the MBL, including daytime, nighttime, pristine marine, pollution-influenced, and combinations of such conditions. Observations of reactive bromine species remain relatively sparse, with measurements typically in the arctic showing elevated concentrations of BrO and Br₂. Bromine nitrate, BrONO₂, to our knowledge has been studied only using model simulations thus far and has not been observed in situ.

Sea-salt aerosols, the largest source of Br_y in the atmosphere, form over the oceans via wave breaking, bubble bursting, and formations of jets.[33][34] SSA concentrations have been shown to correlate with higher wind speeds, as well as wave height and Reynolds number.[35][36][37][38] Aerosol size distributions are dependent on a variety of factors, including humidity, where hygroscopic growth of salt particles can greatly increase SSA surface concentrations.[39] This modulates reactive uptake of Br_y species, as the heterogeneous reaction rates depend on both particle radius and surface area concentration. Reactive uptake coefficients (γ) for reactive bromine remain uncertain despite have a large effect on heterogeneous recycling rates utilized in atmospheric chemistry models. Previous studies have demonstrated a dependence of γ, specifically for reactions with HOBr, to be dependent on both ambient relative humidity and particle pH.[40][41]

1.4 Organic Bromine and Coastal Influences

Organic iodine and bromine-containing compounds have been known to be produced by macroalgae present in the oceans, representing a substantial source of Br and I in seawater.[42][43] So called very short lived bromocarbons emitted from these organisms have the capability to contribute to Br_y in the MBL via oxidation reactions and photolysis.[44][18] These species include CHBr_3 , CH_2Br_2 , CH_2IBr , and CH_3Br , which photolyze on much slower timescales compared to Br_y components. The global distribution of total macroalgae and specific species capable of emitting bromocarbons remains uncertain. However, correlations of reactive iodine (I_y) as well as iodocarbons with low tide have been observed.[45][46] Direct emission of I_2 from exposed macroalgae beds has been attributed as the source of I_y , including the interhalogen species IBr and ICl during low tide.[47] This presents the possibility for a hyper-local source of Br_y from macroalgae at coastal observation sites by way of bromocarbon emission and subsequent reaction, as well as direct I_y emissions and heterogeneous cycling to produce reactive bromine species.

1.5 Dissertation Summary

This dissertation presents a custom-built atmospheric pressure IMR, the "t-IMR", which demonstrates significant improvements in reducing artificial signal from wall effects, producing relatively very low limits of detection useful for observing low concentration (sub-ppt) compounds in the atmosphere. The IMR is optimized to retain large ion-fluxes to the MS detector, while preserving as high of sensitivity as possible. Water vapor dependence and sensitivities for compounds not available for direct calibration are accounted for in detail. Reactive bromine species are observed in the sub-tropical MBL at a coastal site in Bermuda as part of the Bermuda boundary Layer Experiment on the Atmospheric Chemistry of Halogens (BLEACH) field campaign. Local marine, pollution, and other environmental influences are taken into account while examining reactive bromine partitioning based on observed concentrations. Observations are compared with the GEOS-Chem global chemistry model to assess current understanding of the Br_y mechanism

1.6 Publication Plans

Chapter 2 presenting the t-IMR is under review from coauthors and will be submitted for publication as soon as possible. We plan to consolidate and submit the reactive bromine observations presented in chapters 3 and 4 for publication in summer 2025. We also plan to submit the sections in chapter 4 regarding wind speed and tidal relationships with Br_y for publication in summer 2025.

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Chapter 2: Laboratory and Field Characterization of an Atmospheric Pressure Transverse Chemical Ionization Ion-Molecule reaction Region

Abstract

We introduce a custom-built, field-deployable, atmospheric pressure Ion-Molecule reaction Region (IMR) for use with Chemical Ionization Mass Spectrometry (CIMS), the so-called "t-IMR". The design is described in quantitative detail and shows significant improvements in potential measurement interference compared to other IMR configurations, particularly those operating at low pressure. The relatively large laminar flow and inner chamber diameter reduces the probability of sampled air and ion clusters interacting with the Teflon surfaces of the IMR before being detected by Time-of-Flight (ToF) mass spectrometry. This also leads to a substantial reduction in wall effects and artificial background signals for even low volatility organic products, exhibited by alpha-pinene ozonolysis. An electric field is induced perpendicular to flow in the t-IMR to accelerate ions and consequent charged sample clusters to the MS interface. The strength of this field is modulated and optimized to simultaneously maximize total ion flux and instrument sensitivity. A sheath flow apparatus is introduced to provide small N_2 flows counter to ion and sample cluster flow into the MS to reduce the likelihood of particulate buildup and clogs to the pinhole separating the IMR from the MS, ensuring uninterrupted sampling for extended periods of time. Finally, we demonstrate the capability of the t-IMR to be deployed to the field to measure down to sub-ppt level ambient concentrations of important trace gases including reactive bromine at a ground-based site in the marine boundary layer. We find that the t-IMR design considerably reduces artificial signals from surface contact and wall effects, and improves detection of very low concentration species in the ambient atmosphere. Future studies are recommended to evaluate the extent to which humidity effects instrument sensitivity to key compounds for the atmospheric pressure t-IMR setup.

2.1 Introduction

Multiple trace gas species present in the atmosphere at concentrations on the order of parts per trillion (ppt) and below are known to have relatively large impacts on atmospheric composition, the climate system, air quality, and human health. Chemical Ionization Mass Spectrometry (CIMS) has allowed for online and in situ measurements of many such trace gases with high temporal resolution and molecular specificity when coupled to a time-of-flight or orbitrap mass spectrometer having sufficient resolving power and mass accuracy.[1] Chemical ionization has the advantage of preserving the integrity of the molecules being sampled. The softer the ionization process, i.e. the lower the net energy imparted to the analyte upon ionization, the less interference to analyte identification and quantification from chemical or physical processes during sampling. Adduct ionization, where a specific ion such as iodide (I^- , used in all studies herein), nitrate, ammonium, etc, is used to form an ion-molecule cluster, has been shown to be especially soft compared to charge (proton) transfer, direct photoionization, or electron impact.[2][3] A key component of CIMS instruments is the Ion-Molecule reaction Region (IMR), where neutral analyte molecules obtain a charge (positive or negative) via charge transfer, reactive charge transfer, or ion-neutral adduct formation. The resulting analyte ions or clusters can then be guided by electric fields and fluid dynamics inside the mass spectrometer (MS).

The IMR design significantly impacts the sensitivity and selectivity of a CIMS to certain classes of compounds and/or total ion flux, both of which determine the limits of detection (LOD) at which atmospheric components may be measured.[4][5][6][7][8] Many previous IMR designs involving the I^- reagent ion utilize a low pressure chamber (< 0.1 atm). The low pressure has practical and analytical benefits, such as allowing larger apertures for ions to enter the MS, reduced ion-molecule interaction times to minimize secondary ion chemistry without needing electric fields or high flows, and lower absolute water vapor concentrations, as humidity-dependent sensitivities have been reported for multiple compounds across CIMS measurements.[9][10][11][12] However, by reducing the pressure of the IMR dilutes sample molecular number concentration by up to several orders of magnitude.[13] This leads to a lower collision frequency between analytes and reagent ions for a given reaction time and thus lower ultimate sensitivity. In a low pressure IMR, it has been shown that even a relatively small increase in operating pressure can increase sensitivity.[14] For already low concentration species, these issues could prevent in-situ measurements of sub-ppt level compounds.[15] Moreover, the expansion upon sampling through an orifice from approximately 1 atm to <0.1 atm coupled with physical constraints to keep interaction timescales short, leads to turbulent mixing and enhanced wall interactions.

When considering IMR design, the two main objectives to consider include first generating a sufficient and stable stream of reagent ions to produce signal for analyte species. And of equal importance, the

verification that such signals are a true representation of the gaseous sample, ambient or otherwise. This involves disturbing the sample gas as little as possible before it enters the CIMS. Multiple challenges arise in the pursuit of achieving this goal while maintaining a sufficient number of ion collisions for continuous measurement. One such problem is chemical reactions occurring in and on the surfaces of the IMR, which would alter the molecules before detection, thereby creating an artificial chemical signal not present in the actual atmosphere being sampled. One way to reduce this effect is to move the sample through the IMR as quickly as possible to reduce the likelihood of interaction with other molecules and/or surfaces, while ensuring sufficient ion intrusion. The residence time, or average time that an air mass spends in the IMR chamber before entering the CIMS, is controlled mostly by the pumping speed from an external air pump. Another consideration beyond flow speed is turbulent mixing, which is dependent on the pumping scheme and angle at which air enters the CIMS. Turbulence can decrease the likelihood of ion collisions and interfere with total detected signal, if not eliminate signals completely. Designing an IMR such that the inlet flows are as laminar as possible helps to eliminate small eddy formations and turbulence which increase molecular interactions and disturb reagent flows.[16] There are also so-called IMR "wall effects", which refer to a situation where ambient molecules are deposited onto or absorbed into the surface of the IMR to potentially be evaporated and reintroduced into sample flow at a later time. This not only causes an artificial depletion in a signal at the time of sampling, but also can create an enhancement in detection of that particular compound later, both of which misinterpret current ambient conditions and interfere with precise time of day measurements required to understand trace gas chemistry.[17] Advancements in IMR design have been researched in pursuit of rectifying this commonly observed effect.[18][19] Choice of IMR surface material and experimental verification of wall effects are thus crucial to the reliability of resultant chemical signals.

This work introduces and demonstrates the capabilities of a field-deployable atmospheric-pressure "transverse IMR" using iodide reagent ions generated using a vacuum ultraviolet (VUV) lamp. This updated design is based off of a previous transverse IMR setup from Zhao et al,[10] constructed with the intent of minimizing these common problems including turbulent mixing and wall interactions which lead to artificial and/or depleted CIMS signals. We describe in detail its design and evaluate performance based both on metrics determined in laboratory experiments as well as ambient measurements in the field.

2.2 CIMS and IMR Description

We describe a Chemical Ionization inlet coupled to a Time of Flight Mass Spectrometer (i.e. a ToF-CIMS). We utilize a ToFwerk AG high resolution ToF-MS (model L-ToF). The design and operation of the ToF-MS and general coupling to chemical ionization regions has been described previously.[20] [2][17][21] Briefly: analyte

ions and remaining reagent ions are guided through a series of differentially pumped vacuum chambers, by segmented quadrupoles, one in the first stage downstream of the IMR with typical operating pressure of 2 mbar, and the other in the second pumping stage with pressures on the order of $1\text{e-}3$ mbar. Ions are then extracted into the ToF region (pressures typically on the order of $1\text{e-}7$ mbar) where they receive a pulse of energy and fly along a U-shaped path to a Micro Channel Plate (MCP) detector. In this process, the sample molecules are separated by mass due to differences in flight time. From these flight times, exact masses are calculated and binned resulting in the spectrum of ion counts versus mass-to-charge ratios for further analysis. For all data presented in this study, the default timescale of collected spectra is 1 Hz. Integration of peaks in each mass spectrum results in timeseries of all identified species, reported in default units of counts from the MCP in the ToF region. In order to convert detector counts to the relevant atmospheric concentration, a sensitivity value must be determined for every identified species.[6] Sensitivities are typically quantified in units of counts/ppt and are preferably determined by direct calibration, i.e. introducing a known concentration of a given species into the IMR and recording the corresponding instrument response for a set period of time such that the signal is stable and reproducible.

Shown in Figure 2.1 is a schematic of our new transverse IMR, henceforth referred to as the "t-IMR", where the inlet is comprised of a 1 inch (2.54 cm) outer-diameter (OD) TeflonTM tube with 1/16 inch (0.16 cm) wall thickness housed in an 20.3 W x 7.6 H x 3.8 D cm aluminum block, which is secured to the ToF-MS. The distance from the upstream edge of the 1" OD tube (i.e. the entrance to the IMR region) to the reagent intersection/MS ports at the center of the aluminum block housing is 32.4 cm, and the total length of the IMR tube is approximately 47 cm. The aluminum block is used mainly for stability, port alignment, and ability to be electrically grounded. Thus, when mentioning to the t-IMR in this work, we are referring to the 1" OD teflon inlet tube acting as the ion-molecule reaction chamber, which is noted above as longer than the block housing it. This design brings ambient air into the ionization region continuously such that the sampled air flow does not experience any steps in diameter, corners, or other wall materials until it is exhausted beyond the aluminum block and capillary MS entrance area. The 1" OD Teflon tube extends upstream of the housing to ensure development of laminar flow and sampling outside of the overall instrument boundary layer. Figure 2.1 highlights the laminar sample flow of 10 L/min (blue arrow) intersected by reagent ions (red arrow) which are accelerated by the induced electric field created by the applied potential between the ion source exit and the grounded capillary entrance to the ToF-MS, where newly formed analyte ions enter the MS, indicated by the purple arrow. Iodide reagent ions are generated via a gaseous mixture of methyl iodide (CH_3I) and toluene ($\text{C}_6\text{H}_5\text{CH}_3$) carried by ultra-high purity nitrogen gas ($\text{UHP N}_2 \geq 99.999\%$) at a combined standard flow rate of 1.5 liters per minute (LPM). This gas mixture is then introduced into the cavity of an ionization device, ultimately producing I^- reagent ions introduced into the t-IMR at the point

of the applied electric potential, indicated in orange in Figure 2.1.

Shown in the gold-bordered inset of figure 2.1 is a cross-sectional view of the t-IMR, where the sample flow direction points out of the page, reagent ion flow is shown in red, the sample + ion flow into the CIMS in purple, and electric potential application indicated with orange dots (with ground in black), analogous to the rest of the schematic. The critical orifice used to separate the IMR from the small segmented quadrupole (SSQ) region (the MS entrance) is a small cone that is 10 mm in length which extends approximately 2.5 mm into the t-IMR chamber, and has a pinhole of diameter of 0.20 mm where air enters the capillary. The internal cavity downstream side of the orifice is also conically shaped, the diameter expanding to 3.7 mm toward the SSQ region from the pinhole interface. The orifice, highlighted in purple in the inset, is designed specifically to maintain the pressure difference between the IMR at a somewhat dynamic atmospheric pressure on the order of ~ 1000 mbar and the SSQ operating at 2 mbar. Given the small size of this capillary separating the CIMS from the IMR, buildup and/or clogging due to particulates can be a concern depending on operating conditions. This is addressed via the addition of a sheath flow apparatus implemented to provide a small concentric flow of UHP nitrogen gas around the capillary, running opposite in direction to the flow being sampled through it into the MS (shown with green arrows in the inset). This small counter-flow prevents a significant fraction of large particles from depositing onto the capillary which could lead to eventual blocking of the sample orifice. The sheath flow therefore allows for prolonged sampling periods (at least several days) uninterrupted by cleaning that would be otherwise necessary to clear blockages and prevent an interruption in the flow between the IMR and the SSQ chamber. Additionally, this sheath flow likely acts to partially dry the ion flow into the MS, leading to the evaporation of weakly bound water clusters formed when sampling high humidity air.

A diagram of the ionization setup used in all studies presented in this work, is shown in figure 2.S1 . Both the block and inlet tube contain ports for reagent ion flow generated with a VUV photo-ionization device[22], as well as a port for the critical orifice or capillary entrance between the SSQ region of the CIMS and the atmosphere/t-IMR. Use of VUV to generate iodide ions for CIMS work has been demonstrated previously by Ji et al, who report similar instrument sensitivities, reagent ion production, and resultant mass spectra to those obtained with established radioactive sources.[23] Our VUV ionizer setup uses a Heraeus PKS106 UV lamp held in custom stainless steel housing, the base of which is the cavity for ionization, including a female Swage fitting for 1/8" OD tubing (reagent flow input for this study) along with a 1/4" OD output tube (ion output) built in. The 1/8" port acts as the entrance for both the reagent and carrier gases, which here are the CH_3I + toluene and UHP N_2 , respectively. The UV lamp utilizes krypton gas to generate UV ionization light with a photon energy of 10.6 eV while requiring a DC voltage of 1.5 kV. Once in the lamp housing cavity, CH_3I is ionized by the UV radiation supplied by the lamp, aided by toluene acting as a

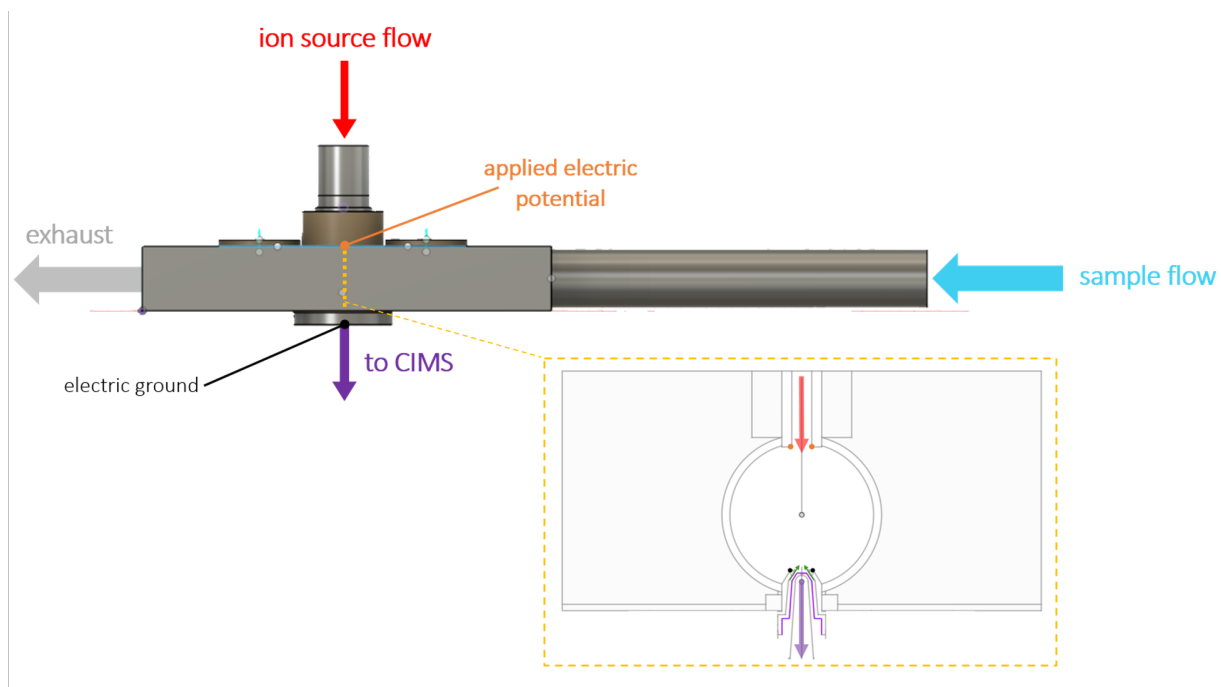


Figure 2.1: Schematic of the transverse IMR (t-IMR). A continuous 1" OD Teflon inlet held in place by stainless housing carries sample air at atmospheric pressure at a flow rate of 10 L/min where it is then intersected at 90° by a 1.5 L/min flow carrying the I^- reagent produced from a VUV ion source, which is accelerated by an electric potential toward the CIMS. The gold dashes in the housing schematic and corresponding inset show the location and a detailed cross section of the t-IMR. Reagent flow is again shown in red while sample + ion flow into the CIMS is shown in purple. For the inset the standard 10 L/min flow through the t-IMR cavity ($\text{ID} = 7/8''$) points out of the page. The critical orifice conical capillary is highlighted with purple outlining. The smaller sheath counter-flow is indicated with green arrows. Electric potential application is shown with orange points, with electric ground in black.

photosensitizer. Optimal flows for instrument operation were determined to be 1.5 LPM through the CH_3I permeation tube channel and 2 standard cubic centimeters per minute (sccm) over the head space of a vial containing a volume of 2-3 mL of toluene.

The VUV setup produces an outflow of I^- ions carried in the UHP N_2 from the VUV housing into the t-IMR chamber. The use of the VUV marks a notable difference between this design and that of Zhao et al (2017), as it does not require the use of salt solutions for ion production as the extractive electrospray ionization (EESI) method does, but rather uses a slow release permeation tube. This prolongs the potential continuous sampling of the t-IMR CIMS, as salt solutions need not be replenished for reagent production, while also avoiding potentially clogging of the capillary delivery tubes involved with EESI. Both theirs and our setups eliminate the need for radioactive sources used in many previous CIMS experiments, which can be difficult to deploy to remote field sites, as well as presenting a higher potential hazard level for operation. Though it is important to note that our VUV device may be replaced by any other ionization instrument (including a radioactive source if so desired) at the user’s discretion.

One notable effect of the specific VUV orientation in this setup is the exposure of sample air to a small amount of UV radiation, which has the potential to change sample composition as well as create O_2^- ions which can create unintended additional analyte ions. These O_2^- cluster peaks may appear at similar mass-to-charge ratios (m/Q s) and potentially complicate the identification of certain compounds clustered with I^- in the negative mode for the CIMS. This has been reported by Ji et al[23] and is diagnosed in our setup mainly by the signal of the fitted compound CO_3^- at m/Q 60 in the mass spectrum. In all laboratory experiments presented here, it is found that the mean CO_3^- signal is always less than 0.5% of the reagent signal ($\text{I}^- + \text{IH}_2\text{O}^-$), in many cases under 0.05%, and does not interfere with the identification and quantification compounds of interest. This is due to the much higher signals for iodide clusters and importantly the mass defect of I^- (separated from O_2^- clusters) easily identified with the high resolution LToF instrument. That said, it is recommended for generally cleaner spectra to reduce sample exposure to the VUV lamp, as done by Ji et al with a 90 degree bend in their reagent delivery line, which is a design element we will likely incorporate into future versions. High CO_3^- signals are typically observed when air leaks are present in the UHP N_2 reagent delivery lines, as even a minuscule amount of air can lead to an O_2 concentration similar to that of CH_3I in the UV-illuminated volume, which would likely result in O_2^- clusters present in spectra.

The t-IMR chamber is sealed against the ionizer and SSQ entrance via, press-fit O-rings and screws holding the block to the CIMS face, such that the t-IMR is only open to ambient air at its entrance and ultimately the external pump throttle to control the flow rate. The ionization and critical orifice ports are aligned for reagent flow to be perpendicular to and combine with sample flow. The standard flow rate chosen for operation of the t-IMR is 10 L/min in an effort to minimize residence time of sample molecules in the

IMR while maximizing total ion counts (TIC) detected by the CIMS, as well as maintaining laminar flow. Laminar flow is achieved given the Reynolds number (Re) calculated by treating the t-IMR as a pipe:

$$Re = \frac{4\rho_{air}V}{\pi\eta d} \quad (1)$$

where ρ_{air} is the density of air (kg m^{-3}), V is the volumetric flow through a pipe ($\text{m}^3 \text{s}^{-1}$), η is the viscosity of air (Pa s), and d is the diameter of the IMR tube (m). The calculation at the ambient temperature of 293 K yields a Reynolds number of $Re = 634$. Flow through a pipe is defined to be laminar if the Reynolds number is determined to be less than 2000 and is considered turbulent if greater than 4000.[24] So for our standard flow of 10 LPM and lower flows, the t-IMR operates within a laminar flow regime. Given this flow rate and the distance from the sample inlet to the CIMS port, the calculated average residence time of sampled molecules is 0.75 seconds.

Reagent ions are introduced orthogonal to the sample flow via both a relatively small carrier flow and a DC electric field which accelerates the ions across the higher atmospheric pressure cross-flow to the pinhole, similar to the previous design. This electric field is achieved with an electric potential bias provided via connecting an external adjustable voltage power supply to the metallic (conductive) exit of the VUV ionizer cavity (see fig 2.S1) and electrically grounding the capillary dividing the CIMS SSQ region from the t-IMR. The subsequent electric force accelerates reagent ions directly across the IMR tube (perpendicular to the flow, see below), colliding and combining with sample molecules, and continuing to the grounded capillary, after which the charged molecules are guided by the standard CIMS octopoles and other internal electronics. The strength of the applied electric field determines ion-molecule interaction time, the total ion current which reaches the capillary/MS, as well as the ion energy and thus the ion-analyte cluster stability. The effect of varying this applied potential and resultant electric field in the t-IMR is presented in this work and, unless otherwise specified, the standard voltage applied to the exit point of the ionizer is 1.5 kV. Ion-molecule interaction time is determined as the time for I^- ions to travel across the t-IMR chamber and calculated by using a simplified electric field strength calculated as $E = \frac{V}{d}$, the applied voltage divided by the distance across the t-IMR chamber (d), i.e. the inner diameter (ID) of the IMR tube, 22.225 mm. Combining the electric field strength with the ion mobility of I^- determined in a previous study to be between 2.15 - 2.49 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ when clustered with 0-2 water molecules,[25] the resulting ion-molecule interaction time is 1.3-1.5 ms. In order to prevent buildup of static charge or induced electric fields on different surfaces, grounding wires are also fixed to the t-IMR metal housing as well as the sheath flow apparatus input. The use of conductive metal (compared with full Teflon block) as IMR housing, as well as a sheath flow apparatus for the capillary entrance to the CIMS, both of which held at electric ground, demonstrate notable improvements

upon the previous crossflow design. These new additions create conditions for more stable instrument signal, longer uninterrupted sampling for ambient measurements, and lower potential electrical interference i.e. from charge buildup. The VUV with applied potential and capillary setup also allow for the CIMS instrument to sample in any orientation.

Background signal determination for CIMS measurements is crucial for accurate signal reporting. This involves a period where sample gases are prevented from entering the CIMS while keeping IMR pressures constant, which results in mass spectra that reflect the so-called background signals for chemical components intrinsic to the CIMS at a given time. These background signals can shift over time for any detected mass, so acquiring background spectra as frequently as possible is important. In this case, the background determination or "zero" signal is acquired by overflowing the t-IMR with UHP nitrogen, a method used in other CIMS studies.[26][18] Here, between 12 and 14 LPM of nitrogen is introduced to the 7/8" ID IMR chamber, acting as an "overflow" of the standard 10 LPM sample flow. The nitrogen delivery apparatus is moved directly in front of the center of the t-IMR inlet and removed when returning to regular sampling. The large amount of UHP N₂ in this configuration is not always practical depending on the sampling location. As we show below, the relatively low wall interactions enable less frequent background determinations. Moreover, alternative background determinations using scrubbers could also be employed instead of UHP N₂. The spectra and subsequent signals recorded during a zero period are used in background determination, as well as limit of detection calculations.[20] Low pressures in the BSQ and ToF chambers of the CIMS are maintained by a Pfeiffer Splitflow turbo pump, which in addition to the SSQ are back by an Ebara model EV-PA 500 pump. The Ebara pump is throttled with a manual valve to achieve a pressure of 2 mbar when the critical orifice is open to ambient pressure.

2.3 Sensitivity and Transverse Electric Field Effects

The ability to set an applied voltage to create an electric field propelling ions generated by the VUV lamp across the t-IMR cavity is critically important to producing signal with the CIMS, and allows the use of such a large sample flow (10 L/min). Without any applied field, total ion counts remain near zero, presumably from physical loss due to ions being forced into the exhaust line by the high t-IMR flow. This result also suggests neutral components of the reagent ion carrier flow arising from the ionization process or precursor gases do not get entrained into the main portion of the sample flow that interacts with the reagent ions. However, even with a small field applied it is apparent that electric forces begin to compensate this kinetic force. It is therefore paramount to characterize the optimal electric field strength in normal operation to maximize signal and sensitivity. The standard electric potential of 1.5 kV applied at the VUV ionizer exit is

chosen based on experiments performed to evaluate changes in ion signals and sensitivity while varying this voltage. The experimental setup includes the t-IMR sampling laboratory room air at the standard 10 L/min flow rate, along with an added 0.040 L/min flow of bromine gas (Br_2) produced by a KINTEKTM commercially purchased Br_2 permeation device, carried by UHP N_2 gas. The permeation tube is kept under constant flow at a temperature of 40°C regulated by heating tape and a thermocouple with digitally monitored temperature readings. The published output of the device held at this temperature is 140 ng/min. The permeation rate is also measured gravimetrically, independently confirming this published rate within 3%. Using this value and the measured flow rates of the carrier N_2 gas and t-IMR, the resultant concentration of Br_2 (in ppt) present in the IMR chamber during this constant addition is calculated. Using measured counts from the CIMS detector for the Br_2I^- cluster peak, normalized to Total Reagent Ion Counts ($\text{TRIC} = \text{I}^- + \text{H}_2\text{OI}^-$) with this known concentration, the sensitivity value for bromine is calculated and tracked throughout the experiment.

When considering the theoretical effect of the applied electric potential, the goal is to have the resultant electric field be sufficiently strong to accelerate enough generated I^- ions across the high volume flow passing through the t-IMR to make it to the capillary CIMS entrance. The stronger this field, the higher the kinetic energy of these ions, which increases the theoretical probability of I^- ion and cluster transmission to the CIMS and therefore total ion signal. However, maximizing kinetic energy is not the singular goal as there is also in theory a point at which the velocity of the lone I^- ions becomes so large that the likelihood of them attaching to analyte molecules in the sample flow begins to decline. The result of such a high electric field would in theory be higher TRIC, but lower signal counts for the compounds of interest which would result in lower instrument sensitivity; along with the safety and power consumption concerns that come with indefinitely increasing the electric potential.

Shown in Figure 2.2 is the result of this experiment, showing the relationships of both Br_2 sensitivity in counts ppt^{-1} per million TRIC with the applied electric potential measured in volts (V) on the left, along with TRIC and total ion counts (TIC) on the right. As the applied voltage is increased, the measured CIMS sensitivity to bromine decreases, while both TRIC and TIC increase. The changes in both are non-linear with electric field strength, showing the larger changes at voltages below ~ 1500 V. Br_2 sensitivity shows a slight exponential decay with applied voltage, decreasing by more than a factor 2 between 300 and 2500 V. TRIC conversely shows a large increase which tapers off at higher voltages. The difference between TIC and TRIC shows a similar increasing pattern, indicating that all other analyte signals present in room air plus that of the bromine added increase as well. Ultimately, the 1.5 kV setting is chosen for t-IMR operation as a compromise between to goal of maximizing both instrument sensitivity as well as total ion counts.

