A COMPARISON OF SATELLITE AND GROUND-BASED RETRIEVALS OF TOTAL COLUMN OZONE AND NITROGEN DIOXIDE, DURING DISCOVER-AQ

A Thesis in

Meteorology

by

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Submitted in Partial Fulfillment of the Requirements for the Degree of

Master of Science

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Abstract

An analysis is presented for both ground- and satellite-based retrievals of ozone and nitrogen dioxide levels from both the Washington, D.C., and Baltimore, Maryland, areas during the NASA-sponsored July 2011 campaign of Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ). Comparisons of satellite and ground retrievals of ozone and nitrogen dioxide levels are necessary to improve satellite-based air-quality forecasts for the lower atmosphere, which is one of the main objectives of the DISCOVER-AQ campaign. Satellite retrievals of ozone and nitrogen dioxide levels are taken from the Ozone Monitoring Instrument (OMI) on the Aura satellite, while ground retrievals of ozone and nitrogen dioxide levels are taken from a network of Pandora spectrometers. Many days during July 2011 illustrate agreement between column nitrogen dioxide and ozone amounts obtained from OMI and the ground-based Pandora spectrometers. However, several days indicate disagreement between the two different retrievals of these column amounts. Three distinct sets of conditions lead to the poor agreement between retrievals from the two instruments, based on analyses of meteorological conditions, local chemistry, transport, and aerosol distribution. Using visible satellite imagery, calculated back trajectories, and aerosol LIDAR observations from the region, it is evident that significant cloud cover often causes inaccurate retrievals of the ozone total column amount, while small, passing cumulus clouds or low aerosol layers causing significant backscatter near the ground can lead to inaccurate retrievals of nitrogen dioxide total column amounts.
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List of Acronyms and Abbreviations

AMF: Air Mass Factor
AOD: Aerosol Optical Depth
API: Advanced Pollution Instrument
ATOVS: Advanced TIROS Operational Vertical Sounders
AVDC: Aura Validation Data Center
BrO: Hypobromite
CESAR: Cabauw Experimental Site for Atmospheric Research
CINDI: Cabauw Intercomparison campaign for Nitrogen Dioxide measuring Instruments
CTM: Chemical Transport Model
CTP: Cross Track Position
D.C.: District of Columbia
DANDELIONS: Dutch Aerosol and Nitrogen Dioxide Experiments for Validation of OMI and SCIAMACHY
DISCOVER-AQ: Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality
DOAS: Differential Optical Absorption Spectroscopy
DOMINO: Dutch OMI NO$_2$
DU: Dobson Units
ECC: Electrochemical Concentration
<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>EOS</td>
<td>Earth Observing System</td>
</tr>
<tr>
<td>FTUVS</td>
<td>Fourier Transform Ultraviolet Spectrometer</td>
</tr>
<tr>
<td>GEOS-5</td>
<td>Goddard Earth Observing System version 5</td>
</tr>
<tr>
<td>GOES</td>
<td>Geostationary Operational Environmental Satellite</td>
</tr>
<tr>
<td>GOME</td>
<td>Global Ozone Monitoring Experiment</td>
</tr>
<tr>
<td>GSFC</td>
<td>Goddard Space Flight Center</td>
</tr>
<tr>
<td>HCHO, CH₂O</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>HYSPLIT</td>
<td>Hybrid Single Particle Lagrangian Integrated Trajectory</td>
</tr>
<tr>
<td>INTEX-B</td>
<td>Intercontinental Chemical Transport Experiment-B</td>
</tr>
<tr>
<td>KNMI</td>
<td>Royal Netherlands Meteorological Institute</td>
</tr>
<tr>
<td>LIDAR</td>
<td>Light Detection and Ranging</td>
</tr>
<tr>
<td>MAX-DOAS</td>
<td>Multi-Axis Differential Optical Absorption Spectroscopy</td>
</tr>
<tr>
<td>MD</td>
<td>Maryland</td>
</tr>
<tr>
<td>MERRA</td>
<td>Modern Era Retrospective-analysis for Research and Applications</td>
</tr>
<tr>
<td>MF-DOAS</td>
<td>Multi-function Differential Optical Absorption Spectroscopy</td>
</tr>
<tr>
<td>MODIS</td>
<td>Moderate Resolution Imaging Spectroradiometer</td>
</tr>
<tr>
<td>MPL</td>
<td>Micro Pulse Lidar</td>
</tr>
<tr>
<td>NAM</td>
<td>North American Mesoscale</td>
</tr>
<tr>
<td>NASA</td>
<td>National Aeronautics and Space Administration</td>
</tr>
<tr>
<td>NATIVE</td>
<td>Nittany Atmospheric Trailer and Integrated Validation Experiment</td>
</tr>
<tr>
<td>Nd:YLF</td>
<td>Neodymium-doped Yttrium Lithium Fluoride</td>
</tr>
<tr>
<td>NH₃</td>
<td>Ammonia</td>
</tr>
<tr>
<td>NO</td>
<td>Nitric Oxide</td>
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</table>
NO₂: Nitrogen Dioxide
NOAA: National Oceanic and Atmospheric Administration
NOₓ: Nitrogen Oxides
NO₃: Total Reactive Nitrogen
O₂: Dioxygen
O₃: Ozone
OCLO: Chlorite
OMI: Ozone Monitoring Instrument
OMPS: Ozone Mapping and Profiler Suite
RMS: Root Mean Square
RRS: Rotational Raman Scattering
SAOZ: *Systeme d’Analyse par Observation Zenithales*
SCIAMACHY: Scanning Imaging Absorption Spectrometer for Atmospheric Cartography
SERC: The Smithsonian Environmental Research Center
SO₂: Sulfur Dioxide
SP: Standard Product
SSMI: Special Sensor Microwave/Imager
TCNO₂: Total Column NO₂
TCO₃: Total Column Ozone
Tg N yr⁻¹: Teragrams of Nitrogen per year
TIROS: Television Infrared Observation Satellite
TOA: Top Of the Atmosphere
TOVS: TIROS Operational Vertical Sounder
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>TOMS:</td>
<td>Total Ozone Mapping Spectrometer</td>
</tr>
<tr>
<td>TTOR:</td>
<td>Trajectory-enhanced Tropospheric Ozone Residual</td>
</tr>
<tr>
<td>UMBC:</td>
<td>University of Maryland, Baltimore County</td>
</tr>
<tr>
<td>UMD:</td>
<td>University of Maryland</td>
</tr>
<tr>
<td>U.S.A.:</td>
<td>United States of America</td>
</tr>
<tr>
<td>USNA:</td>
<td>United States Naval Academy</td>
</tr>
<tr>
<td>UV:</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>V8.5:</td>
<td>Version 8.5</td>
</tr>
<tr>
<td>V8:</td>
<td>Version 8</td>
</tr>
<tr>
<td>VCD:</td>
<td>Vertical Column Density</td>
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“The heavens declare the glory of God; 
the skies proclaim the work of His hands. 
Day after day they pour forth speech; 
night after night they reveal knowledge.”

--Psalm 19:1-2
The Holy Bible, New International Version
Chapter 1: Introduction

1.1: Importance of Satellite Validation for Accurate Air Quality Forecasts

The ability to understand and predict air pollution events has become an increasingly important area of study for the atmospheric sciences in recent years. Hazardous chemicals in the atmosphere are not only are harmful to the environment, but also, near the surface, can cause damage to both permanent structures and human health. According to Kampa and Castanas (2007), hazardous chemicals, including nitrogen oxides (NO$_2$ and NO, collectively referred to as NO$_x$), as well as ozone (O$_3$), in high concentrations near the surface of the earth, can cause health problems for human beings. Health hazards caused by air pollutants can include upper respiratory irritation, chronic bronchitis for adults, acute respiratory infections in children, and increased asthmatic attacks (Kampa and Castanas, 2007). Because of these implications for poor air quality, it is beneficial to be able to make accurate air-quality forecasts using precise retrievals from both ground- and satellite-based instruments.

In July 2011, NASA began a multi-year campaign called Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ). As explained on the project’s website, http://discover-aq.larc.nasa.gov/, the DISCOVER-AQ campaign has three major objectives:

1) Relate column observations to surface conditions for aerosols and key trace gases (O$_3$, NO$_2$, and CH$_2$O).

2) Characterize differences in diurnal variation of surface and column observations for key trace gases and aerosols.
3) Examine horizontal scales of variability affecting satellite retrievals and model calculations.

One of the major problems for satellites measuring air quality on Earth is differentiating between polluted air near the surface and polluted air farther up in the atmosphere. The ability to distinguish between high-level and low-level air pollution is important for the generation of accurate air-quality forecasts. Air-quality forecasts must focus on pollution near Earth’s surface, because this is the pollution that will impact people as they live and breathe. Satellite retrievals of air quality may be improved by making and analyzing comparisons between satellite data and ground-based air quality data that are obtained at the same time.

In this study, we investigate satellite- and ground-based retrievals of both nitrogen dioxide (NO₂) and ozone (O₃). As noted by Seinfeld and Pandis (2006), the only significant source of ozone in the atmosphere is the photolysis of NO₂ at wavelengths < 424 nm:

\[
\begin{align*}
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O} \quad [1] \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad [2]
\end{align*}
\]

As discussed by Boersma et al. (2008), anthropogenic activity is a large and common source of NO₂ in the troposphere, where it has the most immediate effects on human health. Sources of NO₂ include biomass burning, lightning, and soil and aircraft emissions (Herman et al., 2009). The most important NO₂ source is fossil fuel combustion. Table 1 shows the estimated global sources of NOₓ, presented in Chapter 2 of *Atmospheric Chemistry and Physics* by Seinfeld and Pandis (2006).
Table 1: Estimate of Global Tropospheric NO\textsubscript{x} Emissions in Tg N yr\textsuperscript{-1} for Year 2000

<table>
<thead>
<tr>
<th>Sources</th>
<th>Emissions, Tg N yr\textsuperscript{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil Fuel Combustion</td>
<td>33.0</td>
</tr>
<tr>
<td>Aircraft</td>
<td>0.7</td>
</tr>
<tr>
<td>Biomass Burning</td>
<td>7.1</td>
</tr>
<tr>
<td>Soils</td>
<td>5.6</td>
</tr>
<tr>
<td>NH\textsubscript{3} Oxidation</td>
<td>--</td>
</tr>
<tr>
<td>Lightning</td>
<td>5.0</td>
</tr>
<tr>
<td>Stratosphere</td>
<td>≤0.5</td>
</tr>
<tr>
<td>Total</td>
<td>51.9</td>
</tr>
</tbody>
</table>

Seinfeld and Pandis (2006) note that ozone can react with NO in the atmosphere to regenerate NO\textsubscript{2}:

\[
O_3 + NO \rightarrow NO_2 + O_2. \quad [3]
\]

Because both NO\textsubscript{2} and ozone in high levels exhibit harmful effects on human health, we are particularly interested in making comparisons between ground- and satellite-based retrievals of these two chemicals. Repeated comparisons using reliable instruments will allow us to understand the factors that contribute to the best satellite retrievals, which will lead to better satellite products and air-quality forecasts.
1.2: Ozone Monitoring Instrument NO₂ Validation Studies

A number of validation studies using a variety of ground instruments have been performed for the Ozone Monitoring Instrument (OMI) total column NO₂ (TCNO₂) product. (OMI is located on the NASA Earth Observing System-Aura satellite.) Herman et al. (2009) noted that the validation of TCNO₂ measured by OMI is necessary not only to improve the use of satellites in predicting air quality, but also to use satellite data for atmospheric chemistry. Herman et al. (2009) performed two OMI validation analyses. The first analysis was performed using a Pandora spectrometer system at the Goddard Space Flight Center in Greenbelt, Maryland. The second analysis used a multifunction differential optical absorption spectroscopy (MF-DOAS) instrument (Wang et al., 2010) at the Pacific Northwest National Laboratory in Richland, Washington. The MF-DOAS instrument used in this second analysis was built by George Mount’s research group at Washington State University. Both Pandora and MF-DOAS are array detector spectrometers (Herman et al., 2009), meaning that these instruments have the ability to measure absorption spectra at multiple wavelengths simultaneously.

The two validation studies by Herman et al. (2009) indicated that the field of view has a significant impact on satellite retrievals. They found that for cases in which the OMI field of view closely coincided with the location of the ground-based spectrometer in a homogeneous environment, there was generally good agreement between retrievals of TCNO₂ from Pandora and retrievals of TCNO₂ from OMI. However, due to the coarse resolution of OMI, retrievals from OMI in highly polluted regions tend to be biased to low values because adjacent rural regions are averaged with the targeted polluted area. This is largely due to the extremely variable nature of tropospheric NO₂ in time and space (Herman et al., 2009).
Another OMI TCNO$_2$ retrieval validation was performed by Celarier et al. (2008), who used ground-based spectrometers that included both Systeme d’Analyse par Observation Zenithales (SAOZ) and Differential Optical Absorption Spectroscopy instruments in an effort to validate TCNO$_2$ amounts from OMI. Celarier et al. (2008) also noted the difficulty posed by the wide field of view for which OMI TCNO$_2$ retrievals are made, indicating, as Herman et al. (2009) did, that OMI TCNO$_2$ retrievals are biased to low values when compared with ground measurements taken in polluted regions.

In their original study during the Intercontinental Chemical Transport Experiment-B (INTEX-B) campaign in March 2006, Boersma et al. (2008) found that the ability of an aircraft to spiral very near the ground had a large impact on the correlation of OMI TCNO$_2$ amounts to the NO$_2$ column values found by the NASA DC-8 aircraft. In areas that allowed the plane to spiral to very low heights (approximately 1000 feet above the ground), good correlation was observed between the two measurements; however, in regions where the aircraft could not reach low heights during a spiral, particularly in urban regions, large extrapolation of the NO$_2$ column was required to include down to the surface, and correlation between OMI TCNO$_2$ amounts and the aircraft NO$_2$ columns were not as good (Boersma et al., 2008). When the aircraft was unable to spiral sufficiently low, OMI TCNO$_2$ retrievals were often higher than those recorded by the aircraft; however, a large fraction of the aircraft NO$_2$ column was extrapolated in these cases, and the extrapolated fraction of the column was estimated to be 75% uncertain. This study hints that disagreement between OMI TCNO$_2$ amounts and non-satellite based NO$_2$ column amounts may not be solely due to poor resolution of the OMI satellite, but could, in the cases of aircraft NO$_2$ column amounts, be related to poor flight sampling. Flaws in satellite retrievals warrant further study in order to improve satellite-based air-quality retrievals.
Hains et al. (2010) used observations of NO₂ during both the 2006 Dutch Aerosol and Nitrogen Dioxide Experiments for Validation of OMI and SCIAMACHY, (DANDELIONS) and the 2006 INTEX-B campaigns to validate OMI tropospheric NO₂ columns. (SCIAMACHY is the Scanning Imaging Absorption Spectrometer for Atmospheric Cartography.) In the DANDELIONS campaign, ground-based retrievals of NO₂ columns were obtained from three different Multi Axis Differential Optical Absorption Spectrometers, but in the INTEX-B campaign in situ NO₂ profiles were obtained from the University of California at Berkeley Laser-Induced Fluorescence Instrument on board the NASA DC-8 aircraft. Through this study of tropospheric NO₂ columns, it was discovered that improved estimates of surface albedo in the vicinity of OMI NO₂ column retrievals may improve the OMI NO₂ column product (Hains et al., 2010).

The Piters et al., (2012) study using the Cabauw Intercomparison campaign for Nitrogen Dioxide measuring Instruments (CINDI) highlights the importance of comparing ground-based instruments. The CINDI campaign took place from June to July of 2009 at the Royal Dutch Meteorological Institute’s (KNMI’s) Cabauw Experimental Site for Atmospheric Research (CESAR) in the Netherlands. During the campaign, more than 30 different in situ and remote sensing instruments from around the world were gathered at CESAR to determine the accuracy of the various ground-based instruments, and investigate their usefulness in satellite validation. Initial results indicate that MAX-DOAS slant column measurements from multiple instruments agree within 5-10%. Future analysis on data from this experiment will likely have implications for which ground-based instruments are most useful in satellite validation studies (Piters et al., 2012).
For the DISCOVER-AQ campaign, we make comparisons between TCNO2 retrieved by OMI and TCNO2 retrieved by Pandora spectrometers at various sites in Maryland, with a focus on Edgewood, Maryland. For our purposes, TCNO2 describes the amount of NO2 in a given column of air extending from the surface through the stratosphere.

In addition to making comparisons between OMI and Pandora TCNO2 amounts, comparisons are made between Pandora and other surface measurements of and related to NOx levels from a Teledyne API 200 EU NOx Analyzer. Such comparisons lend further insight into the origin of anomalies between the Pandora and OMI TCNO2 amounts.

1.3: OMI Ozone Validation Studies

In addition to OMI NO2 validation studies, there have also been validation studies focusing on the OMI ozone product. McPeters et al. (2008) performed an OMI total column ozone (TCO3) validation study, noting that validation of satellite data is a continually evolving process of comparing satellite-based data to ground-based data, rather than a finite task that can be completed. In their study, McPeters et al. (2008) compared both the OMI-TOMS ozone product and the OMI-DOAS ozone product to an ensemble of ozone data from 76 ground stations in the northern hemisphere. Ultimately, the study revealed good correlation between the OMI-TOMS TCO3 and the ground stations, with the OMI-TOMS TCO3 averages only 0.4% higher than TCO3 averages from the ground stations. The OMI-DOAS TCO3 retrievals exhibited slightly less agreement with the ground station TCO3 retrievals, with OMI retrievals being 1.1% higher on average than retrievals from ground instruments (McPeters et al., 2008).

Anton et al. (2009) performed an OMI validation study of OMI TCO3 using Brewer spectroradiometers on the Iberian Peninsula. Both the OMI Total Ozone Mapping Spectrometer
(OMI-TOMS) and OMI Differential Optical Absorption Spectroscopy (OMI-DOAS) ozone products were compared to the Brewer ozone retrievals from Brewer spectroradiometers located at five ground stations between January 2005 and December 2007. According to the results, “excellent” agreement was found between TCO₃ retrievals from the Brewer spectroradiometers and the TCO₃ retrievals from OMI. The OMI-TOMS TCO₃ amounts averaged 2.0% lower than the Brewer TCO₃ amounts, and the OMI-DOAS TCO₃ amounts averaged 1.4% difference from the Brewer ozone columns (Anton et al., 2009). The authors note that TCO₃ amounts found using the OMI-DOAS algorithm exhibited a greater seasonal dependence than those found using the OMI-TOMS method, which matched ground truth well (Anton et al., 2009).

For the DISCOVER-AQ campaign, we perform an analysis of the OMI-TOMS TCO₃. TCO₃ from OMI is compared with TCO₃ retrieved from the Pandora instruments at various ground sites in Maryland, with a focus on Edgewood, Maryland, where a number of trace gas and aerosol instruments were located.

### 1.4: OMI Validation Study during DISCOVER-AQ 2011

In this work, an OMI validation study is performed for the 2011 DISCOVER-AQ campaign in the Baltimore, MD and Washington D.C. areas. Comparisons are made between Pandora and OMI total column retrievals of both ozone and NO₂ at 11 different ground sites. By making comparisons between both Pandora and OMI at a number of different ground sites, we are able to establish patterns of agreement and disagreement between the ozone and NO₂ products from the two instruments.
At the sites of Edgewood and Beltsville, Maryland, integrated column amounts obtained from ozonesondes launched from those locations throughout July 2011 are also used for comparison to the OMI total column ozone retrievals. Additionally, comparisons are made between the Pandora total column ozone retrievals and the column ozone measurements obtained from the ozonesondes, to provide further insight into column ozone differences among the three instruments.

As noted above, one of the main objectives of the DISCOVER-AQ mission is to relate column observations to surface conditions for aerosols and key trace gases. In this work, an analysis of meteorological conditions, local chemistry, transport, and aerosol distribution is performed on days for which there is significant disagreement between the ground-based Pandora and the OMI satellite retrievals of either ozone or NO$_2$. From this study, three specific sets of conditions are revealed for which the instruments have difficulty retrieving accurately retrievals of either ozone or NO$_2$. The classification of these conditions as problematic for column retrievals indicate ways in which the OMI and Pandora instruments may be improved in the future in order to provide better total column products that may aid in air-quality forecasts.
Chapter 2: Methods and Data

A variety of different methods, instruments, and data were used to complete this study. A discussion of the tools used follows below.

2.1: Overview of DISCOVER-AQ during July 2011

Data for this study was obtained from the NASA Earth Venture sponsored DISCOVER-AQ campaign, a five-year project designed to allow atmospheric scientists to gain a better understanding of air quality measured by satellites. This study focuses on the July 2011 portion of the DISCOVER-AQ campaign.

During July 2011, 13 ground stations were set up in and around Washington, D.C., and Baltimore, Maryland. Instruments, including ozonesondes, Pandora spectrometers, lidars, and NO\textsubscript{x} analyzers, were placed at these sites to measure pollutants and trace gases in the atmosphere. Instruments at ground stations also provided researchers with meteorological data including temperature, relative humidity, wind speed, and wind direction, during the experiment.

In addition to the 13 ground sites, three aircraft obtained measurements of other levels of the atmosphere. Aircraft used for the July 2011 portion of the DISCOVER-AQ campaign were: the University of Maryland’s Cessna 402B, the NASA P-3B, and the NASA UC-12. Aboard these aircraft were spectrometers, a number of trace gas analyzers and particle counters, and lidars. For more information about the aircraft payloads see http://www-air.larc.nasa.gov/cgi-bin/arcstat-d. The aircraft overflew the 13 ground sites, allowing for comparison of ground-based and aircraft measurements. Map 1 gives an overview of the DISCOVER-AQ ground sites and the P-3B aircraft flight path.
Satellite data were also available to researchers for comparisons and validation. In this study, we focus on data from OMI. This work began as a focused study using data products obtained only near Edgewood, Maryland, where the Penn State NATIVE platform was located. However, as analysis of data products from OMI progressed, the study expanded to include data from Pandora spectrometers and OMI at each of the sites shown on Map 1. Data for the comparison of OMI TCNO$_2$ and OMI TCO$_3$ retrievals with ground-based total column retrievals are described.
2.2: OMI

As described by Levelt et al. (2006), the Dutch-Finnish Ozone Monitoring Instrument, hereafter referred to as OMI, was launched on the NASA Earth Observing System (EOS) Aura satellite in July, 2004. Aura has a sun-synchronous polar orbit and crosses the equator at approximately 13:45 local time on a daily basis. The Aura satellite provides 14 orbits per day, travelling at a 98.2º inclination at 705-km altitude. OMI is an ultraviolet/visible nadir spectrograph, and has a spatial resolution of 13 km x 24 km at nadir. Ozone, NO$_2$, SO$_2$, HCHO, BrO, and OCIO are among the trace gases measureable by OMI (Levelt et al., 2006).


The first step of the OMI NO$_2$ algorithm is the determination of slant column abundances for both NO$_2$ and species that interfere with the measurement of NO$_2$ absorption. The vertical NO$_2$ column is then calculated from the slant column. This calculation is accomplished by dividing the slant column density by a calculated air mass factor (AMF) appropriate to unpolluted conditions. After the Vertical Column Densities (VCDs) have been determined, they are globally binned, and spatial filtering is applied in order to estimate the polluted (boundary layer NO$_2$) and unpolluted (free troposphere and stratosphere NO$_2$) components of the VCD.
Table 2: OMI and Pandora Data Retrieval Information

<table>
<thead>
<tr>
<th></th>
<th>OMI NO₂</th>
<th>OMI O₃</th>
<th>Pandora NO₂</th>
<th>Pandora O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Frequency of Retrievals</strong></td>
<td>Once Daily</td>
<td>Once Daily</td>
<td>~ Every 2 minutes</td>
<td>~ Every 2 minutes</td>
</tr>
<tr>
<td><strong>Resolution</strong></td>
<td>13 km along track x 24 km across track (at nadir)</td>
<td>13 km along track x 24 km across track (at nadir)</td>
<td>~ Every 2 minutes</td>
<td>1.6° Field of View</td>
</tr>
<tr>
<td><strong>Measured Wavelengths</strong></td>
<td>405-465 nm</td>
<td>317.5 nm and 331.2 nm</td>
<td>400-440 nm</td>
<td>305-328.6 nm</td>
</tr>
<tr>
<td><strong>Data Version</strong></td>
<td>Level 2 Overpass Data, Version 3</td>
<td>Level 2 Overpass Data, Version 8.5</td>
<td>——</td>
<td>——</td>
</tr>
<tr>
<td><strong>Quality Flags used in OMI/Pandora Comparisons</strong></td>
<td>OMI Cross Track Position (CTP) &lt; 10 or &gt;50</td>
<td>UV Aerosol Index &gt; 0.5</td>
<td>Number of Pandora retrievals in the hour surrounding the OMI overpass &lt; 10</td>
<td>Number of Pandora retrievals in the hour surrounding the OMI overpass &lt; 10</td>
</tr>
<tr>
<td></td>
<td>Distance from center of OMI pixel to measurement site &gt; 60 km</td>
<td>Distance from center of OMI pixel to measurement site &gt; 60 km</td>
<td>Cloud Fraction &gt; 0.2</td>
<td>——</td>
</tr>
<tr>
<td></td>
<td>Cloud Fraction &gt; 0.2</td>
<td>Cloud Fraction &gt; 0.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Finally, if significant amounts of NO₂ were found in the boundary layer, the VCDs are corrected for the polluted component in order to find the final vertical NO₂ column (Chance, 2002).

As described by Chance (2002), and updated in the OMNO2 README File (Krotkov, 2011), major sources of error in the OMI NO₂ algorithm, including Rayleigh scattering, cloud cover, and aerosols, have been accounted for whenever possible in order to provide the best retrievals. Rayleigh scattering most often reduces the signal received by OMI, which leads to a positive bias in the OMI TCNO₂ retrieval; occasionally Rayleigh scattering can amplify the signal received by OMI and create a negative bias in the OMI TCNO₂ retrieval. These biases caused by Rayleigh scattering are corrected by introducing a third order polynomial into the NO₂ retrieval algorithm (Chance, 2002).
Cloud cover also can be problematic for OMI NO$_2$ retrievals because gas below the cloud cover is obscured from OMI, which decreases retrieval sensitivity in this part of the column. The high albedo of the cloud cover can cause increased sensitivity to the part of the column above the cloud height. These issues are corrected in the OMI algorithm by assuming that clouds can be treated as opaque Lambertian surfaces. Optically thin clouds are also treated as opaque, though they are often assigned smaller effective cloud fractions than was actually measured (Chance, 2002). Cloud corrections originