Title
MAX-DOAS measurements of aerosol, HCHO, and NO2 over Los Angeles from an elevated mountaintop site.

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Publication Date
2016

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MAX-DOAS measurements of aerosol, HCHO, and NO$_2$ over Los Angeles from an elevated mountaintop site.

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Atmospheric and Oceanic Sciences

by

Ross Cheung

2016
ABSTRACT OF THE DISSERTATION

MAX-DOAS measurements of aerosol, HCHO, and NO₂ over Los Angeles from an elevated mountaintop site.

by

Ross Cheung

Doctor of Philosophy in Atmospheric and Oceanic Sciences

University of California, Los Angeles, 2016

Professor Jochen Peter Stutz, Chair

Differential Optical Absorption Spectroscopy (DOAS) has become a popular technique for measuring atmospheric trace gases using UV/Vis narrow-band absorption features along a light path through the atmosphere. The UCLA Multi-Axis DOAS instrument (MAX-DOAS) is a ground-based spectrometer currently located at Mt. Wilson, California (1700 meters above sea level) that measures solar scattered light at various viewing elevation angles. Since May of 2010, it has been taking regular measurements of atmospheric pollutants in the boundary layer of the atmosphere in and above the Los Angeles Basin.
This thesis presents the experimental setup and spectral retrievals, as well as results of our observations of measurements of NO₂ and HCHO from Mt. Wilson. Radiative transfer modeling efforts of the deployment at Mt. Wilson will be presented, as well as our efforts to model and account for the effects of clouds and aerosols on MAX-DOAS measurements. Because of the unique challenges presented by aerosols in the ultraviolet and visible light region in a polluted urban boundary layer, new techniques were developed to account for and quantify these effects.

Observations of path-integrated NO₂ and HCHO, some of the primary precursors to ozone formation in the lower troposphere, as well as aerosol extinctions using the UCLA MAX-DOAS will be presented, and the advantages of a mountaintop measurement strategy will be discussed in light of the amount of vertical information that can be retrieved from this approach. The techniques developed to improve the optimal estimation of vertical aerosol extinction profiles and trace gas concentration profiles will be discussed. Finally, an application of these observations uses the ratio of HCHO/NO₂ to study the dependency of ozone formation on nitrogen oxides and VOCs will be presented.
The dissertation of Ross Cheung is approved.

Qinbin Li

Kuo-Nan Liou

Stanley Sander

Jochen Peter Stutz, Committee Chair

University of California, Los Angeles

2016
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ACKNOWLEDGEMENTS

I would like to acknowledge my advisor, Dr. Jochen Stutz, and my committee members, Professor Qinbin Li, Professor Kuo-Nan Liou, and Dr. Stanley Sander.

I’d like to thank Professor Yuk Yung for his continued mentorship over the years, as well as the following members of my research group, both for their help in the preparation and revision of this thesis, as well as their continued support throughout my dissertation research: Fedele Colosimo, Olga Pikelnaya, Nathaniel Brockaway, James Festa, Dejian Fu, Katja Grossman, Steve Hurlock, Max Spolaor, Catalina Tsai, Katie Tuite, and Clare Wong.
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1. Introduction

1.1 Motivation

Despite great progress in combating air pollution during the past few decades through technological innovations and strong environmental legislation, the Los Angeles Basin is still facing significant air quality problems. Great efforts have been made to monitor air pollution levels throughout the South Coast Air Basin.

For decades, air quality monitoring has relied on networks of ground-based observations using a variety of in-situ instruments to measure atmospheric composition, including ozone UV-absorption systems, chemiluminescence NO\textsubscript{x} monitors, particulate matter monitors, and other instruments. The limited number of ground-based stations, however, results in an incomplete spatial coverage, which is further complicated by the potential impact of local emissions. In addition, ground networks were primarily designed to monitor the exposure of humans to various air pollutants and as such are located close to the surface, ignoring air aloft. These observations can be complemented by aircraft, balloon, and satellite measurements, but observations from these more exotic platforms are sparse and expensive. Current surface monitoring networks were also not designed to monitor trace gas emissions, and new technology is needed to observe the concentration and emission of pollutants and greenhouse gases in the long term.

This thesis details efforts to develop a modern remote sensing system and optimal estimation techniques for improved long-term monitoring of the 4D distribution of ozone precursors and other air pollutants, as well as observations from Mt. Wilson, California,
of ozone precursor species, primarily NO$_2$ and HCHO, in the atmosphere above Los Angeles, California.

Remote sensing of atmospheric constituents has had a long history. Early methods concentrated on the measurement of stratospheric trace gases such as ozone (e.g. Molina and Rowland, 1974). In recent years, new developments in remote sensing technologies capable of observing tropospheric constituents have emerged, presenting exciting new opportunities for improving air quality monitoring. Well-known examples of satellite instruments include GOME, SCIAMACHY, and OMI (Platt and Stutz, 2008, and references therein). Ground-based remote sensing is likewise becoming more popular for determining air quality (Hönninger et al., 2003; Sinreich et al., 2005; Pikelnaya et al., 2007, Platt and Stutz, 2008).

In this thesis, I will present a novel approach, which combines the advantages of airborne/satellite and ground-based viewing geometries by performing measurements of air pollutants from a mountaintop. Since May 2010, the UCLA Multi-Axis Differential Optical Absorption Spectrometer (MAX-DOAS) system has been taking measurements at the California Laboratory for Atmospheric Remote Sensing (CLARS) at Mt. Wilson, California, overlooking the Los Angeles basin.

In the following introduction, a brief review of air quality issues in Los Angeles, as well as of VOC/NO$_x$ chemistry, will be given.
1.2. Background of Air Quality issues in LA

In the 1940s, a new type of air pollution was observed in the Los Angeles area. In contrast to the SO$_2$-based smog resulting from coal combustion, most famously observed during the post-industrial revolution in London, this new type of air pollution seemed to occur the most on warm days with plenty of sunlight. It was observed to cause eye-watering while having detrimental effects on agriculture in the Los Angeles basin.

In the 1950s, while investigating the effects of Los Angeles smog on plants, Arie J. Haagen-Smit identified ozone as the primary component of photochemical smog, and linked its formation to the products of automobile exhaust, correctly postulating that hydrocarbons and nitrogen oxides are involved (Haagen-Smit et al., 1952; Haagen-Smit et al., 1953). Ozone has since been identified as a significant public health issue (Lippman, 1993, Bascomb et al., 1996). Since it was initially observed in the Los Angeles area, high ozone levels have since been recorded in most large urban areas around the world. Our knowledge of the chemical processes that result in the accumulation of smog has greatly improved since the 1950s and our current understanding of the chemistry behind ozone formation will be reviewed briefly here.

Ozone is produced through a complex series of reactions that involve volatile organic compounds (VOCs) and a family of nitrogen oxides ($NO_x = NO + NO_2$), both of which can be present in urban and rural atmospheres. $O_3$ photolysis is possible from interactions with sufficiently high energy/low wavelength photons ($\nu < 319$ $nm$):

$$O_3 + h\nu \rightarrow O_2 + O$$  \hspace{1cm} (1.1)
NO\textsubscript{x} sources are varied, but combustion is a significant component of anthropogenic NO emissions, such as the combustion of fuels in automobile engines. Typically, the bulk of the direct production of NO\textsubscript{x} is in the form of NO (>90%). When both NO and NO\textsubscript{2} are in the atmosphere and in the presence of sunlight, they undergo a chemical cycle that is initiated through the photolysis of NO\textsubscript{2} (Blacet, 1952):

\[
NO\textsubscript{2} + h\nu (\nu < 424 \text{ nm}) \rightarrow NO + O \left( ^3P \right)
\]  

(1.2)

This excited oxygen atom reacts with ambient oxygen molecules to form an ozone molecule (Chapman, 1930):

\[
O + O_2 + M \rightarrow O_3
\]  

(1.3)

This reaction is the primary source of ozone in the atmosphere. Once created, the reaction between ozone and NO both serves as a removal mechanism of ozone and as a way to recycle NO\textsubscript{2}:

\[
O_3 + NO \rightarrow NO_2 + O_2
\]  

(1.4)

Rate coefficient calculations have indicated that due to the cyclical nature of equations 1.3 and 1.4, it is impossible for significant levels of ozone to accumulate in the atmosphere.

VOCs refer to the hydrocarbons and other organics that consists of vapor-phase atmospheric organics, excluding CO and CO\textsubscript{2}. VOCs are emitted by a variety of biogenic and anthropogenic sources, and are found at least in some capacity throughout the troposphere. Globally, non-methane VOCs are estimated to be ~10% anthropogenic and ~90% biogenic, although in urban environments anthropogenic sources are typically
significantly more common. The radicalization of VOCs, primarily through the hydroxyl radical OH, allows it along with NO\textsubscript{x} to initiate an oxidation sequence that results in the net accumulation of O\textsubscript{3} in the atmosphere.

It is understood that, although the most typical reaction pathway for atomic oxygen is to collide with O\textsubscript{2} and N\textsubscript{2}, occasionally the O\textsuperscript{(1D)} molecule produced in equation 1.1 collides with a water molecule and produces two OH radicals:

\begin{equation}
O\textsuperscript{(1D)} + H\textsubscript{2}O \rightarrow 2OH
\end{equation}

OH can also be produced through a number of reactions involving Hydrogen Peroxide (H\textsubscript{2}O\textsubscript{2}), nitrous acid (HONO), and formaldehyde (HCHO). The first two compounds are simply photolyzed:

\begin{equation}
H\textsubscript{2}O\textsubscript{2} + hv (\nu < 370 \text{ nm}) \rightarrow 2OH
\end{equation}

\begin{equation}
HONO + hv (\nu < 370 \text{ nm}) \rightarrow NO + OH
\end{equation}

Meanwhile, HCHO undergoes a series of chain reactions:

\begin{equation}
HCHO + hv (\nu < 370 \text{ nm}) \rightarrow H + HCO
\end{equation}

\begin{equation}
H + O\textsubscript{2} \rightarrow HO\textsubscript{2}
\end{equation}

As HO\textsubscript{2} and OH cycle between one another by reacting with NO\textsubscript{x}, they are collectively grouped together as “HO\textsubscript{x}”:

\begin{equation}
HO\textsubscript{2} + NO \rightarrow OH + NO\textsubscript{2}
\end{equation}

The aforementioned reaction of OH with CO or hydrocarbons is typically necessary to initiate the alternate pathways by which ozone is able to accumulate in the troposphere:
\[ RH + OH \xrightarrow{O_2} RO_2 + H_2O \] (1.11)

\[ CO + OH \xrightarrow{O_2} HO_2 + CO_2 \] (1.12)

The RO₂ peroxy compound can then react with NO, converting it to NO₂, and resulting in the formation of ozone through reaction (1.3):

\[ RO_2 + NO \xrightarrow{O_2} R'CHO + HO_2 + NO_2 \] (1.13)

Reactions (1.10) and (1.13) result in the conversion of NO to NO₂, and also act as the dominant reaction pathway for the recycling of OH in the atmosphere, with (1.13) dominating in situations where NOₓ levels are greater than 0.5 ppb, typical in urban and polluted rural sites in the United States and Europe (Sillman, 1999). As a result, the sum of OH, HO₂, and RO₂, collectively termed the “odd hydrogen radicals” often controls the rate of ozone production (Kleinman, 1986). Figure 1.1 is a diagram that shows this entire cycle.
Figure 1.1. VOC-NO\textsubscript{x} photochemical cycle that results in net ozone production. VOCs and NO\textsubscript{x} compete for OH radical. When NO\textsubscript{x} is dominant, its reaction with OH is the primary termination mechanism. Similarly, when VOCs are dominant, it controls the reaction with OH.

1.3. Relationship between NO\textsubscript{x}, VOCs, and Ozone

An important consideration in many environments in which photochemical production of ozone occurs is the relationship between NO\textsubscript{x}, VOCs, and O\textsubscript{3}. A well-
known plot (Figure 1.2) shows the relationship between ozone production, concentration of VOCs, and concentration of NO\textsubscript{x}. The line representing the maximum rate of ozone formation, directly proportional to both the NO\textsubscript{x} and VOC emissions, represents the dividing line between two chemical regimes, the NO\textsubscript{x}-sensitive and VOC-sensitive regime.

In the NO\textsubscript{x}-sensitive regime, also called the VOC-saturated regime or the NO\textsubscript{x}-limited regime, when NO\textsubscript{x} is low, the rate of ozone formation increases with NO\textsubscript{x} in a near-linear fashion. There is generally not enough NO to convert all of the HO\textsubscript{2} into OH, and radical-radical reactions will lead to the termination of the cycle, limiting ozone production. As more NO\textsubscript{x} is added to the system, eventually a maximum of ozone production is reached, where peak OH-cycling occurs. On the other side of this ridge is the VOC-sensitive regime, also known as the VOC-limited or NO\textsubscript{x}-saturated regime, ozone production increases with increasing VOC concentration, and decreases with increasing NO\textsubscript{x} concentrations, as increasing levels of NO\textsubscript{x} result in termination due to OH+NO\textsubscript{2}, rather than OH propagation of the reaction through OH and VOCs. The net result is a reduction in ozone production as NO\textsubscript{x} emissions continue to increase.
Figure 1.2. Modeled ozone concentration in parts per billion, as a function of NO\textsubscript{x} and hydrocarbon emissions. The dots are the emission rates of NO\textsubscript{x} and hydrocarbons from individual simulations. Figure taken from Sillman et. al. (1999).

This highly nonlinear relationship between NO\textsubscript{x}, VOCs, and ozone production complicates policy efforts to combat ozone accumulation in polluted regions. Reducing ambient ozone requires reduction in its precursors, NO\textsubscript{x} and VOCs. However, reducing NO\textsubscript{x} will only result in a reduction of ozone in a NO\textsubscript{x}-sensitive atmosphere. It is even possible to increase ozone production temporarily, if for example NO\textsubscript{x} levels are reduced in a VOC-limited atmosphere.

Though the “ozone isopleth” is often quite complex, and even terms like VOC-sensitive and NO\textsubscript{x}-sensitive are not always clearly defined, the ratio of VOCs-NO\textsubscript{x} is
often used as an indication of the sensitivity, with a high VOC-NO\textsubscript{x} ratio indicating a VOC-limited/NO\textsubscript{x} sensitive regime, and a low VOC-NO\textsubscript{x} ratio indicating NO\textsubscript{x}-limited/VOC sensitive regime. For remote sensing purposes, it is often found that the VOC/NO\textsubscript{x} ratio is a useful marker for the chemical regime of a specific airshed. Although this is not universally true, a parcel of air close to sources of pollutants tends to be VOC-sensitive, as significant levels of NO\textsubscript{x} tends to be emitted close to combustion sources. As the parcel travels downwind, the comparatively shorter lifetime of NO\textsubscript{x} combined with the presence of outside sources of VOCs causes the parcel to evolve into a more NO\textsubscript{x}-sensitive regime. Moreover, in a freshly emitted plume the initial NO\textsubscript{x} supply typically exceeds the available radicals, but as the parcel ages the amount of radicals photochemically produced increases. It is for this reason that the time scales and transportation of ozone precursors is of considerable interest in formulating policy responses to photochemical smog, and why the peak ozone concentrations are often noticed kilometers downwind of major urban centers. This shift in the sensitivity of a plume as it travels downwind has been noticed in a number of 3D models (Milford et. al., 1989, 1994, Sillman et al., 1990).

1.4. Weekend effect, history, chemistry and explanations

One well-documented phenomenon is the difference in ozone and ozone precursors between weekdays and weekends. In many urban environments, higher ozone concentrations have been measured on weekends instead of weekdays, despite the expected greater emissions of primary pollutants during the weekdays due to enhanced
vehicular traffic from the daily commute, as well as commercial operations and trucking patterns. The weekend effect has been observed in locations as diverse as the New York/New Jersey region (Cleveland et. al., 1974), in the Baltimore-Washing DC area, (Lebron, 1975), on the west coast of the United States (Lonnenman et. al., 1974; Levitt and Chock, 1976, Elkus and Wilson, 1977; Altshuler et. al., 1995; Austin and Tran, 1999), in St. Louis (Karl, 1978), in Vancouver, Canada (Pryor and Steyn, 1995), and in Hebei, China (Wang et. al., 2014). It has been shown to be observed primarily in urban areas, with rural areas or areas further downwind often shown to have no weekend effect, or even a reverse-weekend effect (Murphy et. al., 2007a and 2007b).

Since it was first observed, the weekend effect has been shown to have become more pronounced, increasing in strength throughout the 1990s, despite an overall reduction in observed ozone and precursor concentrations during this time period (Fujita et al., 2003), though there is some evidence that the strength of the weekend effect has begun to decline (Wolff et. al., 2015).

In 2003 the California Air Resource Board listed seven commonly proposed explanations for the weekend effect (California Air Resources Board, 2003), which are listed as follows:

1. *Differences in the ratio of VOCs to NOx between weekdays and weekends* – It has been observed that the VOC/NOx ratio drastically changes between weekdays and weekends. In urban areas, where this effect is primarily observed, the local air is typically more VOC-limited, due to the higher emissions of NOx from combustion of automobiles and local industries, while
air downwind comparatively has a lower VOC/NO\textsubscript{x} ratio. It has been demonstrated that commercial diesel vehicles tend to be richer in NO\textsubscript{2} (Marr et. al., 2002a and 2002b, Harley et al., 2005). It has been observed that reduced NO\textsubscript{x} levels on weekends in VOC-limited areas (i.e. urban environments with increased vehicle and industrial combustion, and less influence from biogenic VOC sources) lead to more rapid ozone production. This explanation has been found to be well supported by various studies, for example Blanchard and Fairley (2001), Marr et al. (2002b), and Chinkin et. al. (2003).

2. \textit{NO\textsubscript{x} timing} - Traffic patterns on weekends tend to shift towards the middle of the day, as opposed to distinct morning and evening rush hours. This results in more NO\textsubscript{x} available during times of higher actinic flux, and therefore higher photochemical productivity (Marr et al., 2002b).

3. \textit{Increased weekend emissions} – It has been suggested that the total amount of VOCs and NO\textsubscript{x} emitted is actually greater on weekends than on weekdays. It is important to note that in cities such as Los Angeles in which this study is based, gasoline-powered vehicular traffic throughout the day has been found to be consistent weekday from weekend (Harley et al., 2005).

4. \textit{Aerosol and UV radiation} - Due to a reduced aerosol load due to differences in driving patterns, more solar radiation reaches Earth’s surface on the weekends, enhancing ozone production. Wang et al. (2014) found a higher aerosol content during weekdays than weekends in Beijing China, with an average 3.3% difference in weekday-weekend UV radiation.
5. *Ozone/quenching titration* - lower NO$_x$ emissions on weekends lead to reduced ozone destruction. This is related to the aforementioned NO$_x$ timing, as fresh NO emissions during the weekend morning commute inhibit the production of ozone as the actinic flux is strongest. In addition, OH production, necessary for the entire photochemical cycle that leads to ozone accumulation, is greatly enhanced by the presence of NO$_x$.