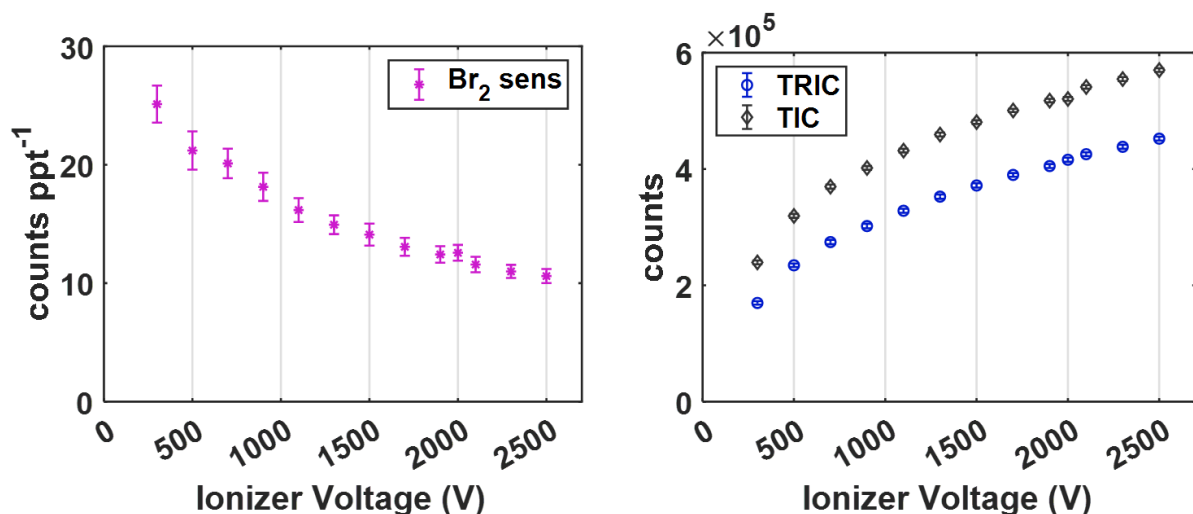


Figure 2.2: (left) Br_2 average sensitivity (counts ppt⁻¹ per 1e6 TRIC) vs. electric potential applied to VUV ionizer and (right) average Total Reagent Ion Counts (TRIC = $\text{I}^- + \text{IH}_2\text{O}^-$ signals) and Total Ion Counts (TIC) vs. ionizer voltage.

2.4 Wall Effects

Another improvement with the transverse design of the t-IMR is the reduction of so-called wall effects. As mentioned in the introduction, wall or memory effects refer to compounds depositing onto IMR surfaces leading to both lower signals for species at the actual time of sampling as well as increased artificial signal later when molecules are liberated from surfaces and reintroduced in the sample flow. Reducing artificial signal is important for all CIMS applications, particularly for those wanting to measure low concentration species. Multiple laboratory studies have been conducted to quantify and reduce this unwanted effect across different IMRs and instrument techniques. Palm et al in 2019 showed that the fast zero technique in their new low pressure IMR significantly reduces memory effects quantified as the "instrument delay time", which is defined as the time it takes for a specific compound's measured signal to return to 10% of its value during a controlled addition to the IMR.[18] In the same study, Palm also provides a summary of how instrument delay time generally decreases with the calculated saturation vapor pressures and subsequent volatilities (or C^* values) of various compounds tested. In other words, less volatile species (lower C^*) generally take longer to evaporate off of IMR surfaces after deposition and will contribute to artificial signal for longer periods of time (longer instrument delay time). The lowest volatility species presented in this study had instrument delay times on the order of 10 minutes or longer. The goal for the t-IMR is to minimize this effect as much as possible by reducing molecule-surface interactions in the instrument.

To characterize our t-IMR in regard to wall effects, experiments were conducted to generate a suite of organic molecules covering a large range in volatility, via alpha pinene ozonolysis. The setup for this

experiment is shown in figure 2.S2. Ozone was generated by flowing approximately 4 LPM of zero air from a Teledyne model 701 zero air generator through an enclosed cavity containing an ultraviolet lamp with output at 254 nm wavelength (Jelight #82-3309-9). Ozone concentrations registered between 900-1000 ppb in a glass flow tube where it was mixed with a 200 sccm flow of alpha pinene + UHP nitrogen gas. This resulted in a suite of organic products detected by the iodide CIMS, including various levels of oxygenated pinene products (i.e. $C_{10}H_{16}O_x$). The products were introduced to the t-IMR by manually moving a 1/2" OD teflon tube outlet from the glass flow tube in front of either the t-IMR entrance or to exhaust. This output was moved in front of the t-IMR for 5, 10, and 30 second pulses repeatedly throughout the experiment to determine if sampling time influences instrument delay on these timescales.

Shown in figure 2.3 are the 1 Hz timeseries of thirty five alpha pinene ozonolysis products from this experiment during a representative 30 second pulse. Relative signals for each detected compound, normalized to their mean value during the 30 second pulse are shown colored by their oxygen-to-carbon atom ratios (O:C), indicating the least oxidized in green (O:C < 0.5) to most oxidized in purple (O:C > 1.5). Also plotted with red dashed lines is the value 0.1, representing the threshold corresponding to 10% of the mean signal for each compound. The absolute signals measured corresponding to concentrations) for these products are consistent across the multiple additions and varied times, reaching the same level with each pulse. The signals drop to below their respective thresholds (red dashed line) on the order of 1-2 seconds after the products outflow tube was removed from the t-IMR, at 22:35:51 (formatted as UTC hh:mm:ss) as illustrated by the bottom plot of figure 2.3 showing a zoomed in view of the end of the 30 second pulse (highlighted in the grey dashed box for the top plot). Two representative organic molecular compositions are included in this plot: $C_{10}H_{16}O_3$, likely a collection of relatively high concentration semi-volatile products, and the much less volatile, more oxygenated products having a composition of $C_{10}H_{16}O_8$. These representative products of α -pinene ozonolysis span multiple orders of magnitude in volatility space. C^* values were calculated at temperatures of 298 K for these two compounds using their saturation vapor pressures as calculated and published by Hyttinen et al (2022) using the SIMPOL methodology outlined by Pankow & Asher (2008).[27][28] The C^* value determined for $C_{10}H_{16}O_3$ is $1.04 \cdot 10^3 \frac{\mu g}{m^3}$ and that of $C_{10}H_{16}O_8$ is $26 \frac{\mu g}{m^3}$ as an upper limit, and $1.7 \cdot 10^{-4} \frac{\mu g}{m^3}$ as a lower limit. This experiment demonstrates that over a wide range of chemical volatility (and molar mass), instrument delay times remain between 1-2 seconds, consistent with inlet residence time. Contextualizing these results with the summary of instrument delay time vs. saturation vapor pressure from Palm et al, the atmospheric pressure t-IMR demonstrates significant improvement in reduction of wall memory effect for lower volatility organic compounds, especially after accounting for the t-IMR residence time of 0.75 s. The t-IMR instrument delay time on the order of 1 second is much less than the 10-minutes reported for low pressure designs. This result is also comparable if not an improvement to

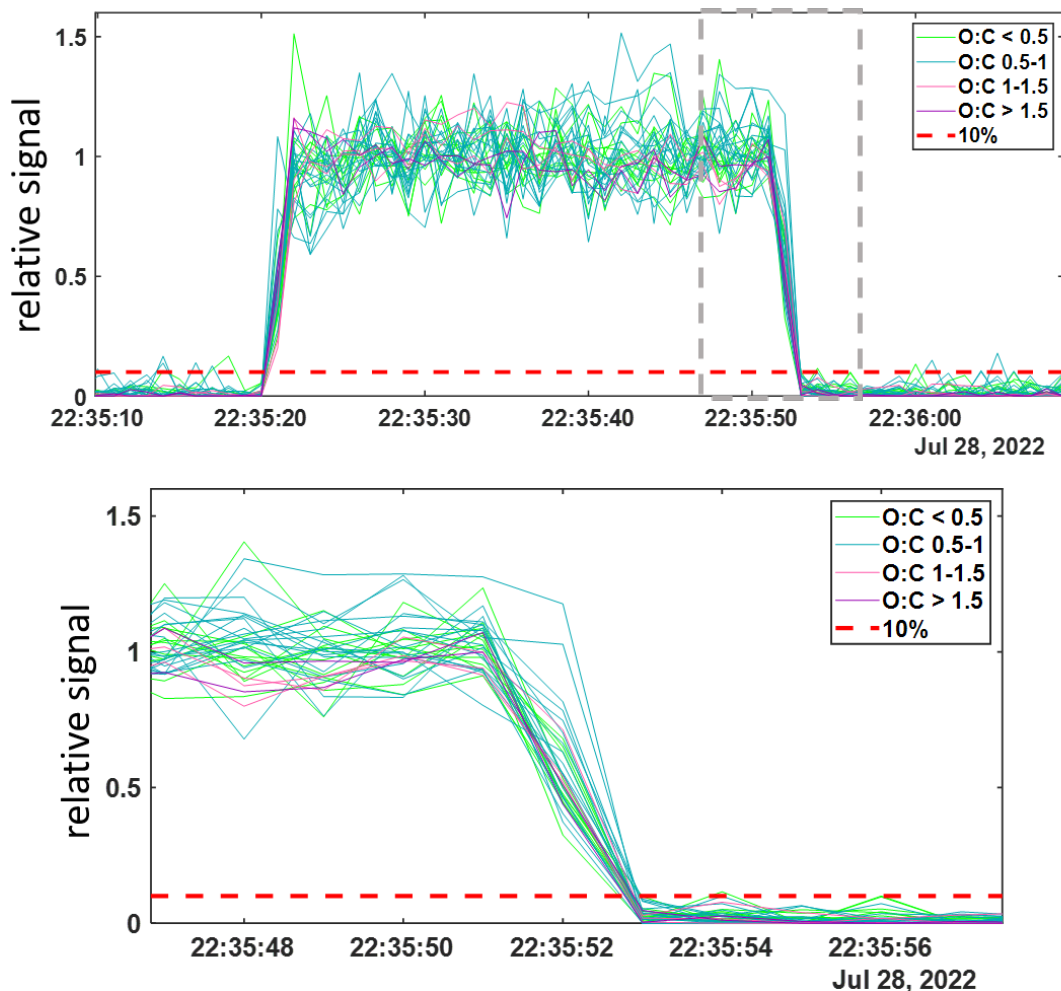


Figure 2.3: 1 Hz timeseries of 35 α -pinene ozonolysis products generated in a laboratory study and detected in the t-IMR. Compounds shown colored by O:C ratio and reported in normalized signals relative to the averaged detected during addition. Relative 10% signal lines shown in red. Bottom plot shows zoomed in view of timeseries as shown in grey box of top plot.

the e-folding time (time for signal to drop to 36% signal) of 1s calculated for the crossflow design presented by Zhao et al for nitric acid.[10]

2.5 In-Situ Observations

The t-IMR was deployed to the field as part of the Bermuda boundary Layer Experiment on the Atmospheric Chemistry of Halogens (BLEACH). The BLEACH campaign took place over two six-week periods from May-June 2022 and January-February 2023. The results presented here will focus on the latter winter leg of the measurements. The t-IMR CIMS was stationed at the Tudor Hill Marine Atmospheric Observatory (THMAO) located on the southwestern shores of Bermuda operated by the Bermuda Institute of Ocean

Sciences (BIOS). The CIMS sampled from atop a 10 meter tower on the shore and was contained in weatherproof housing with an attached air conditioner to assist in stabilizing instrument temperatures. To both accelerate ambient air to the IMR chamber as well as shield the inlet from precipitation and high winds, a 3" diameter secondary inlet was sealed around the 1" t-IMR chamber and was pumped at 110 L/min, of which 10 L/min was sub-sampled by the t-IMR with the same setup of 1.5 kV applied electric potential and iodide ionization scheme described in the previous sections. The additional residence time from this 3" secondary inlet at such a pumping speed is calculated to be 0.76 s. which brings the total residence time for ambient molecules to 1.5 s from entering the outer inlet to the pinhole CIMS entrance. Background signals for a given compound were determined by taking the average signal for that compound during a "zero period" where a flow of 14 L/min of the UHP N₂ gas overflowed the t-IMR by way of a mass flow controller output manually placed in front of the 1" inlet (within the larger 3" sheath inlet). These signals are characterized by a local minimum in the H₂OI⁻ signal, as the ionization region is being overflowed with virtually completely dry nitrogen gas as opposed to the more humid ambient conditions. This "zero" signal is then averaged between multiple overflow periods throughout the campaign and subtracted from the corresponding ambient counts for that detected species. LOD is also calculated using signals recorded during zero periods according to the equation from Bertram et al, giving detection limits on the order of tens of ppq for certain low concentration halogenated species, including HOBr. The t-IMR CIMS in iodide mode is capable of measuring multiple reactive halogen species as well as a suite of organic molecules in the ambient conditions at the site.

Shown in Figure 2.4 is the timeseries as well as the diurnal profile for ambient HOBr measured during the winter BLEACH campaign. Median concentrations are shown in the open circle trace for the diel cycle, with shading representing the 25th and 75th percentiles for the entire sampling period. This data is the result of peak-fitting and integrating 1-minute pre-averaged spectra from the t-IMR CIMS, after which further binning is performed to give a 15-minute data frequency. The timeseries is quality controlled to exclude any calibrations, zeros, or instrument maintenance. Quantum model simulations to calculate the binding enthalpies (BE) to the reagent I⁻ for each of these molecules were performed, as these values correlate with and therefore may be used as a proxy for the relative sensitivities between these species.[29] The calculated BEs are 24.3 and 15.1 kcal/mol respectively for Br₂ and HOBr. The regular calibrations for Br₂ throughout the campaign are used to produce a general sensitivity value for the t-IMR CIMS, which is used for the conversion of instrument signal counts to atmospheric concentration (ppt). Using the binding enthalpy relative to that of Br₂, we scale the measured Br₂ sensitivity value and convert measured signals of HOBr

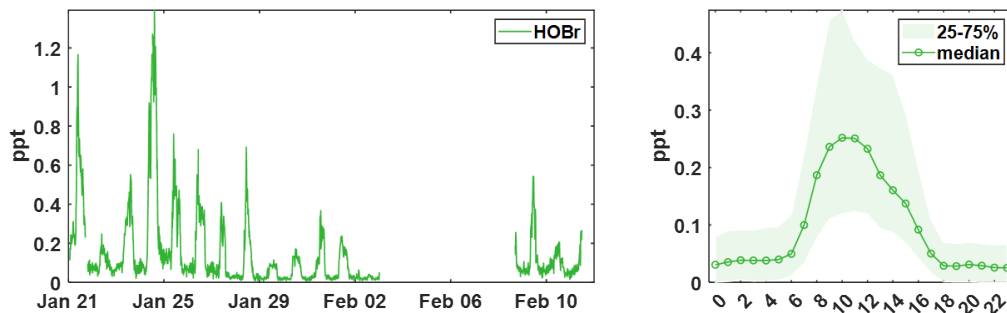


Figure 2.4: (Left) 15-minute averaged timeseries of ambient HOBr concentrations measured during the winter BLEACH campaign and (right) the diurnal profile showing median signal at each hour of day (HOD) in local time. Shading indicates the bounds of the 25th and 75th quartiles for the measured concentrations in each hourly bin.

to atmospheric concentration as well:

$$\frac{\log C_{f,HOBr}}{\log C_{f,Br_2}} = \frac{\Delta H_{HOBr}}{\Delta H_{Br_2}} \Rightarrow C_{f,HOBr} = C_{f,Br_2} \left(\frac{\Delta H_{HOBr}}{\Delta H_{Br_2}} \right) \quad (2)$$

Where $C_{f,X}$ is the instrument sensitivity and ΔH_X is the binding enthalpy for measured compound X. Using equation 2, BE, and the in-field calibrations, the calculated sensitivities for Br_2 and HOBr are respectively 1.5 and 1.3 counts ppt⁻¹ per 1e6 TRIC. Instrument signal counts (from integrating peaks in spectrum) are also normalized to 1e6 TRIC, giving results in atmospheric concentration (ppt) after applying sensitivity values. The daily maximum levels of HOBr vary throughout the campaign, but concentrations reliably increase during daylight hours roughly between 7:00 and 17:00 hours during the winter in Bermuda, corresponding to within the hours of sunrise and sunset for THMAO in Jan-Feb. This aligns with the current understanding of the bromine chemical mechanism in that most gas-phase production of HOBr in the atmosphere requires photochemical reactions.[30][31]

Shown in figure 2.5 is the timeseries and diel cycle for nitric acid concentrations (HNO_3) as measured by the t-IMR CIMS. Similarly to those of the HOBr data, 1-minute averaged spectra were integrated to produce signal counts. However, in this case, the signals are converted to atmospheric concentrations using a direct calibration of the t-IMR after the campaign. The calibration utilizes a custom made permeation device where concentrated nitric acid fills a permeable PTFE tube sealed at each end with solid PTFE caps. The output of this permeation device is determined gravimetrically and converted to units of ng/min, which is then used in conjunction with total IMR flow to determine the concentration in the t-IMR and subsequently the sensitivity to HNO_3 in the same manner as the direct calibrations of Br_2 described earlier. What was determined to be a small contamination of nitric acid on tubing connections involved during

zero periods in the BLEACH campaign made it such that the HNO_3 timeseries could not be background subtracted, though all other quality controls used in the HOBr data are applied here. The diurnal cycle shows median concentrations increasing during daytime hours evident in the shading of the 75th percentile measurements, with a particular period of higher median values in the morning. The relatively elevated concentrations during the day are consistent with the main gas phase production of HNO_3 coming from reaction of NO_2 with OH, requiring photochemistry. This is evidenced by the bottom two plots shown in figure 2.5 which show a zoomed in view of a peak in HNO_3 (cutoff by axis limits in the complete timeseries for clarity) accompanied by NO and NO_2 concentrations on the bottom plot as measured by a Laser-Induced Fluorescence (LIF) instrument. The largest spike in HNO_3 coincides with similar very large spikes in both NO and NO_2 , indicative of both high total NOx and active photolysis. However, there are periods during the night in which HNO_3 is generally elevated and also episodically peaks in concentration. This is likely indicative of nighttime production pathways, presumably hydrolysis of N_2O_5 with H_2O on aerosol surfaces and/or NO_3 reactions with dimethyl-sulfide (DMS) or volatile organic compounds (VOCs). [32][33] Representative mass spectra showing peak fits for both HOBr and HNO_3 as measured with the iodide CIMS are shown in figure 2.S3. These in-situ observations demonstrate the capability of the t-IMR to not only be deployed to the field, but also to measure a diverse suite of compounds down to sub-ppt concentrations while minimizing wall effects and instrument residence time.

2.6 Conclusions

In this work we have characterized a novel atmospheric-pressure IMR inlet (t-IMR) for use with CIMS applications. The crossflow t-IMR is shown to operate under laminar flow conditions with an electric field used to accelerate reagent ions and subsequent ion-ambient molecule clusters across the relatively high-pressure, high flow space to be sampled by the CIMS, resulting in much higher observed ion signals compared to measurements with no applied field, typically by two orders of magnitude. The standard operating electric potential is optimized to retain high total ion signal while also maximizing measured sensitivity. The t-IMR design is also shown to reduce wall memory effects compared to previously studied low-pressure designs, decreasing instrument delay times from the order of minutes to the order of one second for a representative suite of varied volatility organic gases. This increases the measurement reliability of ambient gases even at relatively lower volatilities, particularly improving detection of low concentration species. Results from the first field deployment of the t-IMR demonstrate the capability of the design to sample ambient trace gases continuously, down to sub-ppt concentrations in the case of HOBr.

Operating with the atmospheric pressure t-IMR shows several clear advantages, but also introduces some

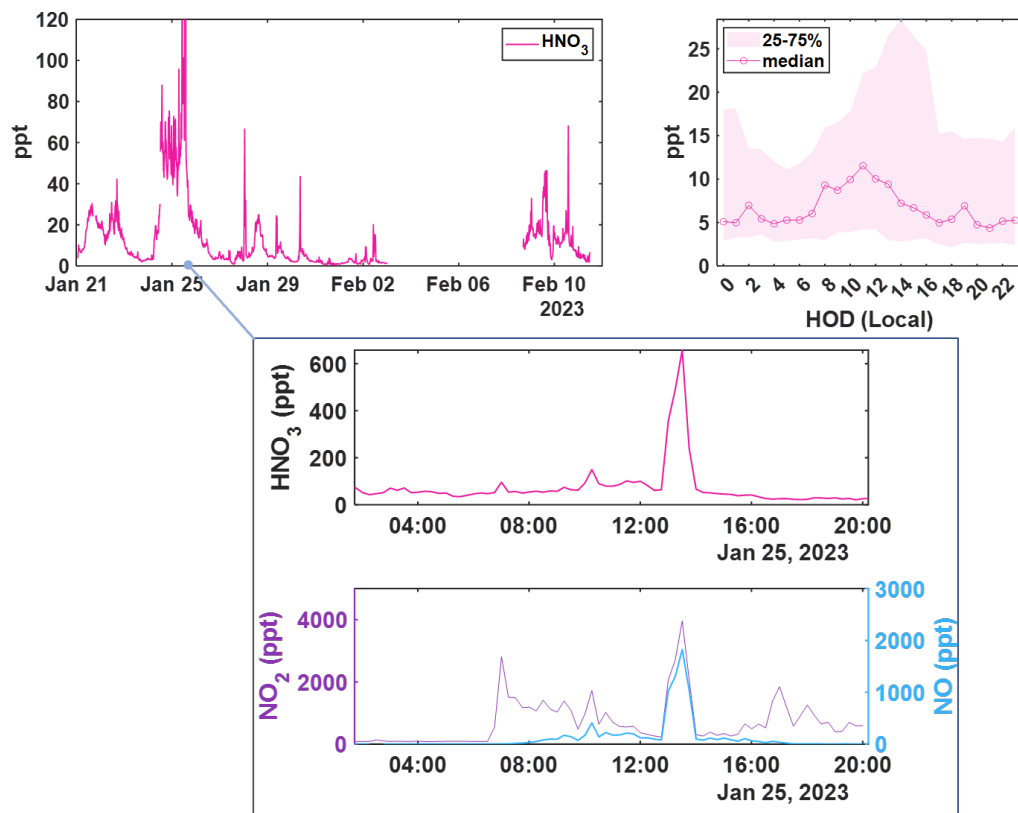


Figure 2.5: (top left:) 15-minute averaged timeseries of ambient HNO_3 concentrations measured during the winter BLEACH campaign and (top right) the diurnal profile showing mean signal at each hour of day (HOD) in local time. Shading indicates the bounds of the 25th and 75th quartiles for the measured concentrations in each hourly bin. (middle:) A zoomed in view of a spike in HNO_3 concentration as measured by CIMS coinciding with (bottom) measurements of NO (blue, right axis) and NO_2 (purple, left axis) as detected by a Laser-Induced Fluorescence (LIF) instrument

limitations, including less control over ambient pressure and humidity changes. While the high flow through the IMR chamber reduces wall interactions and residence time, this does present potential difficulty in background determinations as overflowing with 10 or more L/min of UHP nitrogen gas can be difficult in certain settings where specialty gas quantities are limited. The relatively high sample flow rate also makes it difficult to humidify such a "zero" in applications where a non-dry zero is desired, i.e. with a water bubbler. Since CIMS sensitivity to many compounds has been shown to be somewhat dependent on the amount of water vapor present in the IMR, it is important to quantify the humidity-dependence of sensitivities measured with the t-IMR design. It would also be useful in the future to conduct a sensitivity study for the multitude of organic species that have been measured by iodide reagent chemistry with other IMR designs and conditions for inter-comparison purposes.

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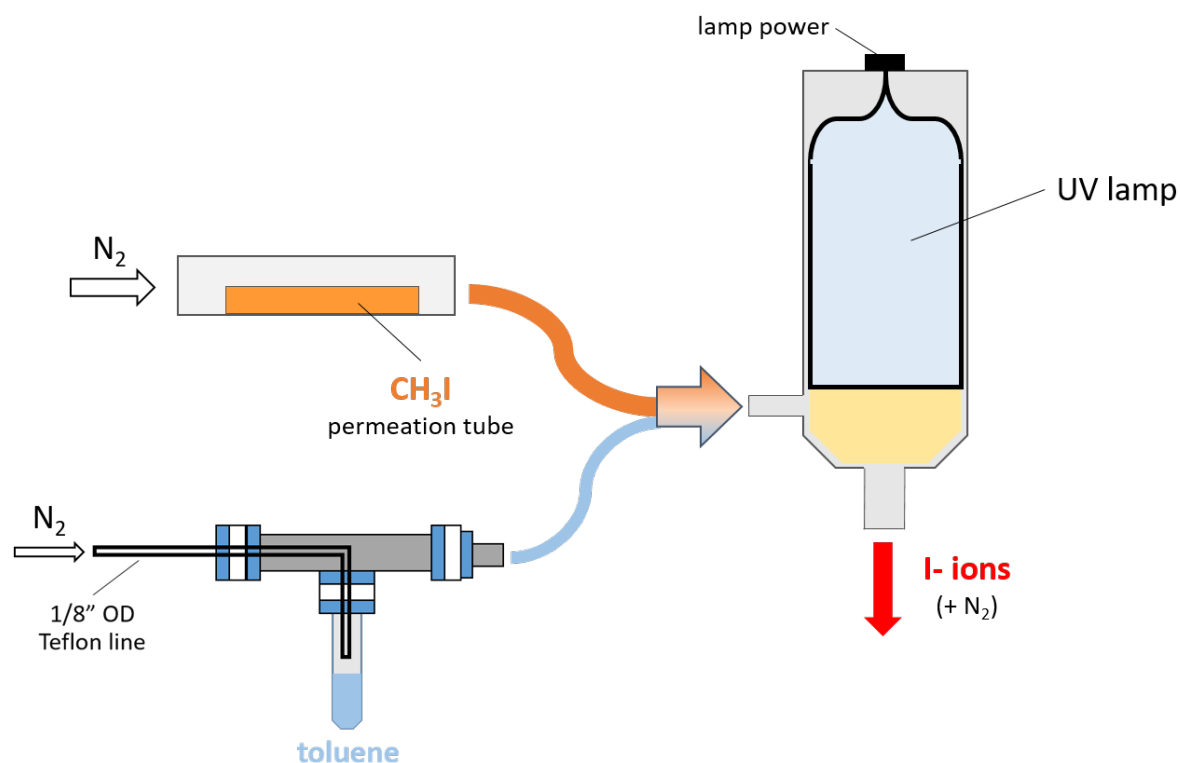


Figure 2.S1: A diagram showing the VUV setup for I^- ion production. UHP N_2 is flown over both a CH_3I permeation tube at 1.5 LPM (orange) and the headspace of a liquid toluene vial at 2 sccm (0.002 LPM, light blue), which combine and enter the VUV cavity illuminated by the UV lamp represented with yellow shading. Resulting I^- ions exit the VUV housing at a stainless 1/4" OD port where an electric potential is applied.

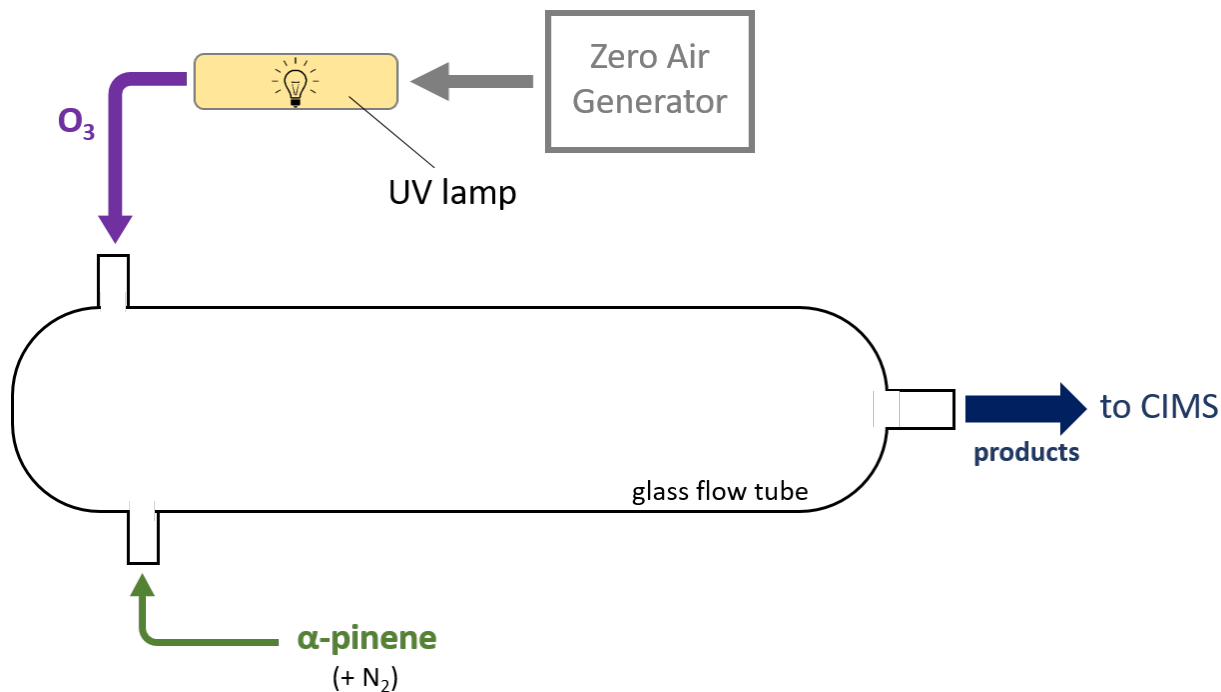


Figure 2.S2: Setup schematic for the alpha-pinene ozonolysis wall effects experiment. A 4 LPM flow from the zero air generator is passed through a chamber illuminated by UV light to produce O_3 which is input into a glass flow tube (purple) along with a 200 sccm (0.200 LPM) flow of gaseous alpha pinene + UHP N_2 (green). Gases mix to form products (dark blue) which are output into the transverse IMR-equipped CIMS.

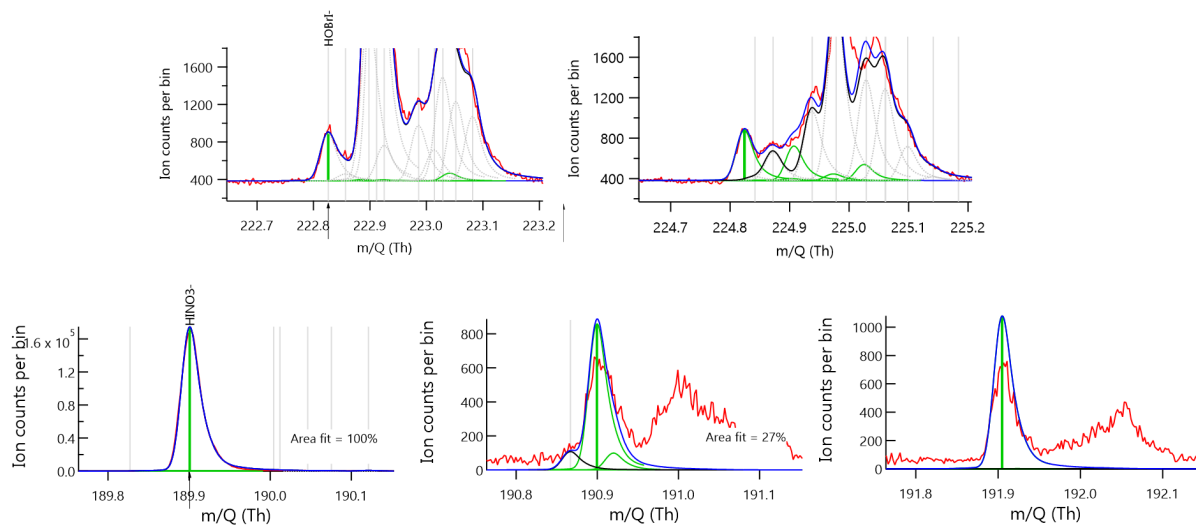


Figure 2.S3: Approximately 15-minute integrated mass spectra showing signal in ion counts vs. mass to charge ratio (m/Q). Red traces indicate raw data while the dark blue show fitted and assigned peaks using an adjusted Gaussian model. Green bars indicate the mass-to-charge positions and fitted intensities for chemical compositions (top) HOBri and (bottom) HNO_3 when clustered to I^- . The additional plots to the right show fits for the respective isotopes, $m+2$ for HOBri and both $m+1$ and $m+2$ for HNO_3 .

Chapter 3: Observations of Reactive Bromine in the Sub-Tropical Marine Boundary Layer

Abstract

Reactive bromine species in the atmosphere affect ozone (O_3) and the cycling of other important trace gases including HO_x and NO_x , with implications for the oxidative capacity of the atmosphere, air quality, and human health. Despite this importance uncertainties remain in the global distribution and chemical mechanism of inorganic bromine, with few in-situ observations, especially outside of polar regions. Here we present results of speciated gas-phase reactive bromine observations made in the Marine Boundary Layer (MBL) at a coastal site in the Northwest Atlantic Ocean, as part of the Bermuda boundary Layer Experiment on the Atmospheric Chemistry of Halogens (BLEACH) campaign. Using an iodide-reagent High Resolution Time of Flight Chemical Ionization Mass Spectrometer (HR-ToF-CIMS) equipped with a custom atmospheric pressure transverse ion-molecule reaction region (t-IMR), we observe sub-ppt levels of atmospheric inorganic bromine compounds including Br_2 , BrCl , HOBr , BrONO_2 , and BrO in the marine boundary layer. To our knowledge, these are the first reported in-situ observations of gaseous bromine nitrate (BrONO_2). An experimental calibration for HOBr produces results for sensitivity in line with previous studies, as well as theoretical calculations involving binding enthalpies used to report measured species in units of ambient concentration. A humidity-dependent sensitivity for Br_2 is obtained for the atmospheric pressure IMR and applied to observational data, finding a non-linear relationship between instrument response and water vapor pressure. Reactions involving BrO , HOBr , and BrONO_2 requiring photochemical activation are investigated. We examine the relationship between reactive bromine levels and surrounding environmental factors including meteorological conditions as well as influence from small local pollution sources and clean marine periods.

3.1 Introduction

Atmospheric halogen-containing species, referring to molecules containing chlorine (Cl), bromine (Br), and iodine (I) atoms, have been of growing importance to researchers over the past few decades due to their capability to influence the climate system and human health. Halogens can greatly affect the oxidation capacity of atmosphere, importantly from the ability of reactive halogens to destroy ozone (O_3) catalytically.[1][2][3][4] Tropospheric ozone is an important greenhouse gas and a pollutant with adverse effects on plant, animal, and human health.[5] The main source of halogens in the troposphere is emission from sea salt aerosols (SSA), from which chlorine and bromine are liberated via acid displacement and debromination reactions, respectively. Other sources include direct emissions from biological activity in the ocean and coal burning power plants.[6][7][8][9][10] Halogenated species also react with HO_x ($=OH + HO_2$) to varying degrees depending on conditions, modulating both the concentrations and ratio of OH and HO_2 , and therefore can have significant impacts on the oxidation capacity of the atmosphere.[11][12] Halogens have been shown to interact with reactive nitrogen species as well, such as NO_x ($=NO + NO_2$), N_2O_5 , and NO_3 which not only influence reactive nitrogen concentrations locally, but can provide longer-range transport of NO_x i.e. via $ClNO_2$. [13][14][10][15] Additionally, halogenated species have been demonstrated to affect the cycling of volatile organic compounds (VOCs), hydrocarbons and mercury (Hg) in the troposphere.[1][16][17][18][19] The Marine Boundary Layer (MBL) is one of if not the most critical sectors of the global atmosphere for ozone sinks. Previous studies have shown the importance of examining and including MBL halogen chemistry on models to correctly predict O_3 and HO_x concentrations, in addition to the baseline photolysis and water vapor reactions.[20]

Inorganic reactive bromine, Br_y ($= Br + 2Br_2 + HOBr + BrO + HBr + BrONO_2 + BrNO_2 + BrCl + IBr$), is of particular importance due to its efficiency in ozone depletion events, and specific reactivity with other atmospheric components (such as mercury) with significant potential influence on air quality and climate. Relatively small concentrations of reactive bromine has been shown to have considerable impacts on tropospheric chemistry, interacting with NO_x , HO_x , O_3 , and dimethyl-sulfide (DMS) cycles.[21] Tropospheric bromine has been demonstrated to have a slightly different chemical mechanism compared with chlorine. The largest global source of gaseous bromine species in the troposphere is the debromination of sea-salt aerosols (SSAs).[22] Other sources of tropospheric Br_y include direct emission from the ocean, coal burning, volcanic eruptions, and transport from the stratosphere.[23][24] The main sink mechanism for Br_y is uptake onto aerosol surfaces, with much smaller contributions from wet and dry deposition.[25] As the dominant source of reactive bromine with the capability to significantly impact concentrations of ozone and the other previously mentioned chemical cycles on a global scale, areas with high SSA concentrations are key in the

pursuit of improving our understanding bromine (and general halogen) cycling in the troposphere.

BrO and HOBr are important components of Br_y reaction pathways, in particular the catalytic ozone destruction cycle:



When this chemical cycle is activated under certain conditions, the result is a net destruction of ozone, production of O₂, and the catalytic cycling of molecular bromine. Reactions 3 and 4 demonstrate the capability of Br_y to impact HO_x concentrations and ratios, in this case by way of reacting with and reducing HO₂ in favor of producing OH. Reaction 3 is temperature-dependent and has been shown to also be influenced by the amount of water vapor present.[26] Because the gas-phase production of BrO and subsequently HOBr require free atomic bromine, they are expected to be highly dependent on active photochemistry and reach significant levels only in the presence of sufficient sunlight (e.g. daytime in the sub-tropical and tropical MBL). While this reaction chain is an important component in the destruction of ozone via bromine chemistry, it is not the only loss pathway of BrO, which is itself photolabile. It can also react with NO_x to either reform free atomic bromine, or bromine nitrate:

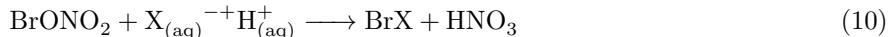
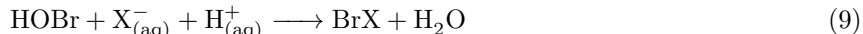


As BrO formation is the main loss of atomic bromine in the MBL (via reaction 1), its subsequent branching reactions and fate have a large impact on the total concentration of and distribution of Br_y among its constituent species. For example, the molecules HOBr and BrONO₂ have slightly different photolytic lifetimes based on actinic flux calculations, with that of HOBr around 12 minutes and that of BrONO₂ approximately 20 minutes during peak photolysis. Therefore if the formation of one is heavily favored over the other, this affects the rate at which molecular bromine may be reformed in a catalytic ozone destruction cycle, or any of the other species mentioned whose chemical cycles interact with bromine. Also evident in equations 6 and 7 is the effect of BrO on the ratio/concentration of NO_x. There is also the possibility for bromine monoxide to

combine with chlorine monoxide (ClO) in the gas phase to form the interhalogen species BrCl and a reaction analogous to equation 2:



Multiple Br_y components can also undergo heterogeneous reactions on SSAs to both partition gas-phase reactive bromine, in addition to changing aerosol chemical composition. Heterogeneous reactions involving HOBr and BrONO_2 are of particular interest, as these reactions consume halogen species (X^- , $\text{X}=\text{ClBrI}$) present in sea spray particles:



The rate at which these heterogeneous reactions occur is dependent on both the gas-phase diffusivity and probability of reaction once in the aerosol for the gaseous species reactant. The unitless reactive uptake coefficient for a given molecule, γ , is defined as the ratio of the number of reactive collisions divided by the total number of gas-particle collisions, ranging from 0 (no reactivity) to 1 (every gas-particle collision results in reaction). The uptake of HOBr onto NaCl particles has been the subject of multiple laboratory studies, and thought to be one of the most important reactions driving the debromination of SSAs, yet the magnitude of its uptake (γ_{HOBr}) remains highly uncertain, along with γ_{BrONO_2} . These coefficients are important to constrain as they are important parameters for models including halogen chemistry, and uptake of reactive gases onto aerosols has been assumed in previous work to be the rate-limiting step for the heterogeneous cycling (and recycling) of halogens in the marine atmosphere.[27]

The multiple pathways for BrO reactions highlight the complexity of identifying contributions from each species to total Br_y concentrations, controlling reactivity with ozone and other important trace gases in the atmosphere. This is particularly important in the MBL where SSAs are predicted to provide a significant source of tropospheric bromine. Thus observational constraints on theorized reactivity for inorganic bromine remain critical to understanding the role of Br_y in global climate and air quality. The first published observations of BrO were reported by Hausmann and Platt in 1994 using a Long-Path Direct Optical Absorption Spectroscopy (LP-DOAS) technique in the Arctic during springtime.[28] Concentrations were recorded up to 17 ppt (with a limit of detection of approximately 4 ppt). There have been multiple studies conducted in Arctic regions which have produced observations of some components of Br_y , while coordinated measurements outside of the Arctic remain sparse. Other studies have reported BrO concentrations in the MBL typically remaining below 10 ppt.[23][29] There also exists evidence for pollution-driven enhancements for

inorganic bromine at coastal sites, particularly for Br_2 and BrO . Proposed causes for this relationship in observations include nitrate chemistry, aerosol pH effects, and local anthropogenic bromide sources near sites of investigation.[30][31][32] Here, we present results containing simultaneous observations of five inorganic, bromine-containing species and components of atmospheric Br_y in the semi-remote subtropical MBL. This includes for the first time, to our knowledge, direct observations of bromine nitrate, BrONO_2 .

3.2 Field Campaign Description and Instrument Setup

The Bermuda boundary Layer Experiment on the Atmospheric Chemistry of Halogens (BLEACH) field campaign took place over two six-week legs, in May-June 2022 as well as January-February 2023. The purpose of the campaign is to investigate halogen chemistry in the marine boundary layer through a suite of gas and particle-phase measurements of chlorine, bromine, and iodine-containing chemical species in the ambient atmosphere. BLEACH also represents the first field deployment of the atmospheric pressure t-IMR-equipped Long Time of Flight Chemical Ionization Mass Spectrometer (LToF-CIMS) described in Chapter 1. The measurements took place at the Tudor Hill Marine Atmospheric Observatory (THMAO) site located on the southwestern shores of Bermuda, operated by the Bermuda Institute of Ocean Sciences (BIOS). The site is positioned approximately 40 meters horizontally from the coastline, ~ 30 m above the sea surface, and is relatively secluded from main roads and other structures in the immediate surrounding area. This along with geographical location of Bermuda makes it an ideal place to observe remote or "clean" marine atmospheric composition, along with intermittent periods of influence from both relatively smaller-scale local anthropogenic activity as well as larger aged and more polluted plumes advected from the east coast of the United States. There have been multiple atmospheric studies conducted at THMAO to investigate NO_x , HO_x , and O_3 chemistry, with few direct observations of halogen-containing compounds.[33][34][35][36] The CIMS was stationed atop a 10 meter tall tower temporarily erected at THMAO for BLEACH, and was complemented by a suite of other instruments including (on the same tower) a low-pressure IMR CIMS operating in both iodide and bromine-adduct ionization modes, a Tunable Infrared Laser Direct Absorption Spectrometer (TILDAS) measuring hydrochloric acid (HCl), and a spectral radiometer. Also present on the ground at the site was an LP-DOAS instrument positioned with a measurement path over the ocean. And atop the permanent THMAO 23-meter sampling tower was a Laser-Induced Fluorescence (LIF) instrument measuring NO_x and ozone, a cascade impactor collecting aerosols and separating by aerodynamic size onto filters to be analyzed offline, and a collection of meteorological instruments providing measurements of humidity, wind speed/direction, temperature, and precipitation.

The t-IMR CIMS was operated from inside weather-proof housing with ports made only for electronics

cables, sampling (the IMR tube), and an air conditioning unit used to assist in stabilizing instrument temperature. To both accelerate ambient air to the IMR chamber as well as shield it from precipitation and high winds, a 3" OD diameter secondary inlet was fixed around the 1" OD IMR inlet and was pumped at 110 L/min using an Agilent model SH110 pump connected through two symmetric ports positioned downstream of the IMR inlet to prevent turbulence in the ionization region. 10 L/min of the ambient 110 L/min flow was sub-sampled by the atmospheric pressure t-IMR, with the standard operating conditions including 1.5 kV electric potential applied to reagent flow described previously. The secondary inlet comprised of brushed aluminum is cylindrical with an oblong cut at the upstream end creating a slightly longer side along the top of the inlet, acting as a rain shield for the pump lines and IMR inlet. Given the dimensions and pumping speed of the secondary inlet, the residence time of this stage is calculated to be 0.75 seconds, which in addition to the residence time of the t-IMR of 0.76 s, brings the total residence time for ambient molecules to 1.51 seconds from the first upstream interaction with instrument inlets to being flown into the MS. The CIMS is operated at a 1 Hz sampling frequency, producing a mass spectrum every 1 second. Iodide reagent ions are produced via the 1.5 L/min flow of CH₃I permeated at ambient temperatures inside the climate-controlled CIMS weatherproof enclosure, mixed with the much smaller 2 sccm flow over the head space of a liquid toluene vial (containing between 3-5 mL toluene, C₆H₅CH₃) and ionized with the VUV lamp, also described previously. The IMR flow is measured at startup using an analogue ball meter fixed to the 1" OD inlet (prior to the secondary inlet installation) while the IDP3 pump is throttled using a needle valve until the desired 10 L/min flow is achieved. The 3" secondary inlet is secured concentrically around the IMR entrance with aluminum blocks to stabilize the inlet along with rubber O-rings sealing all stages of the inlet apparatus to the weather-proof housing box and around the pumping ports.

Instrument background signals are determined by overflowing the IMR chamber with UHP nitrogen at flows typically between 12-14 LPM (at minimum greater than 10 LPM) for a time period of at least 2 minutes. This was achieved during the deployment by manually maneuvering a 1/2" output tube (PTFE with stainless fittings) through the secondary inlet configuration and directly in front of the IMR entrance while controlling N₂ flow with an Alicat mass flow controller (MFC). The signals for a given peak in the mass spectrum during one of these "zero" or instrument background periods is used in calculating the limit of detection (LOD) for that specific compound, per the equation published by Bertram et al 2011[37]:

$$\frac{S}{N} = \frac{C_f[X]t}{\sqrt{C_f[X]t + 2S_0t}} \quad (11)$$

Where S/N is the signal-to-noise ratio, C_f is the calibration factor for molecule X, $[X]$ is its concentration, S_0 is the signal during a zero or background determination for molecule X, and t is the integration time for

its given peak in the mass spectrum. A standard S/N ratio of 3 is applied, which can be used in conjunction with measured background signals, defined sensitivities and integration times to calculate the minimum concentration or instrument LOD, $[X]$.

3.3 Direct Instrument Sensitivity Calibration

Throughout the campaign, the CIMS was calibrated multiple times for Br_2 by adding a known concentration to the IMR for a short period and monitoring the resulting integrated peak signal at the isotopically constrained Br_2 mass-to-charge ratio. Bromine gas was produced via a commercially purchased KINTEKTM permeation tube with a published output rate of 140 ng/min at 40°C. The permeation tube was kept in a custom-built incubator which utilizes PTFE housing and fittings, heating tape and thermocouple to keep the temperature of the device constant at 40°C. The gaseous Br_2 is delivered via a carrier flow of 40 standard cubic centimeters per minute (sccm) equivalent to 0.040 LPM of UHP nitrogen gas directly to the t-IMR (bypassing the secondary inlet) or to an exhaust line when not in use. The published output rate was confirmed gravimetrically after deployment via repeating the incubator conditions and weighing the permeation device over several days/weeks. The weight loss of the tube over time was calculated to be 2.1e-4 g/day with an $R^2 = 0.96$ correlation. Assuming all of the weight lost is due to permeation and evaporation of the Br_2 , which is appropriate given the device is isolated in UHP N_2 carrier flow, this slope can be converted to an independently measured permeation rate of 144 ng/min (within the manufacturer reported error of the device). With this value, the concentration of any gas, X (C_X), in pptv in the IMR at the time of calibration can be calculated assuming stable conditions with minimal loss to tubing walls:

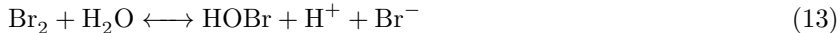
$$C_X = \frac{\delta_X}{m_{mol}} \frac{1}{F} K_g T \cdot 10^{12} \quad (12)$$

where δ_X is the permeation rate of gas X in ng/min, m_{mol} is the molar mass of gas X in ng/mol, F is the largest flow in which the permeation device output is diluted (the t-IMR flow in this case) in sccm, T is temperature in Kelvin, and K_g is the universal gas constant: $82.06 \frac{\text{cm}^3 \text{atm}}{\text{Kmol}}$. With C_x and the measured signal of gas X by the Micro Channel Plate (MCP) detector in the ToF region of the MS in units of ion counts, a sensitivity value or calibration factor can be calculated and reported in units of counts ppt⁻¹. A group of four robust calibrations of bromine performed during BLEACH were chosen and analyzed at the native instrument resolution of 1 Hz to determine sensitivity. Periods of the manual addition are determined from clear and relatively stable increases in the Br_2I^- cluster signal. Approximately 300 of such viable 1-second data points across the four calibrations yield a median, normalized sensitivity of 1.3 counts ppt⁻¹

per 1 million (1e6) TRIC. Without normalizing to reagent ion counts the median sensitivity is calculated to be 4 counts ppt⁻¹. Given the negligible carrier flow of bromine gas compared to that of the t-IMR flow (0.4%), the IMR humidity during the times off calibration is assumed to be equivalent to ambient, which for these periods ranged from 68-77%.

3.4 An Experimental Calibration for HOBr

Given that it is not commercially or otherwise available as a stable chemical, gaseous HOBr must be generated in real time and quantified to achieve a direct instrument calibration. Here we present results from an experimental method to produce and detect HOBr with the t-IMR CIMS, based on previous work performed by Liao et al (2011).[38] The chemical mechanism utilized during the experiment is summarized in equations 13 through 17.



Shown in Figure 3.1 is our experimental setup involving the same permeation device and custom heater used to calibrate for Br₂ mentioned previously, the output from which is passed through a PFA three-way valve. This valve gives the option to either have the gas directly enter the t-IMR to sample as a reference and ensure stable Br₂ signal and sensitivity (bypass), or be passed through a series of up to two chambers containing reactants involved in the mechanism above (shown in the lower path). All paths between the Br₂ permeation tube output and the t-IMR to MS interface remain free of stainless fittings, tubing, etc. as metallic surfaces were determined in previous experiments to interfere with halogenated gas transmission.

The first of the chambers is a PFA tube (with PFA swagelok fittings) containing a wetted slurry of silver nitrate, AgNO₃ + H₂O. This slurry acts to firstly convert Br₂ to HOBr via reaction 13, and also suppress the out-gassing of HBr and/or Br by way of reactions 14-16. The presence of silver nitrate depleting one product of reaction 13 also acts to influence the chemical equilibrium to favor the production of HOBr. The output of the AgNO₃ chamber (#1) is thus a gas-phase mixture of HOBr and Br₂ (as diatomic bromine is

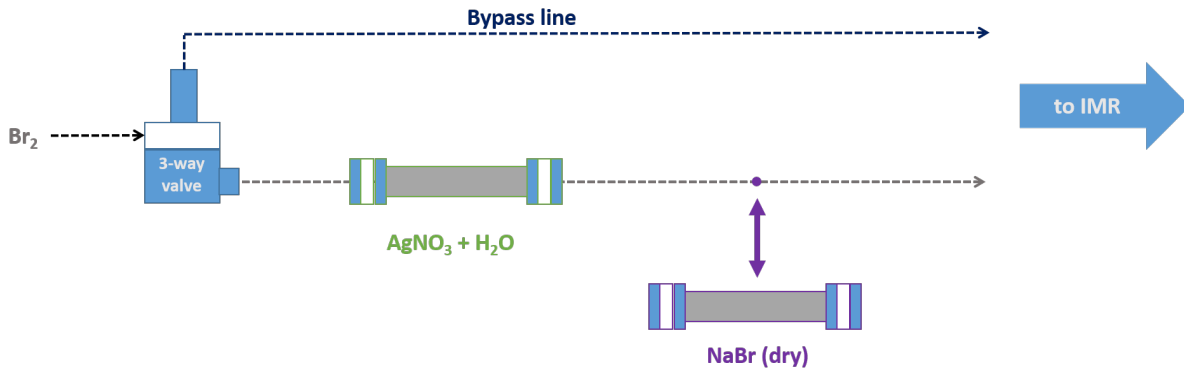


Figure 3.1: Simplified setup for CIMS calibration of HOBr. Br_2 gas is passed through a 3-way valve and then either directly to the Transverse IMR (Bypass line, top path) or through a silver nitrate (AgNO_3) slurry solution and a removable bed of dry sodium bromide (NaBr) crystals (bottom path).

not completely reacted away), the ion counts of which are recorded by the t-IMR-CIMS. The second chamber is an identical tube housing which contains dry sodium bromide, NaBr . By way of reaction 17, this second chamber converts HOBr produced from chamber 1 back to Br_2 . The second chamber is placed in series with the first AgNO_3 tube and removed from the lower path multiple times as the experiment progresses to assess the reproducibility and track the evolution of the relative differences in measured signals of Br_2 and HOBr.

According to the reaction mechanism, the addition of the NaBr chamber (#2) should result in an increase in Br_2 and a decrease in HOBr signals, while the removal of chamber 2 from the path to the IMR should show an increase in HOBr detection back to the levels of the output from chamber 1 and a decrease in bromine signal. By quantifying the absolute differences in integrated peak signal (ion counts) for both compounds, ΔHOBr and ΔBr_2 , the sensitivity (C_f) ratio between the molecules can be calculated assuming that 2 molecules of HOBr generate one molecule of Br_2 in the second reaction chamber:

$$\frac{C_{f,\text{HOBr}}}{C_{f,\text{Br}_2}} = \frac{1}{2} \frac{\Delta\text{HOBr}}{\Delta\text{Br}_2} \quad (18)$$

Shown in figure 3.2 for a representative experiment run is the timeseries of the measured normalized counts per million TRIC for Br_2 and HOBr iodide clusters as well as their respective power series and polynomial fits to provide continuous tracking of the independent timeseries and reduce noise. The middle plot then shows the differences in the respective fits for signals with and without the sodium bromide chamber, i.e. ΔHOBr and ΔBr_2 . And finally, the bottom plot shows the fraction of these (fitted) changes in signal, analogous to the sensitivity of HOBr relative to that of Br_2 , per equation 18. Time zero reflects the point at which HOBr signal is first detected after flowing the bromine gas through the silver nitrate reaction chamber, as the wetted silver nitrate chamber takes a non-negligible amount of time to begin production

and detection of ions for the HOBrI^- cluster. The Br_2 signal steadily increases both with and without the addition of the NaBr reactor, which is attributed mainly to the AgNO_3 chamber drying over time. Silver nitrate is added in excess at the start of the run to eliminate the possibility of being the limiting quantity and step in the reaction process. This leads to a steady increase in ΔBr_2 , contrasting what is shown to be a maximum production and signal for HOBr as evidenced by ΔHOBr fit leveling off around the time of 1000 s. Shown in the bottom plot is a trace for the fraction of the relative signal changes in both compounds, which in steady-state should theoretically be constant. Steady-state is clearly not attainable for this experimental setup, and thus we take the value for $\frac{\Delta\text{Br}_2}{\Delta\text{HOBr}}$ at the time of minimum change (minimizing slope), shown in the orange data points in figure 3.2. After repeating the experiment, we report a range of 0.55 to 1 for the (unitless) fractional sensitivity of HOBr relative to that of Br_2 , which is in reasonable agreement with the value reported by Liao et al (2011). Given that the instrument is independently and directly calibrated for Br_2 , the experimental determination of the fractional sensitivities can be used to produce a value for the sensitivity of HOBr in similar conditions where C_{f,Br_2} is known, or in any case with known Br_2 sensitivity if one assumes this fraction to be constant.

3.5 Indirect Instrument Sensitivity Calculation: Binding Enthalpies

Given that multiple halogen-containing species detected with the t-IMR-CIMS during BLEACH are not commercially available or easily synthesized for reliable direct calibration, other methods to determine their individual instrument sensitivity values are of critical interest. Work conducted by Iyer et al (2016) demonstrates a strong correlation between the CIMS instrument sensitivity and corresponding binding enthalpy for a given molecule to the iodide reagent ion.[39] In this study, the binding enthalpy (ΔH) for a suite of organic molecules is calculated along with respective sensitivities for each species, determined by direct calibration with the CIMS in laboratory experiments. The representative compounds cover a large range of ΔH values from approximately 15 to 28 kcal mol⁻¹ and sensitivities (counts ppt⁻¹) spanning several orders of magnitude. A strong linear correlation is found between the logarithm of the directly measured sensitivities and the binding enthalpy, $\log C_f \propto \Delta H$. For specific application to our bromine observations during BLEACH, the binding enthalpies for several key bromine and chlorine-containing molecules are calculated. Using the calculated binding enthalpies, a sensitivity value via direct calibration for Br_2 , and the log-linear relationship, the instrument sensitivity for the other halogenated species is determined using the following relationship:

$$\frac{\log C_{f,X}}{\log C_{f,\text{Br}_2}} = \frac{\Delta H_X}{\Delta H_{\text{Br}_2}} \Rightarrow C_{f,X} = C_{f,\text{Br}_2} \left(\frac{\Delta H_X}{\Delta H_{\text{Br}_2}} \right) \quad (19)$$

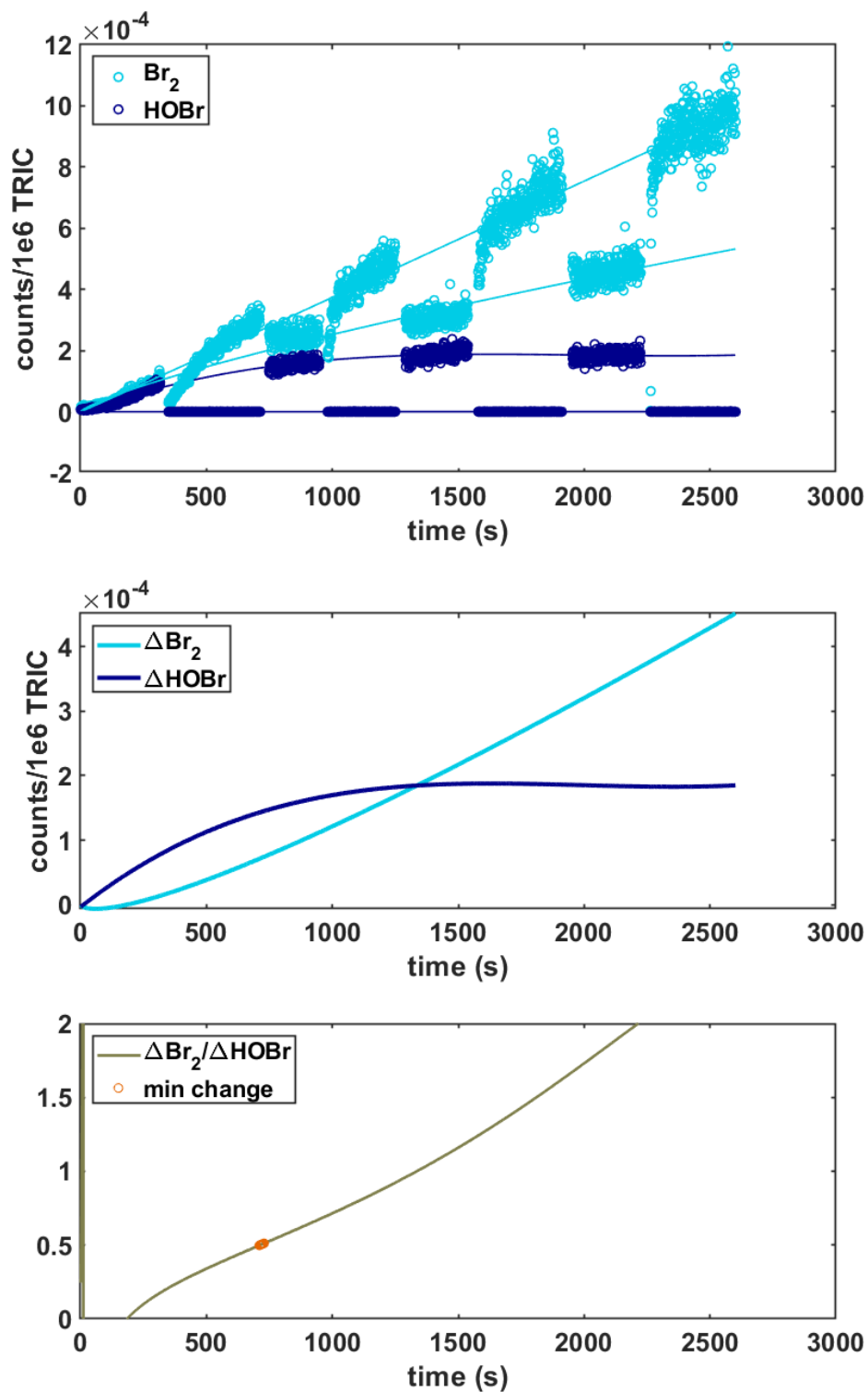


Figure 3.2: [Top] Timeseries of measured signals (circles) in normalized counts per 1 million TRIC for Br_2 (light blue) and HOBr (navy) iodide clusters, along with power series and polynomial fits (solid lines). [Middle] Absolute difference in measured signal fits with and without the addition of NaBr chamber. [Bottom] Fraction of changes in signal traced through experiment (brown solid line), and the values at minimum slope (orange circles).

Compound	Binding Enthalpy (kcal/mol)	Sensitivity (counts ppt ⁻¹)
Br ₂	24.3	1.51
HOBr	15.1	1.29
BrO	13.5	1.26
BrONO ₂	13.3	1.25
BrCl	24.2	1.51

Table 1: Relative binding enthalpies and corresponding sensitivity (per 1e6 TRIC) for five key bromine gas phase species detected by the CIMS during BLEACH.

Here $C_{f,X}$ is the CIMS sensitivity determined for molecule X and ΔH_X is its given binding enthalpy to I^- . Shown in Table 1 are the key bromine-containing species with their corresponding calculated binding enthalpies and subsequent instrument sensitivity for the in-situ calibrations during BLEACH, which again is determined directly for Br₂ and via equation 19 for the remaining compounds. The fractional sensitivity of HOBr to Br₂ based off of this binding enthalpy method is calculated to be ~ 0.8 , which is within the experimental range determined in section 3.4 and in reasonable agreement to the study by Liao et al (2011) referenced therein. The sensitivity ratio of BrO to Br₂ is also approximately 0.8, which is consistent with another study by Liao et al (2012) reporting nearly identical values for the two sensitivity ratios.[40] Our experimental calibration to directly determine an instrument sensitivity range for HOBr along with the values reported in previous studies all serve as independent verification for the use of this binding enthalpy method for reporting concentrations of the detected Br_y as well as the chlorinated species.

3.6 Humidity-based sensitivity Correction

It has been reported in multiple studies that CIMS sensitivity to several classes of compounds is dependent on the humidity, or more specifically, the partial pressure of water vapor (P_{H_2O}) present in the IMR during sampling, which is also dependent on temperature and pressure.[41][42][43][44] During the wintertime BLEACH campaign, temperatures ranged from a minimum of 16°C to a maximum of 23°C and humidity from 51-98%, which combine to give the P_{H_2O} range of 10 to 25 mbar at ambient pressures on the order of 1 atm (1013.25 mbar). As previously mentioned, the ambient humidity is assumed to equivalent to that inside the IMR throughout ambient sampling, which includes periods of direct Br₂ calibration where RH ranged between 68-77%, which translates along with temperature to P_{H_2O} values spanning 16.9-17.5 mbar. This is a relatively small window of water vapor pressures during calibration, thus it is important to quantitatively determine the P_{H_2O} dependence of bromine sensitivity.

This extrapolation is accomplished using a post-campaign laboratory experiment during which Br₂ is delivered to the IMR at a constant rate from the same permeation device deployed during BLEACH. Upstream

of the bromine gas output, the humidity (and thus water vapor pressure) in the IMR is modulated via the addition of UHP N₂ that is both unaltered (dry) and passed through a room temperature bubbler (water held in an air-tight flask with two ports for dry N₂ input and humidified output. The dry and humidified N₂ gas are carried into the atmospheric pressure IMR at varying relative flow rate fractions, with the sum of both remaining constant at 7 LPM, which is slightly less than that of the ambient input IMR flow (8.5 LPM when sampling with 1.5 LPM reagent ion flow). Several minutes are elapsed after step changes in the dry and humidified flows, to allow sufficient time for humidity and Br₂ ion signals to stabilize. Only data during these equilibrated periods are used for sensitivity analysis. Humidity in the t-IMR during laboratory experiments is measured downstream of the ion flow/MS sampling port in the exhaust line using the probe of an Elitech model GSP-6 temperature and humidity logger, positioned upstream of the IMR pump.

Shown in figure 3.3 is the resulting Br₂ sensitivity in counts/ppt (per 1e6 TRIC) scattered against partial water vapor pressure reported in mbar as calculated using the measured humidity during each dry to humidified N₂ flow regime, temperature of the laboratory, and an assumed atmospheric pressure of 1 atm. Both horizontal and vertical error bars represent one standard deviation in P_{H_2O} and sensitivity, respectively. Data from the experimental setup described above are shown with blue markers and labeled as "Lab". Data from direct calibration during the winter 2023 and summer 2022 campaigns are shown in black and red, respectively, with P_{H_2O} in these cases calculated using in situ measurements of humidity, temperature, and pressure at THMAO. A modified gaussian fit is applied to all data from both the laboratory and BLEACH which is shown in purple. The equation for this modified gaussian fit extrapolates from previous work from Lee et al (2014) which determined bromine sensitivity for a low pressure IMR ($P_{H_2O} < 1$)[45] and another study from Zhao et al (2017) reporting that sensitivities for multiple compounds decay at a decreasing rate above a water vapor pressure threshold on the order of 10 mbar.[46] The resulting fit equation has the format:

$$y = k_1 + k_2 \log\left(\frac{x}{k_3}\right) + k_4 \exp(-(k_5 \cdot x + k_6)) \cdot \exp\left(\left(\frac{-(x - k_7)}{k_8}\right)^2\right) + k_9 \exp(-k_{10} \cdot x) \quad (20)$$

where y corresponds to Br₂ sensitivity, x to P_{H_2O} , with k_{1-10} representing constant fit parameters.

The fit shows an initial strong increase in sensitivity with increasing P_{H_2O} , plateauing and reaching a maximum at approximately 10.3 mbar, followed by a slower decline to a gradually increasing asymptote with a value around 0.9-1 counts/ppt at higher humidities/vapor pressures. There is also a decline in sensitivity to 0 at a partial water vapor pressure of 0.1 mbar, which would provide non-real negative sensitivity values for a completely dry sample. Though during ambient sampling in an IMR operating at atmospheric pressure, P_{H_2O} values are not expected to register near this range. This is especially true during the BLEACH23 campaign, where the water vapor pressure values never fall below 10 mbar, as mentioned previously. Therefore, this

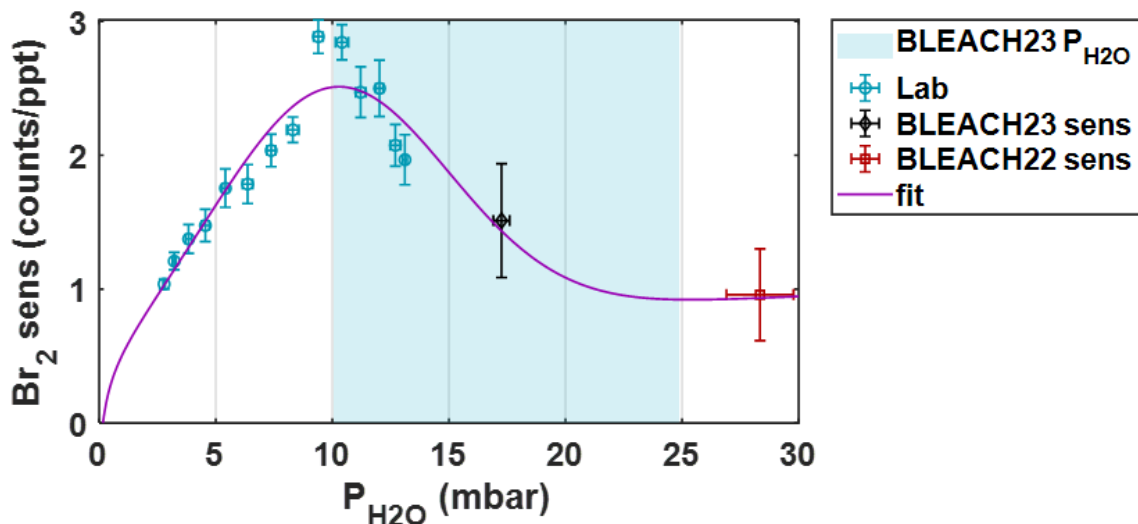


Figure 3.3: Bromine sensitivity vs. partial pressure of water vapor (P_{H_2O}) with data determined from the post-campaign laboratory experiment (blue), and direct calibrations from the winter BLEACH23 (black) and summer BLEACH22 (red) campaigns. A custom modified-Gaussian fit using all data points is shown in purple. Blue shading indicates the range of P_{H_2O} calculated from measured temperature and humidity during BLEACH23 (10-24 mbar)

potentially problematic lower boundary does not affect the humidity-dependent sensitivity correction for the BLEACH campaign measurements.

The modified gaussian fit is used to generate a dynamic sensitivity value for all compounds for which we have binding enthalpies, including the five main bromine compounds discussed in the results section: Br_2 , BrCl , HOBr , BrONO_2 , and BrO . This is accomplished by taking the directly measured Br_2 sensitivity value during BLEACH23 at the corresponding P_{H_2O} value during calibration and converting it to a sensitivity for the other compounds according to equation 19. The fit equation for Br_2 is normalized to a value of 1 at the point of average P_{H_2O} for in-field calibrations, and then multiplied by the singular sensitivities of the given compounds via their respective binding enthalpy ratios. Scaling sensitivity to other compounds at the point of Br_2 calibration periods, and then applying the P_{H_2O} correction ensures that the conversion for all compound signals to concentration from ion signal is based on a direct, in-situ sensitivity measurement under identical conditions. Humidity and temperature measurements at THMAO have the same 1-minute resolution as the pre-averaged CIMS data, resulting in a 1-to-1 timeseries match of P_{H_2O} and thus a 1-minute resolved humidity-corrected sensitivity for these bromine-containing species. Integrated signal counts for the all compounds of interest (clustered to iodide reagent) are normalized to TRIC and subsequently divided by this dynamic sensitivity timeseries, point-by-point, to produce concentration values reported in parts per trillion (ppt) by volume at each 1-minute time step.

3.7 Reactive Bromine Observations

Bromine atoms have two naturally occurring stable isotopes at weights of 79 and 81 amu, which occur approximately in equal abundance: Br^{79} with 50.7% and Br^{81} with 49.3%.[47] Chlorine atoms also have two stable isotopes: Cl^{35} with relative abundance of 75.8% and Cl^{37} with 24.2%.[48] This creates distinct signatures in a mass spectrum for both elements and all compounds that contain them, where a 1:1 ratio is expected for clusters containing one bromine atom at base mass to charge ratio m and the corresponding isotope peak at $m + 2$. Meanwhile an approximate 3:1 ratio is expected for single chlorine-containing species, also for peaks at m/Q m and $m + 2$, respectively.

With ambient atmospheric mass spectrometry, it is common to observe multiple species peaks at the same unit mass, with the possibility of interference between multiple molecules close in mass-to-charge values, depending on resolution. However, halogenated species, including both the bromine and chlorine-containing molecules discussed here as well as iodine (i.e. the reagent ion used here), show a negative mass defect in measured spectra. This means that the exact m/Q position for a halogenated peak is more negative compared to other species, i.e. organic clusters for which iodide mode CIMS is sensitive. This, combined with the high resolving power of the LToF CIMS, separates the peak m/Q position of bromine-containing molecules (clustered to I^-), decreasing the likelihood of interference from overlapping clusters compared with other ambient compounds detected, typically making their identification more robust.

Figure 3.4 shows representative spectra for an ambient sampling period during the BLEACH campaign for the main bromine containing compounds presented in this work. Baseline-subtracted spectra as ion counts (per m/Q bin) as measured by the CIMS are displayed in the red traces for each plot, while green bars show the exact m/Q position and initial fitted peak height for each compound when clustered with the reagent I^- , labeled in green above the corresponding first isotope peak. Isotope ratio patterns of 1:1 are clear for the clusters BrOI^- and HOBrI^- consistent with the single bromine atom in each. For the BrONO_2I^- cluster, the heavier isotope peak at approximate m/Q 269.8 is dwarfed by the peak for I_2O^- , an instrument artifact from iodide reagent chemistry, which is consistently larger throughout sampling. However, the large mass defect and high resolution for the first isotope peak at m/Q 267.8 support the identification of this detected species. Diatomic bromine with a first peak at m/Q 284.74 shows a consistent isotopic pattern of approximately 1:2:1 at masses $m + 2$ and $m + 4$, resulting from the four possible combinations of Br^{79} and Br^{81} . The combination of bromine and chlorine atoms for the BrClI^- also shows an isotopic peak signature consistent with expectation (i.e. the magnitude of the green bars). Save for the one exception with a larger peak overlap, the combination of high mass resolving power, negative mass defect for halogenated sample molecules, and the distinct isotope signature for Br and Cl atoms confirms the spectral identification of these

measured bromine-containing molecules in ambient sampling throughout the campaign.

Shown in figure 3.5 are the timeseries of five key bromine species measured with the t-IMR-equipped CIMS at THMAO, adjusted to local time of sampling (Bermuda, UTC - 4). The sampling frequency of the CIMS is 1 Hz for this campaign, resulting in a mass spectrum every second. This data is pre-averaged to 1-minute spectra before high resolution peak fitting is applied. Shown in the figure are the 15-minute averaged timeseries (applied after 1-minute peak integration). Shown in figure 3.6 are the diurnal cycles measured for each compound. Median concentrations are presented with solid lines and open circle markers, with shading to represent the respective 25th to 75th percentiles of measurements throughout the winter campaign. gray dashed lines indicate the LOD calculated for each compound via equation 12 (for 1-hour time resolution). The missing portion of data from Feb 2-8 2023 is due to a nationwide power-outage in Bermuda and subsequent technical difficulties with getting instruments back online.

Br₂ generally shows the highest concentrations relative to the other key Br_{y*} (= 2Br₂ + HOBr + BrONO₂ + BrO + BrCl) species, with a maximum concentration of 3.7 ppt in the 15-minute average. The median concentration in the diurnal cycle stays below 1 ppt, with an mean concentration of 0.5 ppt for the entire sampling period. There is a clear decrease in most of the signal after the morning of January 27, which marks a distinct shift in multiple components of Br_{y*}. Due to relatively large photolysis rates, gas phase bromine is expected to decrease during the day to near if not completely below detection limits according to most model outputs. And while concentrations are more elevated during the nighttime hours shown in the median signal of the diel trend, there is a lack of a decrease and even small relative enhancement around midday, which becomes more apparent when looking at the 75th percentile of the measurements. A significant daytime source of Br₂ would be required to compensate for and even overtake the large photolytic sink for the days in which concentrations remain above LOD. Nearly all data points in the 1-minute timeseries are above LOD for Br₂.

We report an average concentration of 0.13 ppt for HOBr and maximum of 1 ppt in the 15-minute binned average. Signals reliably increase during daylight hours each day, mostly peaking in late morning and returning to near or below detection limits during the nighttime as is evident in the diurnal cycle in figure 3.6. This is consistent with the current understanding that HOBr production in the gas phase depends on the production of BrO, which is made via photolysis-driven reactions producing free bromine atoms in the atmosphere. Compared to the other three species, there is less of a noticeable drop in HOBr signal after Jan 27th, recording similar daytime maximum concentrations to the preceding period on Jan 31, Feb 2 and 9.

Measurements of BrONO₂ also show a clear daytime enhancement in median concentration, with signals mostly below its corresponding LOD at night. The profile exhibits two local maxima in the early morning at 8 am and in the afternoon at 3 pm, revealing a small local minimum between these hours, where the strongest

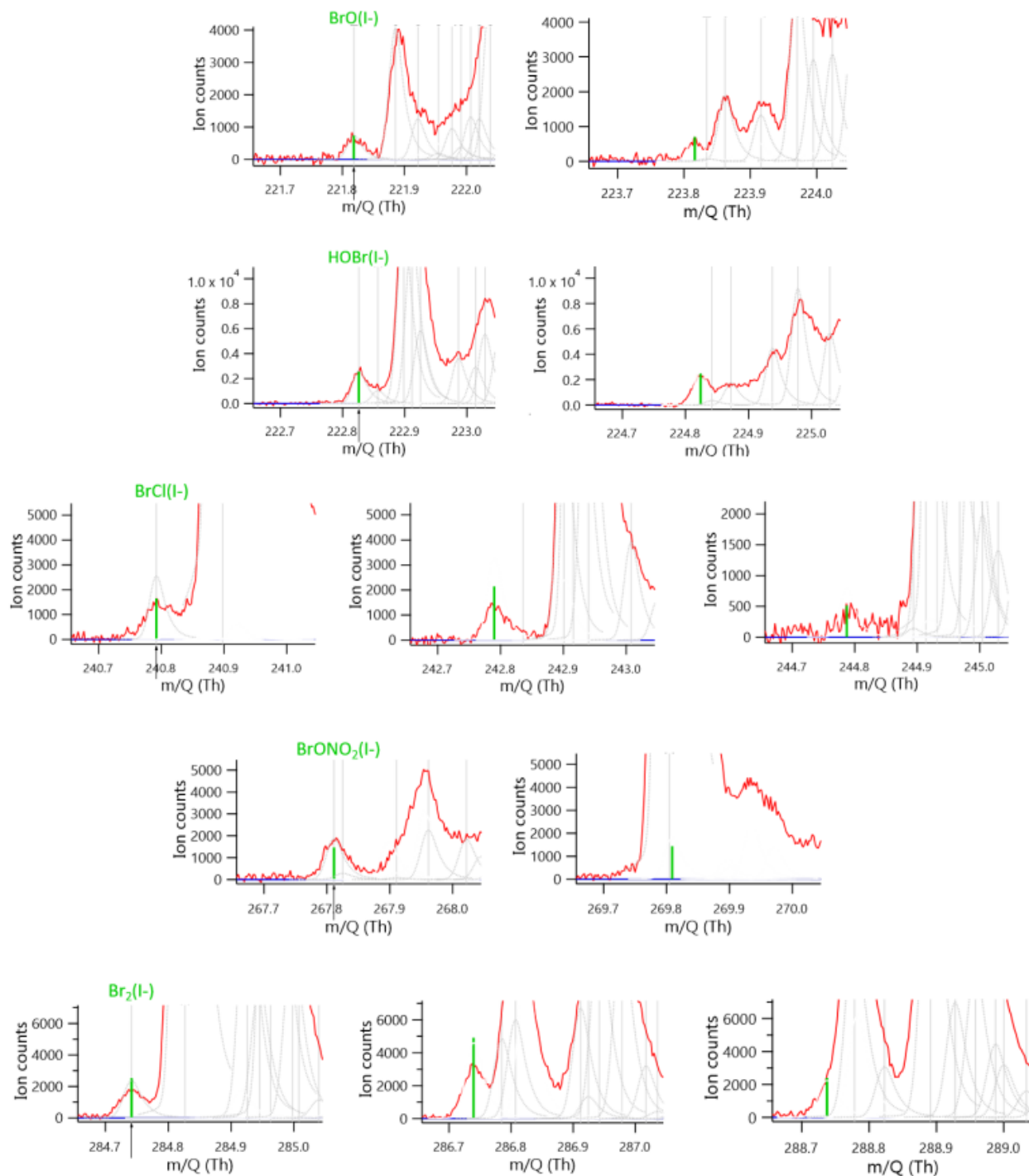


Figure 3.4: Representative CIMS spectra showing peak identification for five bromine-containing species and their isotopes when clustered with I^- . Red traces represent raw spectra (binned ion counts) as measured, while green bars with labels show exact mass-to-charge positions and fitted heights for the peak centers of each compound. Corresponding isotope peaks are shown to the right of each compound.

photolysis rates are expected on typical days with clear skies. The average and maximum concentrations for the campaign respectively are 0.04 and 0.35 ppt. Similarly to HOBr, the diel behavior of BrONO₂ aligns with known chemistry and the idea that photolytically-dependent BrO is also a necessary precursor for its gas-phase production. The local minimum in the observed diel trend aligns with the modeled prediction presented by Liao et al 2012 for their study in Alaska, attributed to a rapid increase in the bromine nitrate photolysis rate around midday.[2] It is also possible that under a NO₂-limited regime, higher NO₂ photolysis during midday i.e. NO_x equilibrium shifting toward NO, would reduce available NO₂ for reaction with BrO to form BrONO₂. Given that the photolysis loss rate of BrONO₂ is assumed in calculations to be less than that of HOBr, which shows no local minimum during midday in the campaign-long diel trend, we postulate that THMAO may indeed be in an NO₂-limited regime concerning bromine nitrate production.

BrO measurements have a relatively low average concentration of 0.06 ppt (below 1-minute LOD of 0.11 ppt) and a maximum of 0.28 ppt. The median signal in the diurnal profile for all hours remains close to detection limits shown in gray, with a slight increase during daylight hours along with the 75th percentile shading, providing limited evidence consistent with photolysis being the dominant production mechanism. The limited detection and consistently low concentrations measured for BrO are somewhat expected in the subtropical MBL given its relatively high reactivity and large amount of loss reactions, including the second largest photolysis rate behind Br₂ among all bromine species presented.

Concentrations are shown for the interhalogen species BrCl with an average of 0.26 ppt and a maximum at 2.6 ppt. There are multiple possible heterogeneous reaction pathways for which BrCl can be produced via HOBr, HOCl, BrONO₂, and ClONO₂ reacting with HBr and HCl in and on the surfaces or SSA particles. There is also one gas phase formation pathway involving BrO reacting with ClO, where the iodide adduct CIMS was not able to detect the latter during BLEACH. BrCl concentrations exhibit a similar drop in concentrations to the rest of Br_y* for the second half of the campaign, though one day later, in this case falling after Jan 28. HOBr also remains stable through this date, reaching an approximately equal daytime maximum on the Jan 27 and 28. The diurnal profile also remains relatively flat, with the only notable small increases in the median concentrations occurring around the hours local sunrise and sunset (7:00 and 18:00), which is more noticeable for the 75th percentile shading. Similar to Br₂, the persistence of BrCl concentrations throughout daylight hours in the campaign-long diel trend is somewhat surprising given that it also has a very large photolysis loss rate. Most model simulation also predict minimum or near-zero concentrations during the day when photolysis is strongest.

Figure 3.7 shows wind roses for the same five major bromine-containing compounds measured during the winter deployment. The 1-minute CIMS data is coordinated with 1-minute wind speed and wind direction data from the measurements at THMAO (on the 23m tower), and then binned into the displayed sectors for

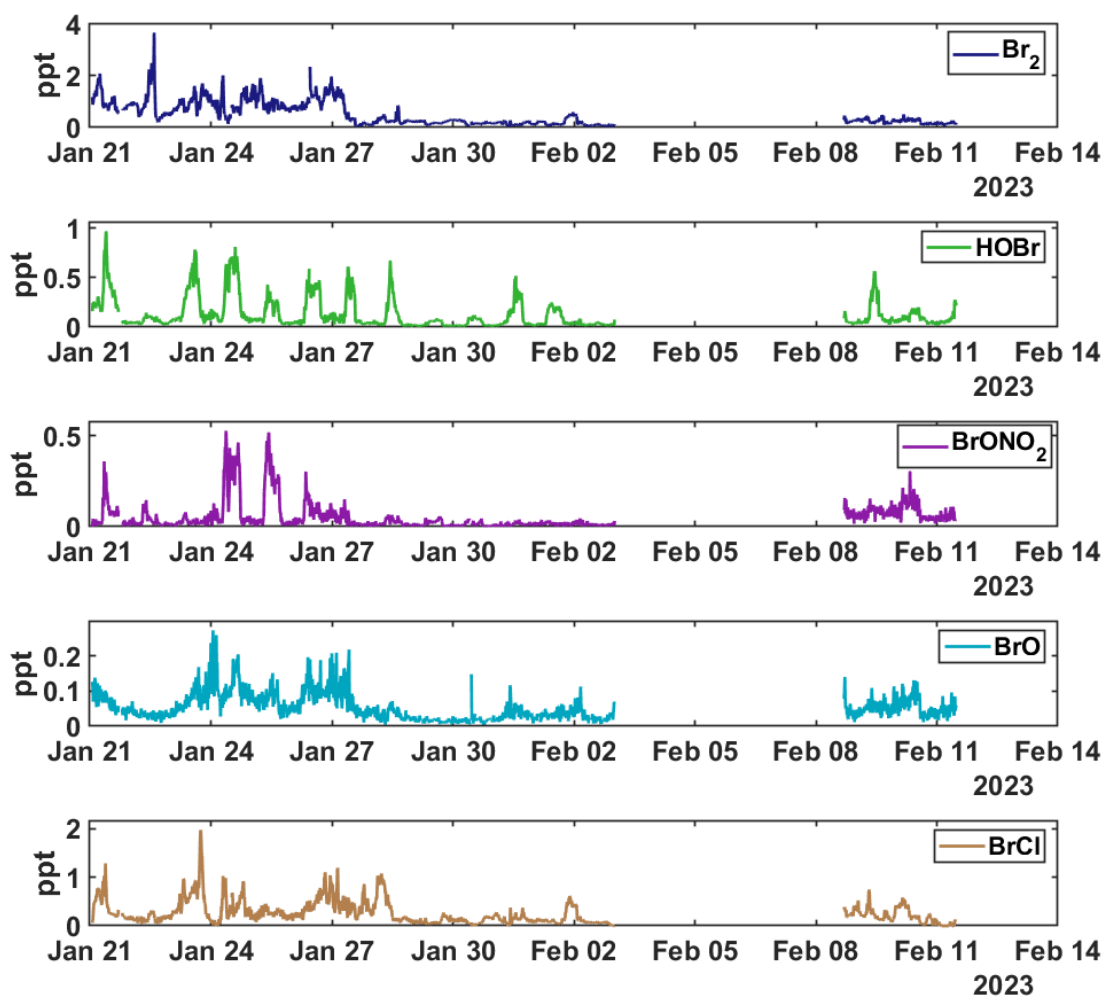


Figure 3.5: 15 minute averaged concentration timeseries of Br₂, HOBr, BrONO₂, BrO, and BrCl as measured by the CIMS at THMAO during the wintertime BLEACH23 campaign.

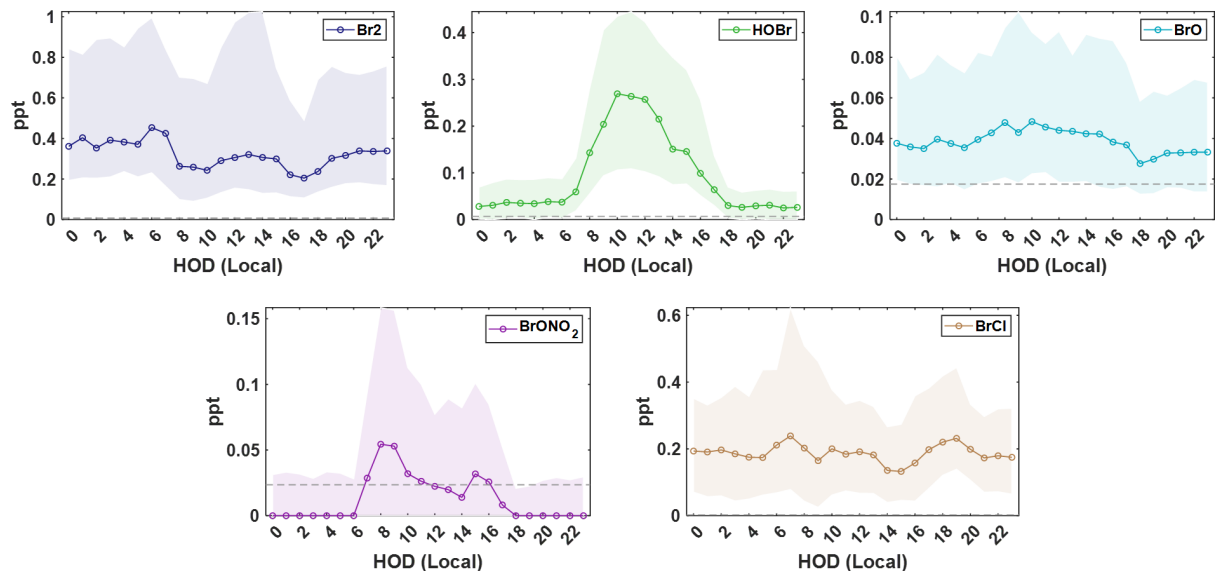


Figure 3.6: Diurnal profiles of Br_2 , HOBr , BrONO_2 , BrO , and BrCl as measured by the CIMS at THMAO during the wintertime BLEACH23 campaign. Each point represents the median concentration for the given compound using all viable data points, while shading represents the 25th percentile of concentrations at the lower limit while the upper shows the 75th. Dashed gray lines indicate the respective limits of detection (LOD) for each.

wind direction. The radial length of each wedge represents the corresponding fraction of data points that fall into that sector. Concentrations are displayed with the color mapping of each wedge, where white and yellow colors represent the lowest concentrations while red and black show the highest. The scaling of this color map changes with each compound and is displayed in the legend for every plot. To ensure that the wind direction bins are robust, data where wind speeds were measured to be below 0.2 m/s are excluded from these plots. This avoids periods of stagnant air causing wind vane instrumentation to idly move in any direction, which would not be representative of genuine easterly or westerly winds, etc. This quality control results in the removal of less than a 2% fraction of CIMS data coverage. Each wind rose only includes data for which concentrations of the given compound are above the respective (1 minute) detection limit, so the wind direction frequencies (wedge radii) deviate slightly between the compounds shown due to different periods of measurement being excluded.

Also shown in the bottom right panel of figure 3.7 is a satellite image of the THMAO site with a purple marker showing the location of the t-IMR CIMS measurements, as well as a zoomed out map of Bermuda with the same marker indicating the location of the site within the island. The inset in the image is a uniformly colored wind rose to show the frequency of all wind directions during CIMS sampling. The standard criteria used by BIOS at THMAO for determining "onshore winds" referring to winds and local air masses originating from over the ocean on site, is to include only wind direction measurements between 210 and 315 degrees

(where 0° is true North), representing the southwesterly to northwesterly sector in the wind rose. This sector is indicated with green dashed lines in the inset frequency wind rose.

Data filtered for Br₂ shows the most uniform wind direction frequency spread, with slightly more data in the westerly wind sector. It also shows the smallest dependence of concentration on wind direction among Br_y* species, with elevated levels shown in almost each wedge. There is a slight enhancement in the north to easterly directions, showing the highest concentrations indicated in the dark red and black colors. BrONO₂ also shows elevated concentrations detected with winds out of the northeastern sector, despite there being less frequent measurements (above its LOD) originating from that direction, though the highest frequency and elevated concentrations for bromine nitrate are shown in the northwesterly wind sector. The north through southeasterly wind sector (~0 - 120°) includes air masses most directly affected by local anthropogenic pollution and land influence. This sector also shows much more frequent and larger NO_x concentrations typically on the order of several hundred ppt and up to a few ppb. This makes sense as the island's only city of Hamilton and power plant are located approximately 9 km from THMAO with a heading between 60-75° i.e. the northeasterly direction.

The HOBr, BrO, and BrCl wind roses show a clear enhancement in concentrations as well as frequency of measurement above LOD mostly in the western half of the wind rose compared to relatively much lower concentrations coming from the east. There are minimal white colored wedges for BrO and BrONO₂ due to their relatively higher 1-minute LOD on the upper end of the range for that concentration range. Approximately 6% of the 1-minute measurements were above the calculated 60 second LOD for BrO, compared to 8%, 53%, 84%, and 87% for BrONO₂, HOBr, BrCl, and Br₂ respectively. This is somewhat unsurprising considering all but BrCl and Br₂ are expected to drop below detection limits in the absence of photolysis and these plots include all times of day. In fact, when accounting for only measurements taken daylight hours (8:00-16:59 local time), measurements above LOD increase to 8%, 15%, 84%, , and respectively for BrO, BrONO₂, and HOBr.

The correlations of HOBr, BrO, and BrCl concentrations in figure 3.7 with local winds coming from the northwest, southwest, and (as a more marginal case) southern directions implies a marine origin or at least influence in their atmospheric chemical sources. This likely stems from gas phase transformations of free atomic bromine (Br) during the day, which can be attributed to photolysis of most Br_y species present in the MBL. This includes compounds liberated from and potentially formed on the surfaces of SSAs. Reaction pathways for formation on and subsequent emission from aerosol surfaces of Br₂, BrCl, and HOBr have been reported.[49] Br is expected to rapidly form BrO, which as stated previously is considered highly reactive as well as photolabile, acting as a branching point for the inorganic bromine chemical mechanism in the presence of sunlight. The enhancements of Br₂ and BrONO₂ with northwesterly winds imply the

same marine-influenced source just discussed for the other compounds in that wind sector. However, the coincidence of some of their highest concentrations with winds from the northeasterly sector suggest an additional local island-based source of bromine, and/or pollution-driven increases in production.

Formation of BrONO_2 is considered exclusive to one reaction dependent on the presence of NO_2 as a reactant with BrO , which is consistent with the generally much higher levels of NO_x measured for local easterly winds. Bromine nitrate also has the longest photolytic lifetime among the Br_{y*} components, a potential reason why it may remain elevated in this wind sector while HOBr and BrO do not. On the other hand, Br_2 also has its highest concentrations registered in the easterly sector and has the highest photolysis loss rate. Thus, a single common source and differences in photolytic loss rates alone are not enough to explain this enhancement for both compounds. It seems probable that there exists some or multiple local bromine-containing source(s) to the east of THMAO and, in the presence of elevated NO_x from anthropogenic activity (local or otherwise), BrONO_2 is quickly and preferentially formed over HOBr . The source(s) could be a strong emitter of diatomic bromine, or secondary reactions (i.e. on SSA surfaces) quickly recycle Br_2 from BrONO_2 (and HOBr) to the gas phase to compensate its relatively much shorter photolysis lifetime.

The possibilities considered for such a local source of reactive bromine include the power plant located in Hamilton, human activity (i.e. small scale coal burning, pool and jacuzzi maintenance, etc.) and enhanced direct organobromide emissions from the Great Bay or other coastlines to the east of THMAO. While bromine has been detected at relatively large levels in coal-burning power plant plumes[10], to the best of our knowledge the plant operating in Hamilton uses heavy fuel oil and diesel as fuel. Wind speeds for the NE/E wind sector throughout the campaign were calmer compared to the westerly counterpart, with a median of 1.7 and maximum of 6.5 m/s for directions between 0-120°, compared to a respective median and maximum of 4.9 and 18.1 m/s for all directions. This along with the distance of ~9 km between the plant and nearly ground level CIMS sampling location makes power plant exhaust seem less likely to be the cause of the easterly enhancement. Average NO_x concentrations in this easterly sector register a mean value of 980 ppt, compared to the mean of 80 ppt for the defined onshore wind sector (210-315°). As mentioned in the introduction, polluted environments and elevated NO_x have previously coincided with increases in observed Br_y , associated with either unknown local sources and/or changes in heterogeneous chemistry via higher aerosol nitrate and changes to pH.

Given that BrONO_2 and HOBr both depend on the photolytic production of BrO during the day, examining the relationship or lack thereof between the concentrations of the two is important for examining existing chemistry and identifying favorable conditions for one product pathway vs. the other. Shown in figure 3.8 is a scatter plot of 30-minute-averaged BrONO_2 vs. HOBr concentrations as measured by the CIMS, colored by NO_2 concentrations reported in ppt as measured by the onsite LIF instrument. Concen-

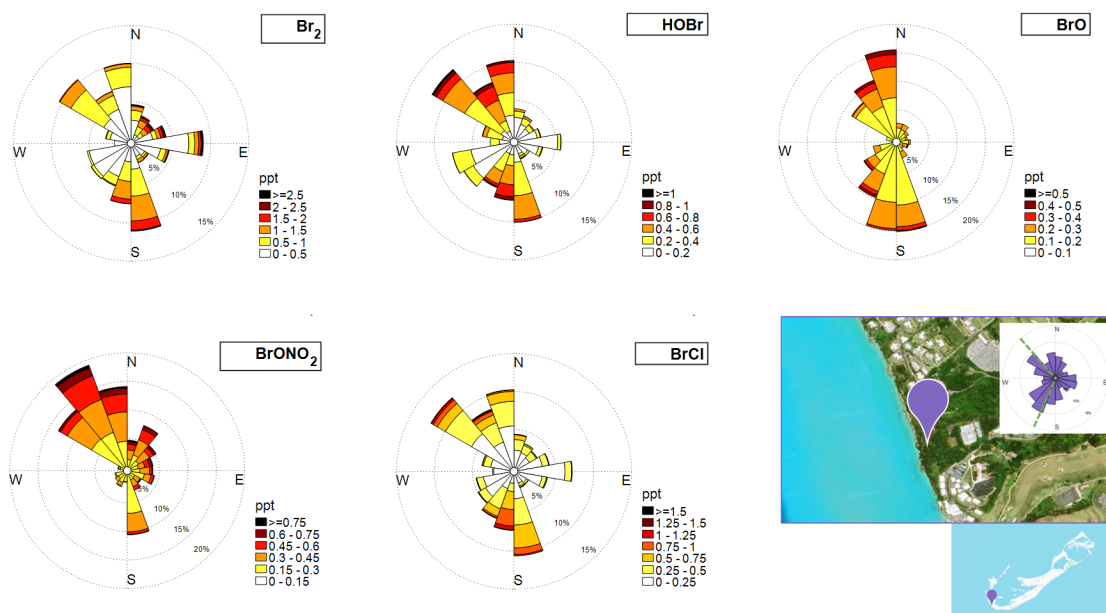


Figure 3.7: Wind roses of five Br_y species measured during BLEACH23. Wedge radii represent the percentage of 1-minute data points that fall into the corresponding wind direction sector. Wedges are colored by corresponding species concentration frequency as noted in the legend for each compound. Points with wind speeds below 0.2 m/s and concentrations below LOD for each compound are not included in the respective plot. A satellite image of the THMAO site (purple marker) is also included in the bottom right with a map of Bermuda [Google maps], as well as a wind rose of the frequency of wind directions for the entire CIMS sampling period.

trations are filtered to only include observations above respective LODs for both compounds detected by CIMS during daylight hours, defined as 08:00 through 16:59 local time in Bermuda for the winter sampling period in January and February. For reference, the local sunrise and sunset times on the first day of data included in this analysis, Jan 20, are 07:19 and 17:41; and for the final day of sampling on Feb 11 they are 07:06 and 18:02. The 1:1 line is shown in the light gray dashed segment in the plot. The general trend with all data shown is that both compounds show coincident enhancements, though not simply linearly. A linear regression fit results in a slope of 0.19 and an R^2 correlation coefficient of 0.28. There is a clear trend looking at the color scale, showing that as NO_2 levels increase, the two become more tightly correlated and BrONO_2 production is more favored as evidence by the increasing slope toward the 1:1 line.

Also presented in the lower panels of figure 3.8 is the same relationship of BrONO_2 to HOBr after separating NO_2 into concentration bins increasing from left to right, where the ranges are given in the title of each plot along with correlation coefficients and p-values. The colorbars (still in units of ppt) for each of these individually binned plots change to reflect the appropriate NO_2 range for each, still with the highest levels represented by magenta colors. As the NO_2 bins increase in concentration, the slope of the linear fit increases, as does the correlation coefficient, maximizing with a linear slope of 1.51 and an R^2 value of 0.88 when NO_2 is above 550 ppt. This indicates more clearly that BrONO_2 production becomes much more favorable and begins to overtake (yet still trends with) the production of HOBr at the higher NO_2 levels, corroborated by the maximum HOBr concentrations remaining below 0.4 ppt in the 30-minute average with the highest NO_2 bin. The lack of correlation and generally much lower BrONO_2 measurements in the smallest bin of < 100 ppt also indicates a potential threshold for NO_2 , below which this formation pathway cannot compete with the alternatives of other bromine-containing species which stem from the loss of BrO , i.e. that of HOBr . Examining this relationship provides some confirmation of the postulated chemical mechanism where gas phase formation of BrONO_2 and HOBr are both dependent on the same reactant, assumed to be the presence of the relatively highly reactive BrO . The dynamic relationship between these two components of Br_y is important to understand as they are known to have different photolysis lifetimes and gas-phase/heterogeneous loss pathways. Thus, changes to their respective levels in the MBL would affect the partitioning between (and the total concentrations of) gaseous inorganic bromine. Adding the layer of NO_2 concentrations demonstrates how this relationship is highly dependent on availability of limiting reactants, and can be affected by pollution levels in marine environments.

THMAO is well positioned to sample air masses originating from over the ocean, capturing natural chemical processes occurring in the MBL. However, it is also subject to influence from anthropogenic activity as well as potential effects of land use and vegetation from the island of Bermuda, especially when significant easterly winds are present as the site is located on the western coastline. In order to account for potential

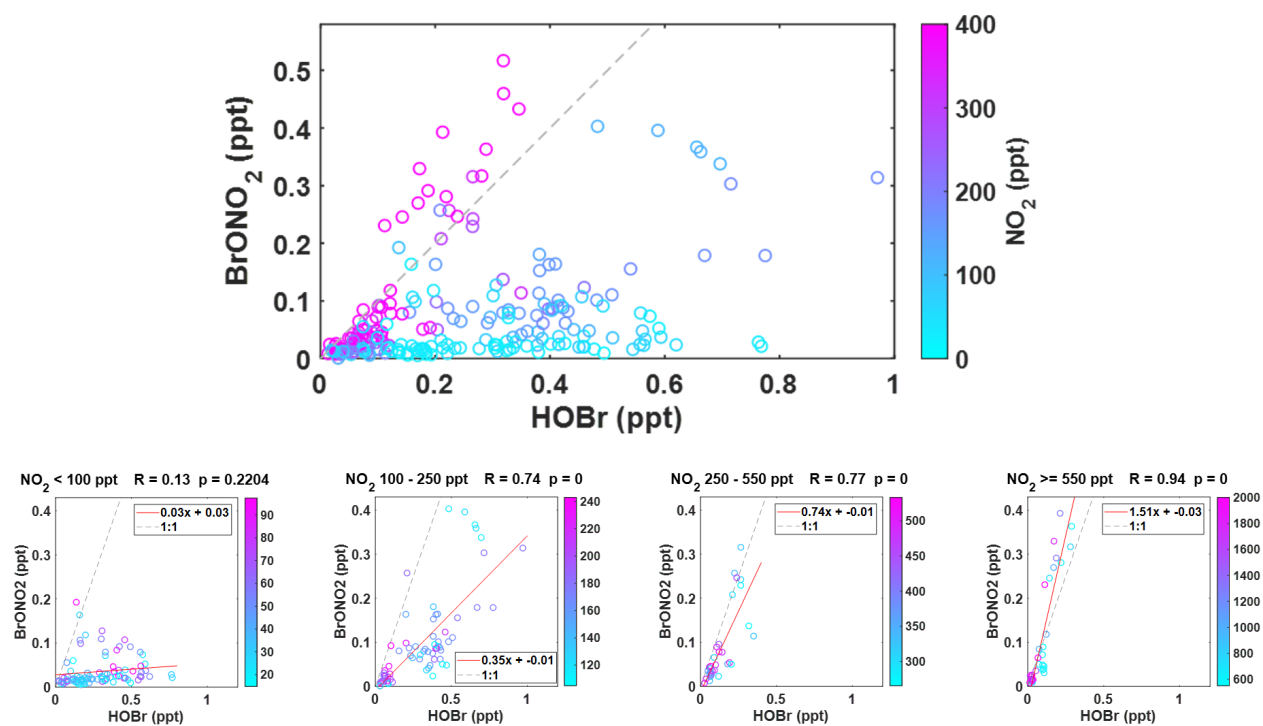


Figure 3.8: Scatter plot of 30-minute average concentrations for BrONO₂ on the y-axis and HOBr on the x-axis, colored by NO₂ concentrations as measured by the LIF instrument, all reported in parts per trillion. Data is filtered to include only concentrations above LOD measured during daylight hours defined as 08:00 - 16:59 local time in Bermuda.

impacts from local activity and attempt to isolate natural atmospheric chemical processes over the remote ocean, filters are applied to data. The identification is based on back trajectories calculated using the NOAA HYSPLIT model[50] as well as in-situ measurements of NO_x and ozone, creating a so-called "clean marine" index for measurements. Shown in figure 3.9 are the diel cycles for the five Br_y^* species detected by the CIMS, filtered to include only these clean marine data points. Median concentrations are given for each hourly bin, along with shading to indicate the 25th-75th percentile ranges. Respective limits of detection are repeated in gray dashed lines. Also shown in the sixth plot is a summary with all five median signals displayed in the same plot. The clean marine periods include over 3600 (1-minute) data points from the CIMS measurements, giving approximately 16% data coverage relative to the entire winter sampling period, during which the winds incident on THMAO are mostly southwesterly. Each hourly bin contains at least 110 (1-minute) sample points except for 16:00 with 87 points. There is slightly more data coverage during the nighttime hours where there are over 170 data points in each bin from the hours of 18:00 - 03:00. Ozone for the clean marine periods has a mean concentration of 42 ppb with a standard deviation of ($\pm$) 5, and a maximum of 48 ppb. NO_2 shows a mean concentration of 44 ± 31 ppt with a maximum of 270 ppt, while NO on average is 3 with a standard deviation of 4 ppt and maximum of 38 ppt.

Median Br_2 observations for this period show the largest shift toward the expected behavior based on its relatively high photolysis rate, where the sustained and even enhanced concentrations during daylight hours is significantly reduced, while higher concentrations buildup after sunset (especially evident in the 75th percentile shading). This reflects the current understanding of the bromine chemical mechanism where typically the strong photolysis rates during the day greatly increase Br_2 loss, outpacing gas-phase production (and/or liberation) which significantly lowers concentrations. Though there remains a slight local enhancement around noon local time in the average, and signals remain above LOD throughout the day. This implies that there is still a somewhat significant marine source of Br_2 during the day, though it is likely either enhanced under polluted conditions, or coincident with and additive to a separate local source peaking during the strongest daily photolysis rates ($\sim$ 12:00-14:00 local). BrCl concentrations in the clean marine periods show a somewhat similar trend throughout the day where median levels remain near 0.2 ppt, though in this case with a drop in signal to near zero at the hour of 9:00 shortly after sunrise recovering to the 0.2 ppt level shortly after. There is also a notable increase in the average compared to the unfiltered data around sunset between the hours of 18:00-19:00.

The diel shape for HOBr remains approximately the same as the unfiltered profile, with a slightly larger and later peak median concentration around midday, which subsequently returns to near or below background after the cessation of active photochemistry. BrO remains near detection limits in the average, with no noticeable enhancement during the day, contrary to the slight increase evident in the campaign-long trend.

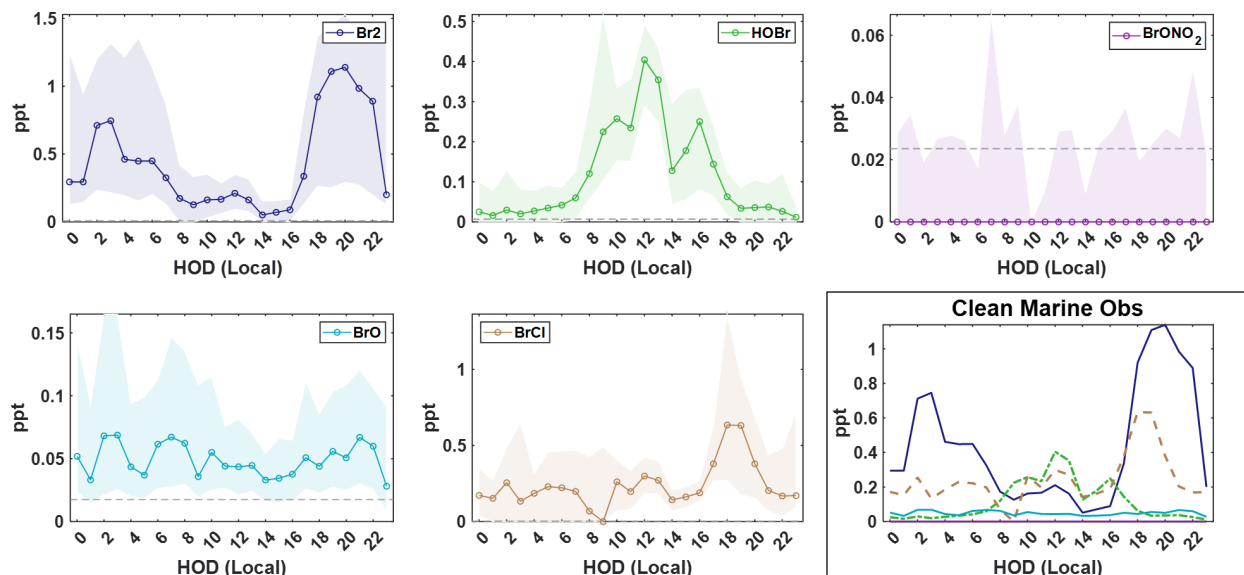


Figure 3.9: Individual diurnal profiles of observed Br_y species during the BLEACH winter leg, filtered to include only data designated as "clean marine-sourced" based on backtrajectory analysis, wind direction, NO_x and O₃ levels. Each plot shows a given compound's median concentration in ppt for each (local) hourly bin and shading to show the 25th to 75th percentiles, and grey dashed traces to indicate the LOD for a given species, with the exception of the bottom right plot which summarizes the median diel cycles for all five species. Br₂ is shown in dark blue, HOBr in green dashes, BrONO₂ in purple, BrCl in brown dashes, and BrO in light blue.

This is indicative that BrO reactivity remains relatively high in the clean marine MBL, where its loss reactions occur on pace or faster than it's formation. Importantly for this clean marine period, the diurnal cycle for BrONO₂ shows what is essentially a complete loss of signal, where the median for each hourly bin is 0 with even the 75th percentile of concentrations at or below the LOD in almost all cases. This indicates what is likely a significant shift in the fate of BrO away from the bromine nitrate production pathway, caused by very low concentrations of NO₂ relative to the rest of the observations. This aligns with the results presented in figure 3.8, suggesting the existence of a minimum NO₂ or NO_x threshold for formation and detectable (above single ppq) levels of bromine nitrate. These clean marine daily cycles along with the wind rose analysis discussed previously present observational evidence for an effect of anthropogenic activity and a generally more polluted environment on the reactive bromine cycle in the marine atmosphere.

3.8 Constraining Heterogeneous Uptake Coefficients

The theoretical heterogeneous reactive uptake rate, k_{het} , of gaseous molecule X onto aerosol surfaces is dependent on the properties of both the gas-phase molecule and size distribution of aerosol:[51]

$$k_{het}^X = \left(\frac{r}{D_g^X} + \frac{4}{v_X \gamma_X} \right)^{-1} A \quad (21)$$

where D_g^X is the gas phase diffusivity ($\text{cm}^2 \text{ s}^{-1}$), v_X is the mean molecular speed (cm s^{-1}), and γ_x is the reactive uptake coefficient (unitless value between 0 and 1) for gas phase compound X . Meanwhile r represents the aerosol average particle radius (cm) and A the surface area concentration ($\text{cm}^2 \text{ cm}^{-3}$). Gas phase diffusivities for the molecules HOBr and BrONO₂ are estimated using the method set by Tang et al using the sum diffusion volume of each atomic component in N₂. [52] Mean molecular speeds are calculated for each species based on their respective molar mass (M_X), along with ambient temperature (T , in Kelvin) measurements taken on site according to the equation:

$$v_X = \frac{8k_B T n_A}{\pi M_X} \quad (22)$$

where k_B is the Boltzmann constant, $1.380649 \cdot 10^{-23} \text{ J K}^{-1}$ and n_A is Avogadro's number, $6.0221 \cdot 10^{23}$. While aerosol filter measurements were conducted for the BLEACH campaign, particle sizing instrumentation was not present at the site, leaving a gap in observational data for both particle radius and aerosol area concentration. However, if the ratio of k_{het} is taken for two molecules, the area concentration (A) and the need of such a measurement is eliminated in the calculation (equation 21), given that both gaseous species are assumed to be well mixed and interacting with the same aerosol distribution. This leaves only the average particle radius to be prescribed when analyzing the effect of reactive uptake coefficients (γ) on the ratio of uptake rates.

Figure 3.10 displays this effect in the form of the uptake coefficient for BrONO₂ vs. that of HOBr, where the contour lines (increasing in value from green to blue color) display the resulting ratio of $\frac{k_{het}^{HOBr}}{k_{het}^{BrONO_2}}$ according to equation 21. For this analysis, an average particle radius of $1 \mu\text{m}$ (10^{-4} cm) is prescribed based on the mean modeled output for wet SSA radius from the GEOS-Chem simulation. As mentioned previously, the uptake coefficients are unitless quantities between values 0 and 1 for any gas phase compound, where 0 indicates that the molecule never undergoes reactions on aerosol surfaces and a value of 1 would mean that there is always a reaction when the species collides with the surface of a particle, implying that the reaction would be limited only by the collision rate of the gas molecule and particles. These quantities are important for models as they affect the speed at which heterogeneous uptake and subsequently gas-phase recycling (in

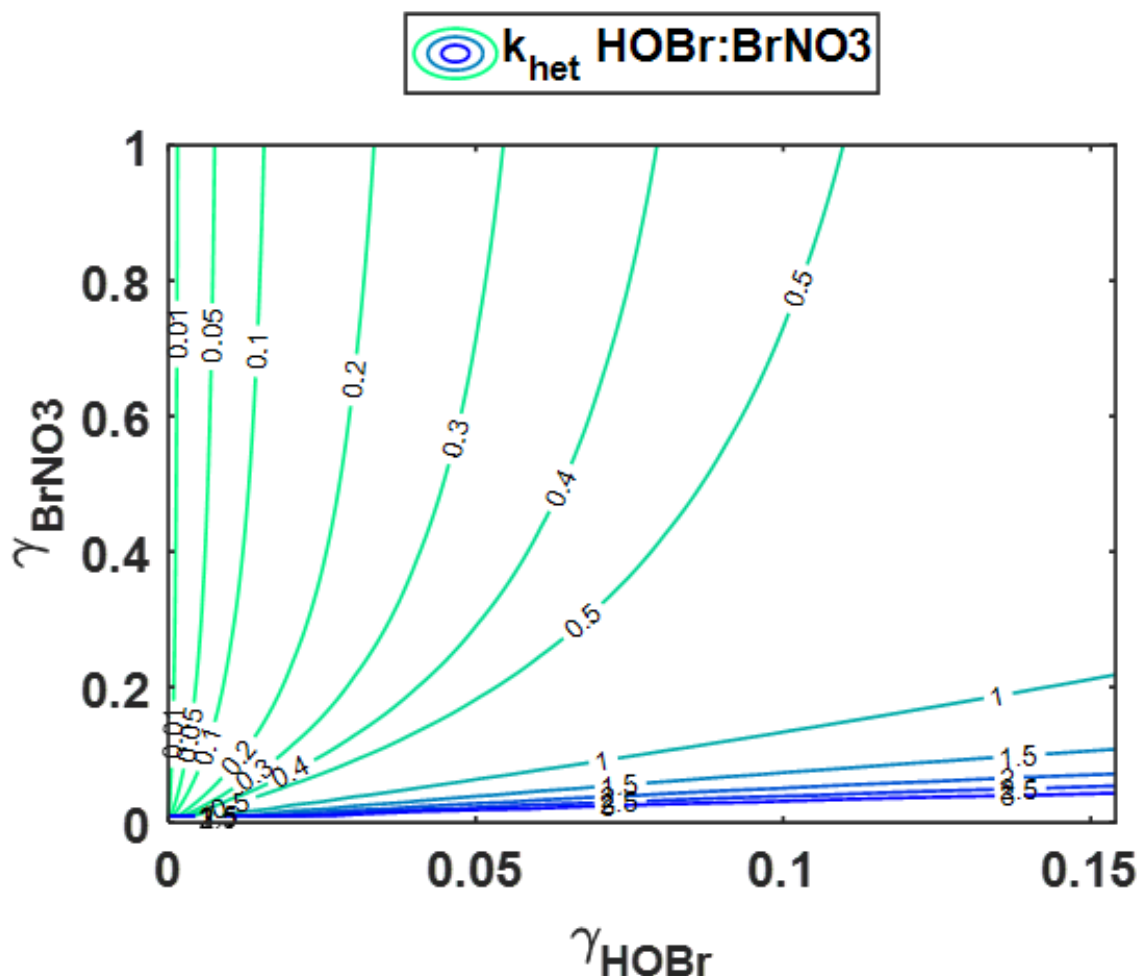


Figure 3.10: Contour plot showing the ratio of heterogeneous uptake reaction rates (k_{het}) for HOBr relative to that of BrONO_2 . Reactive uptake coefficients (γ) for gaseous HOBr and BrONO_2 onto aerosol surfaces are shown on the x and y axes, respectively.

this case for halogens) is represented. Evident in the plot is the organization of the contours as the uptake rate ratio becomes much smaller or larger. As the value approaches zero, one can see that the contours, e.g. the green at a k_{het} ratio of 0.01, become nearly vertical along the y-axis. If this were the true value, it would put a relatively small upper limit on γ_{HOBr} , while leaving γ_{BrONO_2} almost completely unconstrained, meaning that nearly any value between 0 and 1 would result in the given uptake rate ratio. Conversely as $\frac{k_{het}^{\text{HOBr}}}{k_{het}^{\text{BrONO}_2}}$ increases, e.g. the blue contour ratio of 3, shows the opposite where γ_{BrONO_2} would be constrained with a small upper limit while γ_{HOBr} remains unbounded.

In an effort to constrain the uptake coefficients for HOBr and BrONO_2 , $\frac{k_{het}^{\text{HOBr}}}{k_{het}^{\text{BrONO}_2}}$ is estimated independently using an alternative theoretical relationship where we include the gas-phase $\text{Br}_{\text{y}}^{\text{g}}$ measurements made by the CIMS in the MBL. This is accomplished by accounting for total production and loss for the two

gases, and assuming steady state for a chosen sampling period. We apply a generalized total heterogeneous loss term for both species using their heterogeneous reactive uptake rates: $L_{het}^X = k_{het}^X[X]$ and assume that heterogeneous loss and photolysis are much larger than loss due to deposition. Using only this heterogeneous loss term, gas phase reactions, and photolysis, we approximate the total production and loss for both compounds to calculate the change in concentration over time ($d[X]/dt$):

$$\frac{d[HOBr]}{dt} = k_{BrO,HO_2}[BrO][HO_2] - (j_{HOBr} + k_{het}^{HOBr})[HOBr] \quad (23)$$

$$\frac{d[BrONO_2]}{dt} = k_{BrO,NO_2}[BrO][NO_2] - (j_{BrONO_2} + k_{het}^{BrONO_2})[BrONO_2] \quad (24)$$

Where $k_{X,Y}$ represents corresponding gas-phase reaction rates for species X and Y , and j_X is the photolysis rate. Assuming steady state for both compounds, $d[X]/dt$ becomes zero in each equation, which can then be rearranged to solve for k_{het}^X . The ratio of the reactive uptake rates can then be calculated resulting in the following steady-state relationship:

$$k_{het}^{HOBr} : BrONO_2 \equiv \frac{k_{het}^{HOBr}}{k_{het}^{BrONO_2}} = \frac{\frac{k_{BrO,HO_2}[BrO][HO_2]}{[HOBr]} - j_{HOBr}}{\frac{k_{BrO,NO_2}[BrO][NO_2]}{[BrONO_2]} - j_{BrONO_2}} \quad (25)$$

Between the CIMS, LIF, and spectral radiometer instruments, we have coordinated observations during BLEACH23 for all variables in equation 25, other than the gas-phase reaction rates and $[HO_2]$. Values for k_{BrO,HO_2} and k_{BrO,NO_2} (corresponding to gas-phase reaction rates of BrO with HO_2 and NO_2 , respectively), are calculated using the temperature-dependent equations published in the JPL Chemical Kinetics Evaluation number 17.[53] HO_2 concentrations are estimated and prescribed using observations from Elshorbany et al (2022), reaching a maximum of 23 ppt during midday (14:00 local time) and a minimum of less than 0.01 ppt around 06:00.[36]

The concentrations of BrO, HOBr, and $BrONO_2$ as measured by the CIMS in ppt are converted to units of molecules cm^{-3} using temperature and pressure data from THMAO. Data is filtered to include only points where these three compounds were simultaneously measured above their respective detection limits and during daylight hours to account for only the photolytically driven processes. For the steady-state assumption leading to equation 25 to be valid, the concentrations of HOBr and $BrONO_2$ must remain unchanged in time. To satisfy this requirement as closely as possible, a period of time between 14:30 and 16:00 on Jan 25th 2023 is chosen, where the average concentrations and standard deviation for HOBr is 0.64 ± 0.15 ppt and that for $BrONO_2$ is 0.42 ± 0.14 ppt. The number of 1-minute data points in this period which survive the preceding indexing filters is 36. The resulting average of $k_{het}^{HOBr} : BrONO_2$ is 0.05

with a standard deviation of 0.04. Using this value in the context of figure 3.10, an upper limit on the uptake coefficient for HOBr can be defined via equation 21, and visually by following the contour for the upper estimate of $k_{het}HOBr : BrONO_2$ at 0.1 to its maximum value along the x-axis ($\gamma_{BrONO_2} = 1$). This steady-state analysis thus suggests an upper limit for γ_{HOBr} at a value of 0.015. This analysis represents a single point and location of observation for such a limit with multiple assumptions, but is meant to provide observational evidence for constraining the uptake rates utilized in model studies of the bromine chemical mechanism. It also falls into the previously described scenario where a small upper limit is placed on γ_{HOBr} , while γ_{BrONO_2} remains essentially completely unconstrained between 0 and 1.

3.9 Conclusions

With this work we have confirmed the identities and simultaneous measurements of five key gas-phase inorganic bromine species in the semi-remote MBL with a t-IMR CIMS. This includes the to our knowledge the first in-situ observations of bromine nitrate. Direct calibration for Br_2 , along laboratory experiments to estimate sensitivities for HOBr, reinforce the use of binding enthalpy calculations to extrapolate and determine sensitivities for all species measured during the BLEACH campaign. A new detailed humidity-based sensitivity correction of Br_2 at atmospheric pressure is also determined for the atmospheric pressure t-IMR and applied to the relative sensitivities of all halogenated molecules detected with the CIMS.

Online measurements were made for multiple weeks at the Tudor Hill Marine Atmospheric Observatory (THMAO), measuring from MBL air masses generally influenced by marine processes, anthropogenic activity, and a mixture of both. We find that the measured HOBr, $BrONO_2$, and BrO align qualitatively with current understandings of gas-phase Br_y formation and loss pathways, especially when considering the influence of NO_x concentrations from long range transport, passing ships, and local anthropogenic sources present near the sampling site. Br_2 and BrCl show unexpectedly high (or rather lack of a decrease in) concentrations during the day, where photolytic loss has been assumed to dominate and outpace their formation in the natural MBL. This behavior is attributed to either an unknown local source of bromine, enhanced heterogeneous cycling due to higher NO_x and nitrate chemistry, or some combination of both.

The work presented here demonstrates several methods of quality control for the first field deployment and in-situ measurements from the t-IMR, and establishes observational constraints for a large fraction of the established inorganic Br_y species in the sub-tropical MBL. Having this level of constraint provides a benchmark for evaluating the bromine chemical mechanism as we currently understand it. It also allows for further comparison with particle measurements to probe in-situ heterogeneous chemical cycling of bromine, and evaluation of model inputs.

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Chapter 4: Multiphase Reactive Bromine in the MBL: Impacts from Pollution and Tidal Cycles

Abstract

There remain uncertainties in the source attribution and cycling of reactive bromine (Br_y in the Marine Boundary Layer (MBL), especially heterogeneous reactions occurring on the surfaces of sea-salt aerosol (SSA) and other particles. We examine the complex relationship between particulate and gaseous inorganic bromine using five gas-phase species detected by an transverse IMR-equipped Chemical Ionization Mass Spectrometer (t-IMR CIMS) and particle filter measurements taken at a coastal site in Bermuda. A GEOS-Chem model simulation is also used to compare with observations of reactive bromine and address discrepancies in the Br_y chemical mechanism as it is currently understood. The model overestimates all of the observed reactive bromine components, with the largest difference for bromine nitrate (BrONO_2). The effect of pollution on the observations and modeled concentrations is examined via NO_x levels. NO_2 levels in both in situ and in the model are not found to significantly impact the levels of most Br_y components, including BrONO_2 . A strong correlation is identified between reactive bromine and the magnitude of tide height extremes, particularly for low tide. Using linear regression modeling, we find that the height of the last low tide and wind speed are the strongest independently measured predictors of total measured inorganic bromine. The simple linear model using only these two parameters is able to explain 62% of the variance in observations.

4.1 Introduction

4.1.1 Reactive Bromine in a Polluted MBL

Molecular bromine and other Br_y species are known to have significant effects on NO_x ($\text{NO}_2 + \text{NO}$), HO_x ($\text{HO}_2 + \text{OH}$), O_3 , and Hg concentrations, with particular importance in the atmosphere above the remote oceans and polar regions, typically far from anthropogenic activity and direct pollution sources. However,

there are few observations and growing interest among researchers to quantify bromine-containing species in marine environments outside of the arctic and antarctic, i.e. in the tropical and sub-tropical Marine Boundary Layer (MBL). And there are even fewer reports of pollution-related impacts on the inorganic bromine chemical mechanism. It is well known that in the presence of NO_2 , the formation of bromine nitrate (BrONO_2) can change the partitioning and ultimately the fate of inorganic bromine via the following gas-phase reaction sequences:



This branch of Br_y chemistry, explicitly reactions 1 and 2 are evidenced in the BLEACH23 observations presented in chapter 2 and can affect the partitioning of NO and NO_2 . Favorable bromine nitrate production (i.e. high NO_2 conditions) has the potential to shift BrO pathway away from HOBr formation, a well-established mechanism for catalytic ozone destruction. However, reactions 1, 2, and 4 represent a pathway where ozone could also be destroyed catalytically by BrONO_2 formation, where there is a net destruction of O_3 , production of NO_3 , and the reformation of atomic Br . Though under the active photochemistry required for this mechanism, NO_3 may also readily photolyze producing NO_x , O_2 , and O , complicating the net ozone production and loss.[1] There are also heterogeneous pathways for both HOBr and BrONO_2 to react on SSA surfaces and shift reactive bromine concentrations at different rates (see section below).

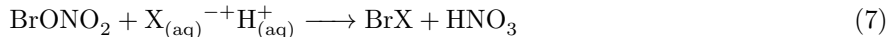
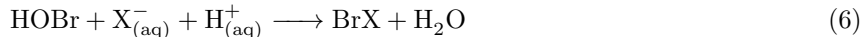
The few studies of bromine chemistry in the polluted MBL have reported elevated BrO and/or Br_2 (as measured by CIMS or DOAS) coincidental with relatively high NO_x levels, typically from continental air masses influenced by anthropogenic activity and associated pollutants.[2][3] Enhanced Br_2 is also observed during the day in some cases, which typically implies a significant local source required to outpace the large photolytic loss. Aside from from significant unknown local sources, explanations for this phenomenon have mostly included nitrogen chemistry impacting halogen reactivity. This includes the idea that higher NO_x can lead to higher aerosol nitrate concentrations which theoretically has the potential to increase the liberation of bromine from aqueous phase in sea-salt aerosol (SSA).[4] BrONO_2 can deposit onto SSA surfaces and react with aqueous HBr , HCl , and H_2O , with a wide range of uptake rates reported depending on environmental

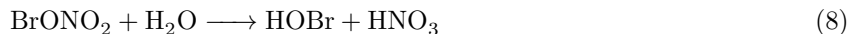
factors such as pH. Bromine nitrate is thought to have the potential to play a large role in halogen release from SSA in high NO_x conditions through such heterogeneous chemistry. Though it is also postulated that in such environments the $\text{BrO} + \text{NO}_2$ would be highly favored and Br_y compounds could be relatively quickly converted back to BrONO_2 during the day.[5] There is also a proposed mechanism for the uptake of N_2O_5 on halide-rich SSA to form BrNO_2 (as well as ClNO_2 and INO_2).[6] Many unknowns remain regarding the effect of pollution and elevated NO_x on bromine chemistry in the MBL, and more observations in such environments will be critical to understanding the full picture of halogen chemistry in the troposphere.

4.1.2 Sea Salt Aerosols and Heterogeneous Chemistry

Sea Salt Aerosols (SSAs) have long been reported as the most significant source of inorganic gaseous bromine in the MBL. SSAs are produced in the marine environment by physical processes in ocean water such as wave breaking (generating sea spray), bubble bursting, and jet formation.[7] These aerosols have the most substantial impact on radiative forcing over the open ocean in the absence of cloud cover, in addition to being a source of cloud condensation nuclei (CCN) themselves.[8] Greater wind speeds have also been shown to correlate with increased sea spray flux and elevated SSA mass concentrations, particularly for coarse particles having diameters above $1\text{ }\mu\text{m}$. [9][10][11] Yang et al (2019) also report more sea spray with higher winds, however they find that wave height and wave Reynolds number are better predictors of SSA concentrations.[12] The size distribution and total aerosol surface area concentration have a large impact on SSA reactivity with gaseous compounds, including reactive halogens. Environmental factors such as relative humidity (RH) also affect aerosol size, where higher humidity causes the swelling of particulates as they absorb water. Hygroscopic growth for NaCl (sea salt) particles has been shown to result in significant increases to measured SSA surface area, by over a factor of 3 at a humidity of 80% when compared to dry aerosol (though this swelling was reduced in the presence of organic matter).[13]

There are many known heterogeneous reactions involving gas-phase reactive halogens on the surface of SSAs, which naturally contain aqueous phase halogen atoms present in seawater (Cl^- , Br^- , I^-). These reactions, depending on species involved, produce dihalogen and interhalogen species which can then be liberated back to the gas phase, depleting the halide levels of salt particles in the process. For reactive bromine, the main heterogeneous pathways involve the uptake of HOBr and/or BrONO_2 onto salt particles:





where $X = \text{Cl, Br, I}$.

The (unitless) reactive uptake coefficient γ_{HOBr} has been demonstrated to be dependent on ambient RH, as well as the size and pH of aerosol particles. Heterogeneous reactivity for HOBr is generally higher for slightly acidic particles compared to alkaline. Though on highly acidified fine particles, particulate bromide has shown enhancements implying a nonlinear relationship with heterogeneous cycling and pH.[14] Pratt and Rossi (2006) found that at least for aerosols less than $1 \mu\text{m}$ in size, that increasing particle diameter gives a larger uptake coefficient. Longer interaction times for gases in larger volume particulates is attributed at least in part to the increased reactive uptake, while higher RH also is associated with fast depletion of HOBr in the presence of salt particles.[15] SSA acidified by sulfate typically results in Cl^- depleted aerosol, causing the uptake of reactive halogens (e.g. HOBr and BrONO_2) to become more dependent on available Br^- (and to a lesser extent, I^-). Ozone concentrations have also been reported to modulate heterogeneous reactions within the bromine cycle. In low ozone (O_3 -limited) regimes, production of Br_2 is thought to stem mostly from gas phase reactions, e.g. the self-reaction of BrO. Though Br_2 concentrations demonstrate a higher sensitivity to heterogeneous chemistry in ozone-rich environments (the Br-limited case).[16]

Reactive bromine has been shown to react with organic aerosol (OA) as well, altering OA composition and potentially the ability to form CCN. Reduced BrO concentrations are observed by Buxmann et al (2015) when adding secondary organic aerosol (SOA) precursors to simulated SSA in chamber experiments compared to those with salt particles alone.[17] Halogenated compounds have even been reported to react with volatile organic compounds (VOCs) and form ultrafine particles themselves.[18] There is clearly much uncertainty remaining regarding the various processes and rates at which reactive bromine (and other halogens) is recycled, especially in regards to heterogeneous chemistry with SSAs and OA. Identifying the main sources/sinks of observed gaseous and particulate bromide in the marine atmosphere will help add constraints to models with highly uncertain parameters and improve our understanding of the impact of MBL Br chemistry on the global atmospheric composition.

4.1.3 Organic Halogen Sources and Coastal Influence

Large fluxes of organic iodine (I) and bromine (Br) species, as well as inorganic iodine compounds, have been observed in coastal MBL studies to be well-correlated with the occurrence of low tides. This is mostly attributed to the exposure of beds of macroalgae, which are thought to produce and emit halogenated organics due to oxidative stress. The first in-situ observations of the relationship between low tides and organohalides is presented by Carpenter et al in their 1999 study based on measurements taken at the remote coastal Mace

Head observatory.[19] Most of the limited reports of tidal influence on halogen measurements have been based out of this field site, potentially due to the well-documented kelp beds, etc with exposure linked to low tides. Both I and Br-containing species have been reportedly produced by such macroalgae, which are considered an important source of iodine and bromine in seawater.[20] Several key bromocarbons including predominantly bromoform (CHBr_3), dibromomethane (CH_2Br_2), and bromiodomethane (CH_2IBr) are considered very short lived substances in the boundary layer and have the potential to contribute a considerable amount of reactive bromine to the atmosphere by way of oxidation and photolysis reactions.[21][22] The global distribution of macroalgae and differentiation between species and their emission of organic (and inorganic) halogen species in different environments remains uncertain.

Concentrations of inorganic iodine species have also been shown to increase during low tides, where direct emission of I_2 from macrophytes is deemed the cause for the tidal correlation between that and HOI. In fact, McFiggans et al observed gaseous atomic I emission rates from macroalgae of I_2 to be an order of magnitude larger than that of organic iodine.[23] Observed enhancements in particle number concentrations/new particle formation provide further evidence of the potential for more active halogen cycling at low tides.[24][25] This effect is evident in the work of Tham et al presenting measurements of interhalogen species, IBr and ICl, along with HOI and I_2 at Mace Head. All four of these compounds exhibit local maxima with low tides, where the interhalogen formation is attributed to enhanced heterogeneous cycling during these periods, e.g. the reaction of HOI with dissolved bromine and chlorine on (sea-salt) aerosol surfaces.[26] While halogen observation studies in the MBL outside of polar regions are sparse, there is a clear line of evidence for coastal source contribution to tropospheric halogen concentrations and influence in reactive halogen cycling. Further observation and source apportionment are necessary when extrapolating ground-based observations at coastal sites to global halogen budgets which include atmospheric chemistry over the open oceans.

4.2 Methods

4.2.1 BLEACH Campaign and Instrumentation

The t-IMR CIMS setup at the Tudor Hill Marine Atmospheric Observatory (THMAO) in Bermuda for the BLEACH campaign is described in more detail in chapter 2. To summarize briefly: the t-IMR samples ambient air at a rate of 10 liters per minute (LPM), sub-sampled from a secondary 3" OD sheath inlet with a flow rate of 110 LPM. The instrument is positioned atop a 10 m tower at the site, approximately 40 m total above the nearby ocean surface. Iodide (I^-) reagent ions are used to detect halogen and other species and generate via methyl iodide and a VUV lamp housing setup. Signals are normalized to reagent, background

subtracted, humidity corrected, and converted to atmospheric concentration (ppt) by direct calibration of Br_2 and relative binding enthalpy calculations for other compounds reported (see Ch. 2). Also stationed at THMAO for simultaneous measurements with the CIMS is a spectral radiometer to measure incident solar fluxes, a Laser-Induced Fluorescence (LIF) instrument measuring O_3 and NO_x concentrations, a collection of meteorological instruments providing measurements of humidity, wind speed/direction, temperature, and precipitation, and a cascade impactor for aerosol collection onto filters for offline measurements.

The cascade impactor used for aerosol speciation is positioned on the permanent 23 m tower at THMAO, utilizing a high volume air sampler for particle collection. High volume flows are turned off during any period of filter exchange or work requiring personnel on the tower, to prevent contamination. The quartz filters used (TE-QMA and TE-230-QZ) are rinsed in 18 M Ω cm water and combusted at 500°C before use. The data presented in this work for the BLEACH23 winter campaign includes 5 aerosol size-cutoff bins based on aerodynamic diameter at the 50% collection efficiency ($D_{p,50}$), in addition to the bulk concentrations (all sizes). The bin sizes are $< 0.6 \mu\text{m}$, $0.6 - 0.9 \mu\text{m}$, $0.9 - 2.3 \mu\text{m}$, $2.3 - 11 \mu\text{m}$, and $> 11 \mu\text{m}$. Active collection for a filter occurred typically at a frequency of ~ 24 hours, with sampling starting around 09:30 local time and stopping the following morning at 09:00 when the filters would be changed. Some extreme weather events prevented filter exchange, resulting in longer sampling periods. The filters are analyzed offline in the laboratory, where they are cut into small pieces and placed in a 50 mL centrifuge tube with 20 mL water. The tube is then weighed and shaken for 30 minutes. Insoluble material is removed from the tube using a $0.2 \mu\text{m}$ poly(ether sulfone) syringe filter. The centrifuge tube and filter masses (after liquid removal) are used to calculate the yield. A coupled ion chromatography (IC) technique is used to measure all species except iodine. Measured concentrations from the IC were blank corrected for all size bins. Yields during this extraction and the calculated total volume during in-situ sampling are used to report ambient aerosol species concentrations in $\mu\text{g m}^{-3}$. Species measured using this technique include sodium (Na), calcium (Ca), magnesium (Mg), chlorine (Cl), bromine (Br), iodine (I), nitrate (NO_3), and sulfate (SO_4).

Tide data was acquired through the National Oceanic and Atmospheric Association tides and currents data repository for station number 2695540, St. Georges Island, Bermuda. Predicted high and low tide heights are reported relative to the Mean Lower Low Water (MLLW) level, which is 19-year averaged height of the each day's lowest tide. A tide height timeseries is obtained by applying a cubic interpolation of the forecasted highs and lows reported to match the CIMS measurement frequency.

4.2.2 GEOS-Chem Model Description

The GEOS-Chem high-performance model version 14.2.3 is used to simulate and examine halogen chemistry in the MBL to compare with observations at THMAO. Stretched grid simulations are used to increase the spatial resolution of the grid box containing the field site to 70 square kilometers. The specific resolution used is C48 S3 with Bermudas location at 32.25°N 64.75°W as the center target. The model utilizes MERRA-2 meteorological fields from the NASA Global Modeling and Assimilation Office. A 22 month spin-up period is implemented from July 2020 to May 2022 for species to reach equilibrium and provide initial conditions more relevant to actual conditions. Tropospheric halogen chemistry in the model is handled according to the systems of reactions described most recently in Wang et al 2021, building upon results reported by Sherwen et al 2016 and Chen et al 2017.[27][28][29] The standard sea-salt debromination mechanism is employed. Hourly output is extracted for both summer and winter legs of the BLEACH campaign. Here, we focus on comparison with the wintertime run spanning from January 15 to February 12 2023. The sea-salt debromination mechanism is included in the model run as is the default for this version.

4.2.3 PLS Regression Technique

Partial Least Squares (PLS) regression is utilized for the CIMS bromine concentrations using the other independent measurements taken at THMAO as predictor variables. It is implemented as a statistical tool to quantitatively determine the significance of wind speed, tide height, and other independent measurements in predicting the behavior of total measured reactive bromine (Br_{y*}). PLS is chosen specifically for its skill in determining the individual contribution of co-varying predictor variables to a linear model. PLS regression takes m observations of n potentially co-varying predictor variables in the columns of (an $m \times n$) matrix, X , and creates a user-specified number (n_{comp}) of "components" using linear combinations of predictor observations, to create a fit for the dependent observations in the $n \times k$ matrix Y (observed bromine in this case, $k = 1$). The model algorithm constructs and performs singular value decomposition using matrices X_0 and Y_0 , which are simply X and Y where the means of each column are subtracted. The function outputs several variables for use in statistical analysis of predictor variables and the fitted response. β is a $(n_{comp} + 1) \times k$ matrix containing the intercept and predictor coefficient estimates for each dependent response variable in Y . The PLS model fit for the observations in Y is thus calculated as:

$$[J_{n,1} \ X] \cdot \beta = Y_{fit} \quad (9)$$

where $J_{n,1}$ is an $n \times 1$ matrix with all entries equal to 1 (accounting for the intercept of the linear fitting model). The model also returns the percentage of variance explained in both X and Y by each component, as well as predictor/response scores, X_S/Y_S , and predictor/response loadings, X_L/Y_L . These matrices can be used to reconstruct the mean-subtracted initial values: $X_0 = X_S X_L'$ and $Y_0 = X_S Y_L'$. Also returned by the algorithm is the $m \times n_{comp}$ matrix W containing PLS weights, defined such that $X_S = X_0 W$. The variable importance parameter or VIP score is a single value for each predictor variable, quantifying its significance in the model, and is calculated as follows (where $\oslash$ denotes element-wise division and $\odot$ element-wise multiplication in a matrix):

$$W_0 = W \oslash \sum_{h=1}^n W_{h,j}^2 \quad (10)$$

$$S = \sum_{i=1}^m X S_{i,j}^2 \odot \sum_{h=1}^n Y L_{h,j}^2 \quad (11)$$

$$VIP = \left[\left(n \sum_{j=1}^{n_{comp}} (S \odot W_0^2)_{h,j} \right) \oslash \sum_{j=1}^{n_{comp}} S_{h,j} \right]^{1/2} \quad (12)$$

The VIP scores, regression coefficients, variance explained, and overall model performance are used to quantitatively examine the individual importance of observed environmental factors (which potentially co-vary) in predicting the measured bromine concentrations during BLEACH23.

4.3 Comparison with GEOS-Chem Simulation

Shown in figure 4.1 are the diurnal profiles for the BLEACH23 winter Br_{y*} ($= 2Br_2 + HOBr + BrO + BrONO_2 + BrCl$) observations along with the same species output from the hourly GEOS-Chem simulation. The CIMS-measured median concentrations in ppt are binned to every hour and shown for each compound. Noting the difference between the y-axis ranges for both, it is clear that generally the GEOS-Chem results show much higher concentrations for all gas-phase brominated species compared to observations, to varying degrees for each species. For Br_2 , the model for the campaign-long average overestimates observed concentrations by a factor of 2-3 and shows levels dropping to near zero during the day, presumably due to its high photolytic loss rate. When further indexing up the comparison, the nighttime (19:00 - 05:59 local) Br_2 average is 4x higher in the model compared to observations, while during daylight (8:00 - 16:59 local) the observed concentrations are almost a factor of 20 larger than predicted. The median in the observed profile does show local minima in Br_2 around sunrise and sunset, but also a local maximum around midday, which implies a relatively large emission source or production mechanism to outpace loss due to photolysis. $BrCl$

shows similar behavior where its predicted levels in GEOS-Chem reduce to near zero during the day and a build up overnight; meanwhile the observations show the absence of a prominent diel trend. There is a small drop in observed concentrations in the late afternoon, as well as relative enhancements around sunrise, midday, and just after sunset in the median. The ratio of average BrCl model concentrations to observations for the campaign is approximately 12:1. Again when considering only data collected during nighttime hours (in the absence of photolysis), this ratio increases to $\sim 23:1$, while during the day the observational mean is 2.5x that of the model. GEOS-Chem also predicts nighttime BrCl concentrations to be nearly 3 times larger than those of Br₂, contrasting the observations from the CIMS which show much lower levels and a ratio on the order of 0.75:1 for BrCl:Br₂.

BrO exhibits the lowest median concentrations throughout the day for both the observational and model summaries. This is consistent with the idea that bromine monoxide is generally more reactive than the other Br_y constituents presented in this work, in addition to being highly photolabile. In GEOS-Chem, concentrations are extremely low and predicted to be below CIMS detection limits outside of the hours 07:00-17:00, and median concentrations peak at approximately 0.7 ppt around 09:00 local time. The shape of the profile is consistent with observations, though again at higher levels by a factor of over 7 during daylight hours. As mentioned previously, the CIMS detection of BrO was below or near detection limits for over 90% of the 1-minute resolved sample points during the campaign.

The median HOBr concentrations show an increase coinciding with sunrise (around 07:00) for both the model and observations, the former rising more quickly to its local maximum. Similar to that shown for bromine nitrate (discussed below), there is a local minimum in concentration around mid-afternoon predicted by the model. This decline is absent in the observational profile, which shows largest concentrations around 10:00-12:00 for the campaign, followed by a swift decrease in signal as the sun sets (sunset times around 17:30-18:00). GEOS-Chem predicts a bimodal shape, with concentration maxima at the hours of 10:00 and 17:00 and residual HOBr lingering slightly longer into the nighttime hours.

BrONO₂ shows distinctly similar shapes between the observed and modeled results, where concentrations increase significantly above the nighttime near-zero background after 06:00 locally, coinciding with sunrise and the beginning of active photochemistry, with concentrations falling in the late afternoon back toward background by sunset, with a slightly larger tail into evening hours predicted by the model (as is the case with HOBr). Both the model and measurements also show a characteristic drop in concentrations around midday with local maxima following at 15:00. This is presumably due to maximum photolysis rates occurring around this time of day, which both increases the direct photolysis and loss of BrONO₂, [30] and impacts the NO/NO₂ ratio, typically shifting in favor of NO and away from the NO₂ required for the gas-phase production of BrONO₂. Though the diel shapes are nearly identical, the model once again over

predicts the concentrations, in this case by nearly two orders of magnitude, where the GEOS-Chem output is approximately 60x higher than the median level measured by the CIMS during daylight hours. As these are the first in-situ observations of bromine nitrate, the similarity in the shape of the diurnal cycles between model and observations is a sign that the theoretical reactions involved in its production and loss are close to reality, while the difference in magnitude suggest the rates of formation and destruction (or heterogeneous uptake) may need further sensitivity experimentation, at least for the MBL conditions at THMAO.

The standard model simulation mostly aligns with observations of NO_x and O_3 in the campaign average, with respective median values of 128 ppt (model) vs 114 ppt (obs) NO_2 , 3.6 vs 2.5 ppt NO, and 43 vs 44 ppb O_3 . Large spikes in NO_x occurring over brief periods in the observations, presumably from passing ships or other local island plumes, are generally not captured by the model likely due to grid resolution treating most of the area chemically as the marine atmosphere without large anthropogenic influence. This leads to much larger higher quantiles and maxima in the observed NO_x compared to the model. Simple sensitivity tests to pollution were also conducted for the GEOS-Chem simulations where two additional runs were performed, the first one having global ship emissions turned off ("ShipOff"), and the second having all anthropogenic emissions excluded globally ("AnthroOff"). Both of these simulations result in lower median NO_2 , by a factor of 2 in the case of AnthroOff, which also shows a decrease in NO and O_3 which is not significant in the ShipOff scenario. When examining the effect of less pollution on the simulated Br_y^* , there is no significant drop in concentrations noticeable in the campaign long diurnal profiles for any species other than BrCl and Cl_2 , which show concentrations on the order of 50% less in the AnthroOff scenario when compared with the standard run. This result is somewhat surprising considering the observed effect of pollution on bromine cycling discussed previously. BrONO_2 concentrations remain close to their values in the diel trend as shown in the standard GEOS-Chem output, despite significantly lower NO_2 concentrations. This suggests that the rate limiting step for the model chemical mechanism is independent of NO_2 availability, at least in the range of 60-130 ppt, contrasting the observational results shown in chapter 2.

4.4 Comparison of Gas-Phase and Particulate Halogen Measurements

As established in the introduction, particle and gas-phase chemistry for halogen-containing species are intrinsically linked via heterogeneous reactions on SSA surfaces and potentially other aerosol species present in the MBL. The inorganic bromine chemical mechanism as it is currently understood specifically includes an inter-dependent array of multiphase reactions that involve both the uptake onto particulates and subsequent

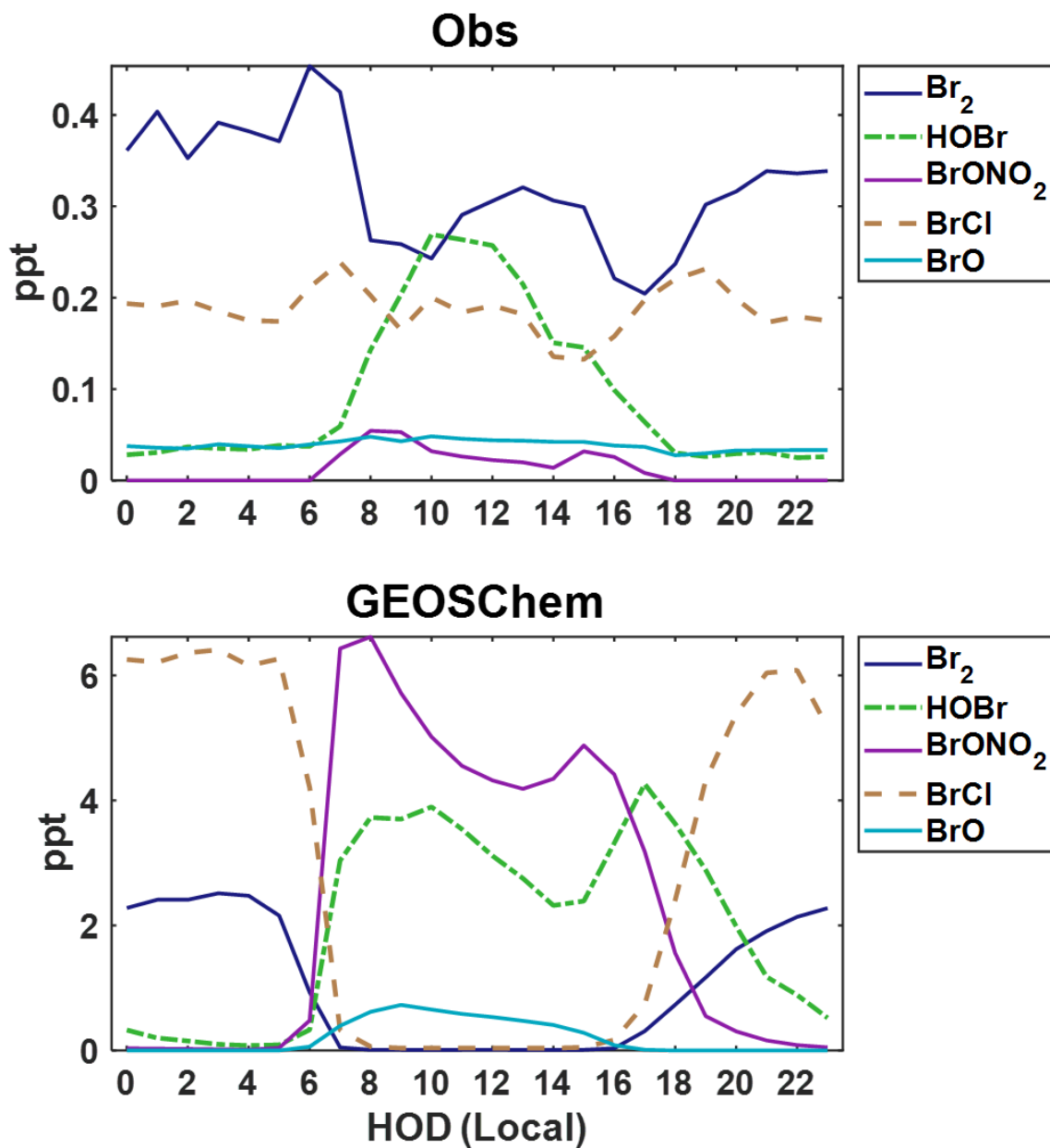


Figure 4.1: Diurnal profiles of Br_y species detected during the winter leg of the BLEACH campaign. The top plot shows observations by the CIMS and the bottom displays the hourly output from the GEOS-Chem simulation, both of which are presented as median concentration in ppt for each (local) hourly bin. Br_2 is shown in dark blue, HOBr in green dashes, BrONO_2 in purple, BrCl in brown dashes, and BrO in light blue.

liberation of gaseous bromine-containing molecules from particle surfaces. It is therefore of great interest to observe bromine levels in the gas and particle phases to gain insight into these important heterogeneous processes. In order to compare particulate and gas phase bromine in common units of mass concentration, concentrations of gaseous Br_y species (reported thus far in units of ppt) are converted to molecules per cubic centimeter (molc cm^{-3}) using the ideal gas law with temperature and pressure measurements taken at THMAO simultaneously with CIMS sampling. Concentrations are then converted further to units of $\mu\text{g m}^{-3}$ of bromine using the atomic weight of $1.327 \times 10^{-16} \mu\text{g}$ for Br. As an example, 1 molc cm^{-3} of Br_2 would correspond to a mass concentration of $2(1.327 \times 10^{-16}) = 2.654 \times 10^{-16} \mu\text{g m}^{-3}$ as it contains 2 Br atoms.

Presented in figure 4.2 are stacked area plots showing the absolute mass concentrations of the measured individual bromine species (panel b) as well as their relative concentration in % to the total Br_{y*} (panel a). Also shown in panels (c) and (d) of the figure are the relative and absolute mass concentrations of particulate bromide as measured by the cascade impactor, respectively. The concentrations are separated into contributions from each aerodynamic size bin, from the finest aerosols with diameters less than 0.6 micrometers (" < 0.6 ") in light blue, to the largest particles over 11 μm in size (" > 11 ") denoted in magenta. The relative contributions to the measured total (bulk) aerosol bromide mass from all particles are shown on the left as percentages. Finally, in the bottom two figures is the general contribution of total observable atmospheric bromine mass from both the gas phase CIMS observations and particle phase filter measurements from the filter collections. Panel (f) gives the absolute bromine mass concentration in $\mu\text{g m}^{-3}$ and relative percentage in panel (e), where the green area represents the fraction present in the gas phase; which is determined from the sum of the mean concentrations of the Br_{y*}^g species (where the g denotes gas-phase), while the dark purple shows particulate bromide (Br^p) from the bulk aerosol filters.

Br_2 is the largest contributor to observed Br_{y*}^g , with over 50% of the mass for all filter periods except one on Jan 27, where the concentration and relative contribution from BrCl is higher than the campaign average. This day also denotes a significant drop in absolute Br_{y*}^g concentrations, which remain relatively lower for the remainder of the campaign. This shift is also evident as the relative mass percentage of gaseous inorganic bromine to the total, which remains below 30% from Jan 27 onward. The largest concentration of Br^p measured on Jan 24-25 coincides with the highest daily maximum wind speeds recorded during the sampling period, as well as the largest particulate sodium loading ($> 13 \frac{\mu\text{g}}{\text{m}^{-3}}$), indicative of elevated SSA concentrations.

Summarized in figure 4.3 is the comparison between the GEOS-Chem simulation and observations for absolute mass concentrations and the relative contribution to total bromide for both the Br_{y*}^g components and the fine and coarse mode aerosol bromide. The data included in this figure are the mean Br_{y*}^g mass concentrations during each filter period, where all measurements shown include only the samples where the

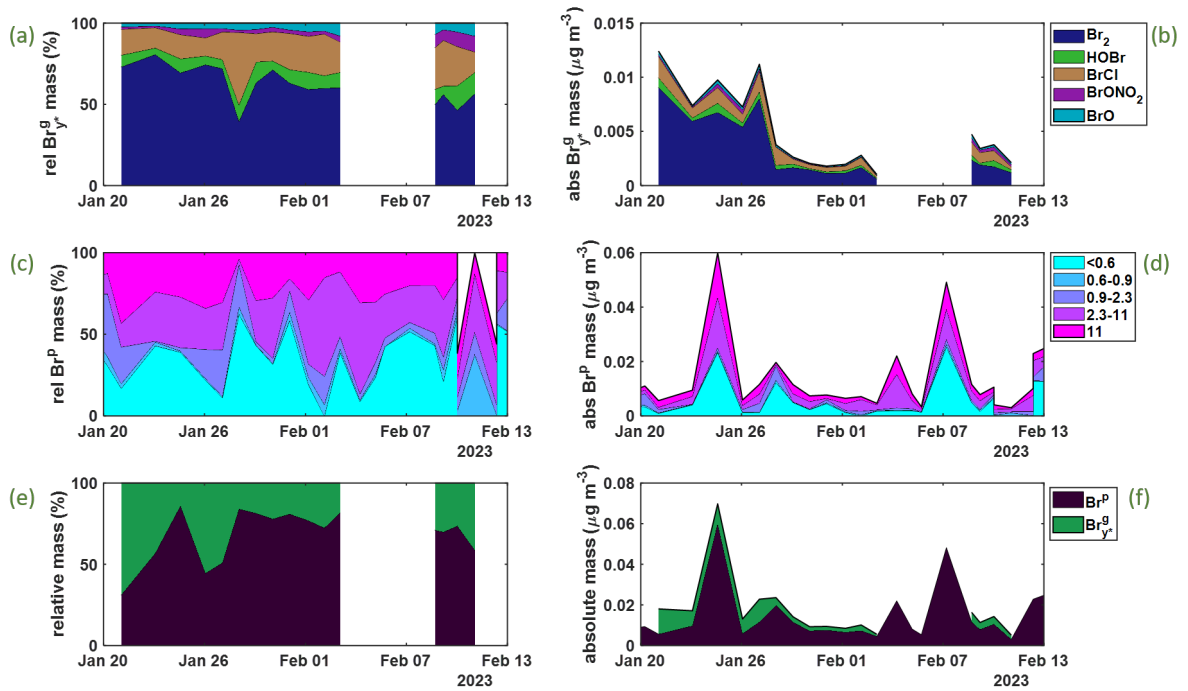


Figure 4.2: Stacked area plots showing relative (left column, %) and absolute (right column, $\mu\text{g m}^{-3}$) contributions from individual components (species and sizes) to bromine mass concentrations in the gas and particle phases. (Top) Gas phase Br mass separated by inorganic bromine species measured by CIMS. (Middle) Particulate Br mass separated by aerodynamic size, reported in microns (i.e. 0.9-2.3 μm in size), as measured by the cascade impactor. (Bottom) Total gas phase Br mass (green) compared with total or bulk aerosol bromide mass (dark purple).

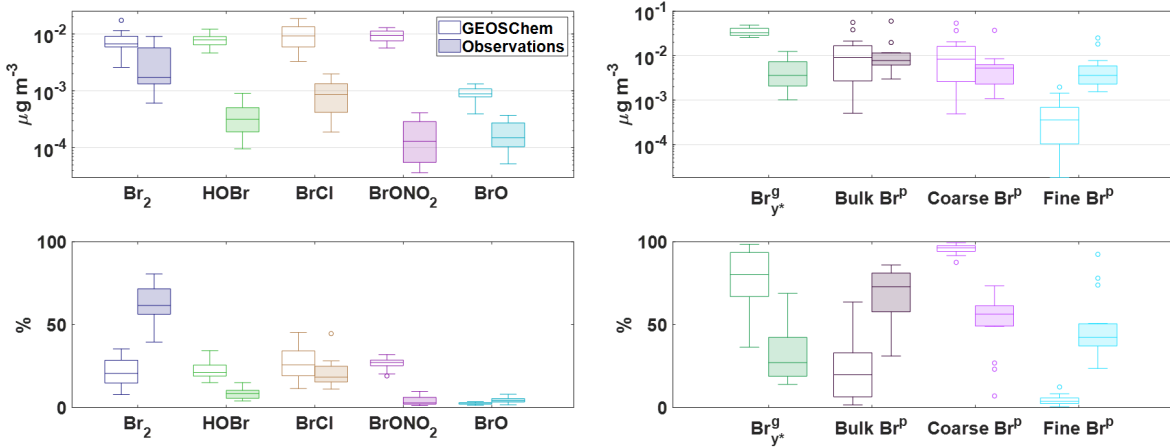


Figure 4.3: Box charts displaying modeled and measured absolute bromine mass concentrations (top panels, with a log-scale y axis) in $\mu\text{g m}^{-3}$ as well as relative contribution to the total (bottom panels) in percentage for the five Br_y components detected during bleach as well as their sum total (Br_{y*}) and aerosol bromide. Values from the GEOS-Chem simulation are shown with unfilled white boxes, while measurements from the CIMS and aerosol filters are shown with filled color boxes.

CIMS was concurrently operational. This leads to the inclusion of 16 filter periods, most of which have a sampling duration of ~ 24 hours. The boxes along the y-axes indicate the 25th to 75th percentiles (the inter-quartile range) of each variable, with the central line representing the median value. Whiskers show the minima and maxima, and outliers (calculated based on inter-quartile ranges) are shown with hollow circle markers. Model results are displayed with transparent white boxes while observations are represented with shading. The top panels show the absolute mass concentration of bromine (for Br_{y*}^g converted from ppt using local temperature and pressure readings) in units of $\mu\text{g m}^{-3}$ on a logarithmic scale. In the bottom plots are relative contributions to the corresponding total bromine measured or modeled in both the gas and particle phases (given as percentages). Total Br_{y*}^g is represented in green for the right two panels, which also include the total or "bulk" particle-phase bromide mass, as well as two individual size bins designated as 'fine' ($< 2.3 \mu\text{m}$) and 'coarse' mode ($\geq 2.3 \mu\text{m}$). In this case, fine mode represents the three smaller aerodynamic size bins for the filter measurements, ≤ 600 nm, 600-900 nm, and 900-2300 nm, as determined by the cascade impactor. Coarse mode includes the sum of particle bromide measured in the two largest size bins of 2300-11000, and ≥ 11000 nm. The relative contributions for fine and coarse mode bromide (%) shown in the bottom right panel are calculated by dividing their absolute mass concentrations by that of the bulk aerosol bromide (sum over all sizes). Br_{y*}^g and Bulk Br^p in the bottom right figure are shown in green and dark purple, respectively, as the respective contribution the sum of both, representing all measured* airborne Br mass (* emphasizing the absence of some gas-phase Br_y components). This shows the relative gas-phase and particle-phase fraction of total detectable atmospheric bromine at THMAO.

Figures 4.3 and 4.1 show a clear over-prediction in the GEOS-Chem simulation of total $\text{Br}_{\text{y}*}^{\text{g}}$ as well as its individual components, now contextualized with the particle phase predictions and measurements. The total $\text{Br}_{\text{y}*}^{\text{g}}$ mass concentration is significantly higher in the model output, by an order of magnitude when comparing the median values from GEOS-Chem against that of the observations. The total (bulk) aerosol bromide mass is captured fairly well in the simulation, showing similar concentration medians and total spread. However, when looking at the size-resolved comparison, the model underestimates median bromide mass in fine-mode particles by an order magnitude. The relative contribution to total measurable Br mass also shows discrepancies, where the model predicts more of the total mass to be in the gas phase ($\text{Br}_{\text{y}*}^{\text{g}}$) with a median of 80% while observations show a median of 27% (with the remaining fraction in the particle phase). The discrepancy between the model and observations for fine mode Br^{p} alone with a median difference of $0.3\text{e-}2 \mu\text{g m}^{-3}$ is not enough to account for the much larger difference of $2.9\text{e-}2 \mu\text{g m}^{-3}$ between the modeled and observed $\text{Br}_{\text{y}*}^{\text{g}}$ median concentrations.

The lack of measurements for all $\text{Br}_{\text{y}}^{\text{g}}$ species leaves the potential for a reservoir species to explain such a large difference in gas-phase mass, e.g. hypobromous acid (HBr) and free atomic bromine, Br. CIMS measurements using iodide as a reagent have been reported to be over 100x less sensitive to HBr compared to Br_2 . [31] In the case of the t-IMR at THMAO, this would mean that its LOD would be 2 orders of magnitude higher, which when applied to its spectral neighbor, HOBr, would mean concentrations less than the order of 10 ppt would not be detectable in the observations. We therefore consider this $\text{Br}_{\text{y}*}^{\text{g}}$ as a lower limit to the actual total gaseous bromine mass. Though even with this caveat, there remain large differences between the GEOS-Chem output and observations for the fractional contribution of $\text{Br}_{\text{y}*}^{\text{g}}$ components to total $\text{Br}_{\text{y}}^{\text{g}}$.

Mass concentrations of other particulate species measured at THMAO are shown in figure 4.4 along with the values modeled in the GEOS-Chem simulation. Analogous to figure 4.3, observations are shown in colored boxes with whiskers extending to the maximum and minimum (outliers in open circles), with log scale on the y-axis for all panels. Fine mode sodium (Na^{p}) and chloride (Cl^{p}) are both underestimated in the model output, the latter by a much larger factor. Bulk Na^{p} and Cl^{p} concentrations show similar medians and spreads between GEOS-Chem and the observed, with coarse mode for both also within uncertainties. Particulate sulfate and nitrate are relatively well represented in the model output across both size bins and consequently in the bulk mass concentrations. Iodine concentrations in the particle phase (I^{p}) are underestimated in both the fine and coarse modes compared to the filter measurements. The underestimation of fine Na^{p} has the potential of contributing to the fine mode halide differences, though the sea-salt production mechanism in the model is relatively simple, and the discrepancy in the fine mode is much smaller than the magnitude of the coarse and bulk Na^{p} concentrations, which are mostly in agreement. While the bulk mass of sea salt

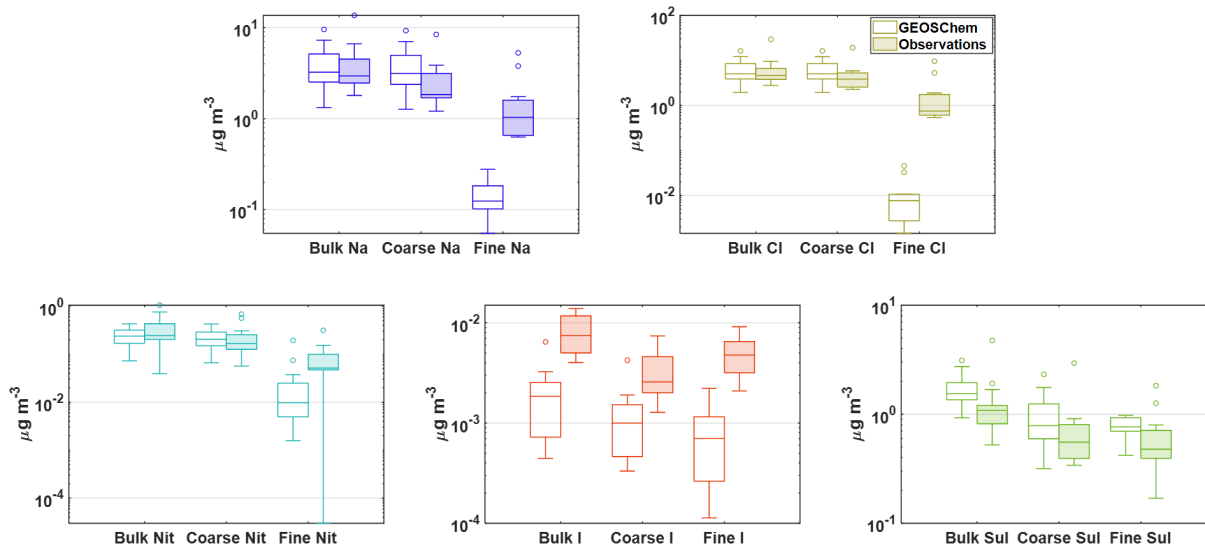


Figure 4.4: Box charts displaying modeled and measured absolute mass concentrations of other species detected from the filters at THMAO. Values shown with a log-scale y axis in units of $\mu\text{g m}^{-3}$ for particulate sodium, chlorine, iodine, sulfate, and nitrate content. Values from the GEOS-Chem simulation are shown with unfilled white boxes, while measurements from the CIMS and aerosol filters are shown with filled color boxes.

alone cannot explain the observed differences in Br_y , the size distribution and thus available surface area may be contributing to the disagreement. Fine mode aerosol halide mass concentrations, Br^{P} , Cl^{P} , and I^{P} , all being measured at concentrations much larger than predicted by the model by varying magnitudes all larger than that of Na^{P} also suggests that either the uptake rate of halogenated molecules onto smaller particles is underestimated, or that the conversion of aqueous halogen species in fine mode aerosol back to the gas phase is too efficient in the model simulation.

4.5 Atmospheric Bromine Dependence on Tide Extremes

Tide data is incorporated into this BLEACH observational dataset based on the previous work done mostly at the Mace Head observatory where a significant link between tides, macroalgae, and observed iodine species is reported. Organic halogenated species have also long been observed to be emitted from ocean ecosystems. Both the iodine and bromine chemical mechanisms interact via gas phase interhalogen reactions, heterogeneous chemistry for both (as well as chlorine) has been evidenced and continues to be investigated. Displayed in figure 4.5 are timeseries for Br_y^{g} in ppt with tide height in meters at local time in Bermuda, the photolysis rate for Br_2 ($j\text{Br}_2$, as determined from the spectral radiometer measurements), as well as the wind speed (WS) and direction (WD), with blue horizontal lines to indicate the modified on-shore wind direction zone of $190\text{--}315^\circ$. The multi-week observational period for BLEACH23 shows the shift in tidal pattern over

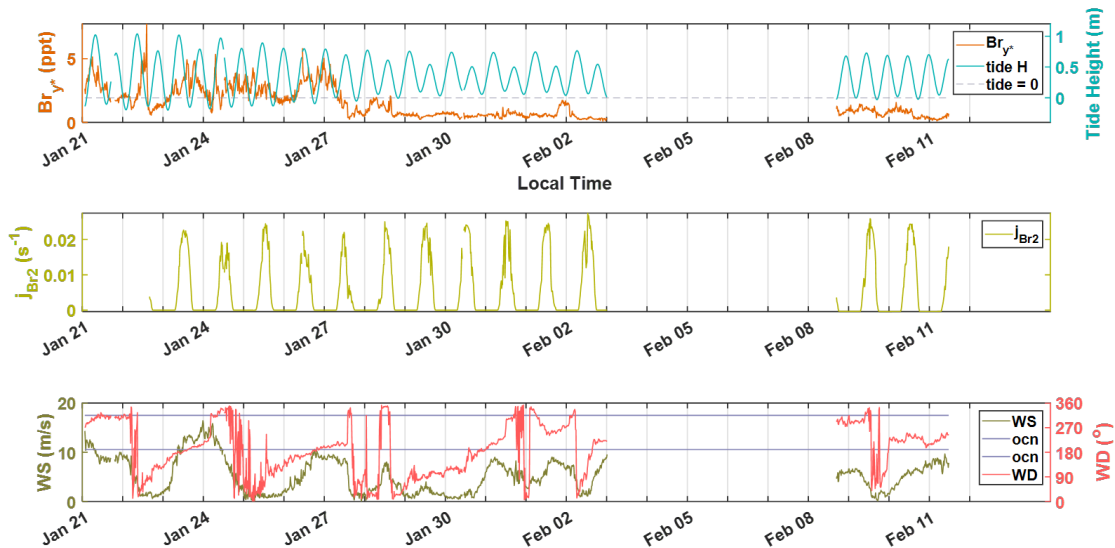


Figure 4.5: 15-minute timeseries showing [Top] total Br_{y*}^g in ppt (orange) with tide height (blue) in meters relative to Mean Lower Low Water (MLLW), which at 0 m is indicated with gray dashes. [Middle] Photolysis rates for Br_2 in s^{-1} (yellow) calculated from spectral radiometer measurements. [Bottom] Wind speeds (WS, brown) in m/s and wind direction (WD, red) in degrees. Horizontal blue lines indicate the beginning and end of the onshore wind direction sector ($190\text{--}315^\circ$)

time, where each day typically encompasses two high tides and two low tides of different intensities. Certain days show high tides around noon and midnight, while low tides occur close to sunrise and sunset times (i.e. Jan 26), and others show the opposite timing for the tidal extrema (i.e. Feb 2). This demonstrates the dynamic relationship between coincident tides and photochemistry, anthropogenic emissions, and other hour of day-dependent processes. Also evident in the tide timeseries are larger envelopes of a secondary oscillation capturing the evolution of the tide extremes, where the magnitude of both high and low tides changes from the beginning of the campaign to their minima near Feb 1. The bottom panel of the figure also highlights time periods where high winds, onshore winds, or the lack thereof coincide with each other as well as the tides. There is no significant correlation observed between wind direction and tide height (or tide extrema) for the campaign measurement period.

No significant relationship is noted between 15-minute averaged Br_{y*}^g and the dynamic tide height at any given time from the higher temporal interpolation of the tide data. However, when examining the magnitude of both high and low tides, strong correlations emerge between detected gas-phase bromine concentrations and the magnitude of these most recent tide *extrema*. A timeseries of most recent low/high tide data are created by taking the value of the tide heights at every low/high tide (i.e. the minimum/maximum) and interpolating this value as a constant until the next low/high tide. This creates a step function-like vector

useful for comparison with halogen measurements (among others taken at THMAO) on multiple timescales. Figure 4.6 displays the distribution of total $\text{Br}_{\text{y}*}^{\text{g}}$ against the binned magnitudes of the last low tide height (panel a), high tide height (c), and wind speeds (e). The box charts show the median, quartile range, minimum/maximum, and outliers of the 15-min averaged $\text{Br}_{\text{y}*}^{\text{g}}$ concentrations for each of the tide extrema and wind speed bins. Medians are connected with the red trace and open circles. The bins are placed at the respective midpoint of a given tide interval, meaning that the last high tide height bin at 0.95 m represents all data where the height of the most recent high tide was ≥ 0.9 m and < 1.0 m.

Gas phase bromine shows a marked increase at the lowest low tide heights, with a significant increase in median (and all values in the spread) noted between the distributions at -0.03 and -0.09 m. The relationship to the last high tide shows slightly smoother escalation toward the highest median $\text{Br}_{\text{y}*}^{\text{g}}$ levels at the most extreme high tide heights. Though in the case of high tides, the displayed outlier values reveal that the larger gas-phase bromine concentrations (above ~ 3 ppt) are observed for all but the lowest height bin (0.55 m). This is in contrast with the low tide bins which show a clear increase in the entire range of $\text{Br}_{\text{y}*}^{\text{g}}$ at the three most negative low tide height bins. When analyzed against wind speed, there is again a notable relationship, where the median concentrations rise and remain elevated after a threshold, in this case around 9 m/s. Similar to the high tides, the enhancement appears more gradual, and there remain outliers and spreads showing elevated bromine concentrations even at low wind speeds, with the highest 15-minute averaged $\text{Br}_{\text{y}*}^{\text{g}}$ actually occurring in the smallest bin of < 1 m/s. The timeseries in figure 4.5 show that while they individually vary, the largest wind speeds for the campaign (i.e. those larger than 10 m/s) occur coincidentally with some of the largest tide extrema, introducing some potential for bias in source attribution. However, when examining wind speeds within the high and low tide height bins, there is no noticeable relationship when examining the median values. A slight enhancement in the 75th quantile and maximum WS are evident at low tide heights under -0.3 ft, but otherwise spreads in the data remain large for each bin.

The tide, wind, and bromine data were also averaged to the aerosol filter collection frequency (~ 24 hours), the results of which are shown in panels b, d, and f of figure 4.6. The average gas-phase bromine concentrations are given on the y-axis and scattered against the average low tide and high tide extremes (panels b and d, respectively) for each filter time period, colored by the average wind speeds. Panel f shows concentrations vs. average wind speed, this time colored by the measured bulk mass concentration of particulate sodium (Na^{p}) in $\mu\text{g m}^{-3}$. Correlation coefficients (R) and p-values measuring the statistical significance of the linear correlations are also given in each scatter plot. In the filter average scatter plots, there is a significant negative correlation with the most recent low tide height ($R^2 = 0.66$, $p < 0.05$) meaning that as the low tide height decreases, more bromine is detected in the gas phase. There is also a similarly strong positive correlation with the high tide heights ($R^2 = 0.74$, $p < 10^{-4}$), meaning that a

larger recent high tide is coincident with elevated Br_{y*}^g for the approximately daily average frequency of filter measurements. It should be noted that the heights of high and low tide extrema are inherently linked, especially on the larger timescale of the 24 hour filter observations, where a higher high tide typically means a lower low tide to follow or vice versa (see figure 4.5). This prevents the defined last low and high tide variables from being fully independent of each other while investigating causality and comparing to the bromine concentrations. This makes it difficult to robustly attribute the clear tidal extrema dependence to either high tide alone, low tide alone, or some combination of both. However, the correlations here in panels a-d show the clear relationship that more extreme tides mean more gas-phase bromine measured at THMAO. There is also a somewhat positive relationship of Br_{y*}^g with the average wind speed during each filter, with a smaller correlation than that of the tide extrema though still statistically significant, with $R^2 = 0.3$ and $p < 0.05$.

As mentioned above, there is no clear campaign-long relationship observed between wind speed and the magnitude of the tide extrema, however the largest wind speeds for the campaign (> 10 m/s) coincide with the largest tide amplitudes. This motivates further study into separating the influence of tides, wind speeds, and potentially other factors on bromine abundance in this coastal marine environment, especially given the sigmoidal shape of median Br_{y*}^g with both the tide extrema and WS. In an effort to explore the respective significance of these variables for the observed bromine, Partial Least Squares (PLS) regression is applied to the CIMS measurements and all other independently available environmental factors. This includes the magnitudes of the most recent tidal extrema (referred to as "Low Tide" and "High Tide" below), the dynamic tide height (i.e. the blue trace in figure 4.5), NO , NO_2 , and O_3 from the LIF instrument, $j_{\text{Br}2}$ from the spectral radiometer, partial pressure of water vapor ($P_{\text{H}_2\text{O}}$, related to specific humidity), pressure (P), temperature (T), and vertical wind speed (VWS) from the sonic anemometer.

PLS analysis takes an input matrix, X, the columns of which contain observations of so-called "predictor" variables, and using a least squares algorithm to generate a model using linear combinations of the predictors in X to best reconstruct the observations of the dependently observed variable(s) in matrix Y. This is accomplished via the generation of a user specified number, n_{comp} , of components. For our purposes, the dependent matrix Y is simply the vector of 15-minute averaged observations of Br_{y*}^g , and the columns of X contain the observations of all previously mentioned meteorological data, NO_x concentrations, etc. Because we seek only to quantify the importance of each predictor in a linear model to recreate the gas-phase bromine observations, the highest possible n_{comp} (the number of predictor variables) is chosen to capture as much of the variance in observed Br_{y*}^g as possible. To eliminate scaling bias, both Y and the columns of X are normalized using respective means and standard deviations (e.g. conversion to z-scores with means centered at 0).

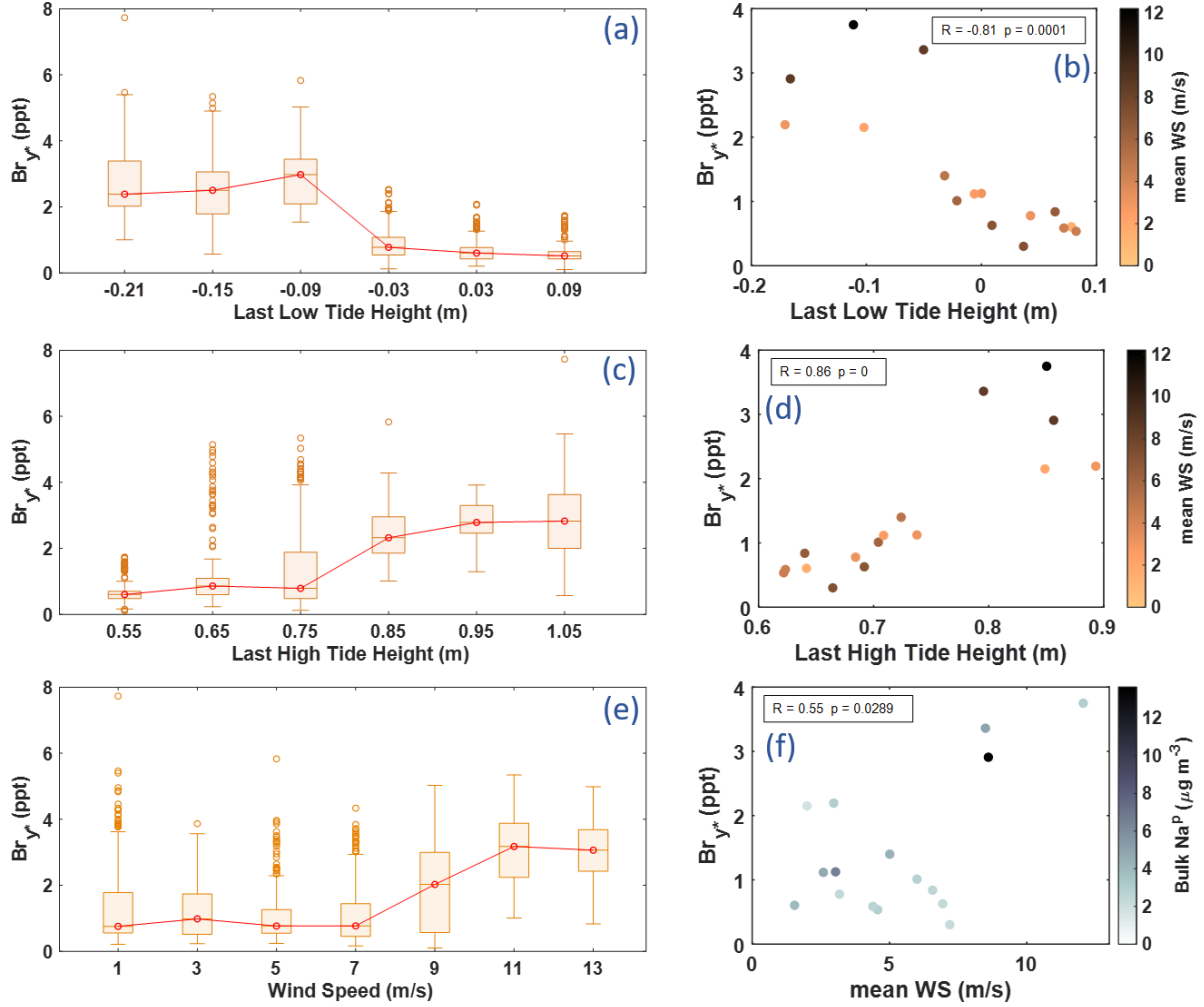


Figure 4.6: Box charts showing the distribution of 15-minute averaged Br_{y*}^g concentrations for binned values of (a) the relatively most recent low tide heights, (c) most recent high tide heights, and (e) coincident wind speeds. Br_{y*}^g is also binned to the aerosol filter sampling time frequency (typically ~ 24 hours) and scattered against the averaged low tide height (b) and high tide height (d) for each filter, colored by average wind speeds. Panel (f) shows Br_{y*}^g scattered against wind speed on the x axis instead colored by bulk (all size bins) aerosol sodium concentrations as measured on the filters.

Figure 4.7 displays the results of a PLS regression applied to the $\text{Br}_{\text{y}*}^{\text{g}}$ concentrations as the dependent variable (Y), using 12 predictor variables measured independently by other instruments at THMAO (columns of X). By introducing the variables jBr2 based on the measurements from the spectral radiometer, as well as NO_x and O_3 by the LIF instrument, some CIMS $\text{Br}_{\text{y}*}^{\text{g}}$ observations are not included in the model due to differences in instrument coverage. This results in the exclusion of only 18% of the 15-minute timeseries data, and when running the model without these variables for complete coverage, the same conclusions are reached. Both the columns of predictor matrix X and the gas-phase bromine concentrations in matrix Y are normalized as z-scores to give equal weight to all independent variables in the model algorithm. The maximum value of $n_{\text{comp}} = 12$ components is used to maximize the variance captured by the PLS model fit.

The cumulative variance explained in the observations by the linear model is shown in panel (a) of the figure. With the 12 predictor variables (and components), the total variance the PLS fit is able to explain in the observed gas-phase bromine is 69%. Panel (e) shows a timeseries of the model fit using the regression coefficients and predictor variables in the blue trace, overlain with the observed values in orange. Panel (c) also shows the observations vs. the model fit, this time as a scatter plot (of the 15-minute averaged data points), colored by the residuals, i.e. the distance from the perfect fit 1:1 line, which is shown in the black dashed trace. The variable importance in prediction (VIP) scores are given in panel (b) for each of the (normalized) predictor variables, with a dashed line representing a threshold value of 1. Regression coefficients for these variables are shown below the VIP scores in panel (d). It should be noted that the PLS model was run with all the data input at different temporal resolutions, from 1-minute to 24-hour averaged measurements. Those results confirm that averaging the data to longer or shorter timescales does not significantly alter the VIP scores or regression coefficients (and therefore the conclusions of this analysis), but only changes the cumulative variance explained in the observations; which is expected because by averaging more data to single point, the variance in the observations is inherently lowered.

The correlation between the model fit and the observed $\text{Br}_{\text{y}*}^{\text{g}}$ shown in panel (c) registers an R^2 value of 0.7 and a mean residual value of 0.42. The variables with VIP scores above the standard threshold of 1 include only low tide, wind speed, and high tide. The low tide and wind speed predictor variables are respectively also assigned the largest and second largest magnitudes for a regression coefficient, meaning they carry the most weight in the components comprising the PLS fit. When considering both of these measures of variable significance, the most recent low tide height and coincident wind speeds are determined to be the most consequential predictors of the measured gas phase bromine concentrations at THMAO. The high level of influence both tide extremes have on the linear model highlight a significant coastal source of (or at least interaction with) reactive halogens.

The PLS model was run again on the same dataset of $\text{Br}_{\text{y}*}^{\text{g}}$ (in matrix Y) using only the two predictor

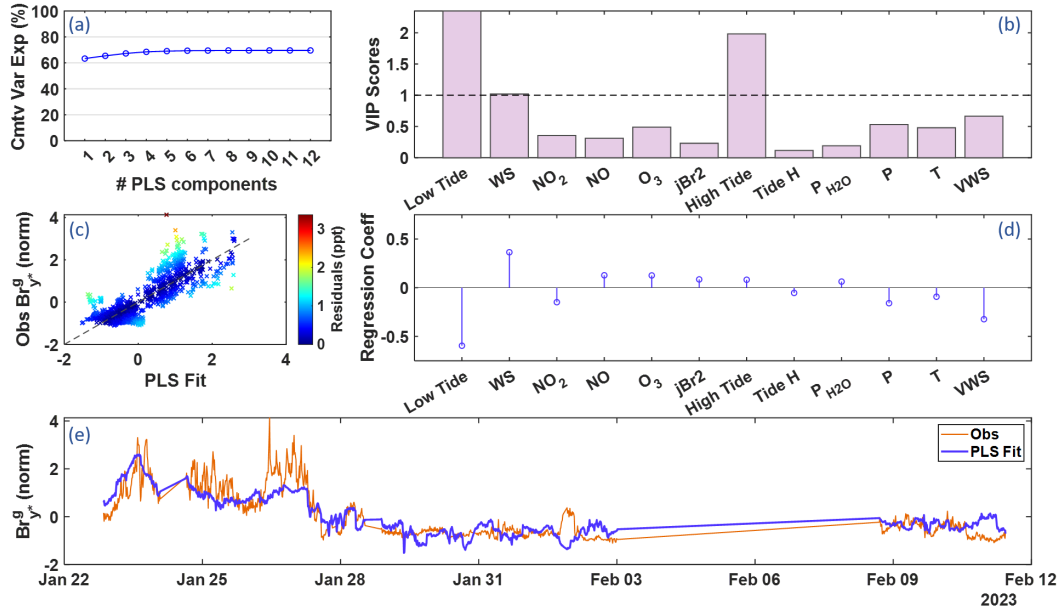


Figure 4.7: Results from the PLS model using 12 independently measured predictor variables. (a) Cumulative variance explained in observed Br_{y^*} by each component in the model. (b) VIP scores for each predictor variable. (c) Scatter plot of 15-minute observed Br_{y^*} concentrations vs. model reconstruction including a 1 : 1 line in gray dashes, colored by residuals. (d) Regression coefficients for the 12 predictor variables. (e) Time series of observed Br_{y^*}

variables of low tide and wind speed. Here, the instrument discrepancies causing some exclusion of CIMS data are no longer relevant since the predictors of NO_x , jBr2, etc are not use. However, time periods where the LIF and spectral radiometer instruments were not running are still excluded for true comparison of this analysis with that shown in figure 4.7. The results of this two-component regression output is displayed in figure 4.8 where a cumulative 62% of the variance in the observations is explained by the linear model fit. The mean residual value in the scatter of the observations vs fit in this case is 0.47.

The VIP scores are lower for both low tide and WS when compared to their values for the run with all 12 predictor variables, with low tide still breaching the threshold value of 1. Wind speed receives a lower VIP score of 0.57 and less weight in this simplified model with a regression coefficient of 0.23 (compared to 0.36 in figure 4.7), while low tide receives more weight in this case with a coefficient magnitude of 0.72 (compared to 0.60). The loss of only 7% of variance explained by the PLS model when excluding 10 of 12 predictor variables, along with only a minor increase in the average residual error in the fit (difference of 0.05), shows that the most recent low tide height and wind speed combined are the most meaningful predictors and biggest drivers for the variance of the observed gas-phase bromine during BLEACH23. From this analysis, it appears that low tide is statistically slightly more important when prescribing a linear relationship with $\text{Br}_{y^*}^g$. However, from the combination of their respective VIP scores and regression weights, both low tide

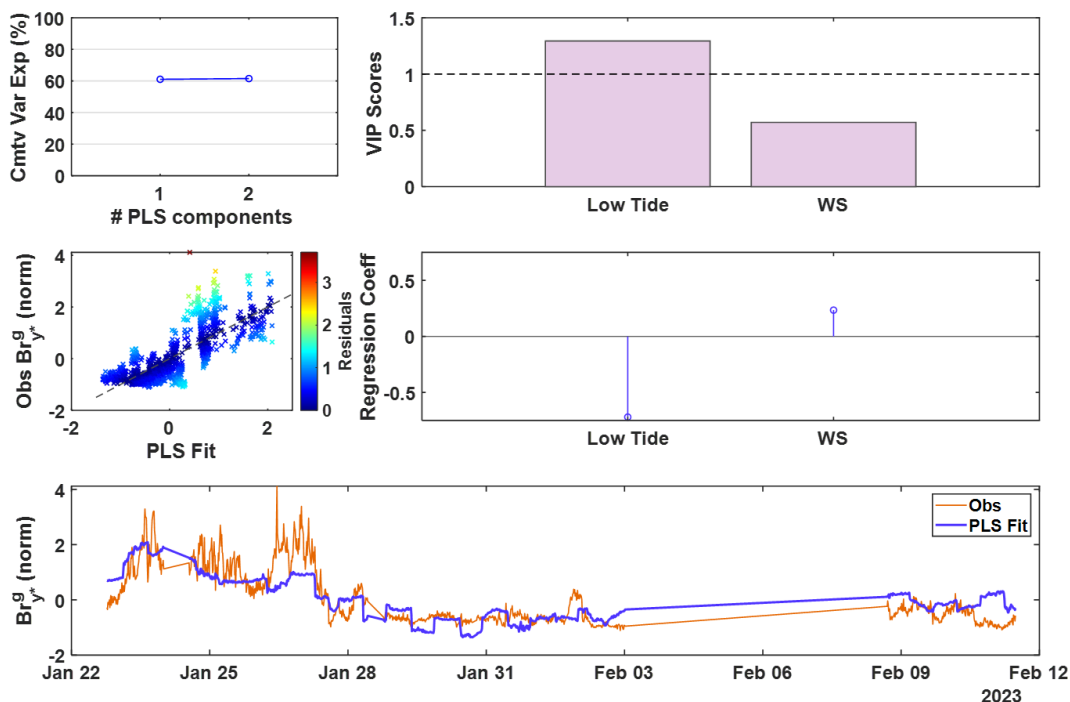


Figure 4.8: Same as figure 4.7 for PLS model results using only low tide height and wind speed as predictor variables.

height and wind speed are shown to be independently important factors in predicting reactive bromine.

There are multiple possible sources responsible for the link between bromine concentrations in the MBL and both tide extrema. Low tides have been linked previously to elevated reactive iodine concentrations in the MBL and attributed to the exposure of iodine-emitting algal beds. It is possible that in the surrounding coastal areas of Bermuda that halogen-emitting algae are exposed during low tide, with a growing source attributable to the magnitude of the low tide height (e.g. the area of exposure). Enhanced SSA concentrations would be expected with an increase in wave height/wave crashing frequency, however larger tide extremes does not intrinsically lead to enhancements in wave heights or crashing. Larger high tide heights would indicate a slightly larger local surface area covered by seawater, potentially increasing the frequency of bubble bursting, jets, and other sources of fine particulates from the ocean surface. Larger tide extrema also lead to a faster change in tide height in a given time frame (assuming high and low tides remain approximately equally spaced in time). This would lead to a faster rate of physical change in water level, which could increase wave activity and SSA formation via wave breaking and bubble bursting. Though, as noted, the best measurable tracer for SSA concentration in the form of Na^{P} , which is generally non-reactive and has a simple physical source in the GEOS-Chem model, shows no obvious correlation with tide extrema.

The identification of a single source or specific relative contributions of these possibilities related to the high and low tide heights is beyond the scope of this work. Further study is recommended into isolating biogenic vs. physical processes that may lead to elevated halogen concentrations in the MBL.

4.6 Conclusions

The GEOS-Chem model simulation run with the halogen chemistry module (including the sea salt debromination mechanism) is demonstrated to output $\text{Br}_{\text{y}*}$ concentrations that are significantly higher than those observed, both in total and considering all individual species. The over prediction remains for almost all inorganic bromine compounds observed when lowering global pollution levels and anthropogenic influence. This implies that NO_2 is not the limiting factor in production of bromine nitrate (BrONO_2), while previous analysis of BrONO_2 , HOBr , and NOx measurements at the coastal THMAO site give evidence that below certain levels of NO_2 , observed concentrations (and presumably the gas phase formation) of BrONO_2 are notably lower.

Particle filter measurements provide further insight into the brominated gas phase species observed by the t-IMR CIMS. Particulate bromide concentrations and total $\text{Br}_{\text{y}*}^{\text{g}}$ show coincident enhancements during the campaign, though the relationship is not entirely linear. The highest levels of both occur during the filter period which encompasses a storm with the largest wind speeds measured during all of BLEACH23. The GEOS-Chem model shows disagreement with observations of measurable atmospheric bromide in the gas vs particles phases, as well as underestimating fine-mode halogen concentrations for Cl, Br, and I. This in conjunction with the observational upper limit on γ_{HOBr} displays the need for further constraint and study of in-situ heterogeneous process which liberate and recycle reactive halogens in the MBL.

Statistical analysis in the form of PLS regression is applied in an attempt to identify potential sources and local influence on the measured reactive bromine. Among all independently measured and potentially co-varying predictors including meteorology, pollutants, etc, the most meaningful for the linear model to approximate $\text{Br}_{\text{y}*}^{\text{g}}$ are the most recent low tide height and wind speed. This indicates a localized coastal source for the observed bromine, in addition to the known sea-salt liberation mechanism. Plausible possibilities for such a source include macroalgae and tide-driven mechanical processes in the ocean relating to sea spray, though identification of a single source linked to the tidal relationship is beyond the scope of this work.

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Chapter 5: Conclusions and Future Work

5.1 Conclusions

Reactive halogens in the troposphere, including inorganic bromine species, have the ability to interact with and modulate concentrations of trace gases important in global atmospheric chemistry including ozone (O_3), nitrogen oxides (NO_x), HO_x , and mercury. This coupling has significant implications for global air quality and climate, yet the partitioning of reactive bromine (Br_y) remains poorly understood with few in situ observations, especially in areas outside of the polar regions. We present the results from the research and development of a new Ion-Molecule reaction Region (IMR) for use with Chemical Ionization Mass Spectrometry (CIMS), its deployment to a field site in the semi-remote Marine Boundary Layer (MBL), and the implications of the observed reactive bromine species at the ground-based coastal location.

The transverse or "t-IMR" design operated at atmospheric pressure is shown to operate at laminar flow conditions, with reduced interactions of analyte molecules with surfaces before entering the MS, as evidenced quantitatively by instrument delay times on the order of 1 second. This gives greater confidence when compared with other low pressure designs that the spectra produced and compounds identified from their high resolution mass-to-charge ratios (m/Qs) are robust and relevant to ambient sampling conditions. The atmospheric operating pressure results in higher signals for ion clusters of interest, while an electric field is employed to accelerate charged clusters across the inner IMR cavity, reducing physical losses to exhaust. The strength of this electric field is shown to have opposing trends with total ion signal and sensitivity to Br_2 , and is optimized at 1.5 kV as a compromise of retaining a relatively large sensitivity while preserving a sufficient total ion flux. The combination of atmospheric pressure sampling, reduced surface interactions/artificial signals, and sensitivity optimization result in an instrument capable of observing sub-ppt concentrations of ambient trace gases, as demonstrated by the observations of HOBr in chapter 1 and other Br_y species in chapter 2.

The dependence of instrument sensitivity on humidity for the atmospheric pressure t-IMR is quantified, fit, and applied to observations of reactive bromine. A dynamic nonlinear fit of relative Br_2 sensitivity vs. water vapor pressure ($P_{\text{H}_2\text{O}}$) is identified for high humidity and temperature, up to $P_{\text{H}_2\text{O}}$ values near 30 mbar. An experimental direct calibration of HOBr is also performed and shows good agreement with

previously reported values as well as those obtained using theoretical binding enthalpies (BEs), providing independent verification for the use of BEs to calculate the sensitivity of other Br_y species.

The t-IMR was deployed to the Tudor Hill Marine Atmospheric Observatory (THMAO) on the southwestern shores of Bermuda to observe halogen chemistry in the MBL. Five key reactive bromine species were observed using iodide reagent ion chemistry: Br_2 , BrO , HOBr , BrCl , and for the first time, BrONO_2 . Online measurements were made for multiple weeks with the t-IMR CIMS, concurrently with other instrumentation giving observations of meteorological data, NO_x , and other trace gases at the site. THMAO experienced a multitude of atmospheric conditions in the MBL, ranging from marine sourced air masses mostly uninfluenced by anthropogenic activity, to highly localized (and occasionally continentally transported) polluted regimes. The concentrations, partitioning, and potential sources of the Br_{y*} ($= 2\text{Br}_2 + \text{BrO} + \text{HOBr} + \text{BrCl} + \text{BrONO}_2$) species are examined using the meteorological factors including wind speed, direction, photolysis rates, pollutant levels, and others. HOBr , BrONO_2 , and BrO levels are found to be qualitatively in agreement with current understanding of Br_y partitioning, especially when considering the large range of NO_x concentrations observed between the clean marine environment and human activity from ships, cars, power generation, etc. Br_2 and BrCl show unexpectedly high concentrations during the day, where loss due to photolysis is typically assumed to overtake their formation mechanisms in the natural MBL. This behavior is attributed to either an unknown local source of bromine, enhanced heterogeneous cycling due to enhanced NO_x and nitrate chemistry, or some combination of both.

Using the observations of Br_{y*} , NO_2 , photolysis rates, as well as prescribed HO_2 concentrations and particle sizes, the ratio of heterogeneous loss rates for BrONO_2 and HOBr is calculated, assuming steady-state for a short period during the campaign. This along with the theoretical values calculated based on the same assumed particle size and calculated diffusivity of the molecules, produces an upper limit to the uptake coefficient of HOBr ($\gamma_{\text{HOBr}} < 0.02$) much lower than that reported in multiple halogen modeling studies (0.1). The uptake coefficient for bromine nitrate remains almost completely unconstrained by this analysis. This presents one observational constraint on the heterogeneous uptake of reactive bromine compounds, which are important values for quantitatively assessing the partitioning among total atmospheric bromine in the MBL.

The observations of Br_{y*} at THMAO are compared with concentrations produced by a GEOSChem model simulation output for the grid box containing Bermuda. The model is run with the most recent standard halogen chemistry module, which includes the debromination of sea salt aerosols (SSAs). Results show that both the total Br_{y*} and the concentration of each contributing compound are significantly higher in the model, by over an order of magnitude in multiple cases. The largest overestimate by the model is for bromine nitrate (BrONO_2), the gaseous formation of which is dependent on the availability of both NO_2 and

BrO (mainly formed via ozone and atomic bromine under active photolysis). Additional model runs with ship emissions and all anthropogenic emissions turned off, respectively, do not show a significant drop in BrONO₂ or total Br_y* toward their observed levels, despite NO_x and O₃ being reduced by approximately a factor of 2 when all emissions are switched off. This indicates that the model production of bromine nitrate (and further partitioning among Br_y components) is not very sensitive to nitrogen oxide and ozone levels, at least at respective concentrations on the order of 200 ppt and 40 ppb.

Filter measurements taken at THMAO also give insight into the gas-phase reactive bromine (Br_y*^g). Particulate bromide (Br^P) shows enhancements in concentration coincident with Br_y*^g, particularly after an overnight event of elevated wind speeds lasting several hours. High wind speeds over open oceans have been shown to correspond to larger SSA concentrations, which would presumably increase the potential for heterogeneous chemistry for reactive halogens in the MBL. The GEOSChem simulation shows a disagreement between the fraction of atmospheric bromine in the particle and gas phases. The model also underestimates fine-mode particle concentrations of chlorine, bromine, and iodine. The observed particle composition indicates an unaccounted for source of halogens in the MBL for the coastal site and/or the need to adjust reaction rates and partitioning as it is understood in the model.

A strong correlation is found between Br_y*^g and tidal extrema, meaning the heights of both the most recent low and high tides for the coasts of Bermuda. As the tide heights become more extreme, i.e. that low tide height decreases and high tide height increases, there is a general increase in measured reactive bromine. A significant relationship in average Br_y*^g is also shown with wind speed. All three of these environmental factors appear to have some threshold value after which the median bromine signal increases. The clearest relationship among these for the total spread in the 15-minute time resolved Br_y*^g (meaning minimum, median, maximum, and quantiles) is with the most recent low tide height. Given that the largest tide extrema coincide with the high wind speed event, statistical analysis in the form of Partial Least Squares (PLS) regression is performed to separate the influence of these co-varying tidal and meteorological factors. Several available meteorological, trace gas, etc measurements taken independently from the t-IMR CIMS are used as predictor variables for the PLS model to generate components that best capture the variance of total detected Br_y*^g. Variable Importance Parameter (VIP) scores along with regression coefficients show that the two most important predictors of gaseous reactive bromine are low tide height and wind speed. The model was re-run using only these two variables as predictors and is able to explain a similar amount of variance in the measured Br_y*^g as the output using all other independent measurements, with low tide height determined to be the most significant indicator. This indicates a localized coastal source of reactive bromine at THMAO, likely in addition to the established SSA debromination mechanism. Possible explanations for such a source include production from macroalgae and mechanical processes in the ocean dependent on the

tide.

Measurement of sub-ppt level halogen species made possible by the development of the t-IMR are quality controlled using several methods including direct calibration, humidity-adjusted sensitivity, and reduced instrument artifacts. The five major components of reactive bromine presented in this work have not been previously reported to be simultaneously observed in-situ above detection limits. These first observations of bromine nitrate specifically have allowed for investigation into effects of pollutant levels on Br_y , as well as provide constraints on and further study into heterogeneous cycling in the marine atmosphere. Coincident observations from colleagues as part of the BLEACH campaign have made possible a detailed examination of gas and particle phase partitioning, while model comparisons point out the potential for future improvements in our understanding of the bromine (and overall halogen) chemical mechanism in the atmosphere. Changing the rates of these reactions in the MBL to better reflect observations has the potential to significantly alter the total oxidative capacity of the atmosphere and trace pollutant concentrations.

5.2 Future Work

Regarding the t-IMR, the significant dependence of Br_2 sensitivity on ambient humidity is accounted for in detail in chapter 2, though for other compounds, especially non-halogenated molecules, the dependence is likely quite different. This presents an opportunity for future work in designing an apparatus to hold water vapor pressure constant in the t-IMR, by delivering humidified air at specified flows. Naturally this would require accurate pressure, temperature and humidity measurements, as well as an automated delivery system based on these conditions to obtain the proper $P_{\text{H}_2\text{O}}$ value. This would also likely involve a water reservoir, introducing the need for both a large amount of ultrapure water (to eliminate contaminants), as well as a need to change out or refill such a reservoir frequently to keep up with a large 10 L/min humidified flow in the IMR. As this would likely be logistically challenging to deploy at a field site, another opportunity for future study is to measure the relationship between the sensitivity for other classes of compounds beyond bromine (e.g. organics at various oxidative states) and water vapor pressure in the laboratory to create multiple standards for future reference. Direct calibration for other compounds is also recommended regardless of a humidity characterization, for both reference and ideally further independent verification of the use of the BE sensitivity method with the t-IMR.

An instrument artifact is identified in chapter 1 for spectra produced with the t-IMR as described, involving O_2^- ion chemistry. The strongest indicator of such chemistry is a peak at m/Q 60 corresponding to the cluster CO_3^- . The unintended production of O_2^- ions is presumably from either small leaks in the reagent chemical delivery system (small amounts of oxygen from ambient air enter before ionization), or from

the exposure of analyte molecules within the IMR cavity to small amounts of UV radiation from the VUV lamp, as it is oriented perpendicular to the flow. Some tests were performed as part of the t-IMR development where small caps of varying shapes and materials with pinholes were placed over the exit of the VUV housing to reduce incident radiation. However it was found that this restricted reagent flow reduced both the total and reagent ion signals detected. It is therefore recommended that a 90° bend be introduced after the VUV housing as part of the t-IMR design (as it has been in similar setups) such that the radiation from the VUV lamp is not incident on the IMR sample flow, theoretically reducing the exposure of ambient oxygen and subsequent production of O_2^- ions. Lastly for the instrument characterization, detailed experiments with instrument voltages are recommended to explore the extent of ion-molecule declustering and a possible dependence on the t-IMR electric field strength.

While the suite of measurements capturing five components of Br_y (and some chlorine compounds including Cl_2 and ClNO_2 , not discussed here) has provided unprecedented insight into reactive bromine chemistry, observations of other species involved in the mechanism are desirable to give even more detail and constraint to our understanding. The use of I^- reagent ions limits the capability for reliable measurements of compounds like HBr due to presumably much lower sensitivity as mentioned previously, as well as atomic bromine (Br). This also prevents the measurement of gaseous iodine compounds such as I_2 , because in order to be detected robustly it would produce the cluster I_3^- , which is already present as an instrument artifact when using iodide CIMS, and is not easily accounted for using the standard reagent normalization. It is therefore recommended for future in-situ observations to employ multiple reagent ion schemes for CIMS operation (e.g. the addition of bromide ionization) to capture the entire range of gaseous halogens above detection limits. This could be accomplished either by fast switching of reagent chemistry for the same CIMS instrument, or the deployment of multiple CIMS instruments measuring with different reagents. Measurements of free atomic Br would also help complete the chemical mechanism picture of Br^y .

We present the first (to our knowledge) observations of BrONO_2 , which closely matches the diurnal behavior predicted in the GEOSChem output here, as well as that in previous model studies which include the $\text{BrO} + \text{NO}_2$ pathway. More in-situ measurements of this compound would be largely beneficial to verify this behavior, as well as provide concentrations observed in other areas and environments. Direct calibration (similar to that of HOBr shown in this work) for bromine nitrate would also provide another independent verification of binding enthalpy methods for halogen-containing species, as well as reduce measurement error. More observations of HOBr simultaneously with BrONO_2 would provide additional in-situ data for the heterogeneous uptake rate analysis and further constrain the uptake coefficients, improving knowledge and efficacy of models handling the partitioning of reactive bromine. Measurements under different environmental conditions could also present observational evidence for potential temperature and humidity-dependent

uptake of halogens onto SSA surfaces. The heterogeneous uptake calculation could also be made more deterministic by accounting for loss due to deposition.

Particle composition measurements with halogen speciation (as well as aerosol pH) at higher temporal resolution would be invaluable in further probing the heterogeneous uptake and production of reactive bromine. In this vain, particle number and size measurements, such as those provided by a Scanning Mobility Particle Sizer (SMPS), are recommended for future study on effects such as aerosol surface area concentration on reactive halogens in the remote MBL where SSAs are thought to be the main drivers of halide and ozone chemistry. As mentioned, the identification of the tidal source behind the significant correlation with $\text{Br}_{\text{y}*}^{\text{g}}$ is beyond the scope of this work. However, this could be accomplished in future studies by way of algae samples taken near THMAO or other future MBL halogen observation sites. Laboratory experiments are also recommended to explore the fate of bromocarbons and iodocarbons known to be emitted from macroalgae. Variables such as UV radiation (photolysis), sea salt surfaces, and more can be investigated for their role in coastal organic (and inorganic) halogen chemistry.

Finally, further sensitivity studies with the GEOSChem halogen module are recommended. Finding methods to lower reactive bromine levels closer to the observations presented here is critical to improving understanding of partitioning between compounds (and phases) and future uses of the model where halogen chemistry is important, e.g. ozone budget analysis. Other simulations such as chemical box models, even simplification to 0-D would be helpful in determining which reactions drive larger changes in marine atmospheric halogen concentrations and their effects on other important trace gases. Organic species are only briefly touched on in this work, though may be an important player in overall halogen reactivity in either the gas or particle phases.

As alluded to (perhaps ad-nauseam) in this work, there are few reported instances of detailed halogen measurements in the MBL, especially outside of polar regions. This provides opportunity for much further research and in-situ measurements to be made in a variety of remote, polluted, and other marine environments to better understand an important, yet poorly constrained subset of atmospheric chemistry involving reactive halogens.