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Development of Optical Spectroscopic Instruments and Application to Field Measurements of Marine Trace Gases

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Development of optical spectroscopic instruments and application to field measurements of marine trace gases

by

Sean Christopher Coburn

B.S., B.A., Newman University, 2007

A thesis submitted to the
Faculty of the Graduate School of the
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This thesis entitled:
Development of optical spectroscopic instruments and application to field measurements of marine trace gases
written by Sean Christopher Coburn
has been approved for the Department of Chemistry and Biochemistry

Rainer M. Volkamer

Christopher Fairall

Date ________________________

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Halogens ($X = \text{Cl, Br, I}$) and organic carbon are relevant to the oxidative capacity of the atmosphere, are linked to atmospheric sulfur and nitrogen cycles, modify aerosols, and oxidize atmospheric mercury. The abundance of halogen radical species in the atmosphere is very low, but even concentrations of parts per trillion (1 ppt = $10^{-12}$ volume mixing ratio) or parts per quadrillion (1 ppq = $10^{-15}$ volume mixing ratio) are relevant for the aforementioned processes. Halogen radicals can be traced through measurements of halogen oxides ($XO$, where $X = \text{Cl, Br, I}$), that are $\sim$1-10 times more abundant. However, measurements of halogen oxides are sparse, partly due to the lack of analytical techniques that enable their routine detection. In Chapters II-IV, I describe the development of a research grade Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) instrument to measure bromine monoxide (BrO) and iodine monoxide (IO) routinely in the troposphere. I present autonomous measurements of BrO and IO in Pensacola, Florida that maximize sensitivity towards the detection of BrO in the free troposphere (altitudes $>2\text{km}$) from ground. The measurements are then coupled to a box-model to assess their impact on the oxidation of mercury in the atmosphere. Chapter V describes the Fast Light-Emitting-Diode Cavity-Enhanced DOAS (Fast LED-CE-DOAS) instrument and first measurements of glyoxal diurnal cycles and Eddy Covariance (EC) fluxes of glyoxal in the marine atmosphere. Glyoxal is the smallest $\alpha$-dicarbonyl and a useful tracer molecule for fast photochemistry of hydrocarbons over oceans. The unique physical and chemical properties of glyoxal pose challenges in explaining this soluble gas over the remote ocean, and recent measurements over the open ocean currently remain unexplained by models. Results from a first cruise deployment over the tropical Pacific Ocean (TORERO field campaign) are presented.
Dedication

To my wife, Melinda, for her unconditional love and constant encouragement
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Chapter I

Introduction

Understanding the chemistry that takes place throughout the atmosphere is a critical aspect of our ability to regulate anthropogenic and monitor biogenic processes that can have significant impacts on factors relevant to short and long term human health. These factors include, but are not limited to: air and water quality (photochemical smog, urban NO\textsubscript{x} levels, acid rain); heavy metal contamination (mercury bioaccumulation in fish); UV radiation exposure (stratospheric ozone destruction); and climate change (aerosols and greenhouse gases).

The work presented in this study aims to assess the effects of halogen distributions on the oxidative capacity of the atmosphere, which is relevant for many processes including catalytic ozone destruction and mercury oxidation; and understanding distributions, sources, and sinks of the Oxygenated Volatile Organic Compound (OVOC) glyoxal over the open ocean. This introductory section will include a brief overview of 1) atmospheric halogens, 2) glyoxal, and 3) the DOAS method.

1.1 Atmospheric Halogens

Inorganic halogens (e.g. BrO, ClO, IO, OBrO, etc.) are an important class of species to monitor because they can play a significant role in determining the oxidative capacity of the atmosphere through reactions with O\textsubscript{3}, NO\textsubscript{x}, and HO\textsubscript{x}. It has been well established that chlorine and bromine species are responsible for the catalytic destruction of stratospheric O\textsubscript{3} over Antarctica during the polar spring (Solomon 1990). Other studies have found that similar
processes are occurring at altitudes less than 1km during polar spring, where measurements reveal near complete removal of boundary layer O$_3$ by halogen species; these phenomena are termed Arctic Ozone Depletion Events (ODEs) (Barrie et al., 1988; Oltmans et al., 1989; Tuckermann et al., 1997). Additionally, it has been found that coincident with the removal of O$_3$ and increase in halogens are times of near complete conversion of gaseous elemental mercury to gaseous reactive mercury in the polar boundary layer. Reactions between atmospheric mercury and halogens are believed responsible for these so called Atmospheric Mercury Depletion Events (AMDEs) (Lindberg et al., 2002; Steffen et al., 2008).

Atmospheric inorganic halogen species have both anthropogenic and biogenic origins. The former is principally industrial halocarbons (chlorofluorocarbons (CFCs): refrigerants, cleaning solvents; and bromofluorocarbons and hydrobromofluorocarbons: fire retardants and extinguishers) with some contributions from methyl bromide (CH$_3$Br: soil fumigant). These species are found mainly in the stratosphere where they play an important role in the catalytic destruction of Arctic and Antarctic O$_3$. The manufacture and use of such compounds has since been regulated by the Montreal Protocol due to their contributions to the aforementioned stratospheric ozone destruction cycle. The latter source mainly comes from oceanic organic halogens (CH$_3$Cl, CH$_3$Br, CH$_3$I, CH$_2$Br$_2$, CHBr$_3$, CH$_2$I$_2$) and to a certain extent oxidation of sea salt halides (Wayne et al., 1995; Keene et al., 1999). Both industrial halocarbons and biogenic organic halogens form inorganic species by photolysis and to a lesser extent, oxidation of organic halogens by OH radicals.
Figure 1.1 Diagram of a generalized atmospheric halogen species reaction scheme ($X = \text{Cl, Br, I}$ and $Y = \text{Cl, Br, I}$).
A general halogen reaction scheme can be found in Figure 1.1 that details many of the major processes these species undergo. Relative contributions of the different halogens to various oxidative processes are typically determined by the chemical composition of the air masses, as this controls the distribution of the halogens between reactive forms and relatively stable reservoirs. In general, chlorine and bromine species are considered the most atmospherically relevant halogens, while iodine species are becoming an area of increased scientific interest due to their ability to form new particles and add to the growth of preexisting particles. Fluorine species are not typically considered as atmospherically relevant in most applications because of their rapid conversion to the stable reservoir HF, which is considered an irreversible loss (Platt and Janssen 1995).

Halogen oxides (XO, where X = Cl, Br, I) are key species in the chemical cycling of halogens in the atmosphere because these radicals react with many other species commonly found throughout the atmosphere (NO\textsubscript{x}, HO\textsubscript{x}, etc.). Additionally, these molecules absorb light in the ultraviolet-visible region of the electromagnetic radiation spectra (300-500 nm) and have relatively large absorption cross-sections (Figure 1.2) which allow them to be measured by many absorption based measurement techniques.
Figure 1.2 Absorption cross sections in the UV/Vis for the halogen oxides. The vertical dashed line represents the cut-off wavelength below which solar radiation does not reach the earth’s surface.
1.2 Glyoxal

Glyoxal is the smallest α-dicarbonyl and is mostly produced from the oxidation of Volatile Organic Compounds (VOCs), making it an excellent tracer for fast oxidative chemistry. These VOCs are both natural (isoprene) and anthropogenic (acetylene, aromatic rings) in origin (Myriokefalitakis et al., 2008; Stavrakou et al., 2009). It can also be directly emitted from sources such as biomass burning, fossil and biofuel combustion (Grosjean et al., 2001; Kean et al., 2001; Hays et al., 2002; Thalman 2013), and has been identified as an important Secondary Organic Aerosol (SOA) precursor (Liggio et al., 2005; Volkamer et al., 2007). Atmospheric removal of glyoxal is driven by photolysis, reaction with hydroxyl (OH) radicals, dry and wet deposition, and uptake to aerosols (Stavrakou et al., 2009). Recent ship-based (Sinreich et al., 2010; Mahajan et al., 2014) measurements and satellite retrievals (Wittrock et al., 2006; Vrekoussis et al., 2009; Lerot et al., 2010) place varying amounts of glyoxal in the atmosphere over the open ocean, which is surprising given the very high Henry’s Law coefficient ($H_{eff}, 4.2 \times 10^5$ M atm$^{-1}$) and relatively short atmospheric lifetime (~2 hours with overhead sun). Currently, the presence of this molecule in the marine boundary layer cannot be explained by global models (Fu et al., 2008; Myriokefalitakis et al., 2008; Stavrakou et al., 2009), but better knowledge of sources and sinks for glyoxal in this environment could lead to a better understanding of the chemical processing producing it and potentially other volatile organic compounds (VOCs).
Figure 1.3 Graphic depicting Lambert Beer’s Law, where incident light ($I_0(\lambda)$) passes through a medium of length $L$ and is attenuated ($I(\lambda)$) before being observed (detector).
1.3 Differential Optical Absorption Spectroscopy (DOAS)

1.3.1 Lambert-Beer Law

The Lambert-Beer Law (Equation 1.1) describes the attenuation of light as it passes through an absorptive layer and forms the basis on which absorption spectroscopy is based.

\[ I(\lambda, l) = I_0(\lambda) e^{-\sigma(\lambda)l \cdot c} \]  

(1.1)

where \( I(\lambda) \) represents the attenuated light, \( I_0(\lambda) \) is the incident light, \( \sigma(\lambda) \) is the absorption cross section of the material attenuating the light, \( l \) is the length of the light path through the material, and \( c \) is the concentration of the material. \( I, I_0 \) and \( \sigma \) are all wavelength dependent parameters, while \( I \) also depends on the length of the light path. Typical units for these parameters in atmospheric chemistry are: \( \sigma(\lambda) \) (cm\(^2\) molec\(^{-1}\)), \( c \) (molec cm\(^{-3}\)), and \( l \) (cm).

Figure 1.3 is a graphical representation of this process. By rearranging Eq. 1.1, one can solve for the optical density (Equation 1.2), which is a commonly referred to parameter in atmospheric chemistry:

\[ \tau(\lambda) = \sigma(\lambda) \cdot l \cdot c = \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) \]  

(1.2)

1.3.2 The DOAS Approach

DOAS is a widely used analytical technique that makes use of the unique absorption structures of different trace gases, which can be used to identify specific gases in the atmosphere (Perner and Platt 1979; Platt and Stutz 2008). It is essentially a numerical high-pass treatment of the Lambert-Beer Law, and for many atmospheric applications of the Lambert-Beer Law, the well-defined relationship in Eq. (1.1) cannot necessarily be applied. This arises for a variety of reasons such as: unknown \( I_0(\lambda) \), variable light paths, or scattering on molecules/aerosols. Some of these obstacles can be addressed, for instance, scattering processes can be accounted for by including extinction due to scattering in Eq. (1.1),
\[ I(\lambda, l) = I_0(\lambda) \cdot \exp\left( - \int_0^l \left( \sum_i \sigma_i(\lambda) \cdot c_i(l) + \varepsilon_R(\lambda, l) + \varepsilon_M(\lambda, l) \right) dl \right) \] (1.3)

where the subscript \( i \) now denotes different absorbing species, and \( \varepsilon_R(\lambda, l) \) and \( \varepsilon_M(\lambda, l) \) represent wavelength (and light path length) dependent extinction due to Rayleigh scattering and Mie scattering, respectively.

However, determining \( I_0(\lambda) \) or knowing the exact light path in the open atmosphere for passive measurements, which utilize scattered sunlight, is virtually impossible. In the DOAS method, this is addressed by further breaking down Eq. (1.3) into all narrow band features, which change quickly as a function of wavelength, and all broadband features, which change slowly as a function of wavelength.

\[ I(\lambda, l) = I_0(\lambda) \cdot \exp\left( - \int_0^l \left( \sum_i \sigma_i'(\lambda) \cdot c_i(l) + \sigma_i^B(\lambda) \cdot c_i(l) \right) + \varepsilon_R(\lambda, l) + \varepsilon_M(\lambda, l) + T(\lambda) dl \right) \] (1.4)

\[ = I_0(\lambda) \cdot \exp\left( - \int_0^l \left( \sum_i \sigma_i'(\lambda) \cdot c_i(l) \right) + P \right) dl \] (1.5)

where the absorption cross section has been separated into its respective narrowband and broadband portions, \( T(\lambda) \) is an instrument transfer function to account for any broadband features inherent to the instrument, and in Eq. (1.5) all broadband features are accounted for by a polynomial, \( P \).

\[ \sigma_i(\lambda) = \sigma_i^B(\lambda) + \sigma_i'(\lambda) \] (1.6)

where the superscript B and the prime represent the broadband and narrowband portions of the absorption cross-section, respectively.

Accounting for all of the broadband processes through the application of the polynomial allows one to work only with the differential absorption structures, hence differential optical absorption spectroscopy. Figure 1.4 is an illustration of this process.

The primary quantity derived from DOAS is the Slant Column Density (SCD),

\[ \text{SCD} = \int_0^l c_i(l) dl \] (1.7)
which is the integrated concentration of the absorber along the light path.

Many applications of DOAS exist as both passive and active techniques; passive meaning the light source is scattered sunlight, and active refers to the use of an artificial light source such as a Xenon-Arc lamp or light emitting diode. In this thesis, instrumentation representative of both forms will be developed and applied towards the measurement of various trace gases in the marine atmosphere.
Figure 1.4 Graphic depicting the concept of differential cross-section (top panel), where $\sigma^0$ is the differential portion and $\sigma^B$ is the broadband portion. The bottom panel demonstrates how incident radiation ($I_0(\lambda)$) is attenuated by absorption according to the cross-section in the top panel.
Chapter II

MAX-DOAS Instrument Development


Goals: This chapter presents the development of a research grade MAX-DOAS instrument, designed and tested for autonomous observations of halogen oxide radicals, and small oxygenated hydrocarbons in the marine boundary layer. Attention is paid to assess the current limitations on the achievable root mean square (RMS) noise, a measure of the sensitivities of this type of hardware.

Methodology: The instrument is described, and sensitivity studies are conducted to systematically assess different parameters, e.g. temperature effects on spectrometer slit width and wavelength pixel mapping, and detector non-linearity, which could be affecting /limiting the signal to noise ratios of MAX-DOAS instruments. This assessment is made through the root mean square (RMS) of the optical density of the residual remaining after the DOAS fitting routine. The RMS limitation associated with each of the parameters listed above is compared to RMS values realized in actual measurements, lending insight onto which factors can play roles in determining the sensitivity of field measurements.

Results/Conclusions: Limitations in RMS by the hardware could be overcome through careful design and control of various instrument parameters (such as instrument temperature and actively addressing detector non-linearity). However, other limitations on RMS are most likely due to
imperfections in the representation of the atmospheric state, i.e., representation of Fraunhofer lines and/or molecular scattering processes. Limitations of the retrieval, such as inaccuracies in the wavelength mapping of reference absorption cross-sections, could also not be ruled out, but as of this point in time might not be surmountable. Improved measurements of molecular spectroscopic parameters, such as higher resolution absorption cross-section measurements, would further benefit these retrievals. By specifically addressing many of these challenges, the achievable RMS of this instrument compares favorably within the high-end of other available MAX-DOAS hardware. We further demonstrate the first detection of BrO, IO, and CHOCHO over the Gulf of Mexico, while also monitoring other trace gases such as HCHO, NO₂, and O₄.

2 Abstract

We designed and assembled the University of Colorado Ground Multi AXis Differential Optical Absorption Spectroscopy (CU GMAX-DOAS) instrument to retrieve bromine oxide (BrO), iodine oxide (IO), formaldehyde (HCHO), glyoxal (CHOCHO), nitrogen dioxide (NO₂) and the oxygen dimer O₄ in the coastal atmosphere of the Gulf of Mexico. The detection sensitivity of DOAS measurements is proportional to the root mean square (RMS) of the residual spectrum that remains after all absorbers have been subtracted. Here we describe the CU GMAX-DOAS instrument and demonstrate that the hardware is capable of attaining RMS values of ~ 6x10⁻⁶ from solar stray light noise tests using high photon count spectra (compatible within a factor of two with photon shot noise).

Laboratory tests revealed two critical instrument properties that, in practice, can limit the RMS: (1) detector non-linearity noise, RMS_{NLin}, and (2) temperature fluctuations that cause variations in optical resolution (full width at half the maximum, FWHM, of atomic emission
lines) and give rise to optical resolution noise, $RMS_{FWHM}$. The non-linearity of our detector is low ($\sim 10^{-2}$) yet – unless actively controlled – is sufficiently large to create a $RMS_{NLin}$ limit of up to $2 \times 10^{-4}$. The optical resolution is sensitive to temperature changes (0.03 detector pixels/°C at 334 nm), and temperature variations of 0.1°C can cause residual $RMS_{FWHM}$ of $\sim 1 \times 10^{-4}$. Both factors were actively addressed in the design of the CU GMAX-DOAS instrument. With an integration time of 60 sec the instrument can reach RMS noise of $3 \times 10^{-5}$, and typical RMS in field measurements ranged from $6 \times 10^{-5}$ to $1.4 \times 10^{-4}$.

The CU GMAX-DOAS was set up at a coastal site near Pensacola, Florida, where we detected BrO, IO and CHOCHO in the marine boundary layer (MBL), with daytime average tropospheric vertical column densities (average of data above the detection limit), VCDs, of $\sim 2 \times 10^{13}$ molec cm$^{-2}$, $8 \times 10^{12}$ molec cm$^{-2}$ and $4 \times 10^{14}$ molec cm$^{-2}$, respectively. HCHO and NO$_2$ were also detected with typical MBL VCDs of $1 \times 10^{16}$ and $3 \times 10^{15}$. These are the first measurements of BrO, IO and CHOCHO over the Gulf of Mexico. The atmospheric implications of these observations for elevated mercury wet deposition rates in this area are briefly discussed. The CU GMAX-DOAS has great potential to investigate RMS-limited problems, like the abundance and variability of trace gases in the MBL and possibly the free troposphere (FT).

2.1 Introduction

Tropospheric halogen species, such as bromine oxide (BrO) and iodine oxide (IO), are of great interest to the emerging debate over the inter-relationships between air quality (Stutz et al., 2002) and climate change since they can destroy tropospheric ozone (O$_3$), which is both toxic and a greenhouse gas; can affect the partition of Nitrogen Oxides (NO$_x$) and Hydrogen Oxides (HO$_x$); may play a role in oxidizing gaseous elemental mercury (GEM, Hg$^0$) to gaseous oxidized
mercury (GOM, Hg$^{2+}$); and, for IO, can form new particles and/or add to the growth of pre-existing particles that may have adverse health effects and can have the potential to cool climate. The detection of halogen oxides, in particular BrO, can pose experimental challenges. For instance, the detection of tropospheric BrO is very difficult due to its relatively low concentrations and its background abundance in the stratosphere. Whereas BrO radicals are typically about ten times as abundant as bromine atoms, both species are in a rapid photochemical steady state. BrO and bromine atoms are very reactive, and are rapidly lost by reaction with oxygenated volatile organic compounds (OVOCs), such as formaldehyde (HCHO) and glyoxal (CHOCHO), HO$_2$ radicals, NO$_x$, or heterogeneous reactions, e.g. on surfaces, or in sampling lines (Atkinson et al., 2007). This leads to considerable analytical challenges with the sampling of these free radicals from the atmosphere by means of in-situ techniques and results in horizontal and vertical distributions of reactive bromine radicals that are very susceptible to gradients in the concentrations of OVOCs, HO$_2$, and NO$_x$. The dependence on reactant gradients poses the question of how representative measurements near ground-level are over the depth of the marine boundary layer (MBL) and throughout the atmosphere. One way to investigate abundance of reactive halogen species is by detecting halogen oxide radicals directly in the open atmosphere using Differential Optical Absorption Spectroscopy (DOAS).

DOAS is a well-established technique (Perner and Platt 1979; Platt 1994; Platt and Stutz 2008) used to identify trace gases by means of their individual differential (i.e. narrow band) absorption structures. In the past, the DOAS technique has been extensively used to measure halogen oxides (Hausmann and Platt 1994; Honninger 2002; Honninger and Platt 2002). Multi-AXis DOAS (MAX-DOAS) is a useful analytical technique that uses scattered sunlight collected at different viewing angles relative to the horizon to measure atmospheric trace gases directly in
the open atmosphere (without the need to draw air through any sampling lines). The integrated
congentrations of trace gases along each line of sight, termed the Slant Column Density (SCD),
are derived using non-linear least-squares fitting of multiple trace gas reference spectra. Each
spectrum is analyzed against a user-defined reference spectrum, which removes Fraunhofer
absorption lines. In a typical DOAS measurement scenario the reference spectrum is recorded in
the zenith viewing direction and at a low solar zenith angle (SZA) in order to minimize the
contribution of the reference SCD from that of the analyzed spectrum. This produces a so called
differential slant column density (dSCD). If the instrument is ground-based and the telescope is
pointed close to the horizon, the increased path length through the surface layer of the
atmosphere makes this technique particularly sensitive to trace gases within the boundary layer
(Honninger and Platt 2002; Honninger et al., 2004). This creates a distinct advantage in the use
of MAX-DOAS to probe the marine/coastal boundary layer.

In the DOAS analysis, the residual structure of the fitting procedure is an indicator for the
quality of the fit. This is usually expressed by the root mean square (RMS) of the residual’s
optical density. RMS of state-of-the-art hardware is typically ~1x10^{-4} or higher (Table 2.1, also
RMS > 10^{-4} for OMI instrument on EOS-Aura, K. Chance, pers. comm, 2010; RMS > 10^{-4} for IO
analysis of spectra recorded by the SCIAMACHY instrument aboard ENVISAT (Schoenhardt et
al., 2008, pers. comm. 2011), i.e., RMS typically does not improve further in accordance with
photon-count statistics. The reasons for this have, to our knowledge, as yet not been elucidated.
There are several parameters that influence the RMS of the DOAS analysis (Platt and Stutz
2008) of solar stray light spectra. These can be divided into (1) hardware limitations (caused by
non-linear detectors, instrument stray light, dark current, under sampling, instrument drifts, etc.),
and (2) limitations in the representation of atmospheric state. The latter combine (2a) numerical
limitations (during convolution of reference spectra, uncertainties in the wavelength pixel mapping, asymmetric or wavelength dependent instrument line shapes, analysis parameters) and (2b) limited knowledge about analysis inputs (e.g., spectroscopic parameters of literature cross-sections, wavelength calibration errors, unknown temperature dependencies, missing reference spectra, or imperfect representation of scattering processes (i.e., Ring)). In particular, the choice of the instrumentation used for the measurement can inherently determine the RMS when acquiring the spectra. Imaging spectrometers with longer focal lengths provide more steady projecting properties; larger size array detectors, and larger slit sizes provide for increased light throughput and thus lower photon shot noise, while smaller spectrometer/detector combinations tend to be more sensitive to temperature variations and optical drift. In part because larger focal length spectrometers and larger detector arrays are disproportionally more expensive, the advantages of small practical devices have recently been driving the development of MAX-DOAS hardware; one example of this is the Mini-MAX-DOAS hardware (Honninger 2002). Mini-MAX-DOAS devices can be easily operated at remote sites, such as volcanoes (e.g. Bobrowski et al., 2003), with just battery power, or be set up quickly at any site, such as on vehicles (e.g. Ibrahim et al., 2010). However, currently available Mini-MAX-DOAS devices are often limited to RMS $\sim 10^{-3}$. In order to detect low concentrations of halogen oxide radicals more sophisticated devices are desirable. State-of-the-art DOAS hardware provides for RMS on the order of $10^{-4}$. Recently, the first measurements with RMS values in the range of $8\times10^{-5}$ have been reported (Friess et al., 2010) with a very stable instrument in the pristine Antarctic environment. Table 2.1 lists selected typical MAX-DOAS instruments and a few of their respective properties, including their RMS values. For a comprehensive look at the performance of the currently available MAX-DOAS instrumentation see Roscoe et al., (2010). The limitations on the
attainable RMS values are one of the driving forces preventing the routine measurement of BrO by means of MAX-DOAS. A BrO dSCD on the order of $1 \times 10^{13}$ molec/cm$^2$ corresponds to a differential optical density of $8 \times 10^{-5}$; however, even lower dSCD values would still be atmospherically relevant, i.e., for oxidizing mercury, and/or could affect the tropospheric ozone background. Using the calculation of path length based on the O$_4$ dSCD described in Sinreich et al., (2010) and using a typical O$_4$ dSCD of $6 \times 10^{43}$ molec$^2$/cm$^5$ a BrO dSCD of $1 \times 10^{13}$ molec/cm$^2$ relates to a mixing ratio of 2-3 ppt BrO. Only small concentrations of bromine atoms (corresponding to <2 ppt of BrO) are sufficient to account for the observed levels of Gaseous Oxidized Mercury, GOM (Holmes et al., 2009). Consequently, low RMS measurements ($<10^{-4}$) are a prerequisite to advancing our understanding of the bromine content of the atmosphere. In order to detect the low optical densities characteristic of BrO column abundances, improvements in the RMS values are a limiting factor.

Measurements by the Mercury Deposition Network (MDN) show that the southeastern United States is a region with elevated mercury wet deposition compared with the rest of the country. This cannot be solely attributed to mercury sources to the atmosphere, which are more abundant in other areas, such as the North Eastern United States industrial corridor, or natural sources that are more dispersed. This discrepancy suggests that the high deposition of mercury to the southeast might be due to the conversion of background atmospheric GEM to GOM, the latter of which is then readily wet-deposited. Whether this process would occur in the boundary layer, in the free troposphere (FT), and/or is a combination of both processes, remains unknown. The ATMOSpeclab at the University of Colorado at Boulder (CU) has developed and characterized a high sensitivity Ground-based MAX-DOAS instrument, the CU GMAX-DOAS. Here we describe the instrument, and present, to our knowledge, the first systematic study of the
factors limiting RMS values as the photon shot noise (PSN) contribution is reduced to $\text{RMS}_{\text{PSN}} < 10^{-4}$. We also present a first application of the CU GMAX-DOAS instrument measuring BrO, IO, HCHO, CHOCHO, NO$_2$ and O$_4$ at a coastal site near Pensacola, FL. This coastal site is in close proximity to a MDN station, and the Gulf of Mexico. The CU GMAX-DOAS was developed to investigate the potential role of halogens in mercury oxidation by measuring the relative abundances and vertical distributions of both BrO and IO.
Table 2.1 Summary of performance capabilities and features of some of the currently reported MAX-DOAS instruments. The notation “n.r.” signifies information that was not reported. The RMS values reported are from typical DOAS evaluation windows ranging from 15 – 40 nm, with the exception of the Pandora Goddard Space Flight Center reference which uses a rather wide window of 130 nm.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>CU GMAX-DOAS¹</td>
<td>Pensacola, Florida, USA</td>
<td>Acton SP2356i</td>
<td>&gt;0.56/110</td>
<td>0.6</td>
<td>2-dimensional CCD detector (PIXIS 400B)</td>
<td>8</td>
<td>0.77</td>
<td>322-488</td>
<td>±0.005-0.06</td>
<td>7x10⁻⁴ – 2x10⁻⁴</td>
</tr>
<tr>
<td>Mini-MAX-DOAS²</td>
<td>e.g. New England, USA/polluted</td>
<td>Ocean Optics USB2000</td>
<td>0.8/50</td>
<td>0.04</td>
<td>1-dimensional CCD detector (Sony ILX511)</td>
<td>0.014</td>
<td>0.7</td>
<td>290-420, 430-460</td>
<td>±0.2</td>
<td>8x10⁻⁴</td>
</tr>
<tr>
<td>Schwampel IUP Heidelberg²</td>
<td>Mexico City/polluted</td>
<td>Acton 300</td>
<td>10/150</td>
<td>0.12 (per viewing direction)</td>
<td>2-dimensional CCD detector (Andor DV420-OE)</td>
<td>6.7</td>
<td>0.7</td>
<td>325-460</td>
<td>± 0.1</td>
<td>2-4x10⁻⁴</td>
</tr>
<tr>
<td>Antarctica IUP Heidelberg³</td>
<td>Antarctica/pristine</td>
<td>n. a., Yobin Yvon grating</td>
<td>1.7/120</td>
<td>0.16</td>
<td>Photodiode array (Hamamatsu ST3904-1024)</td>
<td>2.5</td>
<td>0.5</td>
<td>400-650</td>
<td>n. a.</td>
<td>8.2x10⁻⁵</td>
</tr>
<tr>
<td>Pandora Goddard Space Flight Center⁴</td>
<td>Thessaloniki, Greece, and Greenbelt, Maryland, USA</td>
<td>based on an Avantes spectrometer</td>
<td>n. a./50</td>
<td>0.02</td>
<td>1-dimensional Hamamatsu CMOS</td>
<td>0.025</td>
<td>0.42-0.52</td>
<td>265-500</td>
<td>± 1</td>
<td>&lt; 5x10⁻³</td>
</tr>
</tbody>
</table>

¹ This work; ² Honninger 2002; Sinreich, 2008; ³ Frieß et al., 2004; 2010; ⁴ Herman et al., 2009
Table 2.1 cont’d Summary of performance capabilities and features of some of the currently reported MAX-DOAS instruments. The notation “n.r.” signifies information that was not reported. The RMS values reported are from typical DOAS evaluation windows ranging from 15 – 40 nm, with the exception of the Pandora Goddard Space Flight Center reference which uses a rather wide window of 130 nm.

<table>
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<tr>
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<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MFDOAS</td>
<td>Washington State University⁶</td>
<td>Greenbelt, Maryland, USA</td>
<td>n. a./100</td>
<td>0.54</td>
<td>2-dimensional CCD (PIXIS:2KBUV)</td>
<td>6.9</td>
<td>0.83</td>
<td>282-498</td>
<td>± 2</td>
</tr>
<tr>
<td>Frontier Research Center for Global Change, Japan³</td>
<td>Tsukuba, Japan/ polluted spectrometer (B&amp;W TEK Inc., BTC111)</td>
<td>n. a./10</td>
<td>0.007</td>
<td>1-dimensional CCD (ILX511, Sony)</td>
<td>0.014</td>
<td>0.4-0.55</td>
<td>280-560</td>
<td>n. a.</td>
<td>0.7 - 1.1x10⁻³</td>
</tr>
<tr>
<td>Belgian</td>
<td>Institute for Space Aeronomy⁶</td>
<td>La Reunion</td>
<td>Acton SpectraPro 275</td>
<td>n. a./n. a.</td>
<td>2-dimensional CCD (NTE/CCD-400EB)</td>
<td>8</td>
<td>0.75</td>
<td>300-450nm</td>
<td>n. a.</td>
</tr>
<tr>
<td>IUP Bremen⁷</td>
<td>Ny Alesund, Norway/ pristine</td>
<td>Oriel MS 257</td>
<td>n. a. / n. a.</td>
<td>n. a.</td>
<td>2-dimensional CCD of the Andor DV 440-BU type</td>
<td>6.9</td>
<td>0.5</td>
<td>325-413nm</td>
<td>± 0.1</td>
</tr>
</tbody>
</table>

¹ Herman et al., 2009; ² Irie et al., 2008; ²⁰²¹ Theys et al., 2007; Vigouroux et al., 2009; ⁷ Wittrock et al., 2004; Heckel et al., 2005
2.2 Instrument Description

The CU GMAX-DOAS instrument collects spectra of scattered sunlight between 321.3 and 488.4 nm at different viewing angles, which are then analyzed in order to detect the presence of BrO, HCHO, IO, CHOCHO, NO\textsubscript{2}, and O\textsubscript{4}. The instrument consists of a telescope, located outdoors on an elevated platform to collect scattered sunlight, and the spectrometer/electronics rack, which is kept indoors in an air-conditioned lab and has a two stage temperature control; it contains all of the electrical components needed to operate the instrument, as well as the spectrometer and detector. Fig. 2.1 depicts the instrument components along with their placement and a map of the field sites at which it has been located. When comparing different MAX-DOAS hardware (Table 2.1), the effective slit area, which is the product of the height over which the detector is illuminated and slit width, is a measure of the instrument’s ability to couple in-coming light onto the detector; in this regard, the CU GMAX-DOAS is one of the most light-efficient instruments.

2.2.1 Telescope

The telescope is designed for high light throughput and very low dispersion (cone angle of 0.3\degree). It is comprised of a motor with housing, a rotating prism with housing mounted to the motor axis, and a lens tube. The outer components are made from black anodized aluminum and are protected by a thin polished aluminum shield in order to reduce solar heating of the telescope (Fig 2.1b, c). The rotating prism housing is driven by an Intelligent Motion Systems Inc. MDrive34 Plus motor with internal encoder that is located in the motor housing. The shaft of the motor is attached directly to a custom-made rotating assembly that holds a 5cm x 5cm right angle fused silica prism; and an O-ring sealed sapphire window (optical diameter 50.8 mm, 1mm
During measurement, light is collected via the sapphire window on the main face of the prism housing and enters the prism where it is directed onto an f/4 5cm lens mounted in the opposite direction from the motor onto the prism holder. Both junctions of the prism housing contain two separate O-ring seals to prevent water from entering the prism housing. Additionally, both the prism housing and the lens tube contain small bags filled with silica gel bead drying agent to actively dry the air around the optics and prevent possible condensation on the optical components. The entire prism housing can be rotated 360 degree by changing the motor axis; this rotation defines the elevation angle over which the prism collects light from the atmosphere. The telescope and electronics rack are coupled by optical fibers and electronics cables. The light is focused via the lens tube onto a CeramOptics 10m x 1.7mm silica monofiber that is connected to an OceanOptics 5m fiber bundle consisting of 27 x 200µm fibers. This fiber bundle is configured in a circular arrangement at the fiber junction and then forms a linear array at the spectrometer end. This end of the fiber bundle is directed onto the slit of the spectrometer, which is set at a width of 110 µm. Two filters; a BG3 and a BG38, were placed inside the lens tube to reduce the amount of visible and near infra-red light that could contribute to stray light in the spectrometer, as well as to balance out the light intensity differences between the UV and visible wavelength regions across the detector. The chosen optics maximizes the amount of light collected, thus improving the signal-to-noise ratio and time resolution of measurements.
Figure 2.1 Panel (a) Instrument rack containing ACTON2356i spectrometer (1), PI PIXIS400B detector (2), National Instruments Compact RIO with electronics modules (3), optical mounts to position fibers (4) and power supplies. Panel (b) Telescope with housing of the MDrive34 stepper motor, rotating prism housing, and lens tube for f/4 optics. Panel (c) Outdoor setup of telescope with solar shields to reduce heating of telescope. Panel (d) Measurement sites: OLF located ~20 km northwest of Pensacola, FL, and EPA located in Gulf Breeze, FL ~10 km southeast of Pensacola.
2.2.2 Spectrometer, CCD detector and Electronics Rack

The spectrometer, detector and controlling electronics are housed in a standard 19”
aluminum instrument rack with modifications to the floor and the lid for added stability. The
spectrometer is a Princeton Instrument Acton SP2356i Imaging Czerny-Turner spectrometer with
a PIXIS 400 back illuminated CCD detector equipped with UV fluorescence coating. The
spectrometer was equipped with a custom 500 grooves mm\(^{-1}\) grating (Richardson, 300 nm blaze
angle). This grating gives simultaneous coverage from 321.3-488.4 nm, or a range of 167.1 nm.
The quadratic dispersion equation for the wavelength setting here is
\[
\lambda = 321.27 + 0.125(x) - 2.656 \times 10^{-7}(x^2)
\]
where \(x\) denotes the pixel number, and the linearly approximated dispersion is 0.125 nm pixel\(^{-1}\).
The 110 \(\mu\)m wide slit width corresponds to a linearly approximated spectral resolution of \(~0.68
\) nm FWHM. This has been experimentally determined by means of fitting a Gaussian function to
a mercury atomic line spectrum of the 404.66 nm line to be \(~0.74\) nm. The PIXIS 400B CCD is a
UV-optimized two-dimensional array detector with 400 x 1340 pixels. Our software sets the gain
of the readout register ADC during CCD initialization. This CCD gain is typically set to the
lowest gain value (high capacity mode), which corresponds to a photon-into-count conversion
factor of 16; increasing this gain makes the CCD more sensitive but also reduces the pixel well
capacity, and thus has the primary effect to shorten integration times to reach a certain saturation
level. Notably, the use of the CCD in high capacity mode maximizes the useful well capacity,
and minimizes the attainable RMS noise from a single acquisition. For CCD readout, two rows
are binned to reduce data volume; we use a readout rate of 2MHz (readout noise < 16 electrons
rms), corresponding to a readout time of 134 ms. The CCD is cooled to -70° C to reduce dark
current. The data acquisition software reads a configuration file that specifies a lower and upper
row number for illuminated CCD rows (ROI or ‘region of interest’), and similarly specifies row numbers for “dark” areas of the CCD chip; the latter are used to characterize background in terms of electronic offset, dark current, background and spectrometer stray light. The offset and dark current correction of measured spectra is similar to Wagner et al., (2004). The spectrometer stray light after these corrections was determined to be below 0.1% in our setup. It was verified in laboratory tests that under these operating conditions the detector read-out noise and dark current noise are negligible, and RMS noise essentially follows photon counting statistics. The software saves both a background corrected 1D spectrum, and a full 2D image. For instrument control, a National Instruments CompactRIO electronics chassis, capacity of up to eight modules, was interfaced with our custom built LabVIEW data acquisition code to provide a framework for tracking and controlling numerous instrument parameters, including voltage monitoring, temperature read-back, solid state relay control for software proportional-integral-derivative (PID) temperature stabilization, and fully integrated communications with the telescope motor, spectrometer and CCD detector.

Additional parameters accessible through the software include: selecting and controlling the CCD target saturation level (which represents the ratio of the counts derived from digitizing a spectrum divided by the full dynamic range of the 16-bit ADC used to digitize the spectrum) within a selectable wavelength range, setting upper and lower bounds in which the target saturation level is allowed to vary, automatic determination of the proper integration time to adjust the saturation level within these bounds, automatic rejection of saturated spectra prior to the data storage, and fine tuning the PID parameters used for temperature stabilization of the electronics rack housing as well as the spectrometer. During the software determination of the integration time based on the user defined saturation level inputs, the maximum value from a
single pixel from a specified column range on the CCD is used. This allows us to maintain a target saturation level within a specific wavelength range, even if the relative distribution of intensity across the CCD chip is changing its spectral shape due to changing light conditions, allowing us to optimize a measurement to target a particular trace gas (wavelength range) while not losing information about trace gases measured in a different wavelength range.

Temperature stability is a key component to consider when designing and building MAX-DOAS instrumentation because even small fluctuations can result in changes in instrument properties, such as line shape and dispersion of the spectrometer, and dark current noise in the detector. In order to maintain a stable temperature, the spectrometer was fitted with insulating foam and a small heating foil controlled by a PID loop in the LabVIEW software. Two temperature sensors (Omega PT100 high precision RTDs, accuracy – 1/10 DIN, read out noise: 0.003°C peak to peak) were placed on the instrument, one on the bottom near the heating foil to provide feedback for the PID loop, and one on the top of the instrument to provide information about the temperature gradient over the spectrometer chassis. Additionally, the rack was fitted with an external housing that provided insulation between the inside of the rack and the ambient air. The top of this housing was equipped with 6 single-stage peltier cooling units, used to stabilize the temperature inside the rack. The peltiers are controlled by a series of heavy duty solid state relays that are triggered by a signal received from a PID controlled solid state relay as part of the NI cRIO. With these measures in place, during normal operation, the sensor closest to the heating foil was stable within 0.005°C, while the sensor atop the instrument varied by 0.06°C over an 8 hour period. During this time the rack temperature was stable to within ~0.8°C while ambient temperature varied by more than 6°C. While the detector and fiber mounting hardware are contained within the secondary temperature stabilization unit, they are not necessarily in
thermal equilibrium with the spectrometer, and their temperature is controlled to within the range of temperature variations as measured by the second temperature sensor on the spectrometer, and that inside the instrument rack.

2.3 Laboratory characterization of the CU GMAX-DOAS

The following section describes laboratory experiments to assess spectral drift in the wavelength-pixel mapping, changes in the slit function as a function of temperature, optical resolution across the detector, detector non-linearity, and signal-to-noise levels.

2.3.1 Temperature sensitivity tests

To test the temperature sensitivity of the instrument, atomic line spectra from a PenRay Mercury-Argon lamp were recorded at five different temperatures ranging from 27°C to 40°C. The lines at 334.15 nm (~pixel 104), 404.66 nm (~pixel 667), and 435.84 nm (~pixel 918) were chosen to characterize the shifts (changes in the line center position) and changes in line shape over this temperature range. These three lines were chosen to characterize the spectral projection in the center position of the CCD detector (404 nm line) and off-center of the CCD detector. Tests were performed by first allowing the spectrometer to stabilize for ~1 hour at the desired temperature and then recording the line spectra using the Hg-Ar lamp. The spectra were then analyzed by fitting a Gaussian line shape profile to each of the atomic lines (IgorPro, Wavemetrics). The center position and line width parameters derived from the fitting procedure were used to determine both shifts and line broadening as a function of temperature (Fig. 2.2). Shift is defined as the difference in the center position of the fit for each temperature relative to the position at 30°C; line width
broadening is the difference in the FWHM derived from the fit as compared to a reference FWHM at 30°C. Drift in the wavelength pixel mapping (shift) of this instrument is ~0.1 pixel °C⁻¹. The dependence of shift on temperature is found to be well-represented by a linear regression (Fig. 2.2d). The linear regression coefficients were determined to be 0.08±0.01 pixels °C⁻¹, for the three slopes in Fig. 2.2d, with R² values of 0.95 for the three lines, respectively.
Figure 2.2 Characterization of the spectrometer/detector system with respect to temperature. Panels (a - c) Spectral line shape as a function of temperature for 334 nm, 404 nm, and 435 nm, atomic emission lines of an Hg-Ar lamp. Panel (d) Spectral shift of atomic lines as a function of temperature. Panel (e) Difference in the full width at half the maximum of the line shapes as a function of temperature.
2.3.2 Effect of line-shape broadening on RMS

Table 2.2 illustrates the effect of line shape broadening on the RMS values obtainable during a DOAS fitting procedure. The effect of line shape broadening was determined by convoluting a literature Fraunhofer spectrum (Kurucz et al., 1984) with Gaussian shaped calculated line-shape functions that differed in FWHM by the number of pixels as given in Table 2.2. The convoluted Fraunhofer spectrum was then divided by a Fraunhofer spectrum convoluted using a reference line shape width (here 0.79 nm). These tests were conducted in two wavelength ranges as illustrated in Table 2.2. Since the slit temperature is somewhat buffered by the heat capacity of the spectrometer, its stability is expected to be nearer to the stability of the instrument (~0.06 °C) than that of the rack (0.8 °C peak to peak variations), but it is most likely somewhere between these values. The rack temperature variations showed oscillations with a period of ~30 mins that followed variations in the room temperature of ~7°C, and appeared to be driven by the period at which the room air conditioning (AC) would turn ON/OFF; our second stage temperature control reduced the amplitude of room temperature variations by a factor of ~10 inside the rack. We estimate the instability of our slit temperature, $\Delta T_{\text{slit}}$, as the 1-sigma temperature variability of 10 min averaged rack temperature variations (i.e., assuming a 10 min time constant of the slit to respond to rack temperature changes). Over the course of a day $\Delta T_{\text{slit}}$ was 0.054°C (1-sigma) for periods when the AC was OFF and 0.21°C (1-sigma) when the AC unit was ON. Based on Table 2.2 we expect the attainable RMS$_{\text{FWHM}}$ of our instrument to range from $<1 \times 10^{-5}$ to $5 \times 10^{-5}$ (0.054°C, representative of 80% of the data) and $5 \times 10^{-5}$ to $1.8 \times 10^{-4}$ (0.21°C, 20% of the data), with larger numbers expected in the UV region of the spectrum.
Table 2.2 Calculated RMS dependence on symmetric line shape broadening (Gaussian line shape).

<table>
<thead>
<tr>
<th>Difference (pixels)</th>
<th>Difference (nm)</th>
<th>430-470 nm</th>
<th>330-370 nm</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>1.24E-01</td>
<td>1.50E-02</td>
<td>2.50E-02</td>
</tr>
<tr>
<td>0.1</td>
<td>1.24E-02</td>
<td>1.81E-03</td>
<td>3.07E-03</td>
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<tr>
<td>0.01</td>
<td>1.24E-03</td>
<td>1.84E-04</td>
<td>3.13E-04</td>
</tr>
<tr>
<td>0.001</td>
<td>1.24E-04</td>
<td>1.84E-05</td>
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<td>1.40E-07</td>
<td>2.38E-07</td>
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</table>
2.3.3 Shift Characterization

The numerical uncertainty with which different reference spectra can be mapped onto a common wavelength pixel relation during the non-linear least square analysis of DOAS spectra depends on the absolute accuracy of the wavelength calibration of literature cross-sections. In order to assess the effect of shift error on the RMS, a solar spectrum was copied and one of the copies was systematically shifted by the amounts shown in Table 2.3 and then the spectra were divided. The solar spectrum used was created by co-adding a series of spectra collected at an elevation angle of 80°. Five hundred and sixty spectra, each with an integration time of 5 seconds, were co-added leading to a final spectrum with a total integration time approaching 50 minutes. This many spectra were used in order to obtain a high photon count in the final spectrum for this test. The shift error effect on RMS was determined to be independent of number of photons of the spectrum. The wavelength regions between 430–470 nm and 330–370 nm were used, which corresponds to 323 and 320 pixels, respectively. Table 2.3 shows that in order to achieve an RMS on the order of $1 \times 10^{-4}$ and $1 \times 10^{-5}$ the shift needs to be determined with an accuracy of $\sim 6 \times 10^{-3}$ and $\sim 6 \times 10^{-4}$ pixels for the 430-470 nm range, and $\sim 4 \times 10^{-3}$ and $\sim 4 \times 10^{-4}$ pixels in the 330-370 nm range.

Notably, the uncertainty in the wavelength calibration of literature cross-sections can become limiting if such low RMS is to be realized, in particular when measuring in the presence of abundant trace gases, for instance NO$_2$ in this study. While the DOAS non-linear least-squares fit allows for a shift in the literature cross-sections relative to the wavelength pixel mapping of the instrument, any inherent inaccuracies in the original wavelength calibration during recording of the literature cross-sections could potentially limit the achievable RMS (see Section 2.4.2).
Table 2.3 Calculated RMS noise as a function of shift imprecision for two wavelength ranges.

<table>
<thead>
<tr>
<th>Shift (pixel)</th>
<th>Shift (nm)</th>
<th>RMS (Dev)</th>
<th>OD Delta</th>
<th>RMS (Dev)</th>
<th>OD Delta</th>
</tr>
</thead>
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<tr>
<td>0.1</td>
<td>1.24E-02</td>
<td>1.69E-03</td>
<td>1.43E-02</td>
<td>2.49E-03</td>
<td>1.36E-02</td>
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<tr>
<td>0.01</td>
<td>1.24E-03</td>
<td>1.69E-04</td>
<td>1.42E-03</td>
<td>2.49E-04</td>
<td>1.37E-03</td>
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<tr>
<td>0.001</td>
<td>1.24E-04</td>
<td>1.69E-05</td>
<td>1.42E-04</td>
<td>2.49E-05</td>
<td>1.37E-04</td>
</tr>
<tr>
<td>0.0001</td>
<td>1.24E-05</td>
<td>1.69E-06</td>
<td>1.42E-05</td>
<td>2.49E-06</td>
<td>1.37E-05</td>
</tr>
<tr>
<td>0.00001</td>
<td>1.24E-06</td>
<td>1.69E-07</td>
<td>1.42E-06</td>
<td>2.49E-07</td>
<td>1.37E-06</td>
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</table>
2.3.4 Detector non-linearity

The non-linearity of the detector is a critical property with DOAS applications (Platt and Stutz 2008). Detector non-linearity is particularly important with solar stray light DOAS applications, since it distorts the apparent shape of Fraunhofer lines that are present in the solar spectrum and have to be eliminated accurately in order to make the much weaker atmospheric absorbers visible. Fig. 2.3 presents a theoretical treatment of detector non-linearity for an example solar stray light spectrum recorded with our instrument (Fig. 2.3A). We simulate the distortion of Fraunhofer lines for a 1% non-linearity over 100% saturation, which is typical of state-of-the-art CCD detectors like the one used in this study. Copies of the spectrum were modified (I_{mod}) to reflect recording at 20%, 40%, 60%, 80% and 100% saturation, by multiplication with a wavelength dependent factor calculated as I_{mod} = I_0*(1-(1x10^{-2}*(I_0/100))), where the values in I_0 vary between 1% and 100%, thus reflecting a 0.1% intensity change for every 10% of detector saturation. The DOAS retrieval program, WinDOAS (Fayt and van Roozendael 2001), was used to process spectra from these and all subsequent tests. The software performs a non-linear least-squares fit by simultaneously adjusting the optical cross-sections of relevant atmospheric trace gases in the respective wavelength range to the measured spectra. To account for broad band effects (in particular caused by Rayleigh and Mie-scattering) a third degree polynomial was included. The fitting procedure is performed with the logarithm of the spectra (i.e. in optical density space). Additionally, the software can accommodate shifting the analyzed spectra in order to account for spectrometer drifts, which result in differences in the wavelength pixel mapping between the reference and the analyzed spectrum. In some cases a pre-logarithmic linear intensity offset was included to account for stray light. All of these parameters are adjustable via the software interface and can be optimized for different retrievals,
such as the tests described here. Figures 2.3D and 2.3E show residual spectra from the DOAS analysis (two wavelength windows; 345–360 nm and 425–440 nm, and only including combinations of either a Ring cross-section (Chance and Spurr 1997), a linear intensity offset, neither of these, or both) of simulated spectra with saturation level differences of 80% (100% sample, 20% reference) and 20% (40% sample, 20% reference). The RMS residual is $6 \times 10^{-5}$ and $1.5 \times 10^{-4}$ for 345-360 nm and 425-440 nm, respectively. Illustrated in Figs. 2.3B and 2.3C is the RMS residual structure from the 20% saturation level difference case, as well as a linear intensity offset fit and a Ring reference cross-section calculated from the reference spectrum. It is clear from the similarity of these spectra that the artifact of distorted Fraunhofer lines due to detector non-linearity is strongly cross-correlated, and will modify the fit coefficient of either of these spectra leading to an artificial reduction in the RMS$_{NLS}$. Fitting of a Ring leads to about a factor of 4 reduction in RMS, yet systematic residual structures remain.

Figure 2.4 compares the RMS from these simulations (Fig. 2.4A, and 2.4C) with the RMS from solar stray light spectra (Fig. 2.4B, 2.4D) that were recorded over a wide range of delta saturations. These tests were comprised of taking near zenith spectra at varying detector saturation levels and testing the effect of analyzing either a spectrum of the same saturation level or one of a different saturation level. For these tests, the integration times for the spectra varied due to the manipulation of the saturation level, but for all spectra the number of photons collected was kept near constant (within a few percent) at $10^{10}$ at the maximum. The wavelength windows used for the analysis of this data were also 345–360 nm and 425–440 nm, but since different solar stray light spectra were used additional reference cross-sections needed to be included in the fit. In the UV window, the included cross-section references were: two O$_3$
references (at different temperatures), a Ring spectrum, and an NO\textsubscript{2} reference. In the visible window, the reference cross-sections were the same except only one O\textsubscript{3} was used.

If two spectra from the same target saturation are compared the RMS is statistical, and the derived RMS = 4x10\textsuperscript{-5} and 2x10\textsuperscript{-5} for the 345-360 nm and the 425-440 nm ranges, respectively, compares well with the theoretical value of 3x10\textsuperscript{-5} and 1.7x10\textsuperscript{-5} based on photon counting statistics. However, RMS increases linearly as delta saturation increases, and the linear dependence of RMS\textsubscript{NLin} on delta saturation in the measured data indicates that the detector non-linearity is approximately constant over the full dynamic range of our CCD detector. By comparison of the slope with that from simulations at different detector non-linearities, our detector non-linearity is quantified as 1\% ± 0.3\% for 100\% delta saturation at the two wavelengths (reflecting a factor of 2 different saturation levels at 350nm and 440nm). The manufacturer specified detector non-linearity is given as <1\% in the datasheet, reflecting that our measured non-linearity seems to be slightly higher. Fitting of an intensity offset gives slightly better RMS\textsubscript{NLin} than fitting of a Ring, yet represents an artificial improvement in RMS. Fitting of both Ring and intensity offset can create strong bias in the fit factors for both spectra. The systematic RMS\textsubscript{NLin} residual structures that remain can be on the order of 10\textsuperscript{-4} for large delta saturations in the two spectral ranges studied. At other wavelengths RMS\textsubscript{NLin} is expected to scale with the optical density of Fraunhofer lines.
Figure 2.3 Assessment of detector non-linearity through simulated spectra. Panel A (bottom) depicts an example spectrum with the wavelength intervals analyzed highlighted with the grey background, middle row (panels D and E) shows the residual of the analyses for the two wavelength intervals for four different simulated scenarios, and the top row (panels A and B) demonstrates the spectral cross-correlation between the residual structure due to non-linearity (solid line, no Ring fit and no offset), the Ring fit (dashed line, no offset), and the linear intensity offset (dotted line, no Ring). In panels D and E, the blue and green lines represent data with a saturation level difference (sample – reference) of 80% and depict the results whether including a Ring spectrum in the fitting window (blue line) or not (pink line). The red and black lines represent the corresponding spectra with a saturation level difference of 20%, where the red line is the fit including the Ring spectrum and the black line does not include the Ring.
The limitation in RMS is caused by the shape of Fraunhofer lines and depends on the saturation level at which spectra are recorded. The demonstrated increase in RMS cannot be explained by atmospheric absorbers, which are accounted for in the analysis procedure, and is a strong indication that non-linearities in the detector limit the way that Fraunhofer lines can be characterized with available state-of-the-art CCD detectors. However, Fig. 2.4 also demonstrates that the distortion of Fraunhofer lines from detector non-linearity is not necessarily a problem that limits DOAS RMS. Only an inconsistent use of the detector causes a limitation, due to the inconsistent characterization of Fraunhofer lines, and gives rise to $\text{RMS}_{\text{NLin}}$ to limit the overall RMS. In order to reduce $\text{RMS}_{\text{NLin}}$ to $<5 \times 10^{-5}$ without the need to artificially reduce RMS by fitting an intensity offset or Ring spectrum, the saturation level of the detector cannot vary by more than 6% at 440 nm, and not more than 16% at 350 nm (Fig. 2.4). The solution implemented in the ATMOSpeclab data acquisition LabVIEW code follows the approach described by (Volkamer et al., 2009a). In addition to a given target saturation level two additional variables are set, i.e., the upper and lower limit for the target saturation. These provide not-to-exceed bounds close to the target saturation during the acquisition of spectra, i.e. set here to within 5%. This approach is implemented here in the first field deployment of the CU GMAX-DOAS instrument.
Figure 2.4 Correlation of simulated (A and C) and experimental (B and D) data testing the non-linearity of our CCD detector at two different wavelengths: 350 nm (A and B) and 440 nm (C and D). Coefficients for linear regressions fit to the data were back extrapolated to determine the RMS value corresponding to using 100% of the dynamic range of the detector, and these values are listed for the different fit scenarios in each of the panels.
2.3.5 Signal-to-noise tests

The signal-to-noise as a function of the number of photons collected was characterized using our LabVIEW-based processing tool called the Intelligent Averaging Module (IAM)\(^1\). Scattered sunlight spectra were collected in two modes of operation: (mode1) during normal measurements, where a set of eleven different elevation angles each with an integration time of 60 seconds were scanned during one measurement sequence, and (mode2) during a viewing routine (labelled as field tests) that measured only two elevation angles; 80° (which served as the reference) and 25°, and twenty spectra were taken sequentially at both elevation angles all with 5 second integration times. For all tests, when analyzing spectra in different wavelength regions a line function from each region is chosen to convolute the cross-section reference spectra to help account for differences in line shape across the CCD.

Unless otherwise noted, the WinDOAS settings for all tests included two wavelength regions, between 340-359 nm where BrO is measured and 415-438 nm where IO is measured. The Ring reference was calculated using the DOASIS software (Kraus 2006) from a spectrum measured with our instrument. In the analysis of the set of data collected during normal operations, a routine was used such that each spectrum was analyzed by a close in time reference spectrum; this helped to accurately characterize and eliminate stratospheric absorbers. A new Ring spectrum was created from each new reference and updated in the analysis. For the field tests, IAM was used in two different ways to process these spectra. The first use included adding a specified number of spectra (in this case 4, 16, and 64 spectra) for the viewing angles and then analyzing the resulting spectrum. For the processing

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\(^1\) Intelligent Averaging Module (IAM): Part of the custom built LabVIEW software that allows complex handling and manipulation of the spectra in order to optimize our analysis. This is a powerful tool that allows the user full control over how the data is handled.
of these spectra, the reference spectrum was created by adding 20 sequential individual 80°
spectra (this summed spectrum was then used to calculate the Ring reference spectrum). In
the second method, ratios were created using two sequential spectra of the same viewing
angle, and these ratios were then added together to form the final spectrum that was used in
the analysis. In this method, the final spectra were made of the sum of 500 and 1000 ratio
spectra. For the analysis of these spectra, no reference was used, the Ring was the same that
was used for the first method, and no offset was included. A summary of the cross-section
used in each of these analyses can be found in Table 2.4.
Table 2.4 Summary of the cross-sections used for each of the different analysis settings during the signal to noise tests.

<table>
<thead>
<tr>
<th>Cross-Sections</th>
<th>Field Tests MAX-DOAS Measurements</th>
<th>Field Tests Summed Spectra</th>
<th>Field Tests Summed &amp; Ratioed Spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(340 - 359 nm)</td>
<td>(415 - 438 nm)</td>
<td></td>
</tr>
<tr>
<td>O₃ T = 223 K (Bogumil et al.; 2003)</td>
<td>X X X X X X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₃ T = 243 K (Bogumil et al.; 2003)</td>
<td>X X X X X X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₂ T = 220 K (Vandaele et al.; 1997)</td>
<td></td>
<td>X X</td>
<td></td>
</tr>
<tr>
<td>NO₂ T = 294 K (Vandaele et al.; 1997)</td>
<td>X X X X X X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₄ (Hermans 2002)</td>
<td>X X X X X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IO (Honninger 1999)</td>
<td></td>
<td>X X</td>
<td></td>
</tr>
<tr>
<td>CHÓCHO (Volkamer et al.; 2005)</td>
<td></td>
<td>X X</td>
<td></td>
</tr>
<tr>
<td>H₂O (Rothman et al.; 2005)</td>
<td></td>
<td>X X</td>
<td>X</td>
</tr>
<tr>
<td>BrO (Wilmouth et al.; 1999)</td>
<td>X X X X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCHO (Meller and Moortgat 2000)</td>
<td>X X X</td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>Ring</td>
<td>X X X X X X</td>
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<td>X</td>
</tr>
</tbody>
</table>
Additionally, tests were done with a tungsten lamp in order to assess the instrument’s performance without the influence of Fraunhofer lines. In these tests, sequential spectra of the same photon count, corrected for dark current and electronic offset, were divided in WinDOAS without including an intensity offset or any other cross-section references and not allowing the spectra to shift. This analysis was performed around the maximum of the tungsten lamp (440–465 nm). The division of two spectra that contained ~3x10^{11} photons each allowed us to achieve an RMS of 3x10^{-6}, which compares very well to \( \text{RMS}_{\text{PSN}} = 2.5x10^{-6} \) based on photon counting statistics.

The results from these tests along with the theoretical noise, based on photon counting statistics, are summarized in Fig. 2.5. Theoretical noise based on photon counting statistics was calculated according to the equation

\[
\text{RMS} = ((1/N_{\text{ms}})^2 + (1/N_{\text{rs}})^2)^{1/2}
\]

where \( N_{\text{ms}} \) is the number of photons in the measured spectrum and \( N_{\text{rs}} \) is the number of photons in the reference spectrum. Also included in Fig. 2.5 are results from field measurements of the 155° and 178.5° elevation angles (solid green circles and open green circles, respectively), which typically were in the 6x10^{-5} – 1.4x10^{-4} range (red whiskers give statistics of green points) at high photon count. Increasing the numbers of solar stray light photons, the lowest RMS values achieved by the noise tests were ~1x10^{-5} and ~6x10^{-6} in the 340-359 nm and 415-438 nm ranges, respectively. Such low RMS requires acquisition of >10^{10} photons and takes ~40-50 min with our light-efficient instrument (Fig. 2.5). Figure 2.6 demonstrates that incorporating high light-throughput optics is key to realizing such low RMS in our setup: a single day of data collected in mode2 was analyzed using reference
spectra that differed in the time difference to the analyzed data. As the time difference is increased beyond few 10 minutes, the RMS is observed to increase.

The effect of detector non-linearity has been actively suppressed in these tests by controlling the target saturation level within narrow bounds of 5%. However, the temperature of the slit is expected to vary on a time scale at which heat fluxes equilibrate in our system (few 10 minutes), and the results in Fig. 2.6 are generally consistent with variations in the line shape broadening (see Sect. 2.3.2, Table 2.2). We conclude that the effect of line shape broadening is most likely to explain the empirical observation of increasing RMS with increasing time difference between two spectra (Fig. 2.6), though other factors may contribute as well.
Figure 2.5 Comparison of experimental and theoretical RMS noise vs. photon counting statistics for data collected between 03 March and 25 May 2010, July 2010, and April 2011. Panel (a) for the BrO evaluation range (340–359 nm). Panel (b) for the IO evaluation range (415–438 nm), except for the laboratory tests with a tungsten lamp which were analyzed between 440 – 465 nm. Horizontal lines indicate typical RMS values of other MAX-DOAS instruments: (red dashed line) Mini-MAX-DOAS ($10^{-3}$ RMS); (blue dotted line) research grade MAX-DOAS ($10^{-4}$ RMS). Actual field measurement data is depicted for the 155° and 178.5° viewing angles, (solid light green circles and open dark green diamonds, respectively) from the spring 2010. Field tests from the July 2010 period are depicted with the blue markers. Light blue indicates only co-added spectra (155° elevation angle): 4 spectra (squares), 16 spectra (triangles), and 64 spectra (diamonds). Dark blue indicates co-added ratio spectra (155° elevation angle): 500 ratios (hourglasses); 1000 ratios (triangles pointing up and to the left). The laboratory tests are the red diamonds. The theoretical noise for all the measurement scenarios are the gray horizontal line and the light blue horizontal line. The light blue lines were calculated with a fixed count number for the reference, which was $4 \times 10^9$ photons, while the grey line was calculated assuming the same number of photons in the analyzed and reference spectrum. The red horizontal lines represent the median values for the field measurements with the whiskers containing the 25th and 75th percentile. The top x-axis reflects typical integration times to collect the corresponding number of photons (on bottom x-axis) for this instrument, which was calculated based on a typical value for the 60 second data of $8 \times 10^8$ and $3 \times 10^9$ photons in the UV and visible regions, respectively.
Figure 2.6 RMS as a function of time difference between the spectrum analyzed and the reference. The black lines represent the median, the box edges are the 25\textsuperscript{th} and 75\textsuperscript{th} percentiles, and the whiskers are the 5\textsuperscript{th} and 95\textsuperscript{th} percentiles. In general, using a reference taken close in time to the spectrum analyzed provides better RMS values.
2.4 Field measurements of Halogen Oxides

The CU GMAX-DOAS instrument was deployed at two different field sites in the coastal panhandle of Florida during 2009-2010 (Fig. 2.1d). It operated at the first site, the South Eastern Aerosol Research (SEARCH) network site Operation Landing Field #7 (OLF) (Hansen et al., 2003), from March to May 2009. The current measurement site is a U.S. Environmental Protection Agency (EPA) facility in Gulf Breeze, FL (~10 km southeast of Pensacola, FL). The EPA site is located ~1 km from the ocean and there is a large bay area ~4 km to the North. The instrument has been operating at this site for the time periods May – September 2009, March – May 2010, and July 2010 – February 2011.

2.4.1 Measurement results

At the inland site OLF, we measured NO$_2$, O$_4$, CHOCHO, and HCHO on a regular basis and IO on a few select days. BrO was never detected above the detection limit, likely because both NO and NO$_2$ readily react with BrO, forming reservoir species that can build up in the presence of high concentrations of NO$_x$. Hence, the instrument was moved at the end of May 2009 to the EPA site located in Gulf Breeze, FL. At the coastal EPA site, the following viewing angles from ground level with respect to the northern horizon were applied: 0.8°, 1.5°, 3.8°, 10°, 25°, 80°, 155°, 170°, 176.2°, 178.5°, and 179.2° and each elevation angle utilized a fixed integration time of 60 seconds. These measurements allowed us to measure both to the north over the bay between Pensacola and Gulf Breeze and to the south over the Gulf of Mexico. Measurements from 10 weeks at the EPA site (period from March 11 through May 25 2010) are further discussed here.
During this spring 2010 period the instrument measured 54862 individual spectra (~4600 full sequences of elevation angles) of which 87% were recorded at SZA < 80 degrees; an RMS filter (RMS < 4x10^{-4}) was applied to filter outliers (8% in the HCHO spectral range, 2% in the CHOCHO spectral range). We detected significant BrO in 0.7% of the spectra, IO in ~42%, HCHO in ~65%, CHOCHO in ~32%, NO₂ in ~73%, and O₃ in ~81%. Figures 2.7 and 2.8 show spectral proof for the measurement of these trace gases and Fig. 2.9 and 10 depict time series of the dSCDs for these trace gases from the period between 03 April and 08 April 2010. For all absorbers other than BrO, the detection limit was taken as the 2-sigma noise, which roughly corresponds to 6 times the DOAS fit error (Stutz and Platt 1996). In the case of BrO, an equivalent RMS noise factor was determined to encompass >98% of the negative values for each elevation angle, this factor was used to determine the detection limit. These factors varied between 1.5 and 2.1 times the RMS noise. The average detection limits were approximately 3x10^{13} molec cm^{-2}, 1.3x10^{13} molec cm^{-2}, 4.9x10^{15} molec cm^{-2}, 4.1x10^{14} molec cm^{-2}, and 1.5x10^{15} molec cm^{-2} for BrO, IO, HCHO, CHOCHO, and NO₂ respectively.
Figure 2.7 Spectral proof for the detection of BrO and HCHO. All spectra were analyzed for BrO in the 340-359 nm range and for HCHO in the 337-359 nm range. The BrO fit is from 02 April 2010 at 19:36 UTC in the 155° viewing angle, and the HCHO fit is from 08 May 2010 at 20:28 UTC in the 25° viewing angle.
Figure 2.8 Spectral proof for the detection of IO and CHOCHO. Spectra were analyzed for IO in the 415-438 nm range, while the range of 434-460 nm was used for CHOCHO. The IO fit is from 03 April 2010 at 18:42 UTC in the 179.2° viewing angle, and the CHOCHO fit is from 23 March 2010 at 19:23 UTC in the 3.8° viewing angle.
For IO the measured dSCD decrease with increasing elevation angle. We conclude that IO is mostly located in the MBL. Similarly, most BrO appears to be located in the MBL, but the split in dSCD with elevation angle is less clear. As expected, for both gases the majority of significant data was measured from the southern facing elevation angles suggesting that the coastal or open ocean air masses tend to be more enriched in the halogen oxides relative to those over the land. Radiative transfer calculations were performed in order to determine air mass factors (AMFs) to convert the measured dSCDs into VCDs, but it was found that due to uncertainty in the vertical distribution of these trace gases that using a geometric approximation was sufficient\(^2\). So, using geometric AMFs to convert dSCDs from the 25° (over land) and 155° (over ocean) viewing angles to tropospheric VCDs we calculate daytime (SZA<80°) average VCDs of significant data as ~2x10\(^{13}\) molec cm\(^{-2}\) for BrO, and ~8x10\(^{12}\) molec cm\(^{-2}\) for IO. HCHO, CHOCHO and NO\(_2\) were also observed in the MBL with daytime average VCDs of ~1x10\(^{16}\) molec cm\(^{-2}\), ~4x10\(^{14}\) molec cm\(^{-2}\) and ~3x10\(^{15}\) molec cm\(^{-2}\), respectively.

Field studies (Lindberg et al., 2002; Peleg et al., 2007), laboratory studies (Donohoue et al., 2006), quantum calculations (Tossell 2003; Balabanov and Peterson 2003; Cremer et al., 2008), and modeling studies (Holmes et al., 2006; Selin et al., 2007; Holmes et al., 2009) consistently suggest that a significant conversion of Hg\(^0\) to Hg\(^{2+}\) and possibly mercury bound to particles (PHg) (Murphy et al., 2006) may be attributed to reactive halogens. Despite the growing evidence supporting the role of halogen species, to date most global mercury models still use OH and O\(_3\) chemistry for the conversion of GEM to GOM (Bergan and Rodhe 2001; Selin et al., 2007). These models can reproduce the diurnal patterns of GOM but fail to

\(^2\) Authors wish to note that the use of geometric AMFs for this calculation is a simplification of the radiative transfer process. We have carried out full radiative transfer calculations that varied in the assumptions about the BrO vertical distribution and find this simplification equally represents the uncertainty arising from the lack of knowledge about the true BrO vertical distribution aloft. The calculated BrO VCDs can contain errors on the order of 30% or more.
reproduce the amplitude in GOM. This requires that they infer additional oxidants must exist. First attempts to represent bromine chemistry in models Holmes et al., (2006) resulted in an atmospheric lifetime of GEM against conversion to GOM of 1.4 to 1.7 year (and possibly as short as 0.5 years), indicating that oxidation by atomic bromine would be an important and possibly dominant global pathway for oxidation and deposition of atmospheric mercury. Only small amounts of bromine radicals, equivalent to <2 ppt of BrO are relevant to explain observed trends in GOM (Holmes et al., 2009). Our measurements provide first experimental evidence for the presence of halogen oxides in the marine boundary near Pensacola, FL.

For a systematic characterization of the BrO vertical distribution in the MBL and FT, we propose that further RMS reduction will increase the frequency with which BrO tropospheric column amounts can be detected. However, the height resolution of a ground-based instrument is limited. For BrO located above 6 km altitude, tropospheric and stratospheric BrO become entangled, and the accuracy of tropospheric BrO measurements becomes limited by the need to make assumptions about a stratospheric BrO profile. A solution to this quandary exists by using Airborne MAX-DOAS, or MAX-DOAS from high mountain tops, since the MAX-DOAS technique is always maximally sensitive to absorbers located at or near (within a few km) the instrument altitude (Bruns et al., 2004; Heue et al., 2005; Volkamer et al., 2009a). However, ground based halogen oxide measurements by the CU GMAX-DOAS provide cost-effective means to infer the column abundance of halogen oxide radicals, and can present useful constraints for the halogen atom concentration available to destroy tropospheric ozone and oxidize GEM to GOM.
Figure 2.9 Time series of the dSCDs for BrO, IO, CHOCHO, HCHO, NO₂, and O₄ between 03 April and 08 April 2010 (times are in UTC). This plot is for viewing directions overlooking the bay area. The large circles for each elevation angle represent statistically significant measurements, while the small dots are measurements that do not meet the significance criteria. The average fit errors from the WinDOAS analysis for these elevation angles were 9.8x10^{12} molec cm^{-2}, 2.6x10^{12} molec cm^{-2}, 1.2x10^{14} molec cm^{-2}, 1.9x10^{15} molec cm^{-2}, and 1.6x10^{14} molec cm^{-2} for BrO, IO, CHOCHO, HCHO, and NO₂, respectively.
Figure 2.10 Time series of the dSCDs for BrO, IO, CHOCHO, HCHO, NO$_2$, and O$_4$ between 03 April and 08 April 2010 (times are in UTC). This plot is for viewing directions overlooking the open ocean. The large circles for each elevation angle represent statistically significant measurements, while the small dots are measurements that do not meet the significance criteria. The average fit errors from the WinDOAS analysis for these elevation angles were 7.9x10$^{12}$ molec cm$^{-2}$, 2.2x10$^{12}$ molec cm$^{-2}$, 1.1x10$^{14}$ molec cm$^{-2}$, 1.9x10$^{15}$ molec cm$^{-2}$, and 1.3x10$^{14}$ molec cm$^{-2}$ for BrO, IO, CHOCHO, HCHO, and NO$_2$, respectively.
2.4.2 Discussion of RMS limitations of field measurements

As is shown in Fig. 2.5, the CU GMAX-DOAS instrument is capable of RMS noise of 3x10^{-5} (440nm, 4x10^9 photons) and 6x10^{-5} (350nm, 1x10^9 photons) comparing 60 sec atmospheric measurements collected at different elevation angles. This is in good agreement (within 20%) with the expected photon shot noise if reference photon noise is considered (comparison to the grey line in Fig. 2.5). Such low RMS is, however, not reached on a routine basis. RMS typically ranges from 6x10^{-5} – 1.4x10^{-4} (440nm, 4x10^9 photons), and 8x10^{-5} - 1x10^{-4} (350nm, 1x10^9 photons), with a slightly higher median RMS at visible wavelengths, but close to 1x10^{-4} in both spectral ranges. RMS of 1x10^{-4} is reached on a routine basis by our instrument within 10 sec at 440nm, and within 40 sec at 350nm. At longer integration times RMS becomes essentially independent of the number of co-added photons, wavelength range, and depends only weakly on the elevation angle (5x10^{-5} higher for 1.5 deg vs 25 deg), yet – despite higher photon count – is higher at visible wavelengths than in the UV. In the further we discuss whether changing instrument properties or the representation of atmospheric state are limiting RMS.

For our field data the time difference between a lower elevation angle spectrum and its zenith reference is ~330 seconds, i.e., significantly shorter than the time difference of ~2000 seconds at which the median RMS exceeds 1x10^{-4} in Fig. 2.6. Over such short time scales the RMS_{FWHM} as characterized in Sect. 2.3.2 (Table 2.2) is expected to be <5x10^{-5} at 350nm, and <1x10^{-5} at 450nm, and is not limiting RMS for most of our data. From Sect. 2.3.4 and Fig. 2.4, it follows that intensity changes of 12.5% over the course of acquisition of a single spectrum, coupled with a detector non-linearity of 1% causes RMS_{NLin} of 10^{-4} at 440nm. This RMS_{NLin} can be artificially reduced (by a factor of six) from fitting an intensity offset spectrum (slightly less reduction is expected for fitting a Ring spectrum). Our systematic control of target saturation
provides alternative means to systematically eliminate RMS\textsubscript{NLin} at any target saturation level for practical purposes. In the measurements depicted in Fig. 2.5, the target saturation is actively controlled within ±5\%, i.e., the maximum possible intensity difference is 10\% (actual intensity variations were ~2\% for the cases considered here). It follows from Figs. 2.4B and 2.4D that RMS\textsubscript{NLin} is <7\times10^{-6} and <1\times10^{-5} for the 345-360 nm and 425-440 nm ranges, respectively (with Offset and Ring being fitted in the analysis of our field data). Based on these findings, and consistent with the RMS < 10^{-4} values that are observed in Fig. 2.5, we can rule out that RMS\textsubscript{FWHM} and RMS\textsubscript{NLin} are factors that limit RMS in our field data.

Given that our instrument is capable of RMS much lower than 10^{-4} (Sect. 2.3.5, Fig. 2.5) we conclude that our hardware is unlikely the cause for the RMS limitations observed in the analysis of field data. We believe that it must be our representation of the atmospheric state that is limiting RMS. These factors could be bound to our limited knowledge of spectroscopic parameters of literature cross-sections (uncertain wavelength calibration, unknown temperature dependencies). In an attempt to bind this uncertainty, we estimate the effect of uncertain wavelength pixel mapping on RMS using the NO\textsubscript{2} molecule and our Table 2.3 as an example. The highest wavelength precision is typically achieved by recording laboratory cross-sections using a Fourier Transform Spectrometer (FTS), for which the uncertainty in the wavelength calibration is ~ 0.05 cm\(^{-1}\) (unless special precautions are taken to cross-calibrate wavelength against absolute wavelength standards before and after each spectrometer configuration/beamsplitter change). At 450 nm, or 22222 cm\(^{-1}\), this translates into 0.001 nm uncertainty in the wavelength calibration of the FTS recorded absorption cross-section spectrum, slightly less at shorter wavelengths. At a typical dispersion of spectrometers used in MAX-DOAS applications (0.1 nm/pixel), this corresponds to an uncertainty in the wavelength pixel
mapping of the convoluted reference spectrum of ~ 0.01 pixels at 450 nm. Residual structures occur if strong absorbers like Fraunhofer lines and NO$_2$ are forced onto identical wavelength pixel mappings. Results in Table 2.3 were scaled according to the differences in optical densities, $\delta$ between Fraunhofer lines and NO$_2$. For a NO$_2$ dSCD of 1.5x10$^{17}$ molec cm$^{-2}$ the average scaling factor $\delta_{FH}/\delta_{NO2}$ is 4.3 and 2.6 for the listed Vis and UV wavelength ranges, respectively. This corresponds to a RMS of 4x10$^{-5}$ and 1x10$^{-4}$ for 0.01 pixel uncertainty, which is in principle comparable to the RMS limitations observed in this work. This NO$_2$ dSCD represents an upper limit of the observed dSCD in our field data. Further, the observed RMS depends only very weakly on the elevation angle in our field data. RMS increases by ~50% comparing 25 deg and 1.5 deg elevation angle spectra, for which the air mass factor increases by a factor of ~3. It thus appears that the RMS limitations are less likely to be caused by numerical limitations in our representation of atmospheric absorbers located in the boundary layer, which would leverage the full air mass factor advantage in the lower elevation angles. More likely, other factors play a role in our setup. Nonetheless, the characterization of wavelength pixel mapping at an accuracy of better 0.01 pixels seems pre-requisite to lowering RMS further, in addition to high photon counts and stable instruments. The effects described in Sections 2.3.1, 2.3.2, 2.3.3 and 2.3.4 are examples that can limit the accuracy at which the wavelength pixel mapping is known, yet do not seem to limit our setup. This is the direct result of the active measures taken to stabilize the temperature of the rack/slit, and to control the target saturation of our detector within narrow bounds.

We cannot rule out that an imperfect representation of scattering processes, i.e., non-linear rotational Ring caused by a combination of aerosol scattering and second order molecular scattering (Langford et al., 2007), or missing reference spectra (i.e., vibrational Raman scattering
of N₂ and O₂), are responsible for the higher than expected RMS. Vibrational Raman scattering has been suggested to play a role for zenith sky DOAS measurements of stratospheric absorbers at high SZA (Platt et al., 1997), as well as for liquid water in the oceans (Vountas et al., 2003). Vibrational Raman scattering on gas-phase molecules is today not typically considered in the analysis of MAX-DOAS spectra, which treat only the rotational component of Raman scattering to calculate the Ring reference spectrum (Chance and Spurr 1997; Vountas et al., 1998; Platt and Stutz 2008; Wagner et al., 2009). We are unaware of a discussion of vibrational Raman scattering by gas-phase molecules for tropospheric absorbers measured by MAX-DOAS, where in addition to N₂ and O₂ also H₂O could play a role. The Stokes Raman vibrational scattering cross sections of N₂ and O₂ are about 50, and 100 times weaker than their rotational Raman scattering homologues, yet they are 2 to 3 orders of magnitude stronger for H₂O (Fenner et al., 1973; Bendtsen 1974; Penney and Lapp 1976; Avila et al., 1999; Brodersen and Bendtsen 2003; Avila et al., 2003). In the tropical marine boundary layer O₂ and H₂O add ~30% and <15% relative to N₂ to the vibrational Raman scattering intensity. Several factors in our data make us believe that the lack of an explicit treatment of the vibrational Raman effect is partly responsible for the RMS limitations that we observe: (1) RMS limitations are only observed when comparing spectra between different elevation angles, but not when comparing solar stray light spectra at the same elevation angle; (2) RMS limitations consistently depend only weakly on the elevation angle, as is expected for a limitation caused by a scattering process, but not necessarily for an absorber; (3) a typical rotational Ring δ ranges from essentially zero to ~0.006 on a clear day, and the vibrational Stokes Ring δ can thus reach 1.2x10⁻⁴. This optical density is comparable to the RMS limit we find near 440 nm; (4) The vibrational Stokes Raman scattering of N₂ (vibrational frequency, ωN₂ = 2330 cm⁻¹) has the effect to shift a Fraunhofer line located at 398
nm to 438.6 nm (Stokes Raman scattering); in fact, rotation-vibrational Raman scattering will distribute 398 nm photons over the wavelength range from 434 to 444 nm. We observe larger RMS deviations from theory at longer wavelengths (see Fig. 2.5, and Sect. 2.3.5). Most likely not a single factor can be isolated to explain our observed RMS at high photon counts. Further studies are needed to leverage the full potential sensitivity of our CU GMAX-DOAS instrument.

2.5 Conclusions and Outlook

The instrument properties and the uncertainties surrounding the RMS limited retrieval of BrO and IO from solar stray light MAX-DOAS spectra were explored. A novel CU GMAX-DOAS instrument is described, and characterized, and found capable of achieving RMS $<<10^{-5}$ without any limitations other than photon shot noise in laboratory tests with a tungsten light source, as well as with solar stray light. As pre-requisite for achieving this low RMS we identified that the detector non-linearity of our state-of-the-art CCD detector, as well as changes in optical resolution due to small temperature variations are two key factors that can limit DOAS evaluations of solar stray light spectra at RMS $\sim 10^{-4}$. Both factors were addressed and minimized in the design of the CU GMAX-DOAS instrument.

In a first field deployment, the CU GMAX-DOAS instrument routinely achieved RMS in the range of $8x10^{-5} < \text{RMS} < 1.0x10^{-4}$ and $6x10^{-5} < \text{RMS} < 1.4x10^{-4}$ in all elevation angles, and in the 340-359 nm and 415-438 nm ranges, respectively. We present measurements of BrO, IO, CHOCHO, HCHO, NO$_2$, and O$_4$. These are the first measurements of BrO, IO and CHOCHO over the Gulf of Mexico, providing direct evidence for the presence these halogen oxides in the MBL. BrO in the MBL indicates the availability of bromine atoms as oxidants for elemental
mercury. The relevance of IO in the MBL on the observed elevated mercury wet deposition has been little studied and remains uncertain.

A detailed characterization of RMS noise limitations in our instrument finds that the hardware is not currently limiting RMS at high photon counts. Yet deviations from the expected RMS are observed, and found to be larger in the 415-438 nm range, then at 340-359 nm, despite the higher photon count at the longer wavelengths. The representation of atmospheric state is likely limited by the need to represent vibrational Raman scattering (see Sect. 2.4.2), though other factors inherent to our retrieval algorithm cannot be fully ruled out. To investigate whether it is numerical limitations inherent to our retrieval algorithm or limited information about external analysis inputs that is currently limiting the representation of the atmospheric state, the operation of our hardware with an active DOAS system (e.g. LP-DOAS or CE-DOAS) without Fraunhofer lines, Ring effect, etc., seems to be promising, see e.g., Thalman and Volkamer (2010). The CU GMAX-DOAS hardware has the potential to lower the attainable RMS further, with according benefits for instrument sensitivity and atmospheric discovery.
Chapter III

Ground-based Measurements of Free Tropospheric Trace Gases

Goals: A retrieval was developed to measure partial columns (marine boundary layer, MBL: 0-1 km, free troposphere, FT: 1-15 km, with 2-3 degrees of freedom) of atmospheric trace gases by means of the ground-based MAX-DOAS instrument described in Chapter 1. Factors influencing the DOAS retrieval of BrO from ground will be systematically explored.

Methodology: A case study from the measurements presented in Chapter 2 is used to address the goals mentioned above. Sensitivity studies on the DOAS fitting parameters: intensity offset, wavelength range covered in analysis window, for BrO are presented and optimized. The effect of: choice of the reference spectrum and a-priori, are also assessed with respect to the results of the inversion of measured dSCDs to vertical profiles. Findings from the different sensitivity studies are combined to determine inversion input settings that maximize the sensitivity of the ground based measurements towards the FT.

Results/Conclusions: The measured dSCDs are found sensitive to the retrieval parameters chosen for the analysis: intensity offset, wavelength range of the analysis window, and choice of reference spectrum. These sensitivities are actively addressed which creates only a minor effect on the total VCDs, and partial MBL and FT VCDs. The measured profiles are found sensitive to the inversion grid and a-priori error, which are also optimized for this study; but insensitive to the a-priori and reference spectra that have passed quality assurance filters. By leveraging external information from the chemical transport model WACCM we accomplish the
measurement of vertical profiles of BrO and IO. The profiles are compared with other direct measurements performed by the CU airborne-MAX-DOAS (AMAX-DOAS) over different regions of the tropical Pacific Ocean and are found to be in good agreement.

3.1 Introduction

As described in Chapter 2 the primary result of the DOAS fit retrieval is a Slant Column Density (SCD), which is the integrated concentration of the trace gas along all photon paths. In the case of Multi-AXis DOAS (MAX-DOAS) measurements, (where each spectrum is analyzed against a scattered sunlight reference spectrum) the result is a Differential SCD (dSCD), where differential refers to the difference in the trace gas SCD contained in the analyzed and reference spectrum. As previously mentioned, two scenarios exist for the choice of a reference spectrum: 1) zenith spectra, which refers to a spectrum collected while the telescope is pointing at an angle of 90° above the horizon, are chosen for temporal proximity to data being analyzed (typically resulting in the changing of reference spectrum for each MAX-DOAS measurement scan through the time period); and 2) single zenith spectrum from a period of low solar zenith angle (SZA, the angle of the sun above the horizon) is used to analyze multiple days. The light paths through the upper layers of the atmosphere, as seen by the instrument, change as a function of SZA much more strongly than the light paths at lower altitudes, i.e. the portion of the SCD that is due to absorption at these higher altitudes varies strongly with SZA. By updating the reference spectrum throughout the day, as in method 1, the variability in the reference SCD caused by changes in SZA is represented in each new reference. This means that the contribution to the SCD from the upper atmosphere for the reference and analyzed elevation angles is rather similar and this information is effectively removed in the analysis. This focuses the sensitivity of the
MAX-DOAS scanning geometry on the lower layers of the atmosphere. Conversely, in method 2, where a single reference from a low SZA is used, the contribution of the higher altitudes to the SCD in the reference spectrum is minimized (by the low SZA) and remains constant (single reference). This preserves the information on higher altitudes contained in the measurements.

In this chapter results analyzed using method 2 shall be utilized. The reason for this is to fully leverage the vertical information contained within the measurements. The intent here is to extend the currently used MAX-DOAS retrievals and apply them towards gaining information about the free troposphere (FT) from a ground based measurement. Specifically, I am interested in the retrieval of vertical profiles (and Vertical Column Density, VCDs, which is the vertically integrated concentration of the absorber) of BrO and IO in the FT (although this method is also applied to NO$_2$). Here I present ground-based simultaneous measurements of these molecules in the FT and the method used to achieve these measurements. The presence of these species in the FT can have a significant effect on the chemistry occurring in the atmosphere due to their high reactivity; they can be involved in reactions with O$_3$ (which can lead to changes in the OH), SO$_2$, NO$_x$ (NO$_2$ + NO), and Hg$^0$.

A case study chosen from a cloud-free low aerosol day in April 2010 from measurements, as these are optimal conditions for attempting to retrieve free tropospheric information from ground-based measurements, at a site located in Florida along the Gulf of Mexico is presented here. The inversion of these measurements utilizes an optimized radiative transfer grid, a priori profiles, and optimal estimation input parameters (e.g., a priori error covariance matrix) to maximize the sensitivity to the FT (see Sect. 3.2.3).
3.1.2 Tropospheric BrO and IO

Current methods for monitoring BrO and IO in the FT are limited to satellite, aircraft, balloon-borne, and high-mountaintop measurements (Van Roozendael et al., 2002; Dorf et al., 2006; Theys et al., 2007; Coburn et al., 2011; Theys et al., 2011; Puentedura et al., 2012; Dix et al., 2013), and these studies are sparse. Satellite-borne measurements represent a powerful resource for assessing global distributions and tropospheric VCDs of these species, while the other methods are more representative of these species on regional scales. Additionally, satellite retrievals rely on assumptions made about the vertical distribution of the trace gas being measured, and errors in the a-priori profile can lead to over/under predictions for the derived VCDs. For this reason, extensive work is needed to independently validate measurements from satellites and provide appropriate a-priori profiles.

Van Roozendael et al. (2002) compared ground-based and balloon borne measurements to VCDs of BrO from the Global Ozone Monitoring Experiment (GOME) and found all platforms were consistent with a rather widespread tropospheric BrO VCD of 1-3x10^{13} molec cm^{-2}, once appropriate radiative transfer effects were taken into consideration. Salawitch et al. (2005) and Theys et al. (2011) also report satellite derived tropospheric BrO VCDs (GOME and GOME-2, respectively) for the mid-latitudes of 2x10^{13} molec cm^{-2} and 1-3x10^{13} molec cm^{-2}, respectively. Ground based measurements (Theys et al. 2007; Coburn et al., 2011) in the mid-latitudes also report BrO VCDs that are comparable to the findings from satellites, reporting values of 1-2x10^{13} molec cm^{-2}. Aircraft measurements presented in Wang et al., (2014) find an average of ~1.5x10^{13} molec cm^{-2} BrO VCD in the tropics. All of these studies point to the presence of a ubiquitous layer of BrO in the FT corresponding to a VCD of 1-3x10^{13} molec cm^{-2}. 
If these values are correct, this could account for 20-30% of a total column VCD \(~5-6 \times 10^{13}\) molec cm\(^{-2}\) as seen from satellite (van Roozendael et al., 2002; Theys et al., 2011).

Measurements of IO in the FT are much more sparse, but also seem to indicate the presence of IO in the FT. Puentedura et al. (2012) report ground based measurements of IO from a mid-latitude mountain top site (~2400 m above sea level, asl) and find their data to be consistent with 0.2-0.4 parts per trillion (ppt, 1 ppt = \(10^{-12}\) volume mixing ratio, VMR) IO in the FT. Dix et al. (2013) and Wang et al. (2014) are both aircraft studies that cover the tropical Pacific Ocean and report values that are slightly lower, \(~0.1\) pptv in the FT.

3.2 Instrumentation/Measurements

The instrument and measurement site are identical to that discussed in chapter 1. Only a brief overview will be given here.

3.2.1 Measurement Site

For the duration of the measurements discussed here, the instrument was located at a United States Environmental Protection Agency (US EPA) facility in Gulf Breeze, FL (30.3N 87.2W). This site is ~10km southeast of Pensacola, FL (population appr. 50,000) and ~1km from the coast of the Gulf of Mexico, which enables the measurement of urban and marine air masses (see Figure 2.1 for an overview of the measurement area). The spectrometer and controlling electronics were set-up in the warehouse of the EPA facility, while the telescope was mounted on a support structure on the roof of the warehouse (~10-12 meters above sea level) connected via an optical fiber. The telescope was oriented ~40° west of true north in order to realize a clear view in the lowest elevation angles to the coast. During operation the full 180° range of the
telescope was utilized to enable the characterization of differences between air-masses over land and over the coastal Gulf of Mexico. For the purposes of this study, though, only the viewing direction looking over land (north) will be considered to minimize changes in the radiative transfer calculations due to azimuth effects throughout the day.

3.2.2 Instrumentation

The instrument consists of a Princeton Instruments Acton SP2300i Czerny-Turner grating (500 groove/mm with a 300nm blaze angle) spectrometer with a PIXIS 400B back-illuminated CCD detector. This set up was optimized in order to cover the wavelength range ~321-488 nm with an optical resolution of ~0.68nm FWHM. The spectrometer is coupled to a weather resistant telescope (capable of rotating 180°, 50 mm f/4 optics) via a 10 m long 1.7 mm diameter quartz fiber. During normal field operation this instrument was routinely able to realize RMS (see chapter 1) values on the order 0.9-3x10^{-4}, which pushes the lower end of RMS reported by other MAX-DOAS instruments (see Table 2.1). This system was very stable, with little need for maintenance, and was operated remotely for periods between May 2009 and February 2011 to measure multiple trace gases, including: BrO, IO, NO₂, HCHO, CHOCHO, and O₄.

3.2.3 Inversion method

The inversion method consists of radiative transfer calculations which for this study were accomplished using the radiative transfer model (RTM) McArtim3 (Deutschmann et al., 2011). The method employed here involved: 1) determining aerosol profiles using O₄ dSCDs (Friess et al., 2006; Clemer et al., 2010), 2) using aerosol profiles to calculate weighting functions for the trace gas of interest, and 3) optimal estimation inversion for determining trace gas profiles and
VCDs (Rodgers 2000). Due to the absence of any knowledge on aerosol parameter measurements in the vicinity of the measurement site, assumptions had to be made regarding these inputs to the RTM. These calculations were performed in both the ultra-violet (UV, at 350 nm) and visible (Vis, 483, 450, and 425 nm) regions of the electromagnetic radiation spectrum. The parameters along with their values were: single-scattering albedo (0.98), g parameter (0.7/0.68), and surface albedo (0.03); listed as (UV/Vis) for g parameter.

One important aspect of this study is the choice of the altitude grid used for both the radiative transfer calculations and the inversion. Rather than using uni-distant layers (<1-2 km steps) spanning the altitude range of the trace gas, a grid of varying thickness was utilized. The chosen grid was closely spaced for the lowest portion of the troposphere (0.5 km layer thickness from 0-2km) and changed to a much coarser resolution above 5 km (5 km layer thickness from 5-50 km); the grid used is reflected in SI Table 3.1. This effectively combined the information from multiple altitudes into a single grid point for altitudes where the MAX-DOAS measurements would not necessarily have vertical resolving capabilities.
Figure 3.1 Time series of relevant trace gases and wind direction for the days surrounding 9 April 2010. The different colored points in the trace gas plots represent different viewing elevation angles of the MAX-DOAS instrument as reflected in the legend, where the angle is defined above the horizon. The ozone measurements are representative of two different sites located ~30 km apart: 1) measurements with the University of Colorado in situ ozone monitor at the EPA site (labeled as CU, connected black circles); and 2) in situ ozone measurements made at the OLF site (see Chapter 2 Sect.2.4) (connected red circles).
3.3 Case Study: April 9, 2010

Figure 3.1 shows a time series of several trace gases measured for this study (BrO, IO, NO₂, and O₄) for the week surrounding the day chosen for the case study with April 9ᵗʰ outlined by the blue box. A zeroth order inspection of the O₄ dSCDs made a clear case for the potential of this day to provide an excellent opportunity for two reasons: 1) clear split in and consistent shape of the dSCDs is a good indicator for a cloud free day, and 2) the relatively high dSCDs values (compared with other days) indicates a low aerosol load, enabling the instrument to realize longer light paths (increased sensitivity due to fewer scattering events). An inspection of webcam pictures for the instrument proved the day to be free of visual clouds, and precursory look at the aerosol load confirmed the low values. Figure 3.1 also contains in-situ O₃ measurements (from both the EPA site and the OLF site, see Chapter 2 Sect. 2.4) as well as wind direction measurements from a WeatherFlow, Inc. monitoring station located in Gulf Breeze, FL near the EPA site.

Additionally, data calculated by the Whole Atmosphere Community Climate Model (WACCM, Garcia et al., (2007)) was provided for the case study to help inform different aspects of the retrieval. This model was chosen as the best representation of stratospheric BrO that is currently available, which is an important aspect of this method (see Sect. 3.5.2). Specific models outputs used were: BrO, O₃, HCHO, temperature, and pressure vertical profiles.

3.4 Aerosol profiles

Aerosol profiles were determined through an iterative approach using McArtim to calculate O₄ weighting functions with a given aerosol profile, comparing measured O₄ dSCDs to forward calculated dSCDs, modifying the aerosol profile appropriately, and then recalculating O₄
weighting functions. This process was done for each scan of the case study day (total of 56 scans) in order to determine individual aerosol profiles. The initial aerosol profile used was an exponentially decreasing with altitude extinction profile from a value of 0.01 km$^{-1}$ at 483 nm. This wavelength was chosen for its proximity to the O$_4$ peak absorption structure at 477 nm while avoiding the feature itself as well as absorption structures from other trace gases (i.e. NO$_2$).

The O$_4$ vertical profile used for all calculations and as input to the RTM was based on temperature and pressure profiles available from NOAA’s ESRL Radiosonde Database for locations close to the measurement site. In each step of the iteration the measured O$_4$ dSCDs were compared to the forward calculated dSCDs at each elevation angle of the scan being analyzed, and the differences between these values were used as input for optimizing the modification of the aerosol profile for the subsequent iteration. For this study, the convergence limit was set at a percent difference between the lowest two elevation angle dSCDs of 5%, or if the process reached a limit of 5 iterations without finding convergence the last aerosol profile was used. The limit of 5 iterations was chosen as a compromise between achieving optimal agreement between the O$_4$ dSCDs and data computation time. The results of this process can be found in SI Fig. 3.1 top panels a-d, and the 5% criteria was reached for every sequence.

Once aerosol extinction profiles were determined at 483 nm, which was used to correlate with the strongest O$_4$ absorption band located at 477 nm, they were scaled to 350 nm using the relationship:

$$\varepsilon_{350} = \varepsilon_{483} \times \left( \frac{350}{483} \right)^{-1.25}$$

(Eq. 3.1)

where $\varepsilon_{350}$ and $\varepsilon_{483}$ represent aerosol extinction coefficients at 350 and 483 nm, respectively.
3.5  Troposphere Inversion

Once aerosol profiles for each scan were determined, McArtim was used to calculate weighting functions for the trace gas of interest. From here, the weighting function could either be used to forward calculate trace gas dSCDs based on assumed vertical profiles, or they could be used in conjunction with measured dSCDs in an optimal estimation inversion to retrieve a new vertical profile.

As a zeroth order assessment of the effect of profile selection on forward calculated dSCDs, three different vertical profiles for BrO were used to calculate dSCDs and these were compared to the measured dSCDs. The three profiles were: 1) direct output from WACCM model for the measurement site and case study day; 2) WACCM model output multiplied by 1.4 (40% increase in order to account for any tropospheric BrO not included in the model, or any underestimation of stratospheric BrO in the model); and 3) a case containing a constant VMR of 0.25 pptv from 0-20km then the WACCM model output above 20km. SI Figure 3.1 bottom panels e-g show the results of the forward calculations along with the a posteriori results. Also included is the root mean square (RMS) of the differences between calculated dSCDs (and a posteriori dSCDs) and the measured dSCDs.

3.5.1  A priori Profiles

The a priori profiles for BrO and NO$_2$ utilized in this study were either taken from: 1) a chemical transport model (CTM); 2) the CTM profile scaled in order to account for any tropospheric trace gas not represented in the profile; and 3) from aircraft measurements during the Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated VOC (TORERO) 2012 field experiment (see Chapter 5). These were selected as best “first guess”
scenarios that would be representative of the FT. WACCM output profiles were used for a priori cases 1 and 2. For IO, the three a priori profiles used were: 1) an exponentially decreasing profile (BL value of ~0.25 pptv decreasing to 0.1 pptv in the FT and stratosphere); and vertical profiles measured by the CU-AMAX-DOAS on research flights made in 2010 and during TORERO (cases 2 and 3, respectively), both of which covered the atmosphere over the Tropical Pacific Ocean.

Additionally, the a priori error covariance matrix used in the inversion was constructed to reflect a high level of uncertainty in the lower layers of the atmosphere, accommodating up to several ppt throughout the troposphere. The stratospheric profile was constrained to a 40% uncertainty in the VMR. This was applied in the inversion of all three species, and the corresponding error values (in VMR, except where noted) are found in Table 3.1.
Table 3.1 A priori error values used in the optimal estimation inversion

<table>
<thead>
<tr>
<th>Layer</th>
<th>BrO</th>
<th>IO</th>
<th>NO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0.75</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.5</td>
<td>1000</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.5</td>
<td>1000</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>0.5</td>
<td>1000</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>0.2</td>
<td>200</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
<td>0.2</td>
<td>200</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>0.2</td>
<td>200</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.2</td>
<td>200</td>
</tr>
<tr>
<td>9</td>
<td>40*</td>
<td>0.2</td>
<td>40*</td>
</tr>
<tr>
<td>10</td>
<td>40*</td>
<td></td>
<td>40*</td>
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<td>11</td>
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<tr>
<td>14</td>
<td>40*</td>
<td></td>
<td>40*</td>
</tr>
</tbody>
</table>

*Error above 20 km for BrO and NO₂ is given as a percentage of the input a priori profile
Figure 3.2 Plot showing the results of the iterative approach to determining the SCD contained in the reference spectrum (black), along with the corresponding tropospheric VCD (red).
3.5.2 Reference SCD

One important input for the inversion is the amount of trace gas contained in the reference used for the analysis. This parameter is needed to convert the dSCDs from the measurements to full SCDs, so that the measurements can be directly related to the weight functions from the RTM. Additionally, the value of the reference SCD used influences the a posteriori profile from the inversion. The assumed or derived reference SCD is added to the measured dSCDs prior to input in the inversion, thus the input becomes full SCDs. In our study this was addressed by running the inversion for the trace gas of interest iteratively and updating the reference SCD after each iteration until convergence on the final value was achieved, results from this process are found in Figure 3.2. Once determined, this reference SCD was added to the dSCDs from the fixed reference analysis in order to simulate full SCDs, which represents the appropriate quantity to use in conjunction with the weighting functions.

In the case of BrO, a large portion of the signal for the SCD contained in the reference comes from the stratosphere, making this an important component of this retrieval method. For this reason, the WACCM model was chosen for the “base case” profiles (see Sect. 3.5.1) and was assumed to represent the stratosphere with only a 40% relative error. The error in the stratospheric profile is also assessed with respect to this inversion and the resulting VCDs in Section 3.7.4.

3.6 Results

3.6.1 BrO Inversion

For the actual inversion of the BrO dSCDs, three different a-priori profiles were tested in order to assess the robustness of the inversion, and these were the profiles discussed in Sect.
3.5.1. For reference, diurnal variations in the WACCM model output for BrO vertical distributions can be found in SI Figure 4 panel a while panel b shows the corresponding tropospheric and total VCDs from these profiles. As previously mentioned, the reference SCD determined through the iterative approach was used along with the dSCDs from a fixed reference analysis. Figure 3 shows the results (for one scan at ~45° SZA before solar noon) from the inversions using three different a-priori profiles, panel a contains the vertical profiles in units of concentration (along with the corresponding a priori profiles), panel b shows the vertical profiles in VMR (also with a priori profiles), and panel c shows the averaging kernels from the inversion using the first a priori profile. The averaging kernel gives an indication on where the information in the a posteriori profile comes from, and contains information on the number of independent pieces of information retrieved (degrees of freedom). In an ideal scenario, the averaging kernel for each layer would peak at 1 for that layer. Only slight differences are found in the derived vertical profiles, and it can be seen that the averaging kernels peak twice – once in the lowest layer (from the lowest looking elevation angles) and again between 5km and 20km, where the radiative transfer grid had been optimized. As previously mentioned, a comparison of the a posteriori profile derived BrO dSCDs and the measured dSCDs can be found in SI Fig. 3.1 (bottom panels).

3.6.2 IO and NO₂ inversion

The same basic procedure for the inversion that was used for BrO was followed for IO and NO₂; the major difference being that IO was set up on a grid that only reached to 25km. Additionally, due to the unavailability of WACCM model output for IO the a-priori profiles were chosen from recent publications of aircraft derived IO vertical profiles (Dix et al., 2013; Wang et
al., 2014), as well as a “standard” exponentially decreasing mixing ratio profile. For NO$_2$, the WACCM model output was used in the same manner as BrO with the exception of the last a priori profile being set to a constant 50ppt from 0-20km. The results from the IO inversion for 1 scan at ~45° SZA before solar noon can be found in Figure 4, the results from the same scan for NO$_2$ are in SI Figure 6, and both plots have the same format as found in Figure 3 for BrO. As with BrO, small differences exist between the a posteriori profiles, but overall they show good agreement. Supplementary information Figure 5 shows the comparison between the measured and calculated (from the a posteriori profiles) dSCDs for IO (panel a) and NO$_2$ (panel b). Panel c depicts the resulting RMS value for the differences in the dSCDs, for only one of the mentioned a-priori profiles. This demonstrates the good agreement between measured and calculated dSCDs for the derived a posteriori profiles.
Figure 3.3 Results of the BrO inversion for 1 elevation angle scan at ~45° SZA. Panel a is in units of concentration, panel b is in units of VMR, and panel c is the averaging kernels for the first a priori profile (black, red lines) inversion. Black traces show the a priori profile, colored traces represent a posteriori profiles for: 1) WACCM case (red, solid); 2) WACCM*1.4 (green, dashed); 3) vertical profile from Wang et al. 2014 (blue, dotted).
**Figure 3.4** Results of the IO inversion for the same elevation angle scan as presented in Fig. 3 – layout is also the same as Fig. 3. A priori profiles: 1) exponentially decreasing (red, solid); 2) Wang et al. (2014) (green, dashed); 3) Dix et al. (2013) (blue, dotted).
3.6.3 Diurnal Variation

Using the derived BrO profiles to calculate the SCD contained in all the $90^\circ$ spectra from the case study day is shown in SI Fig. 7 along with the SCDs calculated only using the WACCM model output for reference.

Following the detailed inversion procedure allowed the determination of the diurnal variation in the BL (0-1km), FT (0-15km), and total VCDs for BrO and IO. Figure 5 shows these diurnal variations for BrO in panel c and IO in panel d from the inversion using the first a priori profile along with the corresponding degrees of freedom from the inversions (panels a and b). Similar variations were retrieved from the inversions using the other two a-priori profiles and all data was combined to create average vertical profiles for both BrO and IO. Figure 6 contains these average profiles along (median values shown as the squares) with other reported profiles derived from aircraft observations, which represent the most direct way to assess the vertical distribution of these species. Error bars on the derived vertical profiles reflect the 25th and 75th percentiles of the averaged profiles, in order to reflect the variability in the data. These profiles show surprisingly good agreement with the aircraft measurements and demonstrate the capability of this ground-based MAX-DOAS instrument to derive information on the vertical distribution of trace gases located in the FT.
Figure 3.5 Diurnal variation in the BrO (panel c) and IO (panel d) VCDs (blue: 0-1 km, green: 0-15 km, and red: total), plotted with the corresponding degrees of freedom from the inversion in the top two panels a and b for BrO and IO, respectively.
3.7 BrO Profile Retrieval Sensitivities

In this section sensitivities to different aspects of the BrO retrieval and inversion will be assessed. The parameters of the BrO DOAS retrieval that remained constant were the reference cross-sections included in the fitting routine using the DOAS software WinDOAS (Fayt and van Roozendael, 2001). These included: O\(_3\) (at 223 and 243 K, Bogumil et al., 2003), NO\(_2\) (at 220 and 297 K, Vandaele et al., 1998), O\(_4\) (at 293 K, Thalman and Volkamer 2013), HCHO (Meller and Moortgat 2000), and BrO (Wilmouth et al., 1999). Also included was a Ring spectrum (Chance and Spurr 1997) calculated for the reference used in the analysis.

3.7.1 Intensity Offset

An additional parameter that can be utilized in the DOAS retrieval is an intensity offset, which would be used to help account for any instrument stray light. The instrument employed for this study was designed to actively minimize spectrometer stray light through the use of cut-off filters (BG3 and BG38) and the method of background correction. The background correction is similar to that described in Wagner et al., (2004) and utilizes dark regions on the CCD detector to correct for dark current and offset noise as well as stray light. It was determined that stray light in the instrument was only a few percent (before correction) in the wavelength range 330-360 nm. Fitting an intensity offset should only account for uncorrected stray light and is expected to be on the order of magnitude of the error in the background correction. The fitting of this parameter typically helps reduce the RMS of the fitting routine, thus improving instrument sensitivity. However, preliminary studies found a significant effect on the retrieved BrO dSCDs depending on whether or not this parameter was included in the fitting routine, and that this effect was most pronounced in the narrower fitting windows. In the most extreme case (analysis
window 346-359 nm), retrieved BrO dSCDs changed from \(-1 \times 10^{14}\) molec cm\(^{-2}\) without fitting the intensity offset to values less than zero when an unconstrained intensity offset was included. In all fitting windows tested, utilizing an unconstrained intensity offset resulted in the highest fit factor for the offset and lowest values for the BrO dSCDs, and in some cases lead to significantly negative (non-physical) values. When included in the fitting routine and left unconstrained, it was found that periods of time existed when the fit factor for the intensity offset was more than what was determined to be a reasonable value for this instrument. For this reason, the intensity offset was kept in the retrieval (to help with RMS), but limited to a range determined by the upper limit of this estimated correction \((\pm 3 \times 10^3)\). This led to an average decrease in the BrO dSCD of \(-4 \times 10^{12}\) molec cm\(^{-2}\), but never reached above \(6 \times 10^{12}\) molec cm\(^{-2}\) for SZA < \(~65^\circ\) for the fitting window 338-359 nm.

### 3.7.2 BrO Retrieval Window

Several sensitivity studies were performed to determine the most suitable analysis settings for the BrO retrieval. This was accomplished through a comparison of both O\(_3\) and HCHO dSCD values from the BrO fitting window with dSCDs predicted using WACCM vertical profiles. Also, the effect of different O\(_4\) reference cross-sections was tested with respect to the O\(_4\) dSCD in the BrO fitting window. For the comparison of O\(_3\) and HCHO, WACCM model output profiles were used to forward calculate dSCDs for comparison to measured dSCDs. Five different BrO analysis setting windows were tested: 1) fitting window 345-359 nm with a 2\(^{nd}\) order polynomial; 2) fitting window 346-359 nm with a 2\(^{nd}\) order polynomial (2-band analysis); 3) fitting window 340-359 nm with a 3\(^{rd}\) order polynomial; 4) fitting window 340-359 nm with a 5\(^{th}\) order polynomial; and 5) fitting window 338-359 nm with a 5\(^{th}\) order polynomial (4-band analysis).
The results for two of these windows (2 and 5) both with a constrained intensity offset and without an intensity offset are shown in SI Figure 2. Comparisons of the O₃ dSCDs are found in the top panels, HCHO in the middle panels, and BrO in the bottom panels. It was determined that analysis setting 5) (4-band analysis with 5th order polynomial) including a constrained intensity offset best represented both O₃ and HCHO. These are the analysis settings that were then used to look at the differences between using three O₄ cross sections: 1) Hermans (2002); 2) Greenblatt et al., (1990); and 3) Thalman and Volkamer (2013), shown in SI Fig. 3. While none of the cross sections are able to fully reproduce the O₄ dSCDs from the O₄ optimized window, the Thalman and Volkamer cross-section seems to be an improvement over Hermans and Greenblatt/Burkholder in representing O₄ in the BrO fitting window. Based on the findings of the offset sensitivity tests (Section 3.7.1) and the dSCD comparison tests presented in this section, the dSCDs used for the BrO inversion are from the 338-359 nm fitting window utilizing a 5th order polynomial, the constrained intensity offset, and the Thalman and Volkamer O₄ cross-section.

### 3.7.3 Reference Selection

Another parameter which created sensitivity in the inversion was the choice of reference spectrum. This effect was investigated by running the fixed reference DOAS retrieval with multiple zenith spectra from different times throughout the day. These results were processed in the same manner as described for the general inversion, where the iterative approach was used to determine the BrO SCD contained in each reference and that value was then used as input to the inversion, which was run with three different a-priori profiles. Reference SCD results from the iterative approach were compared with SCDs calculated using the corresponding WACCM
profiles which were multiplied by 1.4 (to account for any error in the stratospheric portion of the profile and any free tropospheric BrO not included in the profile, i.e. a median BrO column abundance). During time of day when the reference SCD is not expected to change significantly (SZA<40°, SCDs from WACCM profiles were ~7x10^{13} molec cm^{-2} and varied by <1x10^{13} molec cm^{-2} during this time) it was found that certain references deviated from this expected behavior (difference between derived SCD and predicted SCD > 2e10^{13} molec cm^{-2}), typically resulting in SCDs that were much lower than expected. It was determined that the relative distribution of the non-zenith elevation angle dSCDs for those particular scans was causing the inversion to converge on these low values for the reference SCD. This was found to create up to a 5x10^{13} molec cm^{-2} difference in the reference SCD (compared to the expected value calculated from the WACCM profile) in an extreme case, which lead to an offset in the derived VCD for any particular reference of 1-2x10^{13} molec cm^{-2}. The comparison of the derived reference SCDs with the estimated SCDs from WACCM enabled the selection of five different references that were deemed suitable for use in further sensitivity studies. This optimization of the reference spectrum resulted in a greatly reduced variability in the derived VCDs to <5x10^{12} molec cm^{-2}.

3.7.4 A-priori Profile Selection

Errors in the retrieved vertical profiles stemming from the inversion itself are determined by the a-priori profile assumption, both the tropospheric and stratospheric components. The effects of the a-priori profile selection were assessed by looking at the variability in the retrieved VCDs and comparing this to the global average. For these tests, the tropospheric and stratospheric portions of the a-priori profile were treated independently, and three different tropospheric portions of the profile and two different stratospheric portions were tested for each
of the five references selected in the previous section. The general structure for the tests were to hold one parameter constant and run all other permutations of the other parameters in order to generate a pool of data associated with the parameter held constant. In all, there were 30 different cases tested (3 tropospheric a-priori profiles x 2 stratospheric a-priori profiles x 5 references = 30), and specifically 10 cases for each tropospheric a-priori, 15 cases for each stratospheric a-priori, and 6 cases for each reference. The averages for each individual case were then compared to the global average created from all 30 cases. It was found that all data fell within error bars of the global average VCD. This indicated that no single assumption of a-priori profile (either the tropospheric or stratospheric components) or reference choice (once optimized) could be singled out to create a systematic bias on the average VCD. The results for the profile associated with the reference used to in the BrO inversion are presented in Table 3.2, where the average represents the average VCD for each case described above.
Table 3.2 Results of the sensitivity studies of a priori profile and reference spectrum on the free tropospheric VCD (1-15 km)

<table>
<thead>
<tr>
<th>Case</th>
<th>Average (molec cm(^{-2}))</th>
<th>Standard Deviation (molec cm(^{-2}))</th>
<th>Number of Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trop0</td>
<td>2.03x10(^{13})</td>
<td>1.50x10(^{12})</td>
<td>10</td>
</tr>
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<td>1.48x10(^{12})</td>
<td>10</td>
</tr>
<tr>
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<td>1.53x10(^{12})</td>
<td>10</td>
</tr>
<tr>
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</tr>
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<td>15</td>
</tr>
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<td>6</td>
</tr>
<tr>
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</tr>
<tr>
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<td>6</td>
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<td>Global</td>
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<td>2.20x10(^{12})</td>
<td>30</td>
</tr>
</tbody>
</table>
3.7.5 **Summary of Sensitivity Studies**

The major finding from these sensitivity studies is that the retrieval parameters associated with the DOAS analysis must be carefully selected as that they proved to create the highest variability in the measured dSCDs, which translates into errors in the derived VCDs. The largest differences were seen when comparing dSCDs from different analysis windows, up to $1 \times 10^{14}$ molec cm$^{-2}$ between the 2-band and 4-band analysis windows, and whether an intensity offset was included in the retrieval. The differences in dSCDs associated with the intensity offset also changed as a function of analysis window; the 2-band analysis had differences up to $1 \times 10^{14}$ molec cm$^{-2}$, while the 4-band analysis this offset sensitivity was greatly reduced, and for all cases remained below $6 \times 10^{12}$ molec cm$^{-2}$. Sensitivities in the inversion of the dSCDs to VCDs were much smaller once appropriate analysis settings were chosen and the largest effect was seen with respect to the reference spectrum selection. It was found that different references could cause deviations in the derived VCDs of $1-2 \times 10^{13}$ molec cm$^{-2}$. Through the careful selection of the reference spectrum, and leveraging external information (stratospheric BrO from WACCM) that facilitates the determination of the SCD contained in the reference spectrum (iterative approach), this sensitivity was reduced to $< 5 \times 10^{12}$ molec cm$^{-2}$. The selection of a priori (both tropospheric and stratospheric components) had the smallest effect on the VCDs once the other parameters (analysis settings, reference selection, and reference SCD) were optimized; resulting in deviations of $< 2 \times 10^{12}$ molec cm$^{-2}$.

3.8 **Conclusion/Discussion**

The ability of a research grade ground based MAX-DOAS instrument to measure free tropospheric VCDs of atmospheric trace gases was assessed utilizing real measurements
acquired during a long term field deployment in Gulf Breeze, FL. A case study day was chosen in April 2010 which exhibited low aerosol loading and cloud free conditions to provide optimal conditions for these measurements. The retrieved aerosol profiles provided input to the radiative transfer model McArtim, which was used to calculate the appropriate weighting functions for the trace gases of interest. An optimal estimation inversion procedure was then used to determine the trace gas vertical profiles from the MAX-DOAS dSCD measurements.

Sensitivity studies were performed on several factors that could potentially play important roles in the determination of the BrO VCDs; 1) inclusion of an intensity offset in the DOAS retrieval; 2) the fitting window used; 3) the choice of O₄ reference cross-section; 4) the choice of reference spectrum used in the DOAS analysis; and 5) the assumptions made on the a-priori profile. Through sensitivity studies it was determined that a 4-band BrO analysis extending from 338-359 nm and the O₄ cross-section of Thalman and Volkamer (2013) were optimal for this data, and that the intensity offset could be included, but needed to be constrained to avoid removing absorption structure from the spectra. After setting these parameters, the choice of reference spectrum was informed through a comparison of the reference SCD determined through the “iterative approach” to the SCD predicted by WACCM (assuming a median BrO abundance profile), which reduced the variability in the VCDs to <5x10^{12} molec cm^{-2}. The references that passed this quality assurance were then used to assess the impact of the choice of a-priori profile for the optimized inversion routine, which was found to impact the final VCDs only minimally. The standard deviations associated with the a-priori profile assumptions for both the tropospheric and stratospheric components (found in Table 3.2) were ~1.5x10^{12} molec cm^{-2} and ~2.2x10^{12} molec cm^{-2}. Combining the uncertainties associated with the different aspects of
the inversion lead to a conservative estimate of the total error of $\sim 1 \times 10^{13}$ molec cm$^{-2}$ for the BrO VCDs.

The vertical profiles from the inversion were condensed into VCDs for both the BL (0-1 km) and the FT (1-15 km), and we were able to determine BL VCDs of $7.7 \times 10^{11}$, $7.6 \times 10^{11}$, and $4.1 \times 10^{15}$ for BrO, IO and NO$_2$, respectively, and FT VCDs of $2.1 \times 10^{13}$ and $4.7 \times 10^{12}$ for BrO and IO.

The vertical profiles derived for BrO and IO show some dependence on a priori, up to 20% difference for BrO and 10% difference (relative to the first a posteriori profile in each case) for IO in the profiles found in Figs. 3.3 and 3.4. However, this makes only a small difference in the free tropospheric VCDs, i.e. <2% difference in BrO and <1% difference in the IO VCDs for those profiles. The percent differences in the BrO VCDs show some diurnal variation but don’t reach more than 5% until SZA>70°; and IO percent differences also show diurnal variation but are always <1.5%.

The retrievals of the BrO and IO free tropospheric vertical profiles are rather similar to those found in several recent aircraft based measurements over the open ocean, as shown in Figure 3.6. The vertical profiles from this study (blue traces), Wang et al., (2014) (red traces), and for IO Dix et al., (2013) (green traces) are shown. The profiles from Wang et al. (2014) are the median profiles of 5 different research flights during TORERO 2012. These flights took place over the course of one month and represent large spatial scales over the tropical Pacific Ocean. The IO profile from Dix et al. (2013) represents a similar latitude range as the TORERO profiles, but took place much farther west over the tropical Pacific Ocean. The IO profiles show a similar vertical distribution (more IO located in the BL as compared to higher altitudes), and the greatest difference is seen between the profile of this study and that of Dix et al. (2013),
which are not within the daily variability (error bars on the profile from this study) at any altitude. The profile from this study contains ~0.1 pptv more IO at 8 km as compared to the other studies, which is a small difference and could potentially be explained by spatial variability. The agreement between the BrO profiles, which is within the daily variability (error bars of the profile from this study) for most altitudes, is remarkable given the vast difference between the air masses sampled (pristine tropical MBL vs continental mid-latitudes MBL). The largest difference, ~1 pptv, here is in the highest altitude point (12.5 km), where the sensitivity in the ground based measurements is starting to drop off (Fig. 3.3).

Additionally, the FT VCDs reported here are in good agreement with the other previously cited values (see Sect. 3.1.2) for BrO and IO. The average BrO FT VCD of ~2x10^{13} molec cm^{-2} falls within the range reported by these other studies (1-3x10^{13} molec cm^{-2}); and the previously noted differences in the IO profiles in the FT lend to a slightly higher VCD than the other reported values, ~5x10^{12} molec cm^{-2} for this study and ~1x10^{12} molec cm^{-2} from Dix et al. (2013). However, these measurements all point to the presence of background amounts of BrO and IO in the FT; and in the case of BrO this can account for a much larger portion of the total column than currently thought.
Figure 3.6 A posteriori profile comparison between this work, Wang et al. (2014), and Dix et al. (2013). Profiles from this work represent the average of the diurnal variation and error bars reflect the 25th/75th percentiles. The profiles from Wang et al. (2014) are the average of 5 vertical profiles measured by the CU-AMAX-DOAS instrument during the TORERO 2012 field experiment, and the IO profile from Dix et al. (2013) is the average of two vertical profiles, also measured with the CU-AMAX-DOAS instrument during research flights testing the instrument in 2010.
Chapter IV

Chemistry of Free Tropospheric Halogen Species and Mercury

Goals: This chapter investigates the impact of elevated BrO, in higher than expected concentrations, and elevated IO in the free troposphere on the oxidation of gaseous elemental mercury (GEM). The chemical identities of oxidized forms of mercury are currently unmeasured. Assumptions about different possible oxidation mechanisms of mercury are discussed in terms of the uncertainties in mercury oxidation rates, product distributions, and spatial distributions in the atmosphere. Oxidation by bromine radicals is one such proposed mechanism that is investigated, and observations of BrO can constrain the concentrations of bromine radicals available in the atmosphere to participate in this reaction.

Methodology: Vertical profiles of BrO and IO in the free troposphere from ground-based measurements (this work, Chapter 3), airborne measurements from the CU AMAX-DOAS instrument during the TORERO 2012 field study, and results from global model simulations will be used in a diurnal steady-state box model to assess the impact of different vertical distributions of BrO on mercury chemistry in the atmosphere. The model results enable distinguishing different oxidation mechanisms through the assessment of chemical reaction products and reaction rates.

Results: These studies show that bromine radicals in the troposphere are the dominant oxidation pathway for GEM; and the vertical distribution of bromine species greatly impacts the GEM oxidation rate. Additionally, the inclusion of recently proposed scavenging reactions for the HgBr adduct can lead to a larger diversity of gaseous oxidized mercury (GOM) products in the
atmosphere than is currently thought. The elevated concentrations of BrO in the measurements relative to the models lead to an increase in the column integral oxidation rate of GEM with respect to bromine radicals by a factor of ~2; this translates into a factor of 2-3 decrease in the GEM lifetime in the free troposphere. Additional reactions of the HgBr adduct in the troposphere increase the rate of scavenging through further oxidation by up to a factor of ~15. These reactions also diversify the chemical identity of GOM which will affect the cycling of mercury through the atmosphere; e.g., changes in the overall aqueous phase partitioning, potential for additional aqueous phase reactions (which can lead to the photo-reduction of GOM to GEM), and through additional decomposition pathways of these species (e.g., photolysis, thermal decomposition).

4.1 Introduction

Mercury in the atmosphere has both natural and anthropogenic sources, and is present mainly in three different forms: gaseous elemental mercury (Hg$^0$, GEM), gaseous oxidized mercury in the form of either Hg$^{2+}$ or Hg$^{1+}$ (GOM), or particulate mercury (Hg$_p$). Natural sources include vegetation, volcanoes, soils, fires, and mineral deposits, while anthropogenic sources are waste incineration, chlor-alkali production, and, primarily, coal combustion (Schroeder and Munthe 1998). Gaseous elemental mercury is relatively inert and is believed to have a long atmospheric lifetime; current estimates range from 0.5 – 1.5 years (Selin et al., 2008), allowing it to be homogeneously mixed at hemispheric scales. GOM is highly reactive with surfaces and very water soluble (Henry’s Law coefficient of HgCl$_2$ = 2.7x10$^6$ M atm$^{-1}$) (Schroeder and Munthe 1998; Lindberg et al., 2007), which leads to a short atmospheric lifetime, on the order of hours (Holmes et al., 2009), due to both wet and dry deposition and possibly uptake to sea salt
aerosols (Selin et al., 2007). Particulate bound mercury refers to mercury species that have been adsorbed to particulate matter or partitioned into aerosols. The lifetime of $\text{Hg}_P$ is very dependent on the chemical composition and size of the particle, as well as the meteorological conditions of the environment in which it is found (Seigneur et al., 1998; Lindberg et al., 2002). A basic diagram of the biogeochemical cycling of mercury is show in Figure 4.1.
Figure 4.1 Basic diagram of the biogeochemical cycling of mercury, where Hg(0) is elemental mercury, Hg(II) is oxidized mercury, and MeHg is methyl-mercury.
It is important to understand the processes that cycle mercury between its various forms (GEM vs GOM vs HgP) because this speciation controls the deposition of mercury to the terrestrial environment, i.e., GOM and HgP are more readily removed from the atmosphere via wet/dry deposition than GEM (Lindberg and Stratton 1998; Bullock 2000). Once deposited, Hg^{2+} can be methylated through biological processes to form the neurotoxin methyl mercury, which has the ability to bio-accumulate in fish tissues and can be enhanced by factors up to 10^6 in predatory fish species relative to water (Schroeder and Munthe 1998; Selin et al., 2010).

4.2 Atmospheric Chemistry of Mercury

Traditionally, ozone and the hydroxyl radical were considered the primary oxidants for GEM in the atmosphere, and these are still the standard reactions used in global mercury models (Selin et al., 2008). The validity of using these reactions has recently become the subject of debate in mercury modeling (Holmes et al., 2009) due to the publication of several thermodynamic studies calling into question the bond strength of the HgO molecule (Tossell 2003; Shepler and Peterson 2003), which is the primary product of these reactions, indicating that these reactions might not be atmospherically relevant. Additionally, evidence is growing that reactions between GEM and bromine species to produce GOM might actually be the dominant pathway for mercury oxidation (Ariya et al., 2002; Tossell 2003; Donohoue et al., 2006).

The relevant mercury chemistry utilized in this study is summarized in Figure 4.2 and includes gas phase reactions, thermal decomposition, gas-particle partitioning (as described in Rutter and Schauer (2007)), and photo-reduction of aqueous phase species to reproduce Hg^0. Two modeling scenarios are presented in Fig. 4.2: panel a ("traditional") and panel b ("revised").
(details in Section 4.4). A summary of all reactions involving mercury compounds and associated rate coefficients can be found in Table 4.1.
Table 4.1 Summary of mercury reactions and rate coefficients used in box-model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate or equilibrium</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Hg}^0 + \text{O}_3 \rightarrow \text{HgO} + \text{O}_2$</td>
<td>$3 \times 10^{-20}$</td>
<td>Hall (1995)</td>
</tr>
<tr>
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<td>Rutter and Schauer (2007)</td>
</tr>
<tr>
<td>$\text{HgO}<em>(aq) \rightarrow \text{Hg}^0</em>(g)$</td>
<td>$1.12 \times 10^{-5}$</td>
<td>Costa and Liss (1999)</td>
</tr>
<tr>
<td>$\text{Hg}^0 + \text{Cl} \rightarrow \text{HgClBr}^3$</td>
<td>$2.2 \times 10^{-32} \times \exp(680 \times (\frac{2}{T} - \frac{1}{298}) \times [\text{M}])$</td>
<td>Donohoue (2005)</td>
</tr>
<tr>
<td>$\text{HgClY} \leftrightarrow \text{HgClY}_(aq)$</td>
<td>$K_{eq}^{1}$</td>
<td>Rutter and Schauer (2007)</td>
</tr>
<tr>
<td>$\text{HgClY}<em>(aq) \rightarrow \text{Hg}^0</em>(g)$</td>
<td>$1.12 \times 10^{-5}$</td>
<td>Costa and Liss (1999)</td>
</tr>
<tr>
<td>$\text{Hg}^0 + \text{Br} \rightarrow \text{HgBr}$</td>
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<td>Donohoue (2005)</td>
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<td>$\text{HgBr} + \text{Y}^4 \rightarrow \text{HgBrY}$</td>
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<td>$\text{HgBrY}<em>(aq) \rightarrow \text{Hg}^0</em>(g)$</td>
<td>$1.12 \times 10^{-5}$</td>
<td>Costa and Liss (1999)</td>
</tr>
<tr>
<td>$\text{HgBr} + \text{Y}^5 \rightarrow \text{HgBrY}^\prime$</td>
<td>$1 \times 10^{-10}$</td>
<td>Dibble et al. (2012)</td>
</tr>
<tr>
<td>$\text{HgBrY}^\prime \leftrightarrow \text{HgBrY}^\prime_(aq)$</td>
<td>$K_{eq}^{1}$</td>
<td>Rutter and Schauer (2007)</td>
</tr>
<tr>
<td>$\text{HgBrY}^\prime_(aq) \rightarrow \text{Hg}^0_(g)$</td>
<td>$1.12 \times 10^{-5}$</td>
<td>Costa and Liss (1999)</td>
</tr>
</tbody>
</table>

1Equilibrium coefficient is parameterized according to Rutter and Schauer (2007): $K_{eq} = (SA-PM)/(SA-PM/10^{(-42.50/T)+10})$, where $SA$ = the specific aerosol surface area, and $PM$ = the particulate mass

2Rate coefficients are given in either cm$^3$ molec$^{-1}$ s$^{-1}$ or s$^{-1}$

3Assumes that the reaction between $\text{Hg}^0$ and Cl is the rate limiting step to form $\text{HgCl}$ which will then quickly react with Br to form $\text{HgClBr}$

4$Y$ = Br, OH

5$Y^\prime$ = HO$_2$, NO$_2$, BrO, IO, I
Figure 4.2 Chemical schematics for the reactions represented in the box model. Left panel represents the “traditional” scenario where only OH and Br are used to stabilize HgBr; and the right panel represents the “revised” scenario where additional stabilization reactions from HO₂, NO₂, BrO, IO, and I are considered.
4.2.1 Reactions of Hg$^0$ with O$_3$ and OH

As previously mentioned, current global mercury models typically use O$_3$ and OH as the primary oxidants for GOM, but recent studies show that these reactions may not be atmospherically relevant (Pal and Ariya 2004; Hynes et al., 2009; Holmes et al., 2009). These processes are summarized in Reactions (4.1-4.3), and both involve the production of mercury monoxide, HgO, the formation of which in the gas phase is subject of debate.

\begin{align*}
\text{Hg}^0 + \text{O}_3 & \rightarrow \text{HgO} + \text{O}_2 \\
\text{Hg}^0 + \text{OH} & \rightarrow \text{HgO} + \text{H} \\
\text{Hg}^0 + \text{OH} & \leftrightarrow \text{HgOH}
\end{align*}

(R4.1) (R4.2) (R4.3)

In a recent thermodynamic study Shepler and Peterson (2003) found that, in the gas phase, HgO is only bound by 17 kJ mol$^{-1}$, while Tossell (2003) calculated this molecule to be unbound. Previous studies on the kinetics of this reaction and the resulting atmospheric implications assume the currently accepted value of 268 kJ mol$^{-1}$ for the binding energy for HgO (Hall 1995; Pal and Ariya 2004). Using the newer binding energy, the enthalpies for the reactions leading to this product become endothermic by $\sim$90 kJ mol$^{-1}$ and $\sim$415 kJ mol$^{-1}$ for ozone (R4.1) and the hydroxyl radical (R4.2), respectively. This makes these reactions energetically unfavorable and unlikely to occur in the gas phase.

Kinetic studies of the reaction with ozone have produced rate coefficients that vary from 0.3-15x10$^{-19}$ cm$^3$ molec$^{-1}$ sec$^{-1}$ (Hall 1995; Pal and Ariya 2004; Sumner 2005), indicating a large uncertainty surrounding this reaction, and all of these studies indicated complex behavior of this reaction system due to wall interactions. Additionally, modeling studies by Bergan and Rodhe (2001) and Seigneur et al., (2006) tested the effects of these rate coefficients in global mercury models and found that the low limit (0.3x10$^{-19}$ cm$^3$ molec$^{-1}$ s$^{-1}$) was too slow to keep GOM levels
close to measured values, while even a median rate coefficient of $7.5 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ was too fast to reproduce global distributions of GOM.

Theoretical calculations of the product of Reaction (4.3), HgOH, have found that this is also a weakly bound molecule with a binding energy $\sim 30-40 \text{ kJ mol}^{-1}$ (Tossell 2003; Goodsite et al., 2004). Goodsite et al. (2004) further calculated rate coefficients for both the formation and decomposition of HgOH via (R4.3), and determined values of $\sim 3 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$ for \text{R4.3}_{\text{forward}} and $\sim 3000 \text{ s}^{-1}$ for \text{R4.3}_{\text{reverse}} at 298K. If these calculations are correct, then the equilibrium of this reaction would be heavily shifted towards reactants.

The summary here is that from all of the studies surrounding Reactions (4.1-4.3) there are still considerable uncertainties pertaining to whether ozone or the hydroxyl radical are atmospherically relevant pathways for the oxidation of GOM. For this study, reactions R4.2 and R4.3 will not be considered; R4.2 due to lack of data indicating this reaction will even occur, and R4.3 due to the negligible overall contribution considering the forward and reverse reactions. However, given the amount of evidence from laboratory studies indicating some role of R4.1 (although this is probably not actually occurring in the gas phase) we will include R4.1 in our box model calculations using the lower bound of the rate coefficient of $0.3 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$.

4.2.2 Reaction of Hg$^0$ with Halogens

Studies investigating reactions occurring between Hg$^0$ and bromine radicals have indicated that this is likely the dominant pathway for the oxidation of Hg$^0$ in the atmosphere with some potential for contributions from chlorine radicals (Reactions 4.4 - 4.5) (Ariya et al., 2002; Tossell 2003; Goodsite et al., 2004; Donohoue et al., 2006; Hynes et al., 2009). Other halogen species ($\text{Br}_2$, $\text{Cl}_2$, $\text{I}_2$, $\text{BrO}$, $\text{ClO}$, $\text{IO}$, $\text{IBr}$, $\text{ICl}$) have been proposed and studied, but most of these
reactions have been deemed too slow to be atmospherically relevant, energetically unfavorable, or at this point in time there is not enough information available to make an adequate assessment (Ariya et al., 2002; Balabanov and Peterson 2003; Raofie and Ariya 2003; Tossell 2003; Shepler et al., 2005; Raofie et al., 2008).

\[ \text{Hg}^0 + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M} \quad \text{(R4.4)} \]

\[ \text{HgCl} \rightarrow \text{Hg}^0 + \text{Cl} \quad \text{(R-4.4)} \]

\[ \text{Hg}^0 + \text{Br} + \text{M} \rightarrow \text{HgBr} + \text{M} \quad \text{(R4.5)} \]

\[ \text{HgBr} \rightarrow \text{Hg}^0 + \text{Br} \quad \text{(R-4.5)} \]

Theoretical calculations have shown both of these reactions to be energetically favorable (Tossell 2003), and kinetic experiments have provided a range of potential rate constants (Ariya et al., 2002; Donohoue et al., 2005; Donohoue et al., 2006). Values for the second order rate coefficients for R4.4 (at 298K and 760 torr) range from \((5.5-100) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\), and \((3.7-30) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) for R4.5. The temperature and pressure dependence of these reactions follow the behavior of a termolecular reaction; positive pressure dependence and negative temperature dependence. At higher altitudes (free troposphere), this will result in competition between the increased stability of the excited adduct \((\text{HgX}^*, \text{ X} = \text{Cl, Br})\) at lower temperatures with the decreased availability of other molecules for collisional stabilization at lower pressure.

Additionally, there have been theoretical studies on the kinetics of these reactions (Khalizov et al., 2003; Goodsite et al., 2012) which provide second order rate coefficients that fall within the range of those determined experimentally, \(~3 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) and \((4-20) \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) for R4.4 and R4.5, respectively. Both of these Hg(I) containing products can be further oxidized through Reactions 4.6 – 4.7.

\[ \text{HgCl} + \text{X} \rightarrow \text{HgClX} \quad \text{(R4.6)} \]
HgBr + X → HgBrX \hspace{1cm} \text{(R4.7)}

where X = Br, Cl. At this point it should be noted that that while the kinetics of the reactions between Hg\(^0\) and Cl radicals are quite fast, chlorine radical concentrations in the atmosphere are typically so low that this pathway is not considered atmospherically relevant. As such, there have been very few studies on the kinetics of R4.6, and the focus in the literature has been towards R4.7. Goodsite et al., (2004) calculated a temperature dependent rate constant for R4.7 as 2.5x10\(^{-10}\)\(\left(T/298 \text{ K}\right)^{-0.57}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\), while Balabanov et al., (2005) calculated rate coefficients for this reaction of (1-30)x10\(^{-10}\) cm\(^3\) molec\(^{-1}\) s\(^{-1}\). The higher of these values represents the low pressure limit, while the lower value represents the high pressure limit.

In a computational study on a variety of HgXY (X = Br, Cl; and Y = Br, Cl, NO, NO\(_2\), O\(_2\), HO\(_2\), BrO, and ClO) Dibble et al., (2012) found that all of these species were bound molecules, albeit some had very low binding energies. Earlier work by Goodsite et al., (2004) and Shepler et al., (2005) investigated similar reactions involving iodine species, finding that Y = I is also a plausible reaction pathway. Based on the evidence presented in Goodsite et al., (2004), Shepler et al., (2005), and Dibble et al., (2012), additional HgX scavenging reactions will be investigated in this study (Reaction 4.7’).

HgBr + X → HgBrX (X = OH, Br, NO\(_2\), HO\(_2\), BrO, I, and IO) \hspace{1cm} \text{(R4.7’)}

There have been few studies dedicated to investigating the potential role of iodine species as direct oxidants of Hg\(^0\) (Goodsite et al., 2004; Shepler et al., 2005; Raofie et al., 2008) (Reaction 4.8).

Hg\(^0\) + X → HgX \hspace{1cm} \text{(R4.8)}

where X = I\(_2\), I, IO
Both reports provide some evidence for the participation of iodine species, which could support the field observations of Murphy et al., (2006) (see Sect. 4.2.1). Raofie et al., (2008) provide the rate coefficient \((1 \times 10^{-19} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1})\) for the reaction with molecular iodine which is too slow to compete with other pathways, and only estimate that the rate coefficient for the reaction with iodine radicals could be comparable to the rate coefficient for the reaction of bromine radicals. Goodsite et al., (2004) calculated a rate coefficient for the reaction with iodine radicals as \(4 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) and a thermal decomposition rate of HgI as \(1 \times 10^4 \text{ s}^{-1}\). These results combined with the lower concentrations of iodine species in the atmosphere most likely make direct oxidation by iodine negligible.
Figure 4.3 Vertical profiles of BrO from the TORERO 2012 field experiment (left panel) and this study (right panel). The TORERO data is comprised of CU-AMAX-DOAS measurements from 5 research flights (orange lines, red is the median) and GEOS-Chem simulations for the corresponding times and locations of the research flights (grey lines). Profiles from this study are from CU-GMAX-DOAS measurements (green line) and from WACCM (black line). These are the medians for the entire day of 09 April 2010.
4.3 Model Description

In this study, a diurnal steady-state box model which follows the framework of (Crawford et al., 1999), where model inputs are initiated and allowed to reach steady-state over several days, was utilized in order to assess the impact of the vertical distribution of BrO in the troposphere on mercury oxidation pathways, sensitivity in oxidation rates to mechanistic assumptions, product distributions and lifetimes. This model was developed by Siyuan Wang, and has been used in previous works in the Volkamer group (Dix et al., 2013; Wang et al., 2014).

For the determination of oxidative pathways, the reaction rates for oxidation of Hg\(^0\) against Br, O\(_3\), and Cl were calculated as a function of altitude for the given reactant vertical profiles, which gives the relative contributions of these reactions to the overall rate of oxidation.

Initializing the box model under two different modes enabled the investigation of sensitivity of oxidation rates to mechanistic assumptions, and in this case the scavenging of the HgBr adduct was studied. The “traditional” model scenario only included Br and OH radicals as scavengers (Holmes et al., 2009), and the “revised” model included the species listed in R4.7; this enabled the comparison of the total rate of HgBr oxidation to HgBrX between the two models. The model also tracks the concentrations of all species as a function of altitude, which gives indications for the product distributions of the various reactions.

Finally, the oxidation rates of Hg\(^0\) for reactions with Br, O\(_3\), and Cl were used to determine the lifetime of Hg\(^0\) against oxidation as a function of altitude.

4.3.1 Initial Conditions

This work expands on that presented in Chapter 3, so conditions representative of the case study presented there will be used to initiate the model. The points mentioned at the end of
Sect. 4.4 are investigated as a function of BrO vertical distributions from four different sources: 1) this study (profile presented in Chapter 3); 2) Whole Atmosphere Community Climate Model (WACCM, see Sect. 4.4.2); 3) CU Airborne-MAX-DOAS (AMAX-DOAS) measurements from the TORERO 2012 field experiment (Wang et al., 2014); and 4) Goddard Earth Observing System – Chemistry Climate Model (GEOS-Chem, see Sect. 4.4.2) profiles. Figure 4.3 shows these vertical profiles for reference. The Hg$^0$ lifetimes are calculated based on each reference profile; and results from modeled profiles will be compared to results from measured profiles. For that reason, corresponding modeled and measured data are averaged in the same ways for both the data presented in this work and that representative of the TORERO 2012 field experiment. In this study, the BrO vertical profile presented at the end of chapter 3 is the average profile for the entire day, so the output profiles from WACCM are also averaged over this day. Similarly, the TORERO data as measured by the CU AMAX-DOAS instrument is the average of 5 different research flights (see Fig. 4.3), so GEOS-Chem data was averaged along these flight tracks during the time each profile was derived. A detailed description of the TORERO measurements and model case studies is given in Wang et al. (2014).

In the box model, input BrO profiles (along with other atmospherically relevant species) are used to determine the concentration of Br radicals available to participate in R4.5 (see Fig. 1.1) Other model inputs were taken as the output profiles from WACCM for the case study day, and these included: temperature, pressure, O$_3$, formaldehyde, and NO$_2$. The vertical profile of IO that was presented at the end of Chapter 3 was also used as input. Aerosol surface area and elemental mercury measurements were used from the TORERO data set and are deemed representative of conditions in the marine atmosphere. Additionally, photolysis rates for a variety of species were calculated using the Tropospheric Ultraviolet and Visible (TUV) Radiation
model. The TUV model was initiated for a Rayleigh atmosphere (aerosol extinction = 0), with O$_3$ and NO$_2$ columns of 380 and 0.3 Dobson Units (DU), respectively, which were derived from the average vertical profiles from WACCM; and calculations from solar noon are used. All parameters with the exception of BrO were held constant for all tests.

When running the box model, the input species (BrO, IO, HCHO, O$_3$, and NO$_2$) are assumed to be in steady-state; and vertical profiles for the inputs can be found in Figure 4.4.
Figure 4.4 Vertical profiles of the input parameters for the box model
4.3.2 External Models

**Whole Atmosphere Community Climate Model (WACCM)** is an atmospheric model that represents the combining of three different National Center for Atmospheric Research (NCAR) numerical models: Model for Ozone and Related chemical Tracers (MOZART) for chemistry; Thermosphere-Ionosphere-Mesosphere Electrodynamics General Circulation Model (TIME-GCM) for mesospheric and thermospheric processes; and Middle Atmosphere Community Climate Model (MACCM) for dynamics and physical processes. For this study, WACCM is used to represent a standard for current knowledge of representing bromine chemistry in the upper free troposphere and stratosphere.

**Goddard Earth Observing System – Chemistry-Climate Model (GEOS-Chem)** is a 3-dimensional model that predicts atmospheric composition by utilizing measurements from GEOS. For the TORERO data set, GEOS-Chem was used to assimilate halogen radical chemistry with physical and chemical processes in order to constrain Br$_3$ in the free troposphere.

4.4 Modeling Results

The primary finding from a comparison of the Hg$^0$ oxidation rates for three molecule used in this study (Br, O$_3$, and Cl) is that the reaction with Br dominates the overall rate throughout the troposphere, independent of initial BrO vertical profile used. The column integral rates are $2.2 \times 10^5$ and $3.4 \times 10^4$ molec cm$^{-2}$ s$^{-1}$ for O$_3$ and Cl, respectively; while the Br rates are $9.0 \times 10^5$, $4.8 \times 10^5$, $7.2 \times 10^5$, and $4.3 \times 10^5$ for the BrO vertical profiles from the CU-GMAX-DOAS measured during this study, the WACCM modeled profile for this study, the CU-AMAX-DOAS measured during TORERO, and the GEOS-Chem modeled profile for TORERO, respectively. All four of the reaction rates from Br are at least a factor of ~2 greater than the contribution from
O₃, while Cl is deemed to be negligible. The vertically resolved rates are shown in Figure 4.5 for all three reactions: Br (blue traces, style indicating initial BrO profile used as input to the box-model); O₃ (red trace); and Cl (green trace); reflecting the contributions of these reactions at different altitudes. Only in the lowest layers of the atmosphere do the rates of oxidation through reaction with O₃ become comparable or greater than those of the reaction with Br. However, it should be noted that for the cases where the rate of reaction with O₃ dominates, the BrO VMR in the lower layers is <0.03 pptv while the O₃ VMR is ~50 ppbv, and in cases where reaction with Br dominates the BrO VMR is <0.3 pptv. For all BrO profiles, the reaction with Br dominates above 4 km and it is this region of the atmosphere that makes the highest contributions to the overall rate of oxidation, this cut-off altitude is indicated by the black dashed line. Additionally, the BrO vertical profiles below 4 km contain the highest amount of uncertainty because most of these measurements are below the detection limits of the instruments.

The BrO vertical profile determined from the CU-GMAX-DOAS measurements presented in this study was used to investigate the impacts of the additional oxidation mechanisms proposed by (Dibble et al., 2012) and the impact of potential iodine chemistry on the oxidation rate of HgBr to HgBrY (see Sect. 4.2.3). Figure 4.6 shows the results of the “traditional” (panel a) and “revised” (panel b) HgBr scavenging schemes as a function of altitude on the rate of HgBr removal through R4.7. In each panel, contributions of individual molecules (colored lines) are shown along with the total removal rate (black lines). Panel c shows the vertical profile of the ratio of the “revised” total rate to “traditional” total rate, which demonstrates the enhancement in the cycling of HgBr when considering the additional scavenging reactions. In the “traditional” model the percent contributions to the total rate of oxidation of HgBr are 69.1% and 30.9% for Br and OH, respectively; and in the “revised” model
the percent contributions are as follows: 72.3% (NO₂); 21.4% (HO₂); 3.5% (BrO); 1.6% (OH); 0.6% (Br); 0.5% (IO); and 0.1% (I). In this case, results from all altitudes can be considered because these removal rates use same BrO vertical profile and are meant to demonstrate the enhancement due to other reactions, as these are limited by the reaction between Br radicals and Hg⁰ (R4.5) in the first place. The greatest enhancement is seen in the lower altitudes (<8 km) (up to a factor of ~20) with the main contribution coming from NO₂ (64.8%). In the lower layers, HO₂ (29.9%) also contributes significantly with BrO contributions increasing with altitude. Reactions with Br and I radicals contribute the least (0.5% and 0.1%, respectively) to these reactions throughout the profile, until >12 km where Br contributions become as important as those of OH.
Figure 4.5 Elemental mercury oxidation rate as a function of species (BrO: blue; O₃: red; and Cl: green) and BrO vertical profile (this work: solid; WACCM: dashed; TORERO AMAX: dotted; and GEOS-Chem: dotted and dashed).
Figure 4.6 also illustrates the increased number of species produced from the additional oxidation mechanisms (see Fig. 4.2 and Sect. 4.3), some of which may have physical and chemical properties compared to the two products of the “traditional” model, which are also products in the “revised” scenario but are present at much lower concentrations. In the “traditional” scenario at 1km, the scavenging products HgBrOH and HgBr$_2$ account for 96% and 4% of the total HgBrX, respectively, and these values drop to 0.24% and 0.01% in the “revised” scenario where HgBrNO$_2$ accounts for 96% of HgBrX. In the “revised” scenario, HgBrNO$_2$ remains the major product throughout the atmosphere, but at the higher altitudes of the free troposphere HgBrHO$_2$ also contributes significantly at 35%, compared to HgBrNO$_2$ at 59%.

Currently, the box-model only accounts for partitioning of these additional species between the gas phase and aerosols; once they are in the aqueous phase they can be photoreduced and reproduce Hg$^0$ in the gas phase from the aerosol. It is expected that these species will go through additional processes in the aqueous phase, which could significantly impact the ultimate fate of the mercury, but at this time there no information on such processes. Additionally, species such as HgBrNO2 and HgBrHO2 could be expected to photolyze under typical atmospheric radiation, but no studies exist that can inform the parameterization of this process.

Using the vertical profiles of Hg$^0$ used in the box-model and the calculated rates of oxidation, the lifetime against oxidation is derived and shown in Figure 4.7. Panel a shows the vertical profile of the resulting Hg$^0$ lifetime for the different BrO vertical distributions (all other parameters remaining constant). Profiles for the data presented in this work are shades of blue (measurements: dark blue; model: light blue) and from the TORERO field experiment are shades of green (measurements: dark green; model: light green). Panel b gives the ratio of modeled to
measured lifetimes for this work (blue) and the TORERO data (green). The dashed horizontal black line represents the 4 km cut-off below which the BrO profiles are uncertain, and the dashed vertical black line (panel b) represents a 1:1 ratio. The largest differences in the Hg$^0$ lifetimes derived from modeled and measured BrO profiles is seen in the free troposphere, where modeled profiles could under predict the lifetime by factors of 2-3.
Figure 4.6 Vertical distribution of the differences in HgBr oxidation rates between the “traditional” (left panel) and “revised” (middle panel) scenarios. The right panel shows the ratio of the total rates of oxidation of HgBr for the two scenarios. The largest enhancement is seen in the lower layers of the atmosphere.
Figure 4.7 Vertical profile of the Hg$^0$ lifetime against oxidation for the four different BrO vertical profiles (left panel): this work (dark blue); WACCM (light blue); CU-AMAX-DOAS from TORERO (dark green); and GEOS-Chem from TORERO (light green). The right panel shows the ratios of modeled vs measured BrO profiles for this work (blue) and TORERO (green). The largest difference is seen in the free troposphere where models tend to under predict BrO.
4.5 **External Field Evidence**

It is well established that bromine induced oxidation of mercury is occurring in the Arctic during polar spring, when Atmospheric Mercury Depletion Events (AMDEs) and Ozone Depletion Events (ODEs) correlate very well with elevated levels of bromine species (Lindberg et al., 2002; Steffen et al., 2008). Peleg et al., (2007), in a study at the Dead Sea, reported measurements correlating bromine monoxide (BrO) and GOM, and in Obrist et al., (2010) these correlations were assessed through a heterogeneous box model which allowed the authors to reproduce the observed AMDE using bromine chemistry. However, the levels of BrO found in these studies (Peleg et al. 2007: background levels of ~5 pptv; maximum of 150 pptv BrO) are not deemed representative for conditions in the terrestrial or marine boundary layer. The chemical link between bromine chemistry and mercury oxidation is particularly relevant in the troposphere, where atmospheric bromine, produced by organic bromine species (CH$_3$Br, CH$_2$Br$_2$, and CHBr$_3$) emitted by biological processes in the ocean or coastal areas and the oxidation of bromine-containing sea salt (see Chapter 1), is thought to be rather ubiquitous (Chance 1998; Fitzenberger et al., 2000; Wagner et al., 2001; Richter et al., 2002; Salawitch et al., 2005; Hendrick et al., 2007; Theys et al., 2007; Coburn et al., 2011; Theys et al., 2011; Wang et al., 2014), although the actual levels present are currently of debate. The measurements of BrO made during this study further add to the spatial distribution covered in the studies listed above.

There have been several field studies aboard aircraft that find the upper troposphere and lower stratosphere to be depleted in elemental mercury (Talbot et al., 2007; Slemr et al., 2009; Lyman and Jaffe 2012). In particular, the instrument used by Lyman and Jaffe (2012) is capable of measuring both GEM and GOM, which enabled them to determine an anti-correlation between GEM and GOM in both the upper troposphere and lower stratosphere. Although all
three reports attribute the low levels of GEM in the upper layers of the atmosphere to oxidative chemistry, the direct measurements of Lyman and Jaffe (2012) provided the first direct link between the two species. Murphy et al., (2006) found that aerosol data collected on research flights aboard the NASA WB-57F and NOAA P3 aircrafts showed a distinct correlation between mercury and iodine, indicating that these species were often present in the same particles. However, they were unable to determine the reason for this relationship, i.e., whether this is a result of oxidation of GOM by iodine containing species or merely a coincidence. More recently, during the Nitrogen, Oxidants, Mercury, and Aerosol Distributions, Sources, and Sinks (NOMADSS) campaign measurements of GOM were assessed using the GEOS-Chem model and it was found that the amount of bromine in the model had to be increased by a factor of three to reproduce the observed GOM (Jaegle et al., 2013). This is also in line with our finding that the global chemistry models tend to under predict bromine in the troposphere, and provides further evidence that this under representation can impact our understanding of mercury cycling in the atmosphere.

4.6 Conclusions/Discussion

The data presented here illustrates the need to better constrain BrO (and possibly IO) in the free troposphere, as that current global models tend to under predict their concentrations, which can have profound effects on processes such as the oxidation of Hg$^0$ to GOM. Past studies have established a link between mercury oxidation and bromine species (Lindberg et al., 2002; Holmes et al., 2009; Obrist et al., 2010), but there are still large uncertainties surrounding the atmospheric implications of these reactions. This is in part due to the ambiguity of the rate of the reaction between Hg$^0$ and Br radicals. Donohoue et al., (2006) measured the rate coefficient in
the laboratory as a function of temperature and pressure and report a value of $1.46 \times 10^{-32} \left(\frac{T}{298}\right)^{1.86}$ cm$^6$ molec$^{-2}$ s$^{-1}$, which is equivalent to $3.7 \times 10^{-13}$ cm$^3$ molec$^{-1}$ s$^{-1}$ at 298K and atmospheric pressure, while Ariya et al., (2002) report a measured rate constant of $3.2 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$ at 298K and atmospheric pressure. Theoretical calculations of these rates produce values within this range (Khalizov et al., 2003; Goodsite et al., 2012). The more recent of these studies produce the slower rate coefficients, but agree very well with each other. However, based on this study even the slower rate coefficients do not change the result of bromine radicals being the major pathway for oxidation in the free troposphere. Even using the slower rate coefficients oxidation by bromine radicals dominates over reactions with O$_3$ and Cl even at very low levels of Br (<1 pptv BrO). This is especially pronounced in the free troposphere where global models tend to under predict halogen concentrations. The agreement between the measured BrO vertical profiles from this study and the TORERO dataset present the potential for this to be a widespread phenomenon given the spatial and climatological differences between the two study locations. Such a ubiquitous layer of BrO could also potentially explain the observations of elevated amounts of GOM in the free troposphere, and might also indicate the presence of a widespread “pool” of GOM.

This would also be particularly relevant for the Southeastern US, where there have been several studies linking deep convective activity to the elevated levels of mercury found in this region (Guentzel et al., 2001; Landing et al., 2010; Nair et al., 2013). The bio-accumulation of methyl mercury in fish tissues introduced in Sect. 4.1 is particularly relevant in this region, where it has been deemed unsafe to eat fish harvested from many of the state’s lakes (Engle et al., 2008; Liu et al., 2008). Wet deposition measurements of mercury far exceed what can be explained through regional sources in the southeast. In fact, Guentzel et al., (2001) estimated that
only 30-46% of the mercury deposited in Florida was a result of local emissions, the other >50% was attributed to long range transport of mercury in the atmosphere. This coupled with the aircraft studies locating elevated levels of GOM in the free troposphere strongly suggest the presence of this global “pool” of mercury in the upper atmosphere that can contribute to deposition on a global scale, which would have a significant impact on future regional and global regulations on mercury emissions. The findings of this study, which indicate that the amount of bromine located in the free troposphere is sufficient to quickly oxidize Hg\(^0\), present an explanation for the findings of these previous studies.

Additionally, the modeling results presented here show that mercury could be a highly dynamic (chemically) species in the atmosphere. The lifetime of Hg\(^0\) against oxidation by bromine radicals dropping to ~40 days in the free troposphere (see Fig. 4.7) is not necessarily consistent with an atmospheric lifetime on the order several months. However, accounting for a more rapid cycling of mercury between GOM and Hg\(^0\) could decrease this discrepancy.

Including the additional pathways for the scavenging of the HgBr adduct as indicated in Shepler et al., (2005) and proposed in Dibble et al., (2012) presents potential mechanisms for the needed reduction of GOM to Hg\(^0\). One such mechanism is the photo-dissociation of HgBrX products containing species that have significant absorption cross-sections in the ultra-violet/visible (UV/Vis) region of the electromagnetic radiation spectrum, e.g. HgBrNO\(_2\), which could reproduce HgBr. This could then thermally decompose or be oxidized again. Another pathway is additional aqueous phase reactions that lead to the photo-reduction of GOM to Hg\(^0\). The diverse products of the additional reactions could significantly impact the cycling between oxidized and reduced form of mercury due to different chemical and/or physical properties as
compared to HgBr$_2$ and HgBrOH. For instance, differences in the solubility of the additional HgBrX products could significantly impact removal of GOM via wet deposition.
Chapter V

Glyoxal over the open ocean: Results from the TORERO Field Experiment


Goals: A Fast Light-Emitting Diode Cavity-Enhanced DOAS (LED-CE-DOAS) instrument to measure eddy covariance (EC) fluxes of glyoxal over the open ocean was developed. The instrument is described, characterized, and was deployed aboard the NOAA research vessel Ka’imimoana during the Tropical Ocean tRoposphere Exchange of Reactive halogen species and Oxygenated VOC (TORERO) 2012 field experiment.

Methodology: EC fluxes are defined as the time averaged covariance between instantaneous deviations from the mean of vertical wind velocities and a physical and/or chemical parameter of interest. This is a well-established and widely used technique for studying surface-air exchange. The Fast-LED-CE-DOAS instrument was operated at ~2Hz and proved to be a “white noise” sensor suitable for EC flux measurements (noise variance ~1200 pptv² over the flux bandpass).

Results/Conclusions: The diurnal variation of glyoxal in the MBL is measured for the first time, and reveals maxima at sunrise (NH: 35±5 pptv; SH: 47±7 pptv) and minima at dusk (NH: 27±5 pptv; SH: 35±8 pptv). Ours are the first EC flux measurements of glyoxal. In both hemispheres, the daytime flux was directed from the atmosphere into the ocean. The maximum fluxes are seen at night (SH: 5.3(±3.3)x10⁻² pptv m s⁻¹; NH: 2.3(±3.1)x10⁻² pptv m s⁻¹) and minimum fluxes
during the daytime (SH: \(-1.6(\pm 3.8) \times 10^{-2}\) pptv m s\(^{-1}\); NH: \(-5.6(\pm 4.1) \times 10^{-2}\) pptv m s\(^{-1}\)). All nighttime fluxes in the SH are significantly greater than zero (SH nighttime average: \(4.7(\pm 1.8) \times 10^{-2}\) pptv m s\(^{-1}\)). By contrast the daytime fluxes are significantly negative (NH daytime average: \(-4.6(\pm 2.3) \times 10^{-2}\) pptv m s\(^{-1}\)). Positive EC fluxes of soluble glyoxal over oceans indicate the presence of an ocean surface organic microlayer (SML), and locate a glyoxal source within the SML. The ocean sink for glyoxal raises questions about the origin of glyoxal, and possibly other oxygenated hydrocarbons over the daytime tropical oceans that warrant further investigation.

5 Abstract

Here we present first measurements of Eddy Covariance (EC) fluxes of glyoxal, the smallest \(\alpha\)-dicarbonyl product of hydrocarbon oxidation, and a precursor for secondary organic aerosol (SOA). The unique physical and chemical properties of glyoxal, i.e., high solubility in water (Henry’s Law constant, \(H = 4.2 \times 10^5\) M atm\(^{-1}\)) and short atmospheric lifetime (~2 hrs at solar noon) make it a unique indicator species for organic carbon oxidation in the marine atmosphere. Previous reports of elevated glyoxal over oceans remain unexplained by atmospheric models. The University of Colorado has developed a Fast Light Emitting Diode Cavity Enhanced Differential Optical Absorption Spectroscopy (Fast LED-CE-DOAS) instrument to measure diurnal variations and EC fluxes of glyoxal that inform about its unknown sources. The fast sensor is described, and first results are presented from a cruise deployment over the Eastern tropical Pacific Ocean (20N to 10S; 133W to 85W) as part of the Tropical Ocean Troposphere Exchange of Reactive Halogens and OVOC (TORERO) field experiment (January to March 2012). Fast LED-CE-DOAS consists of a multispectral sensor to selectively
measure glyoxal (CHOCHO), nitrogen dioxide (NO₂), oxygen dimers (O₄) and water vapor (H₂O) simultaneously, with ~2 Hz time resolution, and a precision of 34 pptv Hz⁻⁰·⁵ for glyoxal. The instrument is demonstrated to be a ‘white-noise’ sensor suitable for EC flux measurements; further, highly sensitive and inherently calibrated glyoxal measurements are obtained from temporal averaging of data. The campaign averaged mixing ratio in the Southern Hemisphere (SH) is found to be 43±9 pptv glyoxal, and is higher than in the Northern Hemisphere (NH: 32±6 pptv; error reflects variability over multiple days). The diurnal variation of glyoxal in the MBL is measured for the first time, and reveals maxima at sunrise (NH: 35±5 pptv; SH: 47±7 pptv) and minima at dusk (NH: 27±5 pptv; SH: 35±8 pptv). Ours are the first EC flux measurements of glyoxal. In both hemispheres, the daytime flux was directed from the atmosphere into the ocean. After sunset the ocean was a source for glyoxal to the atmosphere (positive flux) in the SH; this primary ocean source was operative throughout the night. In the NH, the nighttime flux was positive only shortly after sunset, and negative during most of the night. Positive EC fluxes of soluble glyoxal over oceans indicate the presence of an ocean surface organic microlayer (SML), and locate a glyoxal source within the SML. The ocean sink for glyoxal raises questions about the origin of glyoxal, and possibly other oxygenated hydrocarbons over the daytime tropical oceans that warrant further investigation.

5.1 Introduction

Eddy covariance (EC) fluxes are a well-established and widely used technique to measure surface-atmosphere gas exchange. The EC flux method provides insight into sources and sinks of atmospheric parameters (physical, chemical state variables) suitable to test our process level understanding (Baldocchi et al., 2001). EC fluxes are defined as the time average covariance
between deviations from the mean of vertical wind velocity and deviations from the mean in the
parameter of interest, e.g. here, the mixing ratio of a trace gas:

\[ \bar{F} = \bar{w}'c' = \int_0^{f_n} C_{wc}(f) \, df \]  \hspace{1cm} (1)

where \( F \) is the flux, \( w' \) is the vertical wind velocity component, \( c' \) is the mixing ratio of the trace
gas component, the prime denotes the instantaneous deviation from the mean, \( f_n \) is the Nyquist
frequency of the measurements, and \( C_{wc} \) is the cospectrum.

A requirement of the EC flux technique is that measurements of both vertical wind
velocities and the trace gas of interest are performed at high sampling frequencies, \( f \), (typically a
minimum of several Hz), sufficient to capture a majority of those frequencies that contribute to
the overall flux. Balancing this requirement with preserving sufficient sensitivity in the
measurements is one of the major challenges with developing chemical sensors suitable for EC
flux applications. For mobile deployments, a portable and robust sensor is needed. Further,
additional measurements of platform motion need to be performed, and corrections on the wind
velocity data are needed. A description of the system deployed in this study and the method of
correction is described by Fairall et al., (1997) and Edson et al., (1998), respectively. A particular
challenge arises for EC flux measurements of short-lived species in the marine boundary layer
(MBL), for which concentrations often do not exceed 10s to 100s of parts per trillion (1 pptv =
\( 10^{-12} \) volume mixing ratio (VMR) = 2.46x10\(^7\) molec cm\(^{-3}\) at 298K temperature and 1013 mbar
pressure). As a result of these challenges, ship based EC flux measurements have today only
been reported for the seven molecules: dimethyl sulfide (DMS) (Fairall et al., 2000; McGillis et al., 2001; McGillis et al., 2004; Kondo and Tsukamoto
2007; Miller et al., 2009; Taddei et al., 2009; Miller et al., 2010; Norman et al., 2012), Ozone (O₃) (Bariteau et al., 2010; Helmig et al., 2012), carbon monoxide (CO) (Blomquist et al., 2012), acetone (Marandino et al., 2005; Taddei et al., 2009; Yang et al., 2014), acetaldehyde (Yang et al., 2014), and methanol (Yang et al., 2013). Table 5.1 lists typical concentrations for these molecules in the MBL, and compares them with glyoxal in terms of their Henry’s Law constants (K_H, at 298K), and typical atmospheric lifetimes. Notably, glyoxal is the molecule with the shortest atmospheric lifetime, and is present in the lowest abundance. This short lifetime limits the spatial scale over which glyoxal can be transported in the atmosphere to few 10 km. Further, glyoxal is the most soluble molecule in Table 5.1, i.e. its Henry’s Law constant is 2000, 13860, and 30,000 times larger than that of the other oxygenated hydrocarbons (OVOC) methanol, acetone and acetaldehyde, respectively. The differences in the physical and chemical properties have fundamental implications for the air-sea exchange of glyoxal. For example, while it is possible to supersaturate the surface ocean with acetaldehyde (Zhou and Mopper 1990; Kieber et al., 1990; Millet et al., 2010; Yang et al., 2014) it is impossible to supersaturate the ocean with glyoxal (Sinreich et al., 2010). Studies measuring the waterside concentration of glyoxal have values in the nanomolar (nM) range (Zhou and Mopper (1990): 0.5-5 nM; van Pinxteren et al., (2013): ~4 nM), while based on K_{H,glyoxal} and an airside VMR of 50 pptv the expected seawater concentration should be ~20000 nM. The low glyoxal abundance in the MBL and unique properties make glyoxal a particularly interesting, yet challenging molecule to measure EC fluxes. To the best of our knowledge there are no previous attempts to measure EC fluxes of glyoxal.
## Table 5.1 Overview of Eddy Covariance flux measurements from ships.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>MBL Concentration (pptv)</th>
<th>k_H (M/atm)</th>
<th>Lifetime* (days)</th>
<th>Reference flux measurement in MBL</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>380-400 (x10^6)</td>
<td>0.035</td>
<td>&gt;3x10^5</td>
<td>Fairall et al. (2000)</td>
</tr>
<tr>
<td>CO</td>
<td>60-150 (x10^3)</td>
<td>1x10^-3</td>
<td>16</td>
<td>Blomquist et al. (2012)</td>
</tr>
<tr>
<td>Acetone</td>
<td>700-900</td>
<td>30.3</td>
<td>10</td>
<td>Yang et al. (2014)</td>
</tr>
<tr>
<td>O₃</td>
<td>10-30 (x10^3)</td>
<td>0.011</td>
<td>6</td>
<td>Bariteau et al. (2010)</td>
</tr>
<tr>
<td>Methanol</td>
<td>300-900</td>
<td>222</td>
<td>4</td>
<td>Marandino et al. (2005)</td>
</tr>
<tr>
<td>DMS</td>
<td>20-1500</td>
<td>0.485</td>
<td>0.8</td>
<td>Hubert et al. (2004)</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>200-300</td>
<td>14.1</td>
<td>0.2</td>
<td>Yang et al. (2014)</td>
</tr>
<tr>
<td>Glyoxal</td>
<td>25-80</td>
<td>4.2x10^5</td>
<td>9x10^-2</td>
<td>This work</td>
</tr>
</tbody>
</table>

* Lifetimes calculated against reaction with OH (assuming [OH] = 3x10^6 molec cm⁻³), and photolysis rates calculated for aerosol free, noon time at equator conditions.
Glyoxal, the smallest $\alpha$-dicarbonyl, is largely produced from the oxidation of Volatile Organic Compounds (VOCs) of both natural and anthropogenic origins (Myriokefalitakis et al., 2008; Stavrakou et al., 2009). It can also be directly emitted from sources such as biomass burning, fossil and biofuel combustion (Grosjean et al., 2001; Kean et al., 2001; Hays et al., 2002). Atmospheric removal of glyoxal is driven by photolysis, reaction with hydroxyl (OH) radicals, dry and wet deposition, and uptake to aerosols (Stavrakou et al., 2009). Additionally, glyoxal has been identified as an important Secondary Organic Aerosol (SOA) precursor (Liggio et al., 2005; Volkamer et al., 2007; Fu et al., 2008; Ervens and Volkamer 2010; Waxman et al., 2013). There are currently only few reports of glyoxal measurements over oceans (Zhou and Mopper 1990; Sinreich et al., 2010; Mahajan et al., 2014). These data show significant variability in the abundance of glyoxal (25-140 pptv), and confirm the widespread presence of glyoxal over oceans that had been suggested by satellites (Wittrock et al., 2006; Lerot et al., 2010). Satellites find vertical column densities (VCDs) of 2-4x10$^{14}$ molec cm$^{-2}$ over the Eastern Pacific ocean, comparable to and exceeding the upper range of glyoxal mixing ratios observed in the MBL (assuming all glyoxal was located inside a 1km high MBL). In-situ observations hold great potential to inform this apparent mismatch, but there are currently no previous in situ measurements of glyoxal reported over oceans. While many more (virtually all) measurements of glyoxal have been made over land (Vrekoussis et al., 2009), our understanding of the sources, sinks, and chemical processing of this molecule in continental air masses remains poor. Known continental sources only account for ~50% of the glyoxal budget based on VCDs from the SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) satellite (Stavrakou et al., 2009). Over the tropical ocean, atmospheric models predict virtually no glyoxal (Myriokefalitakis et al., 2008; Fu et al., 2008; Stavrakou et al., 2009); the presence of
this molecule in the remote MBL, thousands of kilometers from continental sources, is surprising and currently not understood (Sinreich et al., 2010).

The University of Colorado Fast Light Emitting Diode Cavity Enhanced Differential Optical Absorption Spectroscopy (Fast-LED-CE-DOAS) instrument was developed to obtain new insights about the sources of glyoxal in the remote MBL. The following sections describe the instrument, characterize performance, and report first results from a ship deployment over the tropical Eastern Pacific Ocean during the TORERO field experiment.

5.2 Experimental

The TORERO 2012 field campaign was an extensive effort to measure a variety of atmospheric parameters and trace gases over the Eastern Tropical Pacific Ocean from aircraft and ships. The ship-based portion of the campaign took place aboard the NOAA RV Ka’imimoana on a research cruise leaving from Honolulu, HI to Puntarenas, Costa Rica between January 25 – March 1 2012 (37 days at sea). Figure 5.1 shows a map with the ship track. Also shown are HYSPLIT 5-day back trajectories for noon and midnight (local time) along the ship track for each day.
Figure 5.1 Cruise track of the NOAA RV Ka'imimoana during the TORERO 2012 field experiment (red trace). The ship set sail from Honolulu, HI on January 25\textsuperscript{th}, 2012 and made final port in Puntarenas, Costa Rica on February 28\textsuperscript{th}, 2012 (35 days at sea). Shown along the ship track are HYSPLIT 5-day back trajectories (initiated at 00:00 and 12:00 LT every day; solid grey lines). The black circles along the trajectories are spaced by 1 day. Air sampled in the northern hemisphere had been over the ocean for at least 2 days prior to reaching the ship, and often did not experience land influences for at least 5 days. Air sampled in the southern hemisphere had been over the ocean for more than 5 days without obvious land/pollution influences. The location of the example glyoxal spectrum is marked by the green star.
5.2.1 Fast LED-CE-DOAS Instrument

Differential Optical Absorption Spectroscopy (DOAS) is a well-established technique that has been successfully used to measure a wide variety of atmospheric trace gases, including glyoxal (Platt 1994). While traditionally DOAS measurements were conducted in the open atmosphere (Platt et al., 1979), the advent of CEAS measurements coupled with DOAS retrievals provides particularly sensitive measurements (Thalman and Volkamer 2010; Ryerson et al., 2013). The multispectral nature of the light sources, such as light emitting diodes (LEDs), add selectivity to enable the simultaneous detection of multiple trace gases, while preserving excellent sensitivity found in other in situ cavity enhanced techniques (e.g., cavity ring down spectroscopy) (Thalman and Volkamer 2010; Ryerson et al., 2013). The Fast-LED-CE-DOAS instrument is a further development of the instrument described in Thalman and Volkamer, (2010). In brief, an LED light source is coupled to an optical cavity enclosed by two highly reflective mirrors, which allows light paths inside the cavity to be realized that are much longer (~2 x 10^4 times) than the length of the cavity itself. The light is collected from the backside of the mirror opposite the LED by an optical fiber and directed onto the spectrometer slit (see Figure 5.3).

For this system, a high-power LED (LedEngin) with peak emission near 465nm was used in conjunction with custom coated mirrors (Advanced Thin Films) with peak reflectivity between 440-470nm. The cavity had a base length of 86cm (74.45cm sample path length) and was coupled to a Princeton Instruments Acton SP2156 Czerny-Turner Imaging Spectrometer with a PIXIS 400B CCD detector (1340x400 pixels or 26.8x8 mm). The spectrometer utilized a custom 1000g mm\(^{-1}\) grating blazed at 250nm which covered the wavelength range from 390-530nm with ~0.75nm resolution (FWHM). The wavelength range observed simultaneously by our system...
was from 430 to 480nm and allowed for the selective detection of glyoxal, NO₂, H₂O, and O₄. Two spectral fitting windows were utilized during this study; one optimized for the retrieval of glyoxal and the other for O₄. The glyoxal fitting window covered the wavelength range from 433-460nm, the O₄ window covered the range 457-487nm, and trace gas reference cross sections for glyoxal (Volkamer et al., 2005), H₂O (measured with this instrument), O₄ (Thalman and Volkamer, 2013), and NO₂ (Vandaele et al., 1998) were simultaneously fitted in both windows. Figure 5.2 shows spectral fit results from the DOAS analysis of these trace gases: the left column shows fits from the glyoxal analysis window for a clean period (no NO₂ contamination from the ship stack) and the right column shows spectral fits from the O₄ window where some NO₂ contamination is present. The water measurement was used to monitor ambient conditions, NO₂ was used as a tracer for sampling the ship stack plume, and the O₄ measurement was used to correct the DOAS data for sampling time lag and inlet characterization (discussed in Sections 5.3.1.1 and 5.3.1.2).
Figure 5.2 Example spectra of molecules measured by the Fast LED-CE-DOAS instrument. The DOAS fits are shown for glyoxal (left panel, 433-460nm fit window), O₄ and NO₂ (right panel, 457-487nm), and water vapor (both windows). The RMS residual for each fit is shown in the top row. The spectra shown here were recorded on 2/14/2012 at ~06:20 LT (glyoxal), and 2/11/2012 at ~13:40 LT (O₄).
The primary measurement of the DOAS technique is Slant Column Density (SCD) which is the integrated concentration of the measured species along all light paths. It is easily converted using Lambert-Beer’s Law to concentration if the light path length within the cavity is known. Two different methods were utilized to experimentally determine the cavity light path: 1) comparison of measured \( O_4 \) SCDs and the calculated concentration of \( O_4 \) within the cavity; and 2) using the ratio of the signal measured in two different pure gases whose Rayleigh scattering cross-sections are well known (Thalman and Volkamer, 2010). For this study, method 2 was employed and \( N_2 \) and \( He \) were used for this process (referred to as mirror curves from this point forward). Mirror curves were taken on a near daily basis which enabled the continuous monitoring of the cavity performance. Additionally, an inherent consistency check exists from the comparison of \( O_4 \) SCD measurements with those calculated from the mirror curve, the Rayleigh scattering cross section of air, and known temperature and pressure (Thalman and Volkamer, 2010). For the duration of the cruise, the peak mirror reflectivity was maintained between 99.9967% – 99.9973%, translating into routine cavity path lengths of 18-20km at 455nm.

In order to accelerate the data acquisition of the instrument to rates sufficient to accommodate EC fluxes, software was developed to simultaneously eliminate shutter movements and decrease readout time (through binning of CCD rows). The final instrument measurement frequency of ~2Hz strikes a balance between time resolution, and the duty cycle dedicated to collecting photons (as compared to read-out time of the CCD). The measurement detection limit with CE-DOAS measurements is typically photon shot-noise limited. We assess the instrument performance by investigating the root mean square (RMS) of the optical density of the residual remaining after the non-linear least squares fitting routine, and comparing it with
the theoretical photon shot noise (Coburn et al., 2011). Individual spectra were summed, and analyzed to improve the signal to noise ratio of the measurements. In an ideal instrument (i.e., completely limited by photo shot noise), the RMS of the fitting routine should follow photon counting statistics, where the theoretical RMS is inversely proportional to the square root of the number of photons collected.

\[
\text{RMS} \equiv \frac{1}{\sqrt{N}} \quad \text{where N is the number of photons collected} \tag{2}
\]

The measured RMS of the Fast LED-CE-DOAS instrument field deployment is compared to the theoretical RMS, and plotted as a function of the number of photons in Figure 5.3. The grey points are raw data at different levels of averaging and the colored squares represent the median values for each set: light blue is the raw 400ms data; dark blue is the sum of 5 spectra (~2s); purple is the sum of 20 spectra (~8s); red is the sum of 100 spectra (~40s); and the green is the sum of 1000 spectra (~8min). As can be seen, the RMS during this campaign fairly closely follows counting statistics for the measured spectra, as well as for different levels of binning. Shown on the right axis is the corresponding 1σ precision for glyoxal.

Appropriate quality assurance filters were applied to the raw CE-DOAS measurements prior to calculating glyoxal fluxes in order to exclude the use of any stack contamination, or otherwise questionable data. These filters removed periods of elevated \( \text{NO}_2 \) (contaminated by the ship stack plume: values greater than ~30 pptv), instability in the cavity (\( \text{O}_4 \) and internal cavity pressure measurements: acceptable pressure range 470-500 torr), and any spectra where the DOAS fitting resulted in RMS values larger than \( 5 \times 10^{-3} \).
Figure 5.3 Fast LED-CE-DOAS instrument performance: sensitivity. The residual noise (RMS) from the DOAS analysis is shown as a function of the number of photons corresponding to different averaging of the data. Grey points represent all data, while colored squares represent their respective mean value; black circles represent the theoretical RMS value determined from photon counting statistics (Coburn et al., 2011). The corresponding 1σ precision of glyoxal is plotted on the right axis.
Figure 5.4 Sketch of the Fast-LED-CE-DOAS setup and plumbing diagram for sampling during TORERO 2012. The N₂ “puff” system is indicated by the red box. Arrows show the direction of flow through various portions of the system. Photographs of this set up can be found in SI Figure 5.1.
5.2.2 TORERO Field Campaign

While the cruise started on 25 January 2012, only data taken 2-28 February 2012 will be considered for this study. The inlet for the cavity was mounted near the top of a 10m jackstaff (18 m above sea level, ASL) on the bow along with the inlets for the CO$_2$ flux system (Blomquist et al., 2014) and the in situ O$_3$ monitor, the sonic anemometer, and a motion system. The sampling line between the inlet and the instrument was ~65m long, and consisted of 3/8” ID coated aluminum tubing (Eaton SynFlex Type 1300). Additionally, an aerosol filter (changed every other day) was included after the inlet in order to prevent collection of sea salt in the majority of the sampling line and keep the air reaching the CE-DOAS system aerosol free. In order to maintain turbulent flow throughout the sampling line, a high flow pump maintained a flow of ~120 L min$^{-1}$ (Lenschow and Raupach 1991). From this main flow, a sample flow of ~9 L min$^{-1}$ was pulled through the cavity. These flow conditions resulted in an operating pressure inside the cavity of ~470-500 torr. This sub-ambient cavity pressure had to be actively addressed due to the sensitivity of optical cavities to fluctuations in pressure (which can de-align the mirrors). This was accomplished by the addition of stabilizing mounts for the mirrors to prevent movement during measurements. Figure 5.4 contains a plumbing diagram for the CE-DOAS system with arrows indicating the direction of air flow at various points along the sampling line. Two pumps and three Mass Flow Controllers (MFCs) were used in this system, the main flow through the sampling line was set at ~120 Lpm (controlled by MFC 1), the smaller sample flow through the cavity was set at ~9 Lpm (controlled by MFC 2), and the calibration gases for the Fast-LED-CE-DOAS system (used for monitoring cavity performance and determining cavity path length) were controlled by MFC 3. Photographs of the inlet, operational cavity, and
instrument rack containing all controlling electronics and spectrometer can be found in the SI Figure 5.1.

5.3 Results

5.3.1 Instrument Characterization

The following sections will describe the characterization of instrument properties pertinent to the measurement of fluxes via the EC technique.

5.3.1.1 Phase correction (N₂ pulse)

Wind sensor data was collected at 10Hz and in order to calculate the glyoxal fluxes the CE-DOAS measurements needed to be synchronized to this data. Rather than degrading the high resolution wind data, the CE-DOAS measurements were first interpolated from 2Hz to 10Hz. Since the trace gas is drawn through an inlet, there is a finite time difference between the instantaneous wind velocity measurements and those of the trace gas measurements. The flux system deployed here includes a method for experimentally determining this correction. The method is described in detail in Bariteau et al., (2010), so only a brief overview will be given here: the inlet is equipped with a fast-switching solenoid valve that injects pure nitrogen (supplied from a compressed air cylinder) into the sample flow. The valve is triggered for 3-5s at the beginning of every hour and the signal used as the trigger is recorded on the same timestamp as the anemometer. This data is used in conjunction with the accompanied drop in the trace gas signal (recorded on a different timestamp) to continuously monitor, and apply a correction to the time stamps prior to correlating both sensors. In the cavity, the measurement of O₄ was used for
this correction. Figure 5.5 contains a plot showing an example of the corrected O\textsubscript{4} signal overlaid on the nitrogen pulse signal (black trace), also shown is the fit of the step response function from method 1 (blue trace). The raw O\textsubscript{4} measurements are shown as black circles, and the interpolated data are the smaller red circles. Two methods were used to determine the phase correction based on the drop in the O\textsubscript{4} signal: 1) fitting of a first order step response function; 2) manual determination. Method 2 involved using O\textsubscript{4} data averages to identify when the N\textsubscript{2} was attenuating the O\textsubscript{4} signal, and from there determining the time at which the signal actually started dropping. Each analysis was performed on hourly data files; 626 files were analyzed and 50 of these files did not meet basic criteria to enable the pulse matching and so were rejected; the total number of usable hours for the flux data was 576. The average difference found between the two phase correction methods was 0.11s and the statistics associated with each analysis can be found in Table 5.2.
Table 5.2 The average phase correction and time response of the Fast-LED-CE-DOAS instrument (with standard deviation) for the two different methods employed in this study. See text for details.

<table>
<thead>
<tr>
<th></th>
<th>Method 1</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phase Correction (s)</td>
<td>Time Response (s)</td>
</tr>
<tr>
<td>Average</td>
<td>-2.54</td>
<td>0.28</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.23</td>
<td>0.16</td>
</tr>
</tbody>
</table>
5.3.1.2 Response Time

The pulse of nitrogen described in the previous section was also used to characterize the response time of the instrument. Introducing pure N\textsubscript{2} gas into the sample flow created a drop in the O\textsubscript{4} signal which was exploited to determine the response time of the instrument. The same two methods employed for the phase correction were used to calculate the instrument response time, which also gave an average difference between methods of 0.11s (statistics in Table 5.2). The instrument response is best determined experimentally, since high frequency flux attenuations can be caused by drawing the sample through the aerosol filter and long sampling line. Here, a low-pass filter function was chosen to represent the attenuation.

\[ H(f) = \frac{1}{1 + 2\pi f \tau_c} \text{ where } \tau_c \text{ is the instrument response time} \] (3)

Using the measured response time and the filter function, the instrument cut-off frequency (\(f_c\)) (the frequency at which the signal fluctuations drop by \(1/\sqrt{2}\)) was calculated, which corresponds to a drop in the signal to 0.5.

\[ f_c = \frac{1}{2\pi \tau_c} \] (4)

Using the average values of the response time of 0.283s and 0.282s for the first-order step response function and the manual determination, respectively, the calculated cut-off frequency is 0.56Hz. The application of the filter function for this system and the effect of the response time on the high frequency attenuation will be discussed in Section 5.3.3.1. These small differences in response time determined from the two methods add certainty about the correction of the flux measurements, as is discussed in more detail in Section 5.3.3.3.
Figure 5.5 Illustration of the phase-correction and time response using O₄. Individual CE-DOAS O₄ measurements (black dots) were interpolated onto the timestamp of the wind sensor (red dots). The N₂ pulse signal (solid black line) is visible as the drop in O₄ SCDs; the data has already been time-shifted to match this N₂ trigger. Also shown is the fit of a step response function (solid blue line) to the drop in the O₄ signal, from which an instrument time response can be determined.
5.3.1.3 Fast measurements

The variance spectra for glyoxal as a function of frequency for a 6 hour time period on 4 February 2012 from 15:00-21:00 UTC are shown in Figure 5.6. Data from both 10 min (purple) and 30 min (light blue) averaging periods are included in this plot.

The constant variance per Hz in the frequency range sampled by the instrument demonstrates that the Fast-LED-CE-DOAS system is indeed a white noise sensor. The horizontal black line represents the integral of the data in the frequency range $6 \times 10^{-4}$ to 1 Hz of ~1600 pptv$^2$. The solid vertical black line depicts the cut-off frequency of the instrument calculated from the average response time of the instrument, and the dashed vertical black lines represent ±1 standard deviation of this data.

5.3.2 Diurnal Cycle Measurements

Analyzing data created from summing 1000 spectra (~8min total integration time) enabled the measurement of a diurnal cycle of glyoxal between 2/2 – 2/28/2012. A time series of these measurements can be found in Figure 5.7 (top panel, left axis). Summing 1000 spectra allowed the realization of an average RMS value of $(1.0 \pm 0.1) \times 10^{-4}$, which translates into an average detection limit of 5.9 pptv; lower detection limits are possible from further averaging of the data. Included in Figure 5.7 are time traces for in situ O$_3$, solar zenith angle (SZA), NO$_2$, RH, ambient air temperature, ambient pressure, wind speed (from the sonic anemometer), and a flag indicating periods that were suitable for EC fluxes.
Figure 5.6 Fast LED-CE-DOAS instrument performance: frequency response for glyoxal. The glyoxal variance distribution per frequency bin for a 6 hour section of data on 4 February 2012 from 15:00-21:00 LT is shown for two averaging periods; 10 min (purple) and 30 min (light blue). The horizontal line represents the integral noise variance (~1600 ppt^2 Hz^-1) at frequencies measured by the instrument (green and grey shading). The solid vertical line represents the cutoff frequency determined from the average time response of the instrument; the dashed vertical lines represent the standard deviation of the time response data (grey background shading); higher frequencies were not measured by our setup (red shading). The Nyquist frequency of our setup is 1Hz.
Figure 5.7 Time series of glyoxal, O₃ and NO₂, as well as meteorological parameters. Grey shaded background represents times suitable for flux calculations; filters included NO₂, cavity pressure, wind direction, wind direction standard deviation, ship heading range, dGly/dt, and the horizontal glyoxal flux components. See text and SI Figure 5.2 for details.
5. 3 3 Ambient Flux Measurements

5.3.3.1 Signal Attenuation

As introduced in Section 5.3.1.2, a low-pass filter function was used to assess the high frequency flux attenuation due to the aerosol filter and sampling line length; Equation (1) can be re-written as Eq. (5):

\[ F_c = \overline{w^T c_m} = \int_0^{f_n} C_{wc}(f)[H(f)]^2 df = \int_0^{f_n} C_{wcm}(f) df \]  \hspace{1cm} (5)

where the subscript \( m \) represents the measured values, see Eq. 1 for other variables (note that the square root appears in the modified equation because only the signal of the trace gas is attenuated).

This relationship can then be used to assess the effect of attenuation on the overall flux by applying the filter function using the Kaimal model neutral-stability cospectrum (Kaimal et al., 1972), derived via Eqs. (6a) and (6b)

\[ \frac{fC_{wc}(f)}{F_c} = \frac{11n}{(1+13.3n)^{1.75}}, \quad n \leq 1.0 \]  \hspace{1cm} (6a)

\[ \frac{fC_{wc}(f)}{F_c} = \frac{11n}{(1+3.8n)^{2.4}}, \quad n \geq 1.0 \]  \hspace{1cm} (6b)

where the surface normalized frequency \( n = f z/\overline{u_r} \), \( z \) is the measurement height, and \( \overline{u_r} \) is the average relative wind speed. Using the calculated “true” and “measured” Kaimal cospectra, an attenuation ratio (\( R_{attn} \)) was derived.

\[ R_{attn}(z, \overline{u_r}) = \frac{\int_0^{f_n} C_{wc,K}(f, z, \overline{u_r})[H(f)]^2 df}{\int_0^{f_n} C_{wc,K}(f, z, \overline{u_r}) df} = \frac{\int_0^{f_n} C_{wcm,K}(f, z, \overline{u_r}) df}{\int_0^{f_n} C_{wc,K}(f, z, \overline{u_r}) df} = \frac{\int_0^{f_n} C_{wcm}(f, z, \overline{u_r}) df}{\int_0^{f_n} C_{wc}(f, z, \overline{u_r}) df} = \frac{F_{xm}}{F_x} \]  \hspace{1cm} (7)

where \( C_{wc,K} \) denotes the Kaimal cospectrum. For the calculation of this ratio, the average value of 0.282s for the instrument response time was used in the filter response function \( H(f) \). The
assessment of this data lead to an average attenuation ratio of 0.947, but never resulted in more than a 10% correction.

5.3.3.2 Flux filtering and results

Two different averaging periods for the glyoxal and vertical wind velocity data were used to determine the glyoxal flux: 10min and 30min, each segment containing a 50% overlap with following segments (11 segments per hour for 10min data, and 3 segments per hour for 30min data). Both averaging periods were used for the data derived from the two methods used for determining the phase correction, creating a total of 4 different flux data sets. Basic filtering criteria were applied to the averaged data segments to reject measurements from undesirable wind sectors (±60° relative wind direction and less than 10° standard deviation) and excessive ship maneuvers (maximum 25° heading range). Additional filtering criteria were applied to exclude outliers in the flux data through the assessment of the horizontal components of the glyoxal flux and the rate of change of glyoxal for each data segment. These filter values were chosen rather arbitrarily through a visual inspection of the data. No significant differences were found between the 4 data sets. Only results from the 30 min data determined from phase correction method 2 will be discussed. While individual flux measurements proved to be noisy, further binning of the 30 min flux measurements reveals trends in the data. Figure 5.8 contains example cospectra from this data, where the average of all data (green trace) scatters around zero. The examples of both positive (red trace) and negative (blue trace) cospectra were created by binning data: from 16 February 2012 21:15 – 2/17 00:45 LT (positive cospectrum); and from 2 February 2012 14:45 – 15:45 LT (negative cospectrum).
Figure 5.8 Cospectra of glyoxal and vertical wind from the flux calculations. The green trace represents the average of all cospectra that passed the quality assurance filters. The positive cospectrum (red) represents data averaged over a period of ~3.5 hours from 2/16/2012 21:15 to 2/17/2012 00:45 LT. The negative cospectrum (blue) represents a ~1 hour average on 2/2/2012 from 14:45-15:45 LT. The background color shading is identical to that in Figure 5.6.
5.3.3.3 Error Sources

The potential sources of error in this data are: 1) inaccuracies in determining the phase shift of the CE-DOAS measurements; 2) high frequency signal loss due to sampling line attenuation; and 3) uncertainty surrounding the noisy raw glyoxal measurements. Phase shift determination was deemed to be rather robust (through the comparison of the values determined using the two different methods), and any small inaccuracies would have negligible effect on the flux data (as assessed by comparing the results from the 4 methods previously mentioned). The high frequency flux loss due to signal attenuation was calculated as being, at most, 10% from the characterization in the instrument response time. Based on the cospectra (Fig. 5.8), it seems that glyoxal efficiently transferred through the sample lines and using the O₄ measurements to characterize sample transfer gives reasonably good agreement.

5.4 Discussion and Conclusions

The Fast-LED-CE-DOAS instrument is a multispectral sensor suitable to measure eddy covariance (EC) fluxes of glyoxal in the remote marine boundary layer (MBL). The measurement frequency of ~2Hz is sufficient to capture ~90% of the glyoxal flux. Inlet and sampling line attenuation was determined using the measured response time of the instrument (0.28±0.14 s, based on O₄ measurements) and accounts for a correction of <10%. Multiple gases are selectively detected simultaneously with glyoxal, and are exploited for our flux measurements as follows: NO₂ measurements are used to identify and filter data affected by stack contamination from the ship; H₂O measurements are used to measure ambient relative humidity; O₄ measurements are used an internal calibration gas to assure control over cavity alignment and mirror cleanliness (Thalman and Volkamer, 2010); further the pulsing of nitrogen
gas into the inlet is monitored from fast high signal-to-noise measurements of O₄ as part of individual spectra. O₄ is then used to characterize sample transfer time through the sampling line, and to synchronize the clocks of the chemical sensor with that of the wind sensor. Two different methods showed excellent control over the phase correction from O₄ measurements (average difference ~0.11±0.10 s), and give confidence in the EC flux measurements of glyoxal.

We have performed the first in situ measurements of glyoxal volume mixing ratios (VMRs) over oceans, and present first EC flux measurements of this soluble and short-lived molecule. Data from the first field deployment of the instrument is presented (35 days at sea). For the VMR data a persistent diurnal trend is observed: glyoxal mixing ratios peak just before dawn (1-hr average maximum in the NH: 43±2 pptv; minimum: 26±1 pptv; maximum SH: 61±1 pptv; minimum: 39±2 pptv), decrease during the day, and reach a minimum in the late evening just after dark (1-hr average maximum in the NH: 36±1 pptv; minimum: 16±1 pptv; maximum SH: 48±2 pptv; minimum: 24±1 pptv); followed by continuous increase through the night. The day-to-day variability in glyoxal is significantly larger than the accuracy of our instrument.

Major advantages with the Fast LED-CE-DOAS instrument to perform precise and accurate measurements of glyoxal are its inherent calibration from observing O₄ (see above) as well as direct calibration from knowledge of the absorption cross section of glyoxal (Volkamer et al., 2005). An earlier prototype version of our instrument has undergone detailed comparison with a large variety of state-of-the-art glyoxal measurement techniques (Thalman et al., 2014, manuscript in preparation⁴). In short, these comparisons revealed an excellent performance.

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compared to other measurement techniques and virtually negligible systematic bias over a wide variety of laboratory conditions. LED-CE-DOAS measurements were found to have the lowest limit of detection (LOD), showed the lowest amount of scatter during calibration experiments (highly precise), and are deemed accurate to within 1-2 pptv glyoxal, or 3.5% at high signal-to-noise, whichever is higher. This uncertainty is smaller than the typical multiday variability in glyoxal over oceans. Indeed, the error bars for multiday averaged data reflect this variability (standard deviation), rather than the instrument precision/accuracy. Despite this significant day-to-day variability, some trends can be seen if data is segregated as a function of time of day (local time) and geographical location. Figure 5.9 shows the VMR (panel a) and EC flux data (panel b) binned as a function of time of day. The data were further segregated for measurements collected in the Northern Hemisphere (NH, blue, 13N to 0) and Southern Hemisphere (SH, red, 0 to 10S); the global average of all data is shown as the grey trace. The number of data points within each bin is given in Table 5.3. For the flux data the error bars reflect the 90% confidence intervals of data within each bin. The shaded regions in the background indicate daytime (yellow) and nighttime (grey), and the average SZA (minimum indicates solar noon) is further shown for reference on the right axis.

The campaign averaged VMR (all data) was 36±9 pptv glyoxal. This is slightly less glyoxal compared to first measurements of glyoxal inside the MBL that found ~80 pptv over the Sargasso Sea (Zhou and Mopper, 1990). It is possible that some continental outflow of terrestrial glyoxal might have contributed to these elevated glyoxal VMR. Sinreich et al., (2010) reported ~63±21 pptv daytime glyoxal over the remote Eastern tropical Pacific Ocean, which is in marginal agreement with the campaign average VMR of our in situ measurements. Recent reports of on average ~25 pptv glyoxal, and no more than 40 pptv over a wide array of ocean
environments (Majajan et al., 2014) are slightly lower than our in situ observations. The comprehensive evidence generally supports the global presence of glyoxal over oceans as indicated by satellites (Wittrock et al., 2006; Lerot et al., 2010). Global glyoxal observations currently remain unexplained by atmospheric models (Myriofekalitis et al., 2008; Fu et al., 2008; Stavrakou et al, 2009), and retrievals remain uncertain (Lerot et al., 2010), and largely untested.
Figure 5.9 Diurnal variation in the glyoxal mixing ratio (panel a) and the glyoxal flux (panel b) in the Northern (blue) and Southern Hemisphere (red). Only data that qualifies for flux calculations has been averaged. Yellow shading indicates daytime, while grey indicates nighttime; the SZA is also shown on the right axis.
Global measurements of glyoxal from satellites agree that the Eastern Pacific Ocean is a
global hotspot for glyoxal over oceans (Wittrock et al., 2006; Lerot et al., 2010). In this context it
is interesting to note that measurements by Sinreich et al., (2010) in a similar season and in a
region that borders that probed here towards the East found average concentration of 63±21 pptv
that agree only marginally within error bounds with the in situ measurements presented in this
study. This raises questions about a longitudinal variation in glyoxal at tropical latitudes, which
had been observed by some satellites (Wittrock et al., 2006), but not by others (Lerot et al.,
2010). Our in-situ measurements in the NH probe a reasonably large longitude range and help
assess this question. We do not find any obvious variation of glyoxal as a function of longitude.
The average glyoxal VMR in the westerly NH cruise segment is 32±5 pptv (average over 7 days;
13N to 0 latitude; 133W to 105W longitude), compared to 31±8 pptv in the easterly NH cruise
segment (average over 7 days; 13N to 0 latitude; 105W to 80W longitude). Early reports from
SCIAMACHY found the annually averaged (year 2005) vertical column density (VCD) of
4.5x10^{14} and 6.0x10^{14} molec cm^{-2} VCD over the western and eastern cruise segments in the NH;
and 3.5x10^{14} molec cm^{-2} over the SH cruise segment (Wittrock et al., 2006). Interestingly,
measurements from the Global Ozone Monitoring Experiment-2 (GOME-2) satellite (Lerot et al.
2010) report ~4.5 x10^{14} molec cm^{-2} in both regions of the NH, i.e., find no evidence for a
longitudinal variation in multi-year averaged data (2007 to 2009); and ~ 3x10^{14} molec cm^{-2} over
the SH cruise segment. The absence of a gradient over 3000 km distance in GOME2 data is
consistent with our data. However, it is interesting to note that the lower limit VCDs of both
satellite instruments correspond to ~183 pptv glyoxal in the NH, and ~120 pptv glyoxal in the
SH (assuming all glyoxal is located inside a 1km high MBL). Such high glyoxal is not confirmed
by our observations, nor by the measurements by Sinreich et al., (2010). We note that the
maximum concentration of 140 pptv reported by Sinreich et al., (2010) presents an extremely rare scenario that is not deemed representative of this dataset (see their Fig. 3c). In situ and ship MAX-DOAS column observations (Sinreich et al., 2010; Mahajan et al., 2014) agree that there is insufficient glyoxal inside the MBL to explain satellite VCDs; this is particularly true over the NH tropical Eastern Pacific Ocean (by a factor 2 to 6). Furthermore, our in-situ data show glyoxal is more abundant in the SH tropical MBL. By contrast, both satellites find ~25-42% lower glyoxal VCDs in the SH compared to the NH. The campaign average VMR during mornings in the SH (47±7 pptv glyoxal) corresponds to ~1.2x10^{14} molec cm^{-2} glyoxal VCD over the SH cruise segment, which is 2-3 times lower than long-time average VCD observed from space. The reason for this apparent mismatch in glyoxal amounts, and reversed hemispheric gradient is currently not understood. A particularly interesting development to investigate the diurnal variation of glyoxal over oceans consists in the TEMPO satellite mission (planned to launch in 2019), which will provide first time-resolved glyoxal VCD observations from geostationary orbit. Our diurnal profiles show further that glyoxal concentrations change by 30% over the course of the day. With the caveat that changes in MBL VMRs may not be indicative of VCD changes, this also implies that ~15% lower VCDs are expected at the time of the OMI satellite overpass (13:45 LT at equator). The differences between satellite and in-situ measurements are as of yet difficult to reconcile. Notably, a direct comparison between in-situ observations and column data is complicated due to the lack of vertical profile measurements of glyoxal at tropical latitudes, different averaging times, and spatial scales probed by in situ and column observations, as well as uncertain assumptions about a priori profiles, cloud screening, and other factors that influence air mass factor calculations. Some of these factors were further investigated from collocated measurements of glyoxal from aircraft during the TORERO project.
The fast in situ LED-CE-DOAS instrument holds great potential for future deployments on research aircraft.

The diurnal variations in our glyoxal flux measurements qualitatively reflect the variations in the VMRs seen in Figure 5.9. The maximum fluxes are seen at night (SH: $5.3(±3.3)\times10^{-2}$ pptv m s$^{-1}$; NH: $2.3(±3.1)\times10^{-2}$ pptv m s$^{-1}$) and minimum fluxes during the daytime (SH: $-1.6(±3.8)\times10^{-2}$ pptv m s$^{-1}$; NH: $-5.6(±4.1)\times10^{-2}$ pptv m s$^{-1}$). All nighttime fluxes in the SH are significantly greater than zero (SH nighttime average: $4.7(±1.8)\times10^{-2}$ pptv m s$^{-1}$). By contrast the daytime fluxes are significantly negative (NH daytime average: $-4.6(±2.3)\times10^{-2}$ pptv m s$^{-1}$). Assuming a dry deposition velocity of $1\times10^{-3}$ m s$^{-1}$ and using an average daytime mixing ratio of glyoxal in the NH of 30 pptv results in an estimated flux towards the ocean of $3\times10^{-2}$ pptv m s$^{-1}$, which is within the error of the measurements. Furthermore, the source of glyoxal from the ocean to the atmosphere is surprising, since glyoxal is so water soluble. Previous observations of positive fluxes of less soluble OVOCs, such as acetaldehyde, have been attributed to super-saturation of subsurface waters in acetaldehyde (Zhou and Mopper, 1990; Yang et al 2014). Glyoxal formation in subsurface waters cannot explain a positive flux to the atmosphere. This is because of the very large effective Henry’s Law coefficient ($K_H = 4.2\times10^5$ M atm$^{-1}$), which causes the equilibrium of glyoxal to be strongly shifted (10$^7$:1) towards the ocean (Volkamer et al., 2009b). The high $K_H$ value of glyoxal is the result of rapid hydration reactions; once hydrated, glyoxal exists primarily in mono- and di-hydrated forms (Ruiz-Montoya and Rodriguez-Mellado 1994; Ruiz-Montoya and Rodriguez-Mellado 1995) that give rise to the 3-5 orders of magnitude higher $K_H$ value of glyoxal compared to other OVOC (see Table 5.1). Ervens and Volkamer (2010) estimated the hydration rate of glyoxal to be 7 s$^{-1}$. This corresponds to a lifetime of glyoxal with respect to hydrolysis of ~140 ms. Unless glyoxal escapes from the
ocean within this time-frame, it will hydrate and is trapped in hydrated forms in the condensed phase. Using Eq. (8)

\[ D = \frac{l^2}{2t} \] (8)

where \( D \) is the diffusion coefficient (assuming a range (0.001-1)x10^{-5} cm^2 s^{-1}, (Finlayson-Pitts and Pitts 2000), \( l \) is distance, and \( t \) is time, we estimate that the time scale of hydration of glyoxal corresponds to a diffusive length scale of only \(~0.5-17\) \( \mu \)m. Such a short distance rules out glyoxal production in sub-surface waters as a source for the positive glyoxal flux. The observation of the positive glyoxal fluxes at night thus locates a glyoxal source inside the organic sea surface microlayer (SML).

The maximum average positive flux (net) that we observe in the SH at night (5.3x10^{-2} pptv m s^{-1}) corresponds to a primary glyoxal accumulation in a 500m high MBL of about \(~4\) pptv over a period of 12 hours. This corresponds to \(~30\%\) of the observed increase in the VMR of glyoxal that is actually being observed over the course of the night. It appears that an additional source of glyoxal is operational in addition to that in the SML that is not captured by the EC flux method. Moreover, the observed daytime negative flux of glyoxal indicates some unknown gas phase source of glyoxal, and likely other OVOCs in the MBL. While negative or neutral fluxes have also been observed for acetone and methanol (Marandino et al., 2005; Yang et al., 2013, 2014), both of these molecules live sufficiently long (acetone: 15 days; methanol: 13 days) that transport from terrestrial sources is likely to contribute to their abundance in the remote MBL. By contrast, any glyoxal lost to the ocean has been produced locally. The daytime lifetime of glyoxal (~2hrs) is too short to explain this source in terms of transport from terrestrial sources.
The widespread positive flux that we observe in both hemispheres at night (more prevalent in the SH) provides direct evidence that the SML is widespread (Wurl et al., 2011), and that oxidation reactions inside the SML are a source for OVOCs. Notably, a recent laboratory study observed the volatilization of several OVOCs (including glyoxal) when O$_3$ was flowed above a polyunsaturated fatty acid film on artificial saltwater in a flow reactor (Zhou et al., 2014). These results provide qualitative confirmation that the oxidation of the SML by O$_3$ can be a source for OVOCs to the gas-phase. However, the production rates found in this laboratory study are insufficient to explain any appreciable portion of the observed glyoxal over the tropical Pacific Ocean. The sources of glyoxal in the remote MBL deserve further investigation.
Table 5.3 Number of points in each time bin from Figure 5.9.

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<th>VMR Data</th>
<th>Flux Data</th>
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<td>300299</td>
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<td>06:00 – 10:00</td>
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<td>275280</td>
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Chapter VI

Summary

This work has presented the development of two different DOAS instruments: a Multi-Axis DOAS instrument, and a Cavity-Enhanced DOAS instrument; for the purpose of measuring halogen oxides and oxygenated volatile organic compounds (OVOCs) in the marine atmosphere. These classes of molecules play integral roles in atmospheric chemical cycles, and measurements of the species can lead to a better understanding of those roles and how they impact many environmentally relevant issues including: air and water quality; heavy metal contamination; ultra-violet radiation exposure; and climate change.

Each section of this thesis has worked towards these ends as follows:

Chapter 2: It was shown that in the development of field deployable MAX-DOAS instrumentation there are significant barriers that can limit the achievable signal to noise of the instrument as assessed through the root mean square (RMS) of the optical density of the residual remaining after the DOAS fitting routine. These barriers were systematically explored and it was determined that some could be overcome through careful design and control of various instrument parameters (such as instrument temperature and actively addressing detector non-linearity). Others, however, are most likely inherent to passive measurements and limited by our ability to accurately represent the atmospheric state, i.e., representation of Fraunhofer lines and/or molecular scattering processes. Limitations of the retrieval, such as inaccuracies in the
wavelength mapping of reference absorption cross-sections, could also not be ruled out, but as of this point in time might not be surmountable. By specifically addressing many of these challenges, the instrument presented was capable of achieving as good or better RMS values of other currently reported MAX-DOAS instrumentation and thus lower detection limits for atmospheric trace gases. This enabled the first detection of BrO, IO, and CHOCHO over the Gulf of Mexico, while also monitoring other trace gases such as HCHO, NO₂, and O₄.

Chapter 3: A case study from the measurements presented in Chapter 2 were further processed in order to assess the capability of ground-based MAX-DOAS instrumentation to measure trace gases located in the free troposphere and quantify those contributions the total column measurement. Additionally, factors influencing the DOAS retrieval of BrO from ground were systematically explored and their impacts on the conversion of MAX-DOAS differential slant column densities (dSCDs, the primary measurement quantity from DOAS) to vertical profiles were assessed. It was found that retrieval parameters for BrO can significantly impact the derived dSCDs, which will also affect the determination of the vertical distribution, and careful attention must be paid in the choice of these parameters. In this study, external information was used to help inform these choices. The inversion of the retrieved dSCDs for BrO, IO, and NO₂ were then utilized in an inversion that was modified in order to maximize the sensitivity of the measurements towards the free troposphere. Using this method, vertical profiles for BrO and IO were derived that were in good agreement with direct measurements performed by the CU airborne-MAX-DOAS (AMAX-DOAS) instrument performed over different regions of the tropical Pacific ocean.
Chapter 4: A diurnal steady-state box model was used to assess the impact of levels of BrO in the free troposphere that are currently higher than what is represented in global chemistry models on the oxidation of gaseous elemental mercury (GEM) to gaseous oxidized mercury (GOM). Also, the effects of additional reactions in the cycling of GOM recently proposed were assessed for the different environments represented by measured input parameters. Vertical profiles derived in Chapter 3 and measured by the CU-AMAX-DOAS instrument during the TORERO 2012 field experiment were assessed against profiles determined from two different global chemistry models (GEOS-Chem and WACCM) for corresponding measurement times. It was found that the lifetime of GEM in the free troposphere could decrease by factors of 2-3 based only on differences between measured vertical profiles of BrO and profiles from global chemistry models, due to the under prediction of BrO in the upper atmosphere by global models. Additional oxidation reactions of GOM would also have a significant effect on the rate of oxidation for the key intermediate species HgBr. These additional reactions also lead to a variety of different products that would, in turn, impact the recycling mercury between oxidized and reduced forms in the free troposphere.

Chapter 5: Here the technique of Light-Emitting Diode Cavity-Enhanced DOAS was extended to application of measuring Eddy Covariance (EC) fluxes of glyoxal in the marine boundary layer over the open ocean. An existing instrument was modified to be suitable for EC fluxes (increased data acquisition rate, stabilized to withstand high flows through the optical cavity), and deployed during the TORERO 2012 field experiment. During this study, the first diurnal cycles of glyoxal were measured over the open ocean and the first EC fluxes of glyoxal in any environment were measured. Considerable temporal and spatial trends were seen in both
the diurnal cycle and EC fluxes of glyoxal, which were not fully consistent with currently available reports from remote sensing instruments. The results of the EC fluxes present evidence of a surface organic microlayer (SML) capable of producing glyoxal (and possibly other OVOCs) over the open ocean, and such a source would have significant impacts on our understanding of global budget for glyoxal. These results also provide further evidence of a photo-chemically controlled gas phase production mechanism for glyoxal in this environment.
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APPENDIX A

SUPPLEMENTARY MATERIAL FROM CHAPTERS 1-5

**SI Table 3.1** Radiative transfer grid used for the free tropospheric inversion.

<table>
<thead>
<tr>
<th>Layer</th>
<th>BrO, NO₂</th>
<th>IO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0 - 0.5</td>
<td>0 - 0.5</td>
</tr>
<tr>
<td>2</td>
<td>0.5 – 1.0</td>
<td>0.5 – 1.0</td>
</tr>
<tr>
<td>3</td>
<td>1.0 - 1.5</td>
<td>1.0 - 1.5</td>
</tr>
<tr>
<td>4</td>
<td>1.5 – 2.0</td>
<td>1.5 – 2.0</td>
</tr>
<tr>
<td>5</td>
<td>2.0 – 5.0</td>
<td>2.0 – 5.0</td>
</tr>
<tr>
<td>6</td>
<td>5.0 – 10.0</td>
<td>5.0 – 10.0</td>
</tr>
<tr>
<td>7</td>
<td>10.0 – 15.0</td>
<td>10.0 – 15.0</td>
</tr>
<tr>
<td>8</td>
<td>15.0 – 20.0</td>
<td>15.0 – 20.0</td>
</tr>
<tr>
<td>9</td>
<td>20.0 – 25.0</td>
<td>20.0 – 25.0</td>
</tr>
<tr>
<td>10</td>
<td>25.0 – 30.0</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>30.0 – 35.0</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>35.0 – 40.0</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>40.0 – 45.0</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>45.0 – 50.0</td>
<td></td>
</tr>
</tbody>
</table>
SI Figure 3.1 Results from the aerosol profile determination using O$_4$ dSCDs (top panels, a-d) and comparison of forward calculated BrO dSCDs using three different profiles (bottom panels, e-f).
SI Figure 3.2 Comparison of O₃ (panels a and b), HCHO (panels c and d), and BrO (panels e and f) dSCDs for different BrO window analysis settings. O₃ and HCHO dSCDs are also compared to WACCM model outputs.
SI Figure 3.3 Comparison of O₄ (panels a and b) and BrO (panels c and d) dSCDs using different O₄ reference cross sections.
SI Figure 3.4 Diurnal variation in the WACCM output for the BrO vertical distribution (panel a), and the corresponding stratospheric and tropospheric VCDs (panel b).
**SI Figure 3.5** Comparison of the a posteriori derived and measured IO (panel a) and NO₂ (panel b) dSCDs, along with the corresponding RMS differences between the individual measurement scans (panel c).
SI Figure 3.6 Results of the NO\textsubscript{2} inversion for 1 elevation angle scan at \sim 45° SZA. Panel a is in units of concentration, panel b is in units of VMR, and panel c is the averaging kernels for the first a priori profile inversion. Black traces show the a priori profile, colored traces represent a posteriori profiles for: 1) WACCM case (red, solid); 2) WACCM*1.4 (green, dashed); 3) constant tropospheric VMR (blue, dotted).
SI Figure 3.7 Comparison of the diurnal variation of the BrO reference SCD between the a posteriori profiles (grey) and WACCM output (black).
SI Figure 5.1 Photographs of the instrument set up aboard the RV Ka'imimoana during the TORERO 2012 field experiment. Left panel shows the instrument inlets, sonic anemometer, and motion system mounted to the jackstaff on the bow of the ship. Middle panel shows the Fast-LED-CE-DOAS instrument, and the right panel shows the instrument rack containing all of the controlling electronics for the cavity as well as the spectrometer/detector.
**SI Figure 5.2** Time series of parameters used to filter fluxes. Grey shaded background represents times suitable for flux calculations, determined only by these parameters. Each data point represents a 30min average with 50% overlap to adjacent points. Horizontal red lines indicate the limits for the different filters.