6. *Surface overnight carryover* - Heavier traffic on Friday and Saturday nights lead to more precursors available at the surface on Saturday and Sunday mornings, as the lack of sunlight prevents the destruction of many of the photochemically active precursors.

7. *Aloft overnight carryover* - Ozone and precursors persist above boundary layer, potentially enhanced by local meteorology with shifting directions of sea breeze at night. Surface and aloft overnight carryover are both related to NO$_x$ timing and titration, and during weekday morning commuter hours, freshly emitted NO$_x$ is often rich in NO, which titrates and prevents ozone accumulation.

1.5. **Outline of future chapters**

In Chapter 2, a discussion about the application of spectroscopy for atmospheric remote sensing will be made, and the measurement techniques used will be introduced, as well as a description of the details of the deployment of the UCLA MAX-DOAS on Mt. Wilson, California.
In Chapter 3 the DOAS analysis will be described, and the cloud classification schemes developed for CLARS will be detailed. The radiative transfer model VLIDORT, and sensitivity studies made to determine both the viability of an aerosol extinction profile optimal estimation, are described. Finally, these results and their implications towards a well-known disparity between the concentrations of modeled and observed O$_2$-O$_2$ collisional complexes will be discussed.

Chapter 4 introduces optimal estimation theory and describes our application of optimal estimation to the MAX-DOAS observations from CLARS, including some new techniques developed to retrieve aerosol optical properties. The advantages of information content from an elevated mountaintop site will be discussed, and results and validation of retrieved aerosol extinction and NO$_2$ vertical profiles will be presented.

Chapter 5 presents an analysis of chemical regime, both on daily/weekly time scales and on seasonal and multi-year time scales, using the ratio of HCHO to NO$_2$ as a measure of VOC/NO$_x$ sensitivity. The quantity of $L_N/Q$ will be introduced, and its implications for the weekend effect and long-term changes in Los Angeles in response to environmental legislation will be discussed.

Chapter 6 will give the conclusions and outlook of this study.
2. Instrumentation

2.1. DOAS method

One of the most common methods of remote sensing of atmospheric trace gases consists of measuring the molecular absorption in solar radiation crossing the atmosphere. Classically, these measurements were performed using direct sunlight, though more modern attempts have also used scattered or reflected sunlight. Most of the techniques make use of the Beer-Lambert Law, which can be expressed in the following form:

\[ I(\lambda) = I_0(\lambda)e^{-\int \sigma(\lambda)C \cdot dL} \]  \hspace{1cm} (2.1)

where \( I_0(\lambda) \) is the intensity of the light source at wavelength \( \lambda \), \( I(\lambda) \) is the intensity of the observed light, \( \sigma(\lambda) \) is the total absorption cross section, \( C \) is the concentration of an absorber, and \( L \) is the path length over which light propagates. Because each photon traverses the entire atmosphere and, in the boundary layer, encounters vastly different mediums, the absorption cross section and trace gas concentration must be integrated over the entire light path length. However, in certain circumstances, one can approximate the Beer-Lambert Law over a relatively uniform medium:

\[ I(\lambda) = I_0(\lambda)e^{-\sigma(\lambda)C \cdot L} \]  \hspace{1cm} (2.2)
The optical depth $\tau$ is a quantity related to the amount of light scattered or absorbed by the atmosphere, and can be expressed in terms of the path length of light through the atmosphere and the absorption and scattering cross section $\sigma(\lambda)$:

$$\tau = \int \sigma(\lambda) \, dL \quad \text{(2.3)}$$

Light transmitted through the atmosphere will be attenuated by scattering due to molecules or aerosols (called Rayleigh and Mie scattering, respectively), and by molecular absorption. However, in practice light transmitted through the atmosphere is attenuated not only by a variety of trace gas absorptions and scattering effects, but also light widening from turbulence, and from the instrument itself.

Differential Optical Absorption Spectroscopy (DOAS) was developed to address these issues by separating the effects of each of these factors to obtain the amount of absorption by a species of interest (Platt and Stutz, 2008). It is based on the principle that the broad-band and narrow-band spectral structures can be separated for certain trace gases that have narrow ($<3$ nm) absorption structures, whereas aerosol extinction, turbulence, and many trace gas absorptions show broad spectral characteristics.
**Figure 2.1.** Separation of broad-band and narrow-band absorptions using DOAS technique (Platt and Stutz, 2008).

If the absorption cross section for each trace gas $j$, can be separated into its constituent parts:

\[
\sigma_j(\lambda) = \sigma_{j0}(\lambda) + \sigma'_j(\lambda)
\]  

(2.4)

where $\sigma_{j0}(\lambda)$ is the broad-band spectral absorption and $\sigma'_j(\lambda)$ is the differential absorption cross section for narrow-band trace gases. The differential optical density $D'(\lambda)$ can be derived from the broad-band or background absorption:
\begin{equation}
D' (\lambda) = \ln \frac{I'_0 (\lambda)}{I (\lambda)} = L \cdot \sum_j \sigma_j' (\lambda) \cdot C_j
\end{equation}

(2.5)

where \( I (\lambda) \) and \( I'_0 (\lambda) \) are the intensity with and without the presence of the differential absorber. The right side of the equation signifies that the differential optical density can be expressed as a sum of the optical depths and concentrations of each individual absorber. This is done with a set of band-pass filters applied to the narrow-band absorption structures of each trace gas; from this the concentration of the trace gas can be derived:

\begin{equation}
C_j = \frac{D_j' (\lambda)}{\sigma_j' (\lambda) L}
\end{equation}

(2.6)

This technique allows for the simultaneous determination of the concentrations of multiple trace gases, over a short time period of minutes or less. Its ability to clearly identify and quantify individual trace gases using their unique differential absorption structures in the open atmosphere makes it an ideal method to measure compounds that are otherwise difficult to observe due to their high reactivity, uptake on sampling lines, or chemical interferences with other trace gases (Platt and Stutz, 2008).
DOAS has been successfully used in the past to measure a number of atmospheric trace species, including HCHO, NO$_2$, BrO, IO, OIO, ClO, I$_2$, and a number of aromatic hydrocarbons (Platt and Stutz, 2008). Since its first applications in the 1970s, DOAS has become a popular method for measuring tropospheric and stratospheric trace gases with narrow absorption features in the UV-vis wavelength rage (Noxon et al., 1975, Platt and Perner, 1983).

2.2. Multi-AXis DOAS (MAX-DOAS)

Among the many realizations of DOAS to measure tropospheric trace gases, Multi-Axis Differential Optical Absorption Spectroscopy (MAX-DOAS), a relatively new class of DOAS implementation, has been gaining popularity over the past ten years. Ground-based MAX-DOAS systems collect scattered sunlight from a number of different viewing angles, allowing the separation of absorptions in the lower troposphere from those aloft (Hönninger et al., 2004). MAX-DOAS systems can be built to be small and are relatively inexpensive. They are simple to operate, and can be automated for long-term operations (e.g. Pikelnaya, 2007). Because the light paths are in the open atmosphere and absorption cross sections are well-known physical constants, calibration is not needed to obtain path-averaged trace gas concentrations. As MAX-DOAS observation paths cross different altitudes of the atmosphere with varying lengths, they provide more information on vertical distributions of trace gases than common in situ measurements. However, this ability, and the conversion of MAX-DOAS observations to trace gas concentrations, introduces challenges as the measured quantity, the path-
integrated trace gas concentration, has to be first converted using complex radiative transfer calculations (Wagner et. al., 2004). MAX-DOAS thus trades the relative straightforward measurements and instrument design for a more complex data analysis.

**Figure 2.2.** Schematic of a typical MAX-DOAS setup, located at the surface, with a positive viewing elevation angle. MAX-DOAS collects scattered sunlight, both off-axis scans and a zenith scan.

MAX-DOAS instruments have been most commonly deployed on the ground looking upwards, but have also been deployed on ships, balloons, or aircrafts, looking in a combination of upwards, downwards, and limb viewing directions (Platt and Stutz, 2008). All instruments have a similar setup, consisting of a spectrometer/detector
combination, a telescope with the ability to aim at different elevation angles, and optics, typically quartz fibers, transferring light from the telescope into the spectrometer.

All MAX-DOAS deployment strategies share a common multi-step approach to analyze the scattered sunlight spectra. In the first step, a concentration of trace absorbers integrated along a slanted light path, commonly called a slant-column density (SCD) is derived. As mentioned previously, because the MAX-DOAS collects light across the entire extent of the atmosphere, the measured concentration \( c(s) \) is integrated over the entire light path \( s \), and so the measured quantity is called slant column density (SCD):

\[
SCD = \int_0^s c(s) \, ds \quad (2.7)
\]

The zenith SCD is usually subtracted in order to remove the effects of stratospheric absorptions and Fraunhofer lines, resulting in the Differential Slant Column Density (DSCD):

\[
DSCD = SCD_{\text{off-axis}} - SCD_{\text{zenith}} \quad (2.8)
\]

The retrieval of the concentration is not straightforward, as the light path through the atmosphere, as well as the various scattering effects due to molecules and aerosols
must be known. Radiative transfer calculations are therefore an important consideration for analyzing MAX-DOAS results.

Various methods have been described in literature to derive vertical profile information of aerosol and trace gases. One common approach relies on calculating two distinct quantities, the Air-Mass Factor (AMF) and the Box Air-Mass Factors (BAMFs). The AMF can be described as a proportionality factor between the SCD and the vertical column density of air from the surface to the top of the atmosphere (Noxon et. al., 1979):

\[ AMF = \frac{SCD}{VCD} \] (2.9)

Then the BAMF is a quantity that represents the contribution of trace gases at certain altitude levels, or vertical “boxes”, to the overall air-mass factor at given atmospheric conditions. These BAMFs are calculated for specific viewing angles of the instrument where each BAMF serves as a measure of the sensitivity at each viewing angle to absorbers at a specific altitude layer. The term “box” refers to discrete atmospheric intervals of height \( \Delta h_i \) at altitude \( h_i \).

The SCD can be expressed in terms of the concentration profile \( C(h_i) \) and BAMFs through the following equation:

\[ SCD = \sum_{i=0}^{n} C(h_i) \times BAMF(h_i) \times \Delta h_i \] (2.10)
Just as SCDs can have the zenith components subtracted to form DSCDs, BAMFs often have their zenith component subtracted to form Differential Box-Air Mass Factors (DBAMFs).

\[
DBAMF = BAMF_{\text{off-axis}} - BAMF_{\text{zenith}}
\]  \hspace{1cm} (2.11)

Typically, a radiative transfer model (e.g. VLIDORT, McMArtim, SCIATRAN) is used to perform forward calculations to simulate MAX-DOAS DSCDs and the BAMFs, which can then be compared to measured DSCDs, and the differences can be inferred (e.g., Li et al., 2010; Pikelnaya et al., 2007; Lee et. al., 2008). This method is especially powerful when there is enough prior knowledge of the state of the atmosphere, such as a clearly defined boundary layer, available information on aerosol optical properties, albedo, etc. If this information is not available these parameters can be varied to match the modeled DSCDs to the observations, often employing look-up tables to speed up the process.

2.3. Application of O₄ to radiative transfer

O₄, or the O₂-O₂ collisional complex, is formed by the collision of two oxygen molecules in the atmosphere. O₄ is a species that is often used to quantify and measure the effects of atmospheric aerosol and other radiative transfer effects on DOAS measurements. This method has several advantages for DOAS applications, and MAX-
DOAS in particular. As atmospheric oxygen is largely chemically inactive, and has a vertical profile that is nearly constant and dependent primarily on temperature and pressure, these properties are transferred to O$_4$ as well. The altitude distribution of aerosols and clouds have an effect on the O$_4$ DSCDs observed by the MAX-DOAS, from which information about the state of the radiative transfer can be derived. O$_4$ absorption bands can be observed throughout the UV and visible wavelength regions, which allows for the wavelength-dependent effects of aerosols to be observed.

It is therefore important to be able to consider the propagation through the atmosphere, in other words the radiative transfer of sunlight from the top of the atmosphere to the MAX-DOAS. As MAX-DOAS measures scattered sunlight, it is sensitive to Rayleigh scattering by air molecules as well as Mie scattering by aerosols in the atmosphere. Photons originating from the Sun travel through the atmosphere through a variety of light paths and their interactions with the atmosphere require the use of radiative transfer models. The spatially and temporally highly variable aerosol scattering is a challenge for the radiative transfer calculations, but also offers the unique opportunity to obtain information about aerosol extinction and aerosol properties. As the optical properties of the aerosol and their vertical profile are often unknown, observed radiances or UV-vis absorptions by the O$_2$-O$_2$ collisional complex, O$_4$, have been used to solve this problem and retrieve aerosol extinction profiles from the MAX-DOAS measurements (e.g., Frieß et al., 2006). O$_4$ has a well-defined vertical profile, which only depends on the atmospheric pressure and temperature profile. As the equilibrium rate coefficient between the O$_2$-O$_2$ collisional complex and molecular O$_2$ is not known O$_4$ concentrations, and by
extension \( O_4 \) slant-column densities, are often expressed in terms of the concentration of molecular \( O_2 \) squared.

![O4 Vertical Profile](image)

**Figure 2.3.** Typical \( O_4 \) vertical concentration profile as a function of altitude, calculated from standard atmospheric pressure and temperature.

\( O_4 \) absorptions can be found in the UV to visible spectral regions (Greenblatt et al., 1990) and \( O_4 \) DSCDs are retrieved with the standard DOAS technique. \( O_4 \) DSCDs can be modeled by radiative transfer models and differences between modeled \( O_4 \) and MAX-DOAS measurements of \( O_4 \) reflect the influence of atmospheric conditions, most notably aerosol extinction and the presence of clouds. For these reasons, \( O_4 \) has been found to be useful for quantifying radiative transfer effects on MAX-DOAS observations.
(Wagner et al., 2004, Frieß et al., 2006). Once the radiative transfer in the atmosphere has been sufficiently constrained, the last step of the analysis involves the simulations of the trace gas DSCDs and a comparison with the observations. As the trace gas profiles are typically the desired results this step is usually performed in reverse, i.e. the observed DSCDs are used to determine the vertical concentration profiles using a numerical inversion technique.

A more serious problem, however, is that the simulation of O₄ SCDs using radiative transfer models has shown a disagreement with MAX-DOAS measurements in numerous studies. Wagner et al. (2009) found the value of the O₄ cross section derived from MAX-DOAS O₄ observations was 25% greater than values determined in a laboratory, speculating that temperature dependence of the O₄ cross section may be the reason why, as atmospheric measurements were made at colder temperatures.

As a result, many studies in the past few years have applied a correction factor to retrieved MAX-DOAS O₄ SCDs of 0.80 to align; the exact reason for this correction factor is not yet known (e.g. Clemer et al., 2010; Wagner et al., 2011). In Section 3.5, we detail some of the analysis and intercomparisons between our MAX-DOAS observations and radiative transfer models, as well as efforts to resolve this difference.

2.4. MAX-DOAS instrument description

The MAX-DOAS was designed for long-term autonomous observations of atmospheric trace gas species, and has been used in past deployments to observe HCHO, NO₂, BrO, IO, OIO, and I₂ (Pikelnaya et al., 2007). The telescope consists of two
elliptical flat mirrors at 45°, the first of which is mounted on a rotating motor, which allows it to scan along the elevation plane, and the second of which reflects light downwards into a third mirror. This setup is itself mounted on a rotating platform with an azimuth motor that allows it to scan along the azimuth plane. The result is that the instrument can rotate both horizontally and vertically, and can point in nearly any direction in its upper hemisphere.

Figure 2.4. Schematic of the UCLA MAX-DOAS, showing the telescope assembly and the spectrometer. Figure from Pikelnaya et al. (2007)

A filter wheel is located in the light path between the rotating stage and a third mirror, which can block light beams to measure background spectra. The third mirror
reflects light onto a 1 mm diameter 5 meters long quartz fiber, which transmits the light to a Czerny-Turner type grating spectrometer (Acton Spectra Pro 300i, 600g/mm grating, 200 µm width entrance slit) coupled to a Hamamatsu 1024 pixel photodiode array (Hoffmann Messtechnik with Hamamatsu S3094 PDA). The spectrometer has a spectral resolution of 0.92 nm and is thermally stabilized at 35°C, while the photodiode array is cooled to -20°C. The telescope has a field of view of ~0.4°. The MAX-DOAS measures in a ~130 nm wide spectral window, the center of which can be determined by software. For the CLARS deployment, the MAX-DOAS initially alternated between a window centered in the UV at 385 nm (320-450 nm), and a window centered in the visible at 530 nm (465-595 nm). After January 2011, the UV window was shifted over to 400 nm (335-465 nm).

2.5. Mt. Wilson/California Laboratory for Atmospheric Remote Sensing

The UCLA MAX-DOAS was installed on Mt. Wilson, California in the spring of 2010, at the California Laboratory for Atmospheric Remote Sensing (CLARS), a facility run by the NASA Jet Propulsion Laboratory. It is located at an altitude of roughly 1706 meters above sea level, at a latitude and longitude of 34° 13’ 28” N and 118° 3’ 25” W, in the San Gabriel Valley directly north of the Los Angeles basin. CLARS is above the polluted boundary layer almost all of the time, and as it overlooks Los Angeles, it presents an excellent vantage point of the lowest several kilometers above a large megacity.
The MAX-DOAS was built to look at upwards (positive) elevation angles, similar to traditional MAX-DOAS instruments. However, for Mt. Wilson it was mounted on a plane at an incline of 22°, with the downwards end facing due south, so that at certain azimuth and elevation angles the instrument is looking downwards (i.e. negative elevation angles) into the basin. The system was set to look in a combination of five azimuth angles (147.36°, 160°, 172.45°, 182.0°, and 240°) and eight elevation angles (+6°, +3°, 0°, -2°, -4°, -6°, -8°, and -10°), geometrically scanning from east to west, both downwards into the boundary layer and horizontally/upwards into the free troposphere.

Beginning at sunrise, the instrument cycles through each of the five azimuth angles, and for each azimuth angle, the eight elevation angles are scanned in sequence. A direct sun measurement through the use of a Spectralon plate (reflectance value of 99%, LabSphere Inc., NH, USA) and a zenith scan is taken as well, after each azimuth scan. Integration times vary depending on the amount of available sunlight, but a typical clear

---

**Figure 2.5.** Viewing strategy of the MAX-DOAS instrument on Mt. Wilson, CA.
sky low solar zenith angle scan will take roughly 5-10 seconds. The angles are viewed first in the UV, and then in the visible light region. Each viewing angle, consisting of a number of averaged scans, will take roughly a minute, and the full azimuth/elevation cycle for both the UV and visible light regions, including zenith scans and direct sun measurements, will typically take 60-80 minutes to complete. At night, Hg emission lines, dark current, and offset spectra are recorded.

The MAX-DOAS began taking measurements on May 24th, 2010, during the CalNex field campaign (Parrish et al., 2014), and except for a few breaks due to equipment failure and adverse weather conditions, it has been running continuously ever since. As of mid-2015 has collected over a million distinct spectra. It is operated by a completely automated set of scripts in conjunction with the DOASIS software package from the University of Heidelberg (Kraus, 2006).

As the control software for the MAX-DOAS assumes a level surface, an appropriate correction factor must be calculated to translate the viewing angles from the plane of the instrument to and from the viewing angles from the plane parallel to the ground. Let $\alpha$ denote the tilt of the plane of the MAX-DOAS with respect to the plane of the ground (here, ~22°), $\theta$ and $\varphi$ denote the elevation and azimuth angles of the plane relative to the ground, and $\theta'$ and $\varphi'$ denote the elevation and azimuth angles at the plane of the MAX-DOAS. We found that the conversion factors from the plane relative to the ground to the plane relative to the MAX-DOAS can be expressed as
\[
\varphi' = 180^\circ + \tan^{-1}[\cos(\alpha) \tan(\varphi - 180^\circ)] \tag{2.12}
\]

for the azimuth, and

\[
\theta' = \theta + \alpha - \sin^{-1}[\sin(\alpha) \cos(\varphi' - 180^\circ)] \tag{2.13}
\]

for the elevation.
3. Analysis

3.1. DOAS analysis

The DOAS approach described in section 2.1 was applied to retrieve NO$_2$, HCHO, and O$_4$ DSCDs from the observed MAX-DOAS radiances. The instrument line function was determined through the use of measured Hg lines. Because the instrument spans from the UV into the visible, in two 130 nm-wide windows, a wide range of wavelength intervals are measured. Initially NO$_2$ was fit in four wavelength intervals, from 323.4-350 nm, 419.5-447 nm, 464-506.9 nm, and 519.8-587.7 nm. HCHO was fit simultaneously alongside NO$_2$ in the 323.4-350 nm region. O$_4$ was observed in three intervals, from 350-390 nm, 464-506.9 nm, and 519.8-587.7 nm, each window encompassing one of the major O$_4$ absorption lines. After January 2011 the shortest-wavelength interval over which NO$_2$ and HCHO were fitted was shifted to 332.8-377.8 nm.

Before each retrieval the measurement spectrum was corrected for dark current and offset, and its logarithm was taken. The retrieval procedure uses various references, including the logarithms of a Fraunhofer reference spectrum measured in the zenith, a simulated Ring spectrum (Vountas et al., 1998), and reference absorption spectra for the major trace gas species in these regions. Each of the reference spectra was convoluted using the instrument function from a Hg line, and was corrected for the I0 effect from the solar spectrum (Aliwell et al., 2002). There have been numerous O$_4$ cross sections reported in the literature, such as Greenblatt et al. (1990), Hermans et. al. (1999, 2011) and Thalmans et. al. (2003). After comparing results we decided to use the O$_4$ reference spectrum from C. Hermans (1999, 2011). O$_3$ and NO$_2$ references were provided by Voigt
et al. (2001) and Vandaele et al. (1998) respectively. For HCHO we used the cross section of Cantrell et al (1990).

The retrieval was performed using a combination of a linear and nonlinear least-squares fit (Stutz et al, 1996, Platt and Stutz, 2008). The measurement spectrum was allowed to stretch and squeeze in wavelength with respect to the reference spectra during the analysis, and the fitting was performed with the DOASIS software package. In addition, a fifth order polynomial was included in the fit.

**Table 3.1.** Wavelength ranges and spectral references used for the spectral retrievals of O₄, HCHO, and NO₂. Note that a zenith solar reference, ring spectra and a polynomial of degree 5 are also included in the fit.

<table>
<thead>
<tr>
<th>Species</th>
<th>Scan</th>
<th>Wavelength Interval (nm)</th>
<th>Fitted Spectral References</th>
<th>Detection Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₄</td>
<td>UV</td>
<td>350-390</td>
<td>NO₂, O₄, HCHO, HONO</td>
<td>7*10¹¹ molec²/cm⁵</td>
</tr>
<tr>
<td>O₄</td>
<td>Vis</td>
<td>464-506.9</td>
<td>NO₂, glyoxal, O₄, H₂O</td>
<td>8*10¹¹ molec²/cm⁵</td>
</tr>
<tr>
<td>O₄</td>
<td>Vis</td>
<td>519.8 - 587.7</td>
<td>NO₂, O₄, O₃, H₂O</td>
<td>5*10¹¹ molec²/cm⁵</td>
</tr>
<tr>
<td>HCHO</td>
<td>UV</td>
<td>323.4-350</td>
<td>HCHO, O₄, O₃, HONO</td>
<td>5*10¹⁵ molec/cm²</td>
</tr>
<tr>
<td>NO₂</td>
<td>UV</td>
<td>323.4-350</td>
<td>HCHO, O₄, O₃, HONO</td>
<td>3*10¹⁵ molec/cm²</td>
</tr>
<tr>
<td>NO₂</td>
<td>UV</td>
<td>419.5-427.9 &amp; 432.4-447</td>
<td>NO₂, glyoxal, O₄, H₂O</td>
<td>1*10¹⁵ molec/cm²</td>
</tr>
<tr>
<td>NO₂</td>
<td>Vis</td>
<td>464-506.9</td>
<td>NO₂, glyoxal, O₄, H₂O</td>
<td>1*10¹⁵ molec/cm²</td>
</tr>
<tr>
<td>NO₂</td>
<td>Vis</td>
<td>519.8 - 587.7</td>
<td>NO₂, O₄, O₃, H₂O</td>
<td>2*10¹⁵ molec/cm²</td>
</tr>
</tbody>
</table>
Figure 3.1 shows examples of the retrievals of O₄, NO₂, and HCHO. The comparison of the laboratory absorption spectrum (red line) with the retrieved spectrum (blue line) shows that all three trace gases were clearly identified. Table 3.1 gives an overview of the various spectral intervals, the trace gases fitted in each interval and the detection limit of the differential slant column density (DSCD), i.e. the difference between low elevation and zenith measurement, of the main trace gas retrieved in each interval. It should be noted that the analysis of NO₂ in four different wavelength intervals is uncommon and that our results are unique in this respect.

Figure 3.1. Example of the analysis of a MAX-DOAS spectrum. The DOAS method fits an absorption spectrum (red) to a retrieved spectrum (blue).

In our analysis, the DOAS procedure calculates an error using the method described in Stutz and Platt (1996). In brief, a correlated least-squares fit is applied to the residuals of the measurement to derive an estimate of the measurement error. The error terms are useful not only for the DOAS applications, but will be used later as the measurement vector for optimal estimation efforts using DOAS results (see Section 4.4)
3.2. Cloud detection algorithm

As with most scattered-sunlight remote sensing applications, clouds represent a challenge, as they are highly variable and strongly impact the observations and the radiative transfer in the atmosphere. However, clouds can be seen in both the O$_4$ and in the measured light intensity detected by the MAX-DOAS, thus allowing their identification. A particular problem for our Mt. Wilson application is the presence of clouds above and below the MAX-DOAS system. Clouds below the instrument are more reflective than the surface and often obstruct the view into the basin, while clouds above the detector attenuate solar radiation and may complicate the radiative transfer calculations.

Figure 3.2. The cloud problem at Mt. Wilson. Data must be filtered for the presence of clouds both above and below the altitude of the MAX-DOAS.
In order to analyze our long-term data-set, we thus developed an algorithm for detecting clouds. To take into account the unique viewing geometry we used a camera that was installed at Mt. Wilson in May 2011, to collect images in the field of view of the MAX-DOAS. Over several months of observations, a large set of clear, partially cloudy, and cloudy observations was obtained. The images were classified into one of three categories: (1) “clear days” in which there were little to no clouds, (2) “low cloud days” in which there was partial or full cloud coverage at negative (downwards-looking) elevation angles, and (3) “high clouds” with partial or full cloud coverage at positive (upwards looking) elevation angles. A clear day reference behavior was established for $O_4$ DSCDs and intensity against solar zenith angle by fitting second order polynomials for the clear sky data for each elevation and azimuth combination.

Comparison of $O_4$ and intensity under cloudy conditions to these fit polynomials show distinct deviations. Generally “low clouds” are extremely reflective and thus greatly increase the intensity of the light received by the MAX-DOAS, while “high clouds” can attenuate the amount of light reaching the MAX-DOAS. $O_4$ DSCDs tend to decrease for low clouds as the light path is shortened relative to a clear view. The effect of high clouds on $O_4$ is more difficult to predict due to the inclusion of the zenith spectrum in the DSCD retrieval. However, any cases where the effect is small and clouds were not identified would not cause a problem since the impact on the radiative transfer is likely minimal.

We found that clear-sky fit polynomials for intensity and $O_4$ are generally consistent for each elevation angle for all seasons. The fit polynomials can thus be applied on our entire set of MAX-DOAS measurements. Based on the statistical distribution of clear day intensity and $O_4$ values we then determined suitable “cutoff
values” for classifying data-points that deviate from the fit polynomial as likely candidates for measurements taken during cloudy conditions (Figure 3.3).

![Deviation from cloud polynomial, Intensity and O₄ DSCDs](image)

**Figure 3.3.** Histogram of deviation from cloud polynomial, when applied to intensity/photon count (left), and O₄ DSCDs (right). The 1- and 2-σ boundaries are shown by the vertical red lines.

We then developed a method for filtering clear-sky data-points from cloudy data-points, using both the measured O₄ DSCDs and intensity, given a sufficiently large number of MAX-DOAS observations. First, ideal fit polynomials to clear sky conditions must be determined:

- Using our Mt. Wilson webcam, get a good sample set of MAX-DOAS measurements, separate “clear days” from “cloudy days”
• For each elevation angle for the set of “clear days”, calculate a second-order fit to both the O$_4$ DSCDs and intensity, with respect to the solar zenith angle when each measurement was taken.

These fit polynomials are generally consistent for each elevation angle, for all seasons. Once the fit polynomials are determined, they can be applied over our entire set of MAX-DOAS measurements, or over a suitably large subset of our data, using the following algorithm:

• Find the measured O$_4$ DSCD and intensity observed at the same time as the measurement

• Using the “clear sky” fit-polynomial, calculate a set of ideal “clear sky” values, and subtract these from the measured values. The absolute value of this difference is taken, with larger values having a higher likelihood of clouds.

• Develop a suitable “cutoff limit”, and remove data-points above or below this cutoff limit. These are largely cloudy data-points. We have used standard deviations from the fit polynomial as a cutoff marker.

Note that care must be taken when setting the cutoff limit. Depending on the size of the dataset fitted and the number of significant outliers, the cutoff level had to be adjusted. It is also important to note that the algorithm can be used for the entire dataset, even when there are no webcam images. The images are used to create the fit polynomials, but the polynomials, once determined, are consistent for all seasons and solar zenith angles.
Figure 3.4. Example of cloud classification, for the month of June 2011. The left two plots show the retrieved $O_4$ separated by “clear” and “cloudy” days, with the fit polynomial to the clear-sky $O_4$ DSCDs by function of SZA (the red line) shown on both plots. The right two plots show the measured intensity from the MAX-DOAS, classified as either clear days or cloudy days, with the fit polynomial to clear-sky intensities shown on both plots. The classification of a day’s worth of data as “clear sky” was kept fairly strict in order to obtain the best “clear sky” cloud polynomial, so it’s worth noting that the “cloudy” days include many days which are only partially or slightly cloudy.
Figure 3.5. Diagram of the cloud sorting routine, from which we are able to systematically identify which of our measurements were taken during cloudy periods.

If the difference is plotted as a histogram, generally clear sky days had roughly Gaussian/random errors, while cloudy days have a long “tail”, so a cutoff of ±1σ or less was set to filter deviations from the cloud polynomial. Figure 3.6 shows the results when this classification scheme is applied to the July 2011 NO$_2$ DSCDs, and the days with clouds are removed. On average, the algorithm flags between 25-35% of the measurements as occurring in the presence of clouds.
It is worth mentioning that over the long dataset over which this algorithm was applied, inconsistencies were found over a long time scale, which we believe is the result of the temperature dependence of O₄ that we describe in section 3.5. In practice, although information may be lost, it is presumably more reliable to filter clouds primarily or solely by measured intensity for longer-term datasets. We have found the sensitivity of this algorithm shows a seasonal dependence that is likely in response to changes in the ambient temperature; the effects of temperature changes on much smaller time scales was not observed amidst the other noise within the O₄ dataset.

**Figure 3.6.** NO₂ DSCDs for July of 2011, before and after the cloud-removal algorithm was applied. The summer of 2011 had an extended “June gloom” period, with unusually high amounts of clouds, so it was a good test for the algorithm.
3.3. Radiative Transfer Modeling

The retrieval of aerosol extinction and trace gas concentration profiles depends heavily on the accurate description of the atmospheric radiative transfer (RT) using a model (RTM). In addition to Rayleigh scattering due to sunlight propagating through the atmosphere, photons reaching the MAX-DOAS will likely interact with atmospheric aerosol particulates. Moreover, due to the downwards-looking viewing geometry at CLARS many photons will have scattered off the atmosphere or, especially at downwards viewing elevation angles, off the surface.

Due to large amount of MAX-DOAS data a fast RTM was needed in our approach. We have thus implemented VLIDORT, which is derived from the first version of the Linearized Discrete Ordinate Radiative Transfer (LIDORT) scalar code (Spurr et al., 2001; Spurr 2006). VLIDORT has been developed for the computation of all the Stokes vector components in a multi scattering multilayer medium. The code is fully linearized, and is able to calculate the polarized radiance field simultaneously with all of the analytic weighting functions with respect to any atmospheric and surface properties (Spurr, 2006). The “linearization” of the code means that VLIDORT expands the simulated radiance field into a Taylor series about a given state of the atmospheric model, thus making the code very computationally efficient. VLIDORT use a “pseudo-spherical” approximation of the radiative transfer equation, which is essential for our observations, in particular for the limb scans.
Table 3.2. VLIDORT input and output parameters. For more information about the calculation of the Jacobian matrices, see section 4.4.

<table>
<thead>
<tr>
<th>VLIDORT inputs</th>
<th>Outputs</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Pressure and Temperature profile</td>
<td><em>Calculated in VLIDORT</em></td>
</tr>
<tr>
<td>• O₃ and NO₂ profile</td>
<td>• Simulated Radiances, with and without absorbers and aerosols</td>
</tr>
<tr>
<td>• Solar geometry (Solar zenith and relative azimuth angle)</td>
<td>• Intensity derivative with respect to aerosol optical depth</td>
</tr>
<tr>
<td>• Altitude of detector</td>
<td>• Intensity derivatives with respect to trace gas absorptions (for O₃, NO₂, and O₄)</td>
</tr>
<tr>
<td>• Viewing elevation angle</td>
<td></td>
</tr>
<tr>
<td>• Aerosol optical depth profile</td>
<td></td>
</tr>
<tr>
<td>• Surface albedo</td>
<td></td>
</tr>
<tr>
<td>• Aerosol Single-Scattering Albedo (SSA)</td>
<td></td>
</tr>
<tr>
<td>• Aerosol asymmetry factor</td>
<td><em>Calculated externally from VLIDORT</em></td>
</tr>
<tr>
<td>• Absorption cross-sections (for O₃, NO₂, and O₄)</td>
<td>• Simulated Slant-column densities from POV of detector</td>
</tr>
<tr>
<td></td>
<td>• Box Air-Mass Factors (BAMFs)</td>
</tr>
<tr>
<td></td>
<td>• Jacobian matrices of O₄ SCDs with respect to aerosol optical depth and relative radiances</td>
</tr>
</tbody>
</table>

VLIDORT uses a user-defined environment, where geophysical atmospheric inputs such as vertical profiles (thermal, trace gases and aerosol), optical parameters (single scattering albedo, asymmetry function, optical thickness, phase function
moments) or spectral properties (cross sections, wavelengths) are defined by the user. Table 3.2 lists the major parameters input and output from VLIDORT.

VLIDORT generates an entire set of intensities and weighting functions that are required for an iteration step in a multi-parameter atmospheric retrieval, with a single call of the model. In addition, Jacobians of trace gas concentration, optical depth, single scattering albedo, phase function quantities, surface emission, surface albedo and other parameters defined by the user, for any set of azimuth and elevation angles, are provided.

Originally there were two versions of VLIDORT, one that modeled upwelling radiation for an instrument at an elevated layer, and one that modeled downwelling radiation for an instrument located at the surface. As we incorporate both upwards and downwards viewing geometries, we have to operate two simultaneous versions of VLIDORT. From now onwards, whenever we mention VLIDORT model runs, two instances of VLIDORT are generally being run simultaneously, one looking upwards and one downwards. In addition, some modifications to VLIDORT had to be made to simulate the measured trace gas DSCDs observed by the MAX-DOAS.

The advantage of the DOAS algorithm is that it results in a reliable measurement of the slant-column density, and for accurate validation such a quantity had to be simulated in VLIDORT. There are two known methods for simulating the SCD in VLIDORT. One method is based on the Lambert-Beer law:

\[
I = I_0 e^{-\sigma \int C \, dl}
\]  
(3.1)
This can be rewritten in the following format:

\[ \int C \cdot dL = \frac{1}{\sigma} \log \frac{I_0(\lambda)}{I(\lambda)} \]  \hspace{1cm} (3.2)

Here \( I \) and \( I_0 \) are the light intensities simulated by VLIDORT. In order to calculate them VLIDORT is run twice, once without the presence of the absorber and once with it. This quantity, the integral of the concentration along a path length \( L \) is, by definition, the SCD. Because this calculation involves taking the ratio of the simulated radiances at each wavelength with and without the presence of the absorber, this method has been now referred to as the “Ratio method” of calculating SCDs.

The other method for calculating SCDs involves the Box-Airmass factors (BAMFs). Due to the discretized nature of dividing the atmosphere into distinct vertical model grid boxes by many radiative transfer models, BAMFs can be calculated at each vertical grid box. As mentioned previously, the SCD can be calculated as a summation of the BAMFs and the vertical concentration within the model grid box:

\[ SCD = \sum_{i=0}^{n} C(h_i) \times BAMF(h_i) \times \Delta h_i \]  \hspace{1cm} (3.3)

This is possible even if the concentration of the absorber is an independent variable, as it is expected that the concentrations of most trace gases will have a negligible effect on the
path length of most photons; molecular (Rayleigh) scattering and Lorentz-Mie scattering likely dominates. It is possible to calculate the BAMF from VLIDORT’s analytically calculated Jacobians of radiance with respect to trace gas concentration \( \frac{dl}{dc} \) using the following expression:

\[
BAMF = -\frac{1}{\sigma l} \cdot \frac{dl}{dc}
\]  

(3.4)

where \( \sigma \) and \( l \) are the absorption cross section and intensity, respectively. The BAMF thus reflects primarily the radiative transfer effects. Theoretically both the BAMF method and the ratio method for calculating SCDs should be identical; in practice we find a small discrepancy between the two that will be discussed in section 3.5.

### 3.4. Sensitivity Studies

In preparation for the retrieval of aerosol optical properties, VLIDORT was used to conduct a number of sensitivity studies, to determine the influence of various parameters on observed \( O_4 \) SCDs. This is, by using \( O_4 \) as a proxy, a survey into the influence various aerosol parameters would have on MAX-DOAS and other remote sensing observations. The parameters tested were chosen based on VLIDORT capabilities and also to be as comprehensive a survey of aerosol properties as possible, and include (1) the Single Scattering Albedo (SSA), (2) the aerosol asymmetry factor \( g \),
(3) the surface albedo, and (4) the boundary layer height and (5) boundary layer extinction respectively.

We were fortunate that the CalNex 2010 field campaign provided us with a variety of direct field measurements of many of these aerosol optical properties, and a rough range of the likely values one would observe above Los Angeles (Thompson et al., 2012). For this study, we chose a “base” run consisting of an aerosol profile of typical average optical properties as observed in the Los Angeles air basin (Figure 3.7). This profile was input in VLIDORT and a model O₄ profile was simulated at the 360 nm wavelength region. Each aerosol parameter was varied individually, to estimate its effect on the O₄ profile. The base profile had a single scattering albedo of 0.92, an asymmetry/g-factor of 0.7, a surface albedo of 0.1 (10%), and an aerosol "box" extinction profile with a boundary layer height of 1 km, and an in-boundary extinction coefficient of 0.1 km⁻¹.
Figure 3.7. “Base” aerosol extinction profile used for the sensitivity study, with a box profile with a 1 km boundary layer height, and a 0.1 km\(^{-1}\) extinction coefficient.

It is worth noting that the variety of aerosol types and consequently aerosol optical properties in urban atmosphere is considerable, and furthermore there are significant spatial and temporal variations in aerosol distributions and properties, compounded by the proximity to emissions sources. VLIDORT and most other radiative transfer models parameterize a single “composite” aerosol profile which is at best an average of the various types out there, which is a known limitation in current atmospheric radiative transfer models.
The Single Scattering Albedo (SSA) is defined as the ratio of the scattering coefficient ($\beta_s$) to the extinction coefficient ($\beta_e$) of an aerosol:

$$\tilde{\omega} = \frac{\beta_s}{\beta_e} \tag{3.5}$$

with non-absorbing aerosols tending to have values approaching 1, and absorbing aerosols having a lower value. Values recorded during CalNex generally show a range from 0.85-0.98 (LeBlanc et al., 2012; Thompson et al., 2012). Two simulations with single scattering albedos of 0.7 and 0.99 respectively were run with VLIDORT, and the resulting O$_4$ DSCDs are shown in Figure 3.8. The total peak-to-peak difference of the O$_4$ DSCDSs at their maximum value is slightly under 8%. Moreover, the effects of the single scattering albedo are primarily seen at downwards-looking (negative) elevation angles, which is intuitive as the bulk of aerosols and of O$_4$ molecules is located near the ground, below the altitude of the MAX-DOAS. Generally a lower single-scattering albedo reduces the O$_4$ DSCDs; one explanation is that with more absorbing aerosols less light is being reflected back to the detector.
Figure 3.8. Effects of single-scattering albedo on O$_4$ DSCDs (top), and relative ratio to O$_4$ SCD with 0.92 SSA (bottom).

The asymmetry factor $g$ is an anisotropy factor used in the Henyey-Greenstein parameterization of light scattering from a spherical particle (Henyey and Greenstein, 1941). The Henyey-Greenstein function allows for the expected value of the phase function $P(\theta)$ to be expressed as a single factor $g$ (Hansen and Hovenier, 1974):
\[ g = \frac{1}{2} \int_{0}^{\pi} \cos \theta \, P(\theta) \sin \theta \, d\theta \]  

(3.6)

which is commonly expressed in terms of the cosine of the scattering angle \( \theta \):

\[ g = \frac{1}{2} \int_{-1}^{1} P(\cos \theta) \cos \theta \, d \cos \theta \]  

(3.7)

The asymmetry factor has been adopted in a variety of radiative transfer models, including VLIDORT. Defined as the average cosine of the scattering function, for a completely forward scattering function the asymmetry factor would be roughly 1, and for an isotropic scattering, \( g = 0 \). In general, at each wavelength the larger particles scatter more light in the forward direction than smaller particles do and consequently have a larger asymmetry factor.

Values of the asymmetry parameter observed in urban environments vary from roughly 0.68-0.75 at 440 nm wavelength (Dubovik et. al., 2002) to 0.85 (Le Blanc et. al., 2012), with a strong dependence on wavelength. For our tests we ran two cases with aerosol asymmetry of 0.6 and 0.8. Figure 3.9 shows the results, highlighting a 6% difference between the two values. Like SSA, we found that the asymmetry is most significant at downwards looking viewing elevation angles, likely for the same reasons described above. A larger asymmetry factor, or in other words stronger forward scattering, resulted in a greater overall O4 DSCD; likewise less forward scattering aerosols resulted in a lower O4 DSCD.
Figure 3.9. Effects of asymmetry factor on modeled O₄ DSCDs (top) and and relative ratio to O₄ SCD with asymmetry factor of 0.7 (bottom)

The surface albedo is a measure of the overall reflectivity of the surface, expressed as the fraction of incident light that is reflected rather than absorbed. While albedo is a persistent concern for downwards-looking remote sensing efforts such as those traditionally located on satellites or airplanes, this survey is the first to consider
downwards looking MAX-DOAS applications, which have traditionally been located near the surface with positive viewing elevation angles.

In addition, it’s worth considering that the average surface albedo observed in a set of scans will be a composite of a variety of albedos of different types. Given the shallow viewing angles considered and the diversity of surfaces in an urban environment, this composite will likely contain a variety of values; for example asphalt pavement can have albedos of 5-10%, concrete pavement of around 15-35%, and dry snow of 70-90% (Hartmann, 1994).

Figure 3.10 shows the results when the albedo is varied from 0.05 – 0.5 (or 5-50%), which encompasses the range of possible values in an urban environment. While there is an effect of roughly 3-4% at all of our viewing elevation angles, consistently at all elevation angles, this is for an extreme range, and while not insignificant, still has overall less of an influence than some of the other aerosol parameters.
Finally, we tested a variety of aerosol vertical extinction profiles. The aerosol extinction coefficient is defined as the inverse of the mean-free path a photon is likely to travel before being influenced by aerosol particles at a specific region of the atmosphere; this is a variable that is likely to change on a frequent basis, and is therefore typically the independent variable to retrieve for aerosol retrieval algorithms. Given the novel nature
of the viewing geometry from CLARS it was predicted that the shape of the aerosol extinction profile would have a significant effect on the CLARS MAX-DOAS measurements, more so than traditional ground-based MAX-DOAS observations.

From prior knowledge it is known that the bulk of aerosol is located close to the ground, and that in typical meteorological conditions in Los Angeles much of the freshly emitted emission have vertical transportation attenuated by boundary layer meteorology, so for this study we parameterized the vertical aerosol extinction profile as a “box” profile that has a uniform extinction from the surface to a set boundary layer height, and a much lower extinction above the boundary layer. This is at best an approximation but captures the general shape of the aerosol extinction profile.

As a result, there are two variables here, the height of the boundary layer and the extinction coefficient within the boundary layer. For the purposes of this sensitivity test the aerosol above the boundary layer had a flat extinction coefficient of $10^{-3}$ km$^{-1}$. For this sensitivity test we varied each parameters separately.

The CalNex 2010 field campaign provided us with Ceilometer data on the boundary layer height, and ground-level extinction coefficient measurements, although these are mainly measured at a wavelength of 532 nm. Figure 3.11 and Figure 3.12 show the results of sensitivity tests for each parameter. Thompson et. al. (2012) saw aerosol extinction coefficients of on average $0.062 \pm 0.044$ km$^{-1}$ at 532 nm. Generally, aerosol extinction tends to increase the shorter the wavelength is, depending on the Ångström parameter, and as our simulation is at 360 nm, we account for a higher possible aerosol extinction. Moreover, it is not uncommon in the Los Angeles air basin for higher aerosol
extinction coefficients to be observed; Thompson et. al. (2012) saw values as high as 0.3 km\(^{-1}\). Thus our sensitivity tests for extinction coefficient ranged as high as 0.5 km\(^{-1}\).

**Figure 3.11.** Effects of boundary layer extinction coefficient on modeled O\(_4\) DSCDs.

The boundary layer height was observed during CalNex by a Ceilometer (Haman et. al., 2012), with values varying on diurnal and on longer time scales. In general a
rough average boundary layer height of 0.5-1.5 km was observed during daylight hours, although values as high as 2 km occurred (Scarino et. al., 2014). This range was simulated in VLIDORT, and the $O_4$ range is shown in Figure 3.12.

![Figure 3.12](image)

**Figure 3.12.** Effects of boundary layer height on modeled $O_4$ DSCDs. The boundary layer extinction is 0.1 km$^{-1}$. 
Table 3.3. Peak-to-peak change in O$_4$ DSCDs when optical parameters are modified. Temperature effects and high-altitude aerosol extinction coefficients are discussed in section 3.5.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range of values</th>
<th>Max. change in O$_4$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albedo</td>
<td>0.05-0.5</td>
<td>3%</td>
</tr>
<tr>
<td>Asymmetry</td>
<td>0.6-0.8</td>
<td>6%</td>
</tr>
<tr>
<td>Single Scattering Albedo</td>
<td>0.7-0.99</td>
<td>8%</td>
</tr>
<tr>
<td>Temperature</td>
<td>280-310 K</td>
<td>25%</td>
</tr>
<tr>
<td>Aerosol Boundary Layer Height</td>
<td>0.5-1.5 km</td>
<td>30%</td>
</tr>
<tr>
<td>Boundary Layer Extinction</td>
<td>0.05-0.5 km$^{-1}$</td>
<td>15%</td>
</tr>
<tr>
<td>High-altitude Extinction</td>
<td>(taken from Sage-II)</td>
<td>8%</td>
</tr>
</tbody>
</table>

At the greatest extent, we see over 30% difference in O$_4$ DSCDs resulting from changes in the boundary layer height, and 15-20% from changes in the boundary layer extinction coefficient. These results suggest that the aerosol extinction shape, especially the boundary layer height, dominates the variation in the O$_4$ DSCDs, although the influence of other aerosol optical properties are significant. These results suggest that an optimal estimation of aerosol extinction profiles can be conducted. Moreover, although albedo is generally a concern for downwards-looking viewing geometries, its effect is more systematic across the viewing geometries. Varying the aerosol optical properties primarily affects O$_4$ DSCDs retrieved from downwards looking viewing geometries.
which is unsurprising given that in our model the bulk of the aerosol is located within the boundary layer.

These tests suggest that the shape of the aerosol extinction profile and the boundary layer extinction coefficient will be the significant variables to consider for any attempt to model radiative transfer, more than any of the other aerosol optical properties. The aerosol extinction profile is therefore the prime focus of any effort to perform a retrieval. The aerosol extinction coefficient is not independent of single-scattering albedo and asymmetry parameter, and thus it is recommended that a “best guess” value of SSA and asymmetry be used to retrieve the “best” extinction profile.

3.5. **Forward modeling of O$_4$ Slant Column Densities**

In preparation for performing optimal estimates of vertical profiles, we compared our initial VLIDORT forward model runs, using known aerosol profiles from the CalNex time period, with measured O$_4$ DSCDs from the same time period. As mentioned previously, there have been discrepancies between O$_4$ DSCDs as modeled by MAX-DOAS systems and by radiative transfer models, the exact reasons for which aren't understood (e.g. Wagner et. al., 2009; Clemer et. al., 2010).

We reconstructed a vertical profile based on CalNex observations of the Los Angeles basin. At the nearby Caltech campus the total column aerosol optical depths was provided observed by the Aerosol Robotic Network (Aeronet) sun photometer (Holben et al., 1998; Holben et al., 2001), while a ceilometer operated by the University of Houston (Münkel et. al., 2007; Haman et. al., 2012) provided observations of the boundary layer.
height. A Cavity Attenuated Phase Shift Spectrometer (CAPS) made _in situ_ measurements of the aerosol extinction coefficient in the 532 nm wavelength range (Massoli et. al., 2010). In order to reconstruct the vertical extinction profile, the aerosol extinction coefficient at the 360 nm O4 band was estimated using the angstrom coefficient provided by the Aeronet station, and the wavelength dependence (Seinfeld and Pandis, 2006):

\[
\frac{\tau}{\tau_0} = \left(\frac{\lambda}{\lambda_0}\right)^{-\kappa}
\]

where \(\kappa\) is the angstrom coefficient.

We assumed again that the aerosol profile followed the “box-profile” as detailed previously. For the model vertical grids below the measured boundary layer height at each time step, the extinction coefficient was set to be that measured by the CAPS instrument. For the grid boxes above the boundary layer, the remainder of the total column optical depth was divided into each vertical grid box. This recreation of the aerosol profile from the CalNex measurements we refer to as the “CalNex reconstruction.”
Figure 3.13. Two sample reconstructions of vertical aerosol extinction profile. This profile is derived through a combination of three measurements from the CalNex field campaign: (1) a total column optical depth measurement, (2) an in situ boundary layer extinction coefficient measurement, and (3) a boundary layer height measurement.

The forward model was run with the CalNex reconstruction of aerosol profiles from roughly May 15th to June 15th, 2010. To take into account the possible 22% uncertainty in O$_4$ absorption cross-sections over the range of 196-296 K (Pfeilsticker et al., 2001), VLIDORT was modified to incorporate a vertical profile of O$_4$ cross-sections, where at each altitude the cross section was scaled using a linear interpolation of the temperature-dependent cross sections as measured by Thalman et. al. (2013). However, even when using temperature-dependent cross-sections, when using a “standard” atmospheric, the model-measurement disparity in O$_4$ DSCDs is observed.
Figure 3.14. Comparison of resulting VLIDORT $\text{O}_4$ DSCDs to MAX-DOAS observations, if input with an aerosol extinction profile derived from CalNex 2010 observations. Without accounting for temperature and high altitude aerosol extinction, the MAX-DOAS $\text{O}_4$ is 15-25% lower than VLIDORT simulations of $\text{O}_4$.

Previous ground-based observations observed a systematic difference of simulated $\text{O}_4$ DSCDs 20-25% smaller than observed (e.g. Wagner et. al., 2009; Clemer et. al., 2010). Interestingly, we found the opposite true for our observations; with the CalNex recreation simulated $\text{O}_4$ DSCDs were routinely on the order of 15-25% higher than those observed by the MAX-DOAS (Figure 3.14). It is possible that as the MAX-DOAS at CLARS is looking in downwards viewing angles at the surface it sees the
opposite effect of traditionally ground-based, which typically observe O₄ DSCDs 20-25% greater than modeled O₄ DSCDs.

3.5.1. Temperature effects

The O₄ disparity has been found to be largely the result of two factors. First, it was found that merely scaling O₄ absorption cross sections by temperature was insufficient. In our initial forward modeling attempts, a standard mid-latitude atmospheric temperature profile was used; in practice the surface temperature in Los Angeles varies greatly on a number of different time scales, but generally within the ranges of 280-310 K.

Although the vertical temperature profile is highly variable, we parameterized the vertical temperature profile with a maximum temperature at the surface, and a linearly decreasing adiabatic lapse rate of 6.5 K/km from the surface, up to a minimum temperature of 190 K roughly around 10 km altitude, creating a tropopause. Real-time temperature data at Mt. Wilson is available from the NOAA National Climatic Data Center (Menne et. al., 2012), which has a monitoring station located at the observatory at roughly 1.7 km above sea level. This profile is used to scale the temperature profile for each time step. Above this altitude, a standard mid-latitude temperature profile was used, since we expect the variability above the tropopause to be at a minimum. Sample recreated temperature profiles are shown in Figure 3.15.
Figure 3.15. Temperature profiles reconstructed using a standard atmospheric lapse rate. This profile is scaled according to the actual recorded temperature at Mt. Wilson at each time step.

Figure 3.16 shows the sensitivity tests for this new temperature profile on VLIDORT simulated $O_4$ DSCDs. Theoretically it is unsurprising that temperature effects would have an effect on $O_4$, as it would affect the pressure and density of the oxygen profile. The resulting disparity in modeled $O_4$ DSCDs due to the 15-30 K range is greater than 20%, almost uniformly at all elevation angles. This influence is often as large as or
greater than the influence of aerosol optical properties on O₄ DSCDs as observed by the sensitivity studies in section 3.4.

![Figure 3.16](image)

**Figure 3.16.** Effects of atmospheric temperature profile, by surface temperature, on O₄ DSCDs.

An observed mismatch between the two methods VLIDORT used to calculate the O₄ DSCDs further suggests that modeling and observations of O₄ DSCDs are highly dependent on temperature. As mentioned in section 3.3, there are two methods for
calculating O₄ DSCDs, the “BAMF method” and the “Ratio method”. Based both on theory, these two methods should give an identical DSCD; and when used to calculate NO₂ DSCDs the results are usually nearly identical, with a difference of under 1%. However, over the same time period a disparity of 5-15% was observed between the O₄ DSCDs calculated by the BAMF method and the DSCDs calculated by the ratio method. It is believed that this disparity may be related to the influence of temperature on the Ratio method, which is largely ignored using the BAMF method; considering the nature of O₄ specifically as an O₂-O₂ collisional, and its relative sensitivity to the pressure and ambient concentration of O₂ in the atmosphere suggest why temperature may have a pronounced effect on O₄. Future efforts to calculate BAMF may be improved by incorporating temperature effects at each altitude level, using temperature-dependent O₄ cross sections (e.g. Thalman et. al., 2013) at each altitude level.
Figure 3.17. Difference between the Ratio method and BAMF method of calculating $O_4$, before and after temperature was correction, using methods detailed in text.

These results suggest that greater attention to atmospheric temperature may be a necessary consideration for future MAX-DOAS deployments. Having real-time meteorological data would allow for the incorporation of a specific temperature profile for each observation into the radiative transfer model.

3.5.2. High altitude aerosol
The other parameter unaccounted for, and discovered to have a disproportionately large effect on $O_4$, was the aerosol extinction profile at altitudes above that of the Mt. Wilson Observatory. As the bulk of aerosols are usually located close to the surface below the boundary layer, it is not uncommon to neglect the aerosol extinction coefficients which are located at higher altitudes, as they are significantly lower.

![Aerosol Extinction Profile](image)

**Figure 3.18.** Examples of the two different aerosol extinction profiles used for this forward modeling study. In this case both the CalNex and Sage reconstruction have identical total column optical depths.

Our modeling studies have shown that “aloft aerosols”, aerosols above the boundary layer up to and including those in the stratosphere, have a non-negligible effect on the observed $O_4$ DSCDs. We compared the aforementioned CalNex Reconstruction, with the “SAGE” reconstruction, which we derived from measurements obtained by NASA’s Stratospheric Aerosol and Gas Experiment II (SAGE-II) Satellite (Rind et. al.,
While the CalNex reconstruction assumes a uniform, comparatively small aerosol profile from the top of the boundary layer to the top of the atmosphere, the SAGE dataset provides aerosol extinction coefficient measurements from the altitudes of 10 to 40 kilometers (Figure 3.18).

As there was relatively little variation in the stratospheric aerosol profile, from the SAGE reconstruction, a “background” aerosol profile from these altitudes was compiled. Above 40 kilometers, a flat aerosol extinction profile of $10^{-7}$ km$^{-1}$ was used; this is even smaller than the background value of the CalNex recreation at these altitudes. Between the top of the boundary layer height and 10 kilometers of altitude there is no data; however VLIDORT showed the best agreement with MAX-DOAS O$_4$ DSCDs when the value of the aerosol extinction at 10 kilometers was extended downwards to the altitude of the boundary layer.
Figure 3.19. VLIDORT simulations using two different aerosol profiles, the CalNex reconstruction and the SAGE reconstruction, compared with the MAX-DOAS observation at the same time.

Figure 3.19 shows the disparity between the O₄ DSCDs calculated by VLIDORT using these two reconstructions. Both of the reconstructions have identical total column optical depths, and yet a difference of between 4-8% between the two has been observed.
Properly constraining the $O_4$ DSCDs is a necessary condition for correctly modeling the radiative transfer of the atmosphere. It has been found that without properly considering temperature effects on $O_4$ and high-altitude aerosol extinction profiles, there exists a disparity between VLIDORT and the MAX-DOAS observations. For the remainder of this dissertation, the temperature correction and high-altitude aerosol extinction coefficients are used. Figure 3.20 shows a comparison of the pre-

**Figure 3.20.** Comparison between MAX DOAS measurement (black), and VLIDORT modeling efforts with (red) and without (blue) temperature and aloft aerosol correction.
temperature and aloft-aerosol corrections with the MAX-DOAS observation at that time. Although there is still not perfect model-measurement agreement, a considerable amount of the disparity has been removed especially at elevation altitudes close to the horizontal, which samples altitudes of which the MAX-DOAS is most sensitive to. The -4°, -6°, and -8° elevation angles are more sensitive to the boundary layer, and therefore it’s likely that the disparity between the forward modeling of O₄ and the MAX-DOAS observations are the result of varying levels of aerosol extinction in the boundary layer which can now be explored through optimal estimation techniques.
4. Optimal Estimation

4.1. Background theory – the Inverse Problem

Forward modeling has been an illuminating first step for performing model-observation validation. However, it operates primarily by selecting a base set of atmospheric profiles and using the model to generate a set of results to simulate the observations from MAX-DOAS measurements. In practice, the MAX-DOAS method generates trace gas DSCDs and the vertical profiles are the unknown quantities of interest. For our analysis, it was found useful to develop a method to calculate an estimate of the vertical profiles of trace gas concentrations and aerosol extinction coefficients from our scattered-sunlight MAX-DOAS measurements. The methods used here fall under the general category of methods developed to solve the “inverse problem”, where from a set of observations the factors that cause it can be solved by working backwards using a model.

Stated in terms of the MAX-DOAS, the retrieval of aerosol extinction and trace gas vertical profiles requires an inversion of the measurement problem, i.e., a reverse calculation from the observed MAX-DOAS DSCDs to the profiles. This method is often commonly called “optimal estimation.” The mathematical basis and solutions of this inverse problem has been described in detail by Rodgers (2000), and will be reviewed here. One of the advantages of optimal estimation, besides its computational efficiency, is that it provides means to systematically weigh the retrievals appropriately with measurement error and error in the prior knowledge of the state of the atmosphere. Frieß
et al. (2006) proposes the use of optimal estimation for the retrieval of atmospheric aerosol extinction profiles from O₄ DSCDs as well as relative radiances. This approach has since been applied in a number of studies, often using parameterizations of the aerosol profile rather than profiles directly (Irie et al., 2008, Clemer et al., 2010). Optimal estimation has also been used to derive vertical profiles of NO₂ (e.g., Preston et al., 1997; Hendrick et al., 2004, 2014; Schofield et al., 2004; Vlemmix et al., 2011), HCHO (Vigoroux, 2009), SO₂ (Pinardi et al., 2014), and BrO (Hendrick, 2007). It should be noted that the retrieval of vertical trace gas concentration profiles of weak absorbers, is a linear problem and thus easier to solve once the aerosol profile is known. More recently, optimal estimation has found application in airborne MAX-DOAS observations (e.g., Dix, 2009, Prados-Roman et al., 2011, Merlaud et al., 2011) and satellite-based DOAS measurements (e.g., Sanghavi et al., 2012). Other methods for solving the inverse problem, such as the Chahine method (e.g. Palazzi et al., 2008) have also been used as well as simpler minimization problems using the residual sum of squares (Halla et al., 2011).

4.2. Retrieval Theory

Traditionally, changes in radiances are used to obtain information about aerosols in remote sensing applications, requiring absolute radiance calibration of instruments. For DOAS applications, it has been found that O₄ DSCDs can be used as the measurement vector to obtain information about aerosol extinction profiles (Wagner et al., 2004, Frieß et al., 2006). This has multiple advantages, among them that boundary
layer measurements, especially at the MAX-DOAS’s low elevation angles, are sensitive to changes in O₄. In addition, the retrieval is less influenced by the effects of clouds. We have adopted this approach here using a forward model $F$ as a description of the physics of the measurement process. $F$ relates the measured vector of O₄ DSCDs, $\mathbf{y'}$, to the state vector $\mathbf{x}$, which, in this case, are the height resolved aerosol extinction coefficients. In the case of the trace gas the measurement vector $\mathbf{y}$ consists of the NO₂ or HCHO DSCDs, and the state vector $\mathbf{x}$ consists of the NO₂ or HCHO vertical concentrations, respectively:

$$\mathbf{y'} = F(\mathbf{x}, \mathbf{b}) + \mathbf{\epsilon}$$  \hspace{1cm} (4.1)$$

Here $\mathbf{b}$ is the parameter vector of other model variables, such as albedo, aerosol optical properties, that are not part of the retrieval. $\mathbf{\epsilon}$ is the error term encompassing both instrumental and model errors. The retrieval strives to determine $\mathbf{x}$ by minimizing the cost function $\chi^2(\mathbf{x})$, which is a quantification of the disparity between the measurements and the model observations:

$$\chi^2(\mathbf{x}) = [\vec{F}(\vec{x}) - \vec{y}]^T S_\epsilon^{-1} [\vec{F}(\vec{x}) - \vec{y}] + [\vec{x} - \vec{x}_a]^T S_a^{-1} [\vec{x} - \vec{x}_a]$$  \hspace{1cm} (4.2)$$

Here $S_\epsilon$ and $S_a$ are the measurement and a priori covariance matrices, respectively, and $\vec{x}_a$ is the a priori knowledge of the state vector. The solution of this problem has been described in Rodgers, (2000). For a linear model function, the solution of this inversion can take many forms. One such example is as follows:
\[
\hat{x} = \left[ K^T S_e^{-1} + S_a^{-1} \right]^{-1} [K^T S_e^{-1} \hat{y} + S_a^{-1} \bar{x}_a ]
\]  

(4.3)

where the matrix \( K \) is the Jacobian, i.e. the multiparameter gradient:

\[
\vec{\nabla} \vec{F}(\bar{x}) = K = \frac{\partial \hat{y}}{\partial \bar{x}}
\]  

(4.4)

For our approach, \( K \) is calculated by VLIDORT as a matrix whose row elements correspond to the measurement vector elements (in our case the measured DSCDs), while the column elements correspond to the quantity of interest in each vertical model grid box (e.g. aerosol extinction coefficient or trace gas concentration).

We have found that this approach can be employed for retrieving vertical trace gas concentrations from the DSCDs obtained from the DOAS algorithm if the effects of atmospheric aerosol on the radiative transfer are sufficiently well known.

As the effects of aerosols on the radiative transfer in the atmosphere are inherently nonlinear, the Linear-Bayesian solution is not always able to retrieve aerosol extinction profiles. Consequently, we have implemented a nonlinear, numerical, iterative approach that uses VLIDORT and the well-established Levenberg-Marquardt algorithm (Levenberg 1944, Marquardt, 1963). VLIDORT is used in each optimization step to calculate a new state vector \( \bar{x}_i \), as well as the Jacobian that is used in the optimization process:
\[
\bar{x}_{i+1} = \bar{x}_i + [(1 + \gamma) S_a^{-1} + K^T S_e^{-1} K]^{-1} \left[ K^T S_e^{-1} \left( \bar{y} - \bar{F}(\bar{x}) \right) - S_a^{-1} (\bar{x}_i - \bar{x}_a) \right]
\] (4.5)

The iteration is started using the \textit{a priori} estimate \( \bar{x}_a \) as the initial estimate \( \bar{x}_i \), and at each step, a newer retrieved profile is calculated. The Levenberg-Marquardt algorithm is an interpolation of the Gauss-Newton method and a Steepest-Descent/Gradient Descent method. The \( \gamma \) parameter determines to what extent each algorithm contributes; for \( \gamma \to 0 \), the algorithm tends towards Gauss-Newton, and for \( \gamma \to \infty \), the algorithm tends towards the steepest descent method. The Levenberg-Marquardt algorithm has the advantage that it optimizes the convergence of the iteration and that it has a very high likelihood to converge to one single result.

The Levenberg-Marquardt algorithm is run until one of several convergence criteria is met. First, after each step the cost function \( \chi^2(\bar{x}) \) is calculated as described above. If at the current step the cost function is improved (i.e., the new aerosol profile results in a reduction in the difference between the observed measurement vector and the modeled measurement vector), the newly retrieved profile is set to be the new iterative state. As Gauss-Newton is ideal for situations in which the true state is close to the current iteration step, \( \gamma \) is reduced, and the algorithm is repeated. Alternately, if the cost function increases, the new retrieved profile is rejected, and \( \gamma \) is increased, adjusting the algorithm in the direction of a steepest descent method. The cost function of the final iterative step also serves as a measure of the quality of the retrieval, with a lower cost function indicating a better fit.
There are many variations of the Levenberg-Marquardt iteration, but Fletcher (1971) suggested that at each stage $\gamma$ be reduced by a factor of two, and increased by a factor of 2 to 10; we currently start $\gamma$ at 0.01 (in other words, in the realm of a Gauss-Newton algorithm), and reduce it by a factor of two and increase it by ten. We found that if the overall retrieved aerosol profile changed by 10% or less after an iteration, additional iterations provide little improvement, so we treat this as a condition for convergence. If too many iterations pass without an improvement in the cost function, or if $\gamma$ becomes too high, the iteration is also halted.

In practice, the vast majority of our aerosol extinction retrievals typically converge in 5-10 iterations, due to the profile changing less than 10% between iterations. In less than ideal conditions, as much as 15 iterations are needed before the algorithm can reach convergence. If the final cost function is less than a set cutoff value, then the trace gas concentration profile can be retrieved; as this can be done with a single stage linear Bayesian retrieval, the trace gas retrieval requires significantly less computational time, and also avoids convergence problems.

The choices of covariance error matrices for the measurements $S_\epsilon$ and a priori estimates $S_\alpha$ were found to have significant effects on the quality of the retrieval. We have found that the error covariance matrices for both the a priori and the measurement vectors are largely dominated by the diagonal elements. As the off-diagonal elements are likely comparatively small we set them to 0, essentially assuming that they were uncorrelated, and that each measurement vector element is independent. The measurement error covariance matrix was thus expressed as a diagonal matrix consisting of the squares of the DSCD retrieval errors from the DOAS procedure:
where $e_\theta$ is the error coefficient from the DOAS fit to the DSCD at elevation angle $\theta$.

For NO$_2$ and O$_4$, this error is an absolute error, typically on the order of 1-5%. As it is believed that the retrieval error should dominate the measurement error term, other random, systematic, and model errors are ignored.

The \textit{a priori} error covariance matrix is more difficult to estimate. The coefficients $e_i$ of the \textit{a priori} error covariance matrix may vary considerably, as the daily atmospheric conditions in Los Angeles can change drastically, but the chosen values significantly affect the convergence of the retrieval algorithms, and as such must be selected carefully. It is possible to parameterize the \textit{a priori} covariance matrix using error coefficients, similar to how the error covariance matrix is determined above:

\[
S_a = \begin{bmatrix}
(e_1 \cdot x_1)^2 & \cdots & 0 \\
\vdots & \ddots & \vdots \\
0 & \cdots & (e_n \cdot x_n)^2
\end{bmatrix}
\]  \hspace{1cm} (4.7)

The choice of error coefficients can have a significant effect on the final retrieval. Error coefficients that are too small can constrain the estimates to the \textit{a priori} values and also fail to represent the volatility of boundary layer conditions above Los Angeles. However, too large of an error estimate can result in unstable retrievals due to the aforementioned
under-posed nature of the inverse problem. Unfortunately, unlike the error covariance matrix, the choice of the \textit{a priori} covariance matrix is not as straightforward. For the synthetic studies detailed in section 4.4, this error coefficient model, consisting of a diagonal \textit{a priori} error covariance matrix was used.

\section*{4.3. Information Content}

An important question for the quality of the retrievals is the amount of vertical information that can be retrieved. The optimal estimation technique provides tools to perform such an analysis. The gain matrix $G$ describes the sensitivity of the retrieval $\hat{x}$ to the observations $\hat{y}$, such that

$$
G = \frac{\partial \hat{x}}{\partial \hat{y}} = \hat{S} K^T S_e^{-1} \quad \text{where} \quad \hat{S} = (K^T S_e^{-1} K + S_a^{-1})^{-1}
$$

Significantly, $\hat{S}$ is the error term of the retrieval. This can then be used to determine the averaging kernel $A$, a quantity that measures the impact of each of the state vector elements on the retrieval:

$$
A = \frac{\partial \hat{x}}{\partial \hat{x}} = \frac{\partial \hat{x}}{\partial \hat{y}} \frac{\partial \hat{y}}{\partial \hat{x}} = GK \quad \text{(4.8)}
$$
The averaging kernel $A$ is a square matrix whose elements range ideally from 0 to 1; if an element is close to 1, the state vector elements will change almost perfectly with the true atmospheric state, even without an \textit{a priori} constraint. An averaging kernel of 0 suggests no information from the true atmospheric state at all. It is possible to obtain averaging kernels outside of this range. For averaging kernels greater than 1, the retrieval is overly sensitive to the individual state vector at certain points, and for averaging kernels less than 0, the retrieval is anti-correlated to the state vector. For regions of the atmosphere where there is little to no influence, it is possible to see slightly negative averaging kernels that may still be within the noise. Simply speaking, the averaging kernels serve as an indicator for the sensitivity of the retrieved quantity to the true value of the quantity being measured at each altitude layer, with the peak of each averaging kernel corresponding to the altitude of maximum sensitivity, and the width of the averaging kernel indicating which altitude layers the MAX-DOAS is sensitive to.

Inevitably, improvements in radiative transfer modeling and \textit{a priori profile} and error characterization can improve these averaging kernels. The degrees of freedom are the number of independent parameters that can be obtained through this optimal estimation. They are determined by taking the trace (or sum of the diagonals) of the averaging kernel matrix. Both the averaging kernels and degrees of freedom are used to determine the quality of the retrieval for each set of observations.
4.4. Description of optimal estimation for MAX-DOAS

VLIDORT was configured to analytically calculate Jacobians for both stages of the two-step process detailed in Figure 4.1. For the aerosol retrieval, $K$ is defined as the partial derivative of each measured $O_4$ DSCD with respect to aerosol optical depth per altitude. For the trace gas retrieval, $K$ is defined as the partial derivative of each measured trace gas DSCD with respect to the vertical concentration profile of that trace gas. The details of these modifications are detailed below.

Traditionally, for the purposes of satellite-based retrievals, Jacobian matrices were designed for measurements consisting of radiances observed by a spectrometer. As such, the Jacobian provided by VLIDORT natively takes the form:

$$\frac{\partial I}{\partial C} \quad (4.9)$$

where $I$ is the measured intensity and $C$ is the concentration of the absorber at each height interval $j$. Some modifications to the Jacobian matrix were required for our circumstance. For a MAX-DOAS trace gas retrieval using calculated DSCDs, where the state vector consists of the concentration at each of the $j$ height intervals, $C_j$, our desired final form is the Jacobian matrix:

$$\frac{\partial DSCD_i}{\partial C_j} \quad (4.10)$$
where the measurement vector consists of all \( i \) DSCDs that are in a single vertical scan of measurements taken at a single azimuth viewing angle, for seven different elevation viewing angles (-8°, -6°, -4°, -2°, 0°, +3°, +6°) with 0° being the horizontal limb-scanning mode. As the MAX-DOAS instrument typically takes a full vertical scan of these elevations within a time span of 15 minutes, we assume that this set of measurements samples the bulk of the atmosphere from the surface to the level of CLARS near simultaneously.

As mentioned previously, VLIDORT calculates the SCD of a trace gas using the ratio method:

\[
SCD = -\frac{1}{\sigma} \log \left( \frac{I}{I_0} \right) 
\]

We can therefore express the calculation of the Jacobian matrix as such, by taking the partial derivative of the SCD expression, to calculate a format in terms of \( \frac{\partial I}{\partial C} \):

\[
\frac{\partial SCD}{\partial C} = \frac{\partial}{\partial C} \left( -\frac{1}{\sigma} \log \left( \frac{I}{I_0} \right) \right)
\]

\[
= -\frac{1}{\sigma I} \frac{\partial (I)}{\partial C}
\]

\[
= -\frac{1}{\sigma \cdot I} \frac{\partial I}{\partial C}
\]

\[ (4.12) \]
which is the transformation of the Jacobian \( \frac{\partial I}{\partial c} \) into \( \frac{\partial SCD}{\partial c} \).

In order to perform the Levenberg-Marquardt iteration to retrieve vertical aerosol extinction profiles from measured O\textsubscript{4} DSCDs, the Jacobian needed is to be of the form:

\[
\frac{\partial DSCD(O_4)}{\partial \varepsilon} \quad (4.13)
\]

where \( \varepsilon \) is the aerosol extinction coefficient at each altitude layer. This is the ideal form for a retrieval in which the measurement vector consists of O\textsubscript{4} DSCDs. If, for this case, \( \sigma \) is the absorption coefficient of O\textsubscript{4}, \( I \) and \( I_0 \) are the VLIDORT simulated radiances with and without the presence of aerosols in the atmosphere, then we can derive an expression for the necessary Jacobian matrix by evaluating the derivative by the chain rule, and applying the Lambert-Beer Law:

\[
\frac{\partial DSCD(O_4)}{\partial \varepsilon} = \frac{\partial}{\partial \varepsilon} \left( \frac{1}{\sigma} \log \left( \frac{I}{I_0} \right) \right)
\]

\[
= \frac{1}{\sigma} \frac{\partial \left( \log \left( \frac{I_0}{I} \right) \right)}{\partial \varepsilon}
\]

\[
= \frac{1}{\sigma} \frac{\partial \left( \log (I_0) - \log (I) \right)}{\partial \varepsilon}
\]
In order to calculate \( I \) and \( I_0 \), VLIDORT is run twice, both times with completely identical atmospheric parameters, except that \( I_0 \) is calculated with a completely aerosol-free atmosphere; in effect \( I_0 \) is calculated in a Rayleigh scattering-only atmosphere. Thus, the resulting Jacobian matrix is sensitive to only the influence of aerosols on the \( O_4 \) DSCDs.

**Figure 4.1** Schematics of the “two-stage” retrieval of aerosol from MAX-DOAS \( O_4 \) DSCDs and then the trace gas retrievals from the retrieved MAX-DOAS trace gas DSCDs (e.g., \( NO_2 \) and HCHO).
Figure 4.1 shows the general schematic used for retrieving vertical profile following the “two-stage” method, where for each observation an aerosol extinction profile is retrieved first, followed by a separate inversion step for the vertical trace gas profile. A set of wrapper codes was set up to perform these retrievals. Two versions of VLIDORT were created, one to calculate O$_4$ DSCDs and simulate aerosol effects, and the other to calculate NO$_2$ DSCDs and vertical trace gas concentrations.

At each stage, atmospheric parameters to best simulate the conditions at the time of each measurement are input into VLIDORT, and MAX-DOAS DSCDs are simulated using conditions and viewing geometry as close to the actual MAX-DOAS measurements as possible. The matrix transformations detailed in this section are performed in the wrapper code, using intensity Jacobians generated by VLIDORT, and the optimal estimation routines are done at each step. This process can be performed on specific sets of measurements, and can also be automated to be performed automatically over large amounts of data, along with filtering of clouds using the algorithms detailed in section 3.2.

### 4.5. Theoretical Retrievals

We performed extensive tests on the retrieval using a number of synthetic aerosol extinction profiles as well as a number of NO$_2$ vertical concentration profiles. These profiles were chosen to recreate typical atmospheric conditions observed at Mt. Wilson. Using VLIDORT, a sample “true” aerosol extinction profile was simulated and a set of
synthetic O$_4$ DSCDs was obtained. Using these O$_4$ DSCDs as the measurement vector, an aerosol profile was retrieved and compared to the true state. In addition to testing our retrieval codes, these tests allowed us to better understand the behavior of the retrieval. The tests were conducted at a 360 nm wavelength, in the ultraviolet region, which corresponds to a strong O$_4$ absorption. Our distribution of VLIDORT was configured to use the Henyey-Greenstein parameterization that modeled aerosol optical properties as a function of aerosol asymmetry and single-scattering albedo (Henyey et al., 1941), and as such for this study VLIDORT simulated an aerosol profile that had an asymmetry of 0.68, and a single-scattering albedo of 0.99. The single scattering albedo was chosen as a rough composite of values observed at the CalNex ground site (Dubovik and King, Thompson et. al., 2012), while the asymmetry factor was chosen as an average value among observed aerosol asymmetry parameters (Andrews et. al., 2006; Dubovik and King, 2008). Our weighting functions suggested that most of the scattered sunlight observed by the MAX-DOAS scatters off the atmosphere and not off the ground, but nevertheless a surface albedo of 10%, roughly corresponding to what has been observed over urban environments, was used.

The a priori profile used for this theoretical simulation consisted of a vertical “box”, in which a boundary layer of a certain height was set, below which elevated aerosol extinction and NO$_2$ concentrations were simulated. Except for when the effects of a variable boundary layer on information content was being tested (Table 4.2), we used a 1 km boundary layer height. Above the boundary layer, extremely small amounts of aerosol and trace gas concentrations were used, to simulate a comparatively clean free
troposphere. For this study, we used an exponentially decreasing aerosol extinction profile with increasing altitude, starting at the top of the boundary layer.

To create a set of synthetic MAX-DOAS DSCDs, a synthetic “true state” was created by taking the \textit{a priori} aerosol vertical extinction profile and increasing the extinction coefficient at all altitudes by 50%. This “true state” was input into VLIDORT, which then simulated a set of $O_4$ DSCDs. These DSCDs were then substituted for the measurement vector for the nonlinear Levenberg-Marquardt algorithm. We also made VLIDORT simulations with a synthetic true state that was only 50% of the \textit{a priori} aerosol extinction at all altitudes. We used the error coefficient parameterization of the \textit{a priori} error covariance matrix, $S_a$, as described in section 4.2, where the off-diagonal elements of the covariance matrix were set to zero, while the diagonal elements were set to the square of a set percentage of the \textit{a priori} aerosol extinction profile. As the aerosol extinction is extremely small above the boundary layer, this essentially allows the retrieval to primarily fit the extinction in the boundary layer. The measurement error covariance matrix’s ($S_e$) off-diagonal elements were also set to zero, while the diagonal elements were set to the square of an error coefficient times the simulated $O_4$ DSCD; henceforth the percentage of the error coefficient will be used to describe the error of the $O_4$ DSCDs. The percentage used was found to have a significant effect on the convergence of the retrieval. We experimented with measurement errors ranging from several percent of the $O_4$ DSCD (the MAX-DOAS can typically retrieve down to a 1% retrieval error from the DOAS fit), down to measurement error of 0.1% of the $O_4$ DSCD, which is significantly better than what is currently possible with MAX-DOAS instruments.
Figure 4.2 shows two examples of such a theoretical retrieval for the same profile and two different errors of the O₄ DSCDs. The right panel illustrated the averaging kernel of the retrieval, which quantifies the impact of each of the state vector elements on the retrieval. Based on this sensitivity analysis, we can also determine the amount of information that theoretically can be retrieved from the Mt. Wilson observations. In the case of aerosol extinction, for realistic atmospheres the number of independent pieces of information can vary greatly depending not only on the measurement and a priori error estimates, but also on a number of optical parameters and on the size and shape of the vertical aerosol extinction profile.
Figure 4.2. Examples of theoretical aerosol extinction profile retrievals with measurement errors of 0.1% (top) and 1% (bottom). The retrieval algorithm has a number of degrees of freedom of 4-5, and is thus able to retrieve the profile with four to five pieces of independent information, depending on the measurement error.
Table 4.1. Dependence of the theoretical DOFs of aerosol extinction retrievals on measurement and *a priori* error. These results were derived for a 1 km high boundary layer with an aerosol extinction of 0.1 km$^{-1}$.

<table>
<thead>
<tr>
<th>A priori error</th>
<th>Measurement error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2%</td>
</tr>
<tr>
<td>10%</td>
<td>3.94</td>
</tr>
<tr>
<td>20%</td>
<td>4.49</td>
</tr>
<tr>
<td>50%</td>
<td>4.89</td>
</tr>
<tr>
<td>100%</td>
<td>5.23</td>
</tr>
<tr>
<td>500%</td>
<td>5.73</td>
</tr>
</tbody>
</table>

Table 4.1 shows the degrees of freedom for the theoretical aerosol retrievals for a combination of measurement errors and *a priori* errors used in this study, as defined by the error-coefficient parameterization. As expected, the information content can be greatly improved by improvements in instrument precision; this highlights the advantages of making improvements in future generations of monitoring instruments. It is worth noting that one can obtain artificially high information content by increasing the *a priori* error to unreasonably high levels (essentially removing the influence of the *a priori* estimate), but the resulting retrieval is under-posed and quickly becomes unstable. Likewise, by having extremely high measurement errors of 5% or more, the amount of information that can be retrieved is sharply reduced. However, for typical conditions the MAX-DOAS measurement error is roughly on the order of 1-3%, and the best retrieval results are found when the *a priori* error is roughly 25-50% of the *a priori* profile. In
these cases our theoretical simulations suggest that 3-4 degrees of freedom are obtainable by our retrievals.

Table 4.2 shows the results of theoretical retrievals for a variety of atmospheric aerosol vertical profiles where two parameters are varied, the boundary layer aerosol extinction coefficient (assuming a well-mixed extinction in this boundary), and the boundary layer height. These all assume a free tropospheric profile that exponentially decreases with height, starting from the top of the boundary layer. For these tests, the measurement error is fixed at 1%, while the \textit{a priori} error covariance matrix is set at 25%, which from the above table is a relatively low error estimate.

\textbf{Table 4.2}. Theoretical DOFs for an aerosol extinction retrieval with a 1\% measurement error and a 25\% \textit{a priori} error. The likely observed conditions for the South Coast Air Basin are bolded.

<table>
<thead>
<tr>
<th>Boundary Layer Height (km)</th>
<th>0.05</th>
<th>0.1</th>
<th>0.25</th>
<th>0.5</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3.66</td>
<td>3.63</td>
<td>3.56</td>
<td>3.41</td>
<td>2.93</td>
</tr>
<tr>
<td>0.5</td>
<td>3.65</td>
<td>3.61</td>
<td>3.49</td>
<td>3.15</td>
<td>2.64</td>
</tr>
<tr>
<td>1.0</td>
<td>3.63</td>
<td>3.56</td>
<td>3.35</td>
<td>2.77</td>
<td>2.09</td>
</tr>
<tr>
<td>1.5</td>
<td>3.59</td>
<td>3.48</td>
<td>2.97</td>
<td>2.82</td>
<td>2.16</td>
</tr>
<tr>
<td>2.0</td>
<td>3.57</td>
<td>3.43</td>
<td>2.81</td>
<td>2.42</td>
<td>1.62</td>
</tr>
</tbody>
</table>
When only a small amount of aerosol extinction is present in the boundary layer, there is very little difference in changing the boundary layer height, as the atmosphere is largely optically thin down to the surface. However, as the aerosol extinction increases, the boundary layer gets increasingly opaque, and the degrees of freedom of the retrieval is greatly reduced. Perhaps unsurprisingly, for extremely low aerosol extinction profiles, there is very little influence of boundary layer height on degrees of freedom. For extinction coefficients around 0.05 km$^{-1}$, consistently around 3.6 degrees of freedom are observed. When the boundary layer is extremely low (0.1 km), very little information is lost as aerosol levels increase, but for higher boundary layers, more information is lost; as much as a degree of freedom or more with a 1 km boundary layer height, and more than that for significantly elevated layers. If, however, we look at typical environments with a 1 km boundary layer height, and aerosol extinction coefficients in the boundary layer limited to 0.1-0.3 km$^{-1}$, we are able to consistently obtain about 3-3.5 degrees of freedom.

As the MAX-DOAS is observing in an urban environment that is typically highly polluted, the loss of information in high aerosol regimes poses a challenge for aerosol retrievals. This effect has been observed in our actual retrievals from Mt. Wilson. However, the most extreme examples in Table 4.2 tend to be significantly greater than what is typical, and in Los Angeles the boundary layer height and boundary layer aerosol extinction are not independent of one another, as they are treated in this theoretical retrieval. Although they are sensitive to local emissions and grow throughout the day, boundary layer height and extinction are not independent of one another and often are inversely related. The results of these tests thus indicate that with a 25-50% $a$ priori
error, standard retrieval error for our O$_4$ DSCDs, and typical aerosol conditions in Los Angeles, we can see between 3.5-4.5 degrees of freedom in typical polluted cases.

We similarly performed theoretical retrievals for NO$_2$ vertical profiles from simulated DSCDs. A fixed aerosol profile with a boundary layer height of 1 km, and a boundary layer extinction of 0.25 km$^{-1}$ was used for these tests. Like the aerosol retrievals, VLIDORT was given an a priori NO$_2$ vertical concentration profile, and a set of NO$_2$ measurements was simulated by varying the a priori profile by 50%, using this as a “true” NO$_2$ state, and generating a set of NO$_2$ DSCDs. We experimented with both a linear Bayesian inversion and the nonlinear iterative Levenberg-Marquardt inversion, but found that although there was a slight improvement with a Levenberg-Marquardt inversion, it came at the cost of significantly greater computational costs and as such it was decided to rely on the Linear-Bayesian inversion for our NO$_2$ retrievals.
Figure 4.3. Examples of theoretical NO\textsubscript{2} trace gas profile retrievals with measurement errors of 0.1\% (top) and 1\% (bottom). The retrieval algorithm has a number of degrees of freedom of 4-5, and is thus able to retrieve the profile with four to five pieces of independent information, depending on the measurement error.
Figure 4.3 shows two retrievals of synthetic NO\textsubscript{2} DSCDs, using a simulated NO\textsubscript{2} true state within VLIDORT. Again, depending on whether the measurement error ranges from 0.1 to 1\%, the degrees of freedom from our theoretical retrievals ranges from 4.5 to 5.5. Due to the idealized conditions the retrieved information content is higher than what is practically observed in the atmosphere, although the information content is still larger than was previously observed.

Table 4.3. Theoretical DOFs from NO\textsubscript{2} concentration retrievals by measurement and \textit{a priori} profile error for a boundary layer aerosol extinction of 0.1 km\textsuperscript{-1} and a boundary layer height of 1 km.

<table>
<thead>
<tr>
<th>\textit{A priori} error</th>
<th>Measurement Error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.2%</td>
</tr>
<tr>
<td>10%</td>
<td>4.95</td>
</tr>
<tr>
<td>20%</td>
<td>5.59</td>
</tr>
<tr>
<td>50%</td>
<td>6.23</td>
</tr>
<tr>
<td>100%</td>
<td>6.69</td>
</tr>
<tr>
<td>500%</td>
<td>6.98</td>
</tr>
</tbody>
</table>

Table 4.3 shows the degrees of freedom for the theoretical NO\textsubscript{2} retrievals for a combination of measurement errors and \textit{a priori} errors. We see a greater variability in the retrieved degrees of freedom, compared to what we see in Table 4.1 for the equivalent test of our aerosol retrievals; this we attribute to the greater sensitivity of our retrievals to NO\textsubscript{2}, compared to aerosol extinction. We would also like to call attention to the
observed improvements in information quality that are possible if the measurement error of current DOAS systems is improved. Table 4.4 shows the degrees of freedom for a variety of atmospheric NO$_2$ vertical profiles, defined by boundary layer NO$_2$ concentration and boundary layer height. Note that Table 4.4 is conducted for one specific aerosol profile, and the actual retrieved profiles are likely to be influenced by higher aerosol extinction coefficients.

Table 4.4. Theoretical DOFs from NO$_2$ concentration retrieval by shape of a priori estimate of vertical concentration profile with a boundary layer aerosol extinction of 0.1 km$^{-1}$.

<table>
<thead>
<tr>
<th>Boundary Layer Height (km)</th>
<th>NO$_2$ boundary layer concentration (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td>0.1</td>
<td>4.62</td>
</tr>
<tr>
<td>0.5</td>
<td>4.62</td>
</tr>
<tr>
<td>1.0</td>
<td>4.65</td>
</tr>
<tr>
<td>1.5</td>
<td>4.67</td>
</tr>
<tr>
<td>2.0</td>
<td>4.73</td>
</tr>
</tbody>
</table>

Nevertheless, from an elevated mountaintop position, in the absence of an opaque aerosol layer, the UCLA MAX-DOAS is expected to see roughly 3.5-4 degrees of freedom if the a priori profile is constrained to 25-50% of its base value; in practice deviation from this value often leads to either highly unstable retrievals, or little deviation from the a priori profile.
It is of note that this is purely the information content from retrievals from measurements conducted solely in the 360 nm wavelength O₄ absorption band, and we can see typically greater degrees of freedom than is typically observed from ground based observations. A survey of recent efforts to perform vertical profile retrievals of NO₂ and similar trace gases using primarily ground-based upwards viewing MAX-DOAS instruments suggest degrees of freedom of, respectively, 1.5-2 (Clemer et. al., 2010), 2-3 (Vlemmix et. al., 2011), ~1 (Sinreich et. al. 2013), 0.7-2.1 (Wang et. al., 2014), and ~2 (Coburn et al., 2014). In comparison, despite variations depending on choice of a priori profile and error constraints, this theoretical study find that we are consistently able to find 4-5 pieces of information from our retrievals.

In practice we have found that using a priori errors of 25-50% lead to stable retrievals of both aerosol extinction and trace gas concentration. The a priori error estimate also must encompass the range to which the true state can vary, which in the turbulent boundary layer of polluted environments can vary considerably, so it is unrealistic to expect improvements in a priori error. Improvements in the measurement error percentage, however, are possible with improvements in instrument resolution and quality, and in DOAS retrievals of slant columns; we find that if instrument error can be further reduced, these reductions will have a significant impact on the quality of the vertical profiles retrieved.
4.6. Aerosol Lookup Table

As previously mentioned, the MAX-DOAS scans a full set of vertical elevation angles at a single azimuth angle, and the DOAS algorithm provides a set of measured DSCDs of O$_4$ and NO$_2$ at each of those elevation angles, taken at typically no more than 15 minutes apart from one another. We used the aforementioned “two-stage” retrieval to take advantage of the CLARS scanning sequence by first retrieving the aerosol extinction profile using MAX-DOAS O$_4$ measurements. Then, this aerosol extinction profile is retained, while the Linear-Bayesian algorithm is used to retrieve the NO$_2$ vertical profile.

We encountered numerous challenges to obtaining a successful convergence using the non-linear Levenberg-Marquardt algorithm. As mentioned in section 3.5.1, in recent years, the temperature dependence in O$_4$ absorption cross sections has been found to be potentially non-trivial, up to 22% over the range of 196-296 K (Pfeilsticker et. al., 2001), and existing uncertainties in O$_4$ absorption cross sections may present significant sources of error. For our forward modeling of O$_4$, we have used a standard atmospheric temperature profile in VLIDORT, and combined this with a linear interpretation of the O$_4$ cross sections at a number of temperatures, as measured by Thalman and Volkamer (2013), in order to create a variable vertical profile of O$_4$ cross sections. As with the forward model, real-time temperature data at Mt. Wilson from the NOAA National Climatic Data Center (NOAA NCDC) were incorporated into an estimated temperature profile assuming a 6.5 K/km lapse-rate; this was done using measurements as close to the time of the DOAS measurements whenever possible (Menne et. al., 2012). Figure 4.4 shows the influence temperature can have on our VLIDORT modeled O$_4$ DSCDs, once
both the temperature dependent $O_4$ cross sections and the temperature sounding is incorporated into VLIDORT.

![Temperature Effects on $O_4$]

**Figure 4.4.** Effects of temperature on modeled $O_4$ DSCDs. These DSCDs are all generated with an identical aerosol extinction profile (1 km boundary layer height, 0.1 km$^{-1}$ extinction) and viewing geometry. Here temperature effects are incorporated into VLIDORT using both temperature dependent $O_4$ cross sections, and the vertical temperature profile.

An even larger challenge may be the day-to-day variability in the aerosol profile. The aerosol content of Los Angeles varies on a day-to-day basis, to the extent that using a
single “standard” profile as an *a priori* estimate will be largely inadequate for modeling the sheer variety of aerosol profiles present over years of data. It is not sufficient to model just the boundary layer aerosol extinction value varies; we have found that the retrieval often struggles to capture the variation in boundary layer height adequately.

Aerosol optical properties have a large influence on O₄ DSCDs and vary greatly on short temporal scales (Thompson et. al., 2012). In section 3.4, we showed sensitivity tests of various optical properties, finding as much as a 10% change in modeled O₄ DSCDs due to variations in single scattering albedo, a 6% change from variations in aerosol asymmetry factor, and 3-4% change from variations in surface albedo. However due to lack of information, our retrieval assumes a fixed “best” value for aerosol asymmetry factor and single scattering albedo. This effect may be mitigated by the fact that the aerosol extinction coefficient is not independent of these optical parameters; errors in the estimates of aerosol optical parameters will be reflected and compensated for in the retrieved aerosol extinction, with a minimized effect on the retrieved trace gas vertical profile.

To improve the convergence of the data, we adopted the use of a look-up table in conjunction with the optimal estimation. Optimal estimation routines are mathematically complex and are highly demanding on computational power, requiring multiple instances of the radiative transfer model to be run per-measurement. The computational demands of optimal estimation routines scale with the size of the dataset to be considered; sufficiently large datasets such as those generated by autonomous MAX-DOAS systems thus require large amounts of computational time to analyze.
It is important to note that traditionally lookup tables were used as the sole retrieval mechanism (e.g., Li et. al., 2010). Lookup tables have traditionally been popular because a retrieval algorithm that consists of simple comparisons to a lookup table are easier to implement, and as all of the necessary radiative transfer calculations can be performed once, i.e. the computational demands do not scale with the size of the dataset to be compared with (e.g., Rahman et. al., 1994; Mitchell et. al., 1993; Grey et. al., 2006). On the other hand, the quality of the retrieval is highly dependent on the quality of the model and the measurements, and as the inherent errors due to model and measurement uncertainty, or the errors due to a lack of knowledge of the physics of the system being considered, are not taken into account when comparing the system to a lookup table, an argument can be made that a simple lookup table comparison is “less correct” than optimal estimation models. In addition, the number of situations to incorporate in a lookup table can be immense, as each additional state variable to consider adds a layer of complexity to the table, and to correctly account for the “resolution” of the atmosphere often requires an interpolation among the dimensions of the lookup table.

Here, we implemented combining lookup tables with our existing optimal estimation routine. This is essentially combining the two methods in a way designed to complement each other. A lookup table was created for the purpose of choosing a suitable a priori aerosol extinction profile, as well as other unfitted factors for the retrieval. The selected a priori aerosol profile was then input into the Levenberg-Marquardt algorithm which, using VLIDORT as the forward model, is used to retrieve the best vertical extinction profile.
Table 4.5. Parameters used to generate the lookup table. Every combination of these parameters was incorporated into a separate VLIDORT run, and a set of $O_4$ DSCDs corresponding to each profile was generated. Overall 15,876 separate profiles were generated. This table was then used to generate 

<table>
<thead>
<tr>
<th>Parameter (units)</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boundary Layer Height (km)</td>
<td>0.4, 0.6, 0.8, 1.0, 1.2, 1.5</td>
</tr>
<tr>
<td>Boundary Layer Extinction (km$^{-1}$)</td>
<td>0.01, 0.025, 0.05, 0.1, 0.3, 0.5</td>
</tr>
<tr>
<td>Solar Zenith Angle (°)</td>
<td>0, 10, 20, 30, 40, 50, 60, 70</td>
</tr>
<tr>
<td>Solar Relative Azimuth Angle (°)</td>
<td>0, 10, 20, 30, 40, 50, 60, 70, 80</td>
</tr>
<tr>
<td>Surface Temperature (K)</td>
<td>280, 285, 290, 295, 300, 305, 310</td>
</tr>
</tbody>
</table>

To create the lookup table, VLIDORT was run for a wide variety of atmospheric conditions. For this analysis, every permutation of five variables was run: (1) solar zenith angle, (2) solar relative azimuth angle, (3) boundary layer extinction, (4) boundary layer height, and (5) temperature. (3) and (4) describe the “box model” parameterization of the vertical aerosol distribution, with the substitution of the SAGE II aerosol extinction coefficients for values above 10 kilometers, as described in section 3.5.2. (1) and (2) represent the solar viewing geometry, which are necessary to simulate the conditions at each time step. Each profile and geometry combination was input into VLIDORT, which was run in a forward mode to generate a set of $O_4$ DSCDs for each of the MAX-DOAS viewing elevation angles (+6°, +3°, 0°, -2°, -4°, -6°, -8°, and -10°) corresponding to
every possible combination of the above five values. As is standard for lookup tables, the

calculation of the O$_4$ DSCDs is the computationally intensive state, as calculating this

lookup table took roughly a week due to number of radiative transfer calculations, but

this only needs to be done once, and afterwards all of the values are compiled together in

a table.

Table 4.5 details the parameters used to generate the lookup table, as well as the

values of each parameter tested. These were chosen to have a breath to encompass the

variety of day-to-day and year-round conditions observed in the Los Angeles air basin.
The number of values to use for each parameter was chosen to be a compromise between

the resolution of the lookup table and computational time. Overall, it took roughly a

week to generate the 15,876 profiles resulting from these elements. Figure 4.5 shows a

sample of lookup table elements from one specific solar viewing geometry.

When performing aerosol retrievals, we are therefore able to compare our

measured O$_4$ DSCDs with the lookup table and choose the parameters whose modeled O$_4$

DSCDs have a minimum residual sum of squares difference from the measured O$_4$

profile. The NOAA NCDC dataset was used to find the temperature at Mt. Wilson at
the time of each measurement, while the solar geometry is measured as part of the

operation of the MAX-DOAS.
Figure 4.5. Sample of O$_4$ DSCDs (top) and corresponding vertical aerosol extinction profile (bottom) for a variety of elements of the lookup table corresponding to one solar viewing geometry.

A subset of the lookup table consisting of the $n$ table values that correspond to the current viewing geometry and measured ambient temperature are selected, and from this subset the boundary layer height and boundary layer extinction coefficient corresponding to the best match are selected. Typically $n$ is roughly 100-150 elements, and is largely a factor of the resolution of the lookup table. We found it inconsistent to choose merely the “best” value for boundary layer height and aerosol extinction, and so a weighted
average of the resulting O₄ DSCDs of the \( \sqrt{n} \) elements with the smallest residual sum of squares (RSS) between the lookup table and MAX-DOAS O₄ DSCDs is made, with the RSS used as the weighting factor. We had also experimented with summing all \( n \) elements, but as that incorporated a number of unphysical elements the resulting average O₄ DSCD showed a large mismatch between itself and the observed O₄ DSCDs. The table is calculated such that there is less than a 50% difference in extinction coefficient in the boundary layer between each lookup table profile, and as such with a 50% error applied to this retrieval, we are able to cover a wide range of values. Figure 4.6 shows an overview of this process.

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**Figure 4.6.** Overview of incorporation of lookup table into aerosol retrieval. A set of O₄ DSCDs from the MAX-DOAS is compared to the lookup table to find the best matches. From this an aerosol extinction profile is generated and used as the *a priori* for the optimal estimation.

Partially due to the computational demands of generating lookup tables, optical depth and aerosol SSA were not included as additional variables in the lookup table. Since each element of the lookup table consists of a unique combination of the above five variables, the total number of elements consists of the products of the total number of values tested for each variable. As a result each additional variable included in the table adds another dimension, and increases the run time.

As mentioned previously, aerosol asymmetry and single scattering albedo is not independent of aerosol extinction as well, and the lookup table is not the ideal mechanism for retrieving these values in the presence of an under-posed problem. Because our method can be considered a cross between the lookup table and optimal estimation methods, we are only interested in an “initial guess”, relying on the optimal estimation to obtain our best estimate of the true state of the atmosphere, and as such we can incorporate a simpler lookup table to give us a number of initial atmospheric states, and do not have to rely on the interpolation of our lookup table to retrieve an estimate of a final aerosol profile with a good resolution.
4.7. Aerosol Retrieval

With the lookup table providing parameters, we are able to generate improved *a priori* profiles, as well as incorporate local temperature data into our retrievals. We applied these techniques to our full retrievals based on observed MAX-DOAS DSCDs. Figures 4.4 and 4.5 shows some typical retrieval of the aerosol extinction profile from optimal estimation from measured O$_4$ DSCDs, for a variety of conditions. The error-bars are calculated at each altitude level from the *a priori* and measurement error covariances as described in Rodgers (2000):

\[
\hat{S} = (K^T S^{-1}_e K + S^{-1}_a)^{-1}
\]

The results show the capability of retrieving realistic aerosol extinction profiles that exhibit a clear boundary layer and reasonable extinction values. It should also be noted that the retrieval yields different extinction values and boundary layer heights for both days.
Figure 4.7. Sample aerosol retrieval and averaging kernels, based on MAX-DOAS retrieved O$_4$ DSCDs, on June 26th, 2010. The algorithm used the combined lookup table-optimal estimation technique, and the aerosol extinction coefficients are retrieved in the 360 nm wavelength region.
Figure 4.8. Sample aerosol retrieval and averaging kernels, based on MAX-DOAS retrieved O$_4$ DSCDs, on June 24th, 2010. The algorithm used the combined lookup table-optimal estimation technique, and the aerosol extinction coefficients are retrieved in the 360 nm wavelength region. Here, although the lookup table provided a lower boundary layer height \textit{a priori}, the retrieval resulted in a much higher boundary layer height.

Our analysis of the averaging kernels suggests that the retrievals are less sensitive to the lowest several hundred meters of the atmosphere, where the majority of the aerosol particles reside. However, it should be noted that the MAX-DOAS collects data over a large horizontal area, so the variability may be smoothed due to the averaging over a large region. It is also generally the case that, although the MAX-DOAS is sensitive to
the altitude around which the instrument is located, the bulk of the signal is located within the boundary layer, and thus from the surface nearest the ground is the greatest variation.

We also expect that improvements in the ability of radiative transfer models to capture aerosol scattering effects would significantly improve our ability to model its effects on our O$_4$ DSCDs, and consequently our retrievals of aerosol extinctions.

![Aerosol DOFs from retrievals, CalNex 2010](image)

Figure 4.9. Histogram of degrees of freedom (number of independent pieces of information retrievable from the algorithm) from aerosol retrieval, using MAX-DOAS observed O$_4$ DSCDs.
Figure 4.9 shows the histogram distribution of the degrees of freedom for two months of measurements from CLARS, from May 24\textsuperscript{th} to July 11\textsuperscript{th}. This period roughly corresponds to the CalNex 2010 field campaign. In general we are often able to see at least 4 degrees of freedom, with a spread of between 3.5-5 between this period; this has been borne out through analysis of longer time periods. This suggests that we are able to see on average 3.5-5 independent pieces of information; although the majority of this seems to be at the altitudes of 500 meters or higher, if this region is well constrained by the \textit{a priori}, the retrieval is sensitive to aerosol information in the lower 500 meters, where the majority of the signal is coming from.

The validation shows that after accounting for aloft aerosols and temperature effects, we are able to capture the total column optical depth, even though the averaging kernels near the surface are low. Obtaining the boundary layer height accurately is a persistent challenge that may be particularly difficult due to the a number of factors, among them the wavelength at which these retrievals are being made (360 nm), which in the UV makes the penetration into the boundary layer difficult; this factor is only enhanced during high aerosol events, during which the path length is further reduced. However, for the purposes of retrieving the total column optical depth, the algorithm has resulted in generally good agreement with the ground measurements, which for the purposes of retrieving trace gas retrievals is typically sufficient.

An Aeronet station was operated at Caltech since early 2010, before the start of the CalNex field campaign, and has been operational mostly continuously, with several gaps for when the instrument was being calibrated. Some periods were also impacted by the reduced performance of the instrument, especially in the UV. It should be noted that
the Aeronet station and the UCLA MAX-DOAS do not sample the same airmass, as they are located 10 miles away from one another, and are sensitive to different altitude regions. To compare the aerosol extinction retrieval with the aerosol optical thickness, AOT, from the Aeronet station, we integrated the extinction profile retrieved from the MAX-DOAS data vertically. Figure 4.10 shows the results of this comparison. Generally the gaps in the MAX-DOAS data correspond to data-points in which the cloud sorting algorithm flagged it as cloudy data.

**Figure 4.10.** Comparison of retrieved total column optical depth from VLIDORT/MAX-DOAS inversion with local Aeronet station. Note that the Aeronet Station is located at the Caltech campus, while the MAX-DOAS samples a large horizontal airmass to the east of the Aeronet station
4.8. NO\textsubscript{2} Retrievals

After each aerosol retrieval, we then retrieve the NO\textsubscript{2} vertical concentration profile with the Linear Bayesian algorithm, as described in Section 4.1. This retrieval is largely similar to that of the theoretical retrieval of NO\textsubscript{2}, with retrieved MAX-DOAS NO\textsubscript{2} DSCDs as the measurement vector. NO\textsubscript{2} retrievals were only performed after a successfully converged aerosol retrieval, and generally the information content is greater for our trace gas retrievals, and so a lookup table was not used. Instead, an \textit{a priori} profile with a boundary layer height similar to that found in the aerosol retrieval was used. This profile was run through VLIDORT, and a set of synthetic NO\textsubscript{2} DSCDs were generated. A rough scaling factor was calculated based on the difference between the synthetic and actual NO\textsubscript{2} DSCDs; this scaling factor was applied to the boundary layer NO\textsubscript{2} concentration value. This method was found to be sufficient for a first-pass \textit{a priori} estimate. Overall, VLIDORT is only run one additional time.

Figure 4.11 and Figure 4.12 show two retrievals of NO\textsubscript{2} vertical profiles on two different days. In both cases a clear boundary layer can be identified. Figure 4.7 shows a typical retrieval during ideal clear-sky conditions near noon-time. We have found that once the factors such as aerosol extinction vertical profile, ambient temperature, and boundary layer height have been taken into account, the NO\textsubscript{2} retrieval proves quite capable of capturing a wide variety of variation in the boundary layer.
Figure 4.11. Sample NO$_2$ vertical concentration profile retrieval and averaging kernels, from near-noon local time, June 26$^{\text{th}}$, 2010, in roughly ideal clear-sky conditions. This retrieval was done with a Linear Bayesian retrieval, following a retrieval of the aerosol extinction profile.
Figure 4.12. Sample NO$_2$ vertical concentration profile retrieval and averaging kernels from early morning measurements, 8:30 AM PST, May 29$^{th}$, 2010. Despite greater airmass and reduced sunlight and NO2, the retrieval has a greater capacity to find a posteriori values far from the a priori profile used.

Figure 4.13 shows a comparison of our retrieved NO$_2$ mixing ratios using this method during the CalNex 2010 period, compared to in situ measurements taken by the ARB ground monitoring station, located in Azusa, CA. It is worth noting that the region just above the surface corresponding to the 100 meter VLIDORT model grid box is one that the averaging kernels suggest the least sensitivity to the true state, and yet we are able to get relative good agreement with the ARB-observed NO$_2$ observations.
Figure 4.13. 100 (red) and 500 (blue) meter VLIDORT ground-station retrieval, compared to the local ARB ground monitoring station in Azusa.

Notably the ARB monitoring stations are largely *in situ* and thus do not sample the same airshed; the vertical profile retrieved by the inversion not only encompasses the bottom 3 kilometers of the atmosphere, but also due to the light paths samples a horizontal area that stretches roughly 10 kilometers and includes air over urban areas ranging from residential areas, industrial areas, and highways. It is thus likely that each vertical profile is a composite of a vast airshed. The few high values of NO$_2$ retrieved by the inversion are not necessarily artifacts of the retrieval; the high NO$_2$ event on 6/22 was observed in the MAX-DOAS DSCDs, which were significantly higher than is typical.
Figure 4.14. Histogram of Degrees of Freedom (number of independent pieces of information retrievable from the algorithm) from Linear Bayesian inversion using MAX-DOAS observed NO$_2$ DSCDs.

Figure 4.14 shows the histogram of retrieved degrees of freedom from the CalNex period. We have now been able to consistently retrieve roughly 5.5 degrees of freedom of information. This is a full degree of freedom greater than was observed in earlier versions of this retrieval. Improvements in error characterization and a priori estimates seem to have largely resulted in this improvement.
5. Determining ozone production efficiency

5.1. HCHO / NO\textsubscript{2} ratio

As mentioned previously, ozone formation results from a series of photochemical reactions involving nitrogen oxides (NO+NO\textsubscript{2}) and volatile organic compounds (VOCs), and thus in the past it has been common for control strategies to focus on mitigating the emissions of either species, depending on whether the current chemical regime is NO\textsubscript{x}-limited or VOC-limited (Dodge, 1987). In some places, including California, both are regulated.

A method that has recently become popular for column density measurements has been the use of ratios of trace gas SCDs of NO\textsubscript{x} to VOCs as a method of looking at ozone sensitivity. In previous studies, a “proxy” has been used for VOCs, and the ratio between it and NO\textsubscript{2} has been taken. Sillman (1995) was the first to suggest using indicator species for ozone-NO\textsubscript{x}-VOC sensitivity and suggested HCHO as a proxy as it is a relatively short-lived oxidation product of many reactions, and is often positively correlated with many peroxy radicals. The HCHO/NO\textsubscript{2} ratio thus acts as an indicator of the chemical regime of the atmosphere. Recently, this approach was applied to space-based observations of HCHO and NO\textsubscript{2} (e.g., Martin et. al., 2004). A modeling study by Duncan et. al. (2010) used a ratio of HCHO/NO\textsubscript{2} < 1 as an indicator of a NO\textsubscript{x}-limited/VOC sensitive chemical regime, while HCHO/NO\textsubscript{2} > 2 was indicative of a VOC-limited/NO\textsubscript{x} sensitive regime. The region with a ratio between 1 and 2 is a
“transition zone” indicating that a reduction of both NOx and VOCs will likely result in a reduction of ozone.

5.2. \( P(O_3) \) and \( \mathcal{L}_N/Q \)

The rate of production of \( O_3 \), \( P(O_3) \), can be calculated from the amount of NO and peroxy radicals (Seinfeld and Pandis, 2006):

\[
P(O_3) = k_{eff} ([HO_2] + [RO_2])[NO]
\]

This cycle continues until radicals are removed through radical/NOx and radical/radical reactions. For example, the following reactions:

\[
OH + NO_2 \rightarrow HNO_3
\]
\[
HO_2 + HO_2 \rightarrow H_2O_2 + O_2
\]

are the two most common chain termination reactions. It is important that the chain termination reactions can be divided into two classes, radical removal through radical+NOx reactions (i.e. the \( OH + NO_2 \rightarrow HNO_3 \) reaction), and radical removal through radical+radical reactions (i.e. the \( HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \) reaction).

The analytic quantity \( \mathcal{L}_N/Q \) has become popular as a measure of the sensitivity of \( P(O_3) \) to NOx and VOCs. \( \mathcal{L}_N \) is the rate of total, irreversible radical removal through
reactions with NO$_x$, while Q is the rate of radical production. If $L_R$ is the loss rate due to radical-radical reactions, then one can obtain the following expression:

$$Q = L_R + L_N$$

This quantity can be considered the fraction of free radicals removed from the atmosphere through reaction with NO$_x$. Given that radical-radical reactions dominate in lower NO$_x$ regimes, and that radical-NO$_2$ reactions (i.e. $OH + NO_2 \rightarrow HNO_3$) dominate in higher NO$_x$ regimes, it was found that $L_N/Q$ approaches 1 in high NO$_x$ (VOC limited) regimes and 0 in low NO$_x$ (NO$_x$ limited) regimes (Kleinman 1997, Kleinman 2001).

Kleinman et al. (1997) found that $L_n/Q = 0.5$ is a natural transition point between NO$_x$ and VOC limited conditions, when performing rate calculations from field observations based in Nashville, Tennessee. Average $L_n/Q$ ratios have been found as high as 1 in New York City (indicating a VOC limited regime), and roughly 0.5 in Houston, Texas and Mexico City (Mao et al., 2010).

During CalNex 2010, as previously mentioned a number of gas-phase and aerosol-phase measurements were taken in the LA basin. Griffith et. al. (2016) in particular took in situ measurements of OH and HO$_2$ by laser-induced fluorescence-fluorescence assay by gas expansion (LIF-FAGE) technique which suggested that when the ratio of HCHO/NO$_2$ was equal to 0.55, the crossover-point for $L_n/Q$ of 0.5 is crossed. Although this value is lower than the HCHO/NO$_2$ ratio of 1-2 used in Duncan et. al. (2010), this crossover point is based on observations and samples air much closer to what is observed at Mt. Wilson, so it is likely more accurate.
Figure 5.1. Plot of HCHO/NO$_2$ vs. LN/Q for the surface observations during CalNex 2010 field campaign (P. Stevens, personal communication)

5.3. CLARS HCHO/NO$_2$ ratio

Figure 5.2 shows the results during the CalNex field campaign when the ratio of HCHO SCDs and NO$_2$ SCDs observed by the MAX-DOAS are taken. The ratio is calculated using the HCHO and NO$_2$ DSCDs retrieved from the 323-350 nm wavelength range band, so that radiative transfer effects affect both DSCDs equally. It is expected that the ratio should thus cancel out the majority of these effects. The observations from two different elevation angles, one (-4°) looking downwards into the basin and boundary layer, and the other (0°) looking horizontally out into the free troposphere. The daily average for daylight hours is shown, and the days that correspond to weekends are shaded.
in gray. Note that May 29-31st was the Memorial Day holiday weekend in Los Angeles, and as it was a public holiday it can be assumed that traffic patterns reflect that of weekends.

![Daily Averaged HCHO/NO₂ ratios during CalNex 2010](image)

**Figure 5.2.** Daily averaged HCHO/NO₂ ratio during CalNex 2010 analyzed at the same wavelength (323-350 nm) to cancel out radiative transfer effects. Weekends are the shaded regions in grey. The 0.55 HCHO/NO₂ “crossover” point is shown, detailing the empirical cutoff between NOₓ and VOC-limited chemical regimes.

The observations from the downwards looking elevation angle (-4°) have a consistently lower ratio than that of the horizontal viewing angle (0°), as it is more sensitive to the polluted boundary layer, which is considerably more VOC-limited. A weekday/weekend difference in the HCHO/NO₂ ratio was observed, with a consistently higher ratio on weekends, corresponding to a period of reduced NOₓ sensitivity. This
represents the aforementioned “weekend effect” which has been observed in Los Angeles in the past (see Chapter 1).

**Figure 5.3.** Monthly averaged NO$_2$ (top) and HCHO (middle) DSCDs observed in the Los Angeles Basin from Mt. Wilson, California, at the -4° viewing elevation angle.

Day-to-day variations are possible using this method, but given the time scale of the MAX-DOAS observations from CLARS, this ratio method can be applied to look at longer-term (seasonal) observations. Figure 5.3 shows the monthly averaged HCHO/NO$_2$
ratio over a multi-year period (from 2011 to 2014), alongside the long-term monthly averaged NO₂ and HCHO DSCDs. As there are fewer data points for weekends as opposed to weekdays, the uncertainty is larger, but as was seen in the daily averaged results from CalNex in 2010, the weekend ratio is typically larger than the weekday ratio. Moreover, a yearly reduction in NO₂ is observed, which roughly matches the 11% per year observed by Russell et al. (2010), but which seems to have largely occurred on weekdays. It is possible that this improvement is the result of the state of California’s stricter regulation of trucks and diesel fuel.

A strong seasonal dependence with larger values during the summer can be seen in the monthly mean ratios, with a maximum in August or September, and minimal values during winter months. This suggesting that summers in Los Angeles are in a more NOₓ-limited regime. The exact reason for this trend is not quite understood, but seems to be largely driven by seasonal trends in HCHO, that are not as prominent in the NO₂ DSCDs.

Figure 5.4 looks at the weekend effect in greater detail. The cloud-sorted DSCDs for all of 2011 were separated depending on weekday versus weekend for both HCHO and NO₂, and the DSCDs are averaged by the hour to show the diurnal patterns. A strong weekday-weekend discrepancy is seen in NO₂, which is largely absent in HCHO. The trend of higher HCHO/NO₂ ratios observed on weekends, and consequently the weekend effect, seems to be largely driven by the weekday/weekend discrepancy in NO₂ rather than that of VOCs.
Figure 5.4. Hourly averaged NO$_2$ DSCDs (top) and HCHO DSCDs (bottom), for downward-looking elevation angle, separated by weekdays and weekends. The error bars show variance from the hourly averaging.
During CalNex 2010, Griffith et. al. (2016) took measurements of ozone production and OH reactivity in Los Angeles, and from this diurnal averaged values of $L_{N/Q}$ were calculated, using an analytical expression developed by Kleinman et. al. (2001) and the RACM2 model; the results are displayed in Figure 5.5.

![Figure 5.5](image)

**Figure 5.5.** $L_{N/Q}$ values observed during CalNex 2010, showing calculation from analytical equation (Kleinman et. al., 2001) and RACM2 model, comparing weekday, weekend, and holiday values. Figure taken from Griffith et. al. (2016).

Both analytical calculation and model results found that $L_{N/Q}$ is greater than the 0.5 cutoff point during weekdays and weekend mornings, but less than 0.5 on weekend afternoons and holidays. This suggests that in Los Angeles the production of ozone is
typically VOC-limited, but the weekend effect is the result of weekends and holidays being NO\textsubscript{x}-limited. The NO\textsubscript{x} DSCDs observed by the MAX-DOAS agree with these results, seeing a strong decrease in NO\textsubscript{x} levels on weekends.

It is also noteworthy that, given the aforementioned correlation between $L_N/Q$ and HCHO/NO\textsubscript{2}, as shown in Figure 5.1, it is possible to validate the results of Griffith et. al. (2016), and extend them for a much longer time scale. During CalNex, calculated $L_N/Q$ values ranged from 0.25 to 1, which from in situ data corresponds to HCHO/NO\textsubscript{2} ratios of roughly 0.1 to 1.5. Over this same time period, the MAX-DOAS detected HCHO/NO\textsubscript{2} ratios of roughly 0.1 to 1 in downwards looking viewing angles, even though it is less sensitive to the bottom 500 meters of the atmosphere. This result suggests that the MAX-DOAS HCHO/NO\textsubscript{2} ratios are consistent with what has been observed, and that the MAX-DOAS can be used to extrapolate and extend this analysis over longer time periods.

Given that NO\textsubscript{x} reductions are ongoing due to environmental legislation, we have already observed a multi-year reduction in NO\textsubscript{x} levels in our monthly averaged observations. It is therefore reasonable to expect a reduction in the strength of the weekend effect. We thus investigated the changes in ozone sensitivity over our dataset over a multiple year period. Figure 5.6 shows the change in the difference between the monthly averaged weekend ratio and weekday ratio. A linear best fit line is applied to this monthly average over the three year period, which suggests that the difference between the weekday to weekend ratio has dropped from roughly 2 to 1.5 over the time period from 2011 to 2014. This matches the trend of the lessening of the weekend effect that has been observed by others (Wolff et al., 2013; Baider et. al., 2015).
Figure 5.6. Ratio of the difference between HCHO/NO$_2$ ratios observed on weekends versus weekdays. For this plot the monthly average for weekdays is divided by the monthly average of weekends at each data point. The red line is a linear best fit, and a reduction in the difference in the ozone sensitivity over the 2011-2014 period can be observed.
6. Conclusions and Outlook

6.1. Conclusions

A Multi-Axis DOAS instrument was installed on Mt. Wilson, California, in May of 2010, and operated for the next five years continuously measuring differential slant column densities of O₄, HCHO, and NO₂. In addition to the length and scale of this deployment, other major novel features of this deployment included taking observations in both the UV and visible light regions. Most notably, the MAX-DOAS instrument was deployed on an elevated mountaintop location with a downwards looking viewing angle, making it an ideal vantage point for long-term observations with an excellent view of the Los Angeles air basin.

This approach presents unique challenges, but also unique opportunities. Contrary to traditional MAX-DOAS deployments, which often last no more than a few days to as much as a few months, this long-term deployment of the MAX-DOAS allowed for observations of seasonal and multi-year trends in ozone precursors, including likely responses to increasing legislation of motor vehicles and especially commercial trucks.

The roughly consistent viewing geometry and conditions, combined with the size of our dataset, allows for the creation of a robust algorithm for sorting and classifying measurements made in the presence of clouds, based on observed O₄ DSCDs and radiances.

MAX-DOAS is a relatively new application of the DOAS technique, and the optimal estimation of vertical profiles of trace gas concentrations to MAX-DOAS observations is an application of inverse modeling techniques that is currently undergoing
active innovation by the community. This problem is significantly complicated by the scattered-sunlight nature of MAX-DOAS observations, which are often performed in polluted environments in the lower troposphere, which necessitates the observation and retrieval of aerosol optical properties, typically simultaneously with the trace gas profile retrieval.

The VLIDORT radiative transfer model was integrated with a set of wrapper codes to process large volumes of data sequentially, analytically calculate Jacobian matrices linearizing VLIDORT, and perform a “two-step” optimal estimation algorithm. The first step consists of a nonlinear Levenberg-Marquardt retrieval of vertical aerosol extinction coefficients from MAX-DOAS observed O$_4$ DSCDs. The aerosol profile retrieved in the first step is then incorporated back into VLIDORT, which produces another set of Jacobian matrices; these matrices are then used to perform a Linear-Bayesian retrieval of vertical trace gas concentrations of NO$_2$, using MAX-DOAS observed NO$_2$ DSCDs as an input.

Developing the aerosol retrieval proved to be challenging, as our radiative transfer modeling efforts with VLIDORT show a similar model-measurement disparity between measured O$_4$ DSCDs than is commonly observed by the community, i.e. measured O$_4$ DSCDs are on average roughly 15-25% greater than modeled O$_4$ DSCDs (Wagner et. al., 2009; Clemer et. al., 2010). Sensitivity tests using VLIDORT were performed to determine the effects of single scattering albedo, asymmetry factor, surface albedo, aerosol extinction vertical profile, and temperature on O$_4$. Our tests show that single scattering albedo can change O$_4$ DSCDs by ~8% peak-to-peak, asymmetry factor could have a 6% effect, and surface albedo 3%. Temperature, however, can have as much as a
20% difference in the simulated O$_4$ DSCDs over the temperature range observed in Los Angeles. Given that the maximum variation we observed in our sensitivity tests due to variation in aerosol extinction is 30%, this influence is considerable. Traditionally, the DOAS community has not considered temperature effects during MAX-DOAS deployments, but our model-measurement agreement of O$_4$ DSCDs was significantly improved by incorporating temperature data from the local NOAA National Climatic Data Center at Mt. Wilson to create a custom atmospheric temperature profile for each retrieval.

One other feature found to have a significant effect on O$_4$ DSCDs is the high altitude aerosol profile. Here we define it as aerosol above the boundary layer, and especially above 3 kilometers. Traditionally, attempts to perform radiative transfer modeling of ground-based remote sensing observations tend to assume that aerosol extinction coefficients above the polluted boundary layer tend to be “negligible” and thus a sufficiently small background aerosol extinction coefficient is used for higher altitudes. While it is true that aerosol extinction coefficients drop significantly above the boundary layer, our modeling efforts suggest that, as these are integrated over the vertical height of the atmosphere, higher altitude aerosol extinction coefficients have a measurable effect on O$_4$ DSCDs. When incorporating aerosol extinction coefficients observed by NASA's (SAGE-II) Satellite (Rind et. al., 1997) into VLIDORT’s aerosol profile between 10 and 40 kilometers, modeled O$_4$ DSCDs had an additional 4-8% difference.

It is our recommendation that future MAX-DOAS deployments consider local meteorology data and incorporate temperature effects into their radiative transfer modeling efforts, as well as incorporating higher altitude aerosol extinction
measurements into their radiative transfer models. It is significant that after incorporating the corrections to aerosol profile and temperature into VLIDORT we are able to model \( \text{O}_4 \) DSCDs without using the 0.8 “correction” factor MAX-DOAS groups have been applying to their retrieved \( \text{O}_4 \) DSCDs.

Information content analysis suggests an additional advantage of performing lower troposphere observations from an elevated mountaintop position. A set of tests were performed where synthetic \( \text{O}_4 \) DSCDs were generated by VLIDORT, and then were input into our two-stage optimal estimation routine. This was repeated for a wide range of aerosol profiles, and simulating a variety of instrument and \textit{a priori} error estimates, and in each case the total information content, quantified as degrees of freedom, was measured. The degrees of freedom of the retrieval depend greatly upon the atmospheric conditions simulated as well as the error estimates of both the \textit{a priori} profile and the measurements. Nevertheless, our simulations show that the aerosol retrieval is consistently able to retrieve on average 3.5-4.5 degrees of freedom, and the \( \text{NO}_2 \) retrieval is consistently able to retrieve 3.5-4 degrees of freedom. In ideal conditions, as much as an additional degree of freedom can be observed on top of that. It is significant that, consistently ground-based MAX-DOAS observations are able to retrieve on average 1 degree of freedom, and in the best-case 2 degrees of freedom. Our results suggest there is an advantage to using our method of locating a MAX-DOAS on an elevated mountaintop site, both because of the increased information content as well as the improved vantage point over a major urban center.

The two-step optimal estimation has been successfully applied to a range of MAX-DOAS observations. A special challenge for the application of the aerosol
retrieval to MAX-DOAS O₄ DSCDs is the selection of the *a priori* aerosol extinction profile. Often there is little information on the aerosol extinction profile on any given day in Los Angeles, and yet the choice of the aerosol extinction profile to use as an *a priori* was quickly proving to be the largest impediment to the successful convergence of the algorithm. In order to improve the convergence, VLIDORT was used to generate a lookup table consisting of O₄ DSCDs generated for a wide variety of solar viewing angles, aerosol profiles, and background temperature. Then, for each viewing geometry and temperature, the aerosol extinction profile corresponding to the modeled O₄ DSCD that best matches the measured O₄ DSCD is used as the *a priori* for the optimal estimation of aerosol. As the Levenberg-Marquardt algorithm is an iterative method, the lookup table effectively provides a best “first step” estimate for the iteration. Thus, this method can be considered an integration of a more traditional lookup table method with more modern optimal estimation techniques.

Using this approach, our analysis has indicated that the aerosol retrieval is capable of retrieving total column optical depth and shows good agreement with the local Aeronet station located at the nearby Caltech campus during the CalNex 2010 period. There is a limited capacity to retrieve information about aerosol extinction within the boundary layer, which is ultimately limited by the lack of information and sensitivity to the lowest 500 meters of the atmosphere. Nevertheless, by constraining the aerosol, this retrieval allows us to perform retrievals of NO₂ concentrations in the boundary layer that show good agreement with local California Air Resource Board NO₂ monitoring stations.

In parallel with our optimal estimation efforts, we investigated the use of HCHO/NO₂ ratios, a technique that has been successfully used to analyze VOC/NOₓ
chemistry previously (Martin et. al., 2004, Duncan et. al., 2010). Given the length of our dataset observed from Mt. Wilson, the HCHO/NO$_2$ ratio can not only reflect changes in the South Coast air basin on an hourly and daily basis due to changes in traffic patterns, but also trends over long time periods. Analysis of this ratio shows a clear weekday/weekend disparity in VOC-sensitivity, with weekends significantly less VOC-sensitive. Analysis of MAX-DOAS NO$_2$ and HCHO DSCDs suggest that this disparity is driven primarily by differences in NO$_2$ concentrations, which are significantly higher on weekdays. Thus, on weekends ozone production efficiency is much higher than on weekdays, in accordance with existing theories as to the cause of the weekend effect. Interestingly, HCHO has a comparatively small weekday/weekend difference. Analysis of the ratio over multiple years also suggests that over the period of our observation the weekend effect has been declining in strength, likely the result of the state of California’s legislation of diesel truck traffic slowly taking effect over the lifetime of commercial vehicles.

6.2. Outlook

These results suggest the potential and feasibility of this method for performing long-term observations of trace gases over urban areas and other locations, as well as for the ability of the MAX-DOAS to observe aerosols. There exists great potential in continuing to conduct measurements from Mt. Wilson. Given the demonstrated ability to use $L_N/Q$ to calculate the ozone sensitivity over a long enough time period, MAX-DOAS measurements can be used to observe ozone sensitivity over multiple year time scales.
Given the ability of the MAX-DOAS to run autonomously for a multiple year period, there exists the potential to observe the long-term changes in VOC/NO\textsubscript{x} sensitivity and ozone production efficiency, as well as observe the daily, weekly, and seasonal patterns in the chemical regime above Los Angeles.

The optimal estimation also proves promising. Retrievals of NO\textsubscript{2} have been proven to be consistent with local \textit{in situ} measurements. Retrievals of other trace gases are a natural next step for optimal estimation using our method. Initial efforts have focused on HCHO vertical profile retrievals. Generally, the larger the measurement error of the trace gas DOAS retrieval, the more challenging the optimal estimation problem; as retrieval errors of NO\textsubscript{2} have been the lowest, retrievals of NO\textsubscript{2} have naturally been the most straightforward to implement of all of the trace gases in the current field of view of the MAX-DOAS instrument. However, in addition to HCHO, HONO and CHOCHO have notable absorption features in the MAX-DOAS’s spectral range.

The ability to retrieve aerosol optical properties from MAX-DOAS observations is both one of the most challenging aspects of MAX-DOAS, and yet improvements here offer great benefits. This study demonstrates the benefits of increased information content on the ability to retrieval aerosol optical depths. It may be able to overcome the barrier imposed by limited information content by performing an analysis incorporating simultaneous inverse modeling of multiple wavelengths. Previously, MAX-DOAS aerosol retrievals focused on using a single wavelength, and while this study uses the 360 nm O\textsubscript{4} band, many other MAX-DOAS instruments focus on using the 477 nm band (Frieß et. al., 2016); the UCLA MAX-DOAS retrieves this band as well. Focusing on multiple wavelengths for this retrieval may provide the information necessary to better
resolve the boundary layer height and extinction, though this has never been done simultaneously before due to the complexity of the inverse problem; among other problems, uncertainties in the Ångström parameter must be determined. An additional technical challenge would be the increased computational time required to generate Jacobian matrices. Nevertheless, the situation of a MAX-DOAS onto an elevated mountaintop layer offers great promise for future long-term observations of not only atmospheric trace gases, but also aerosols.
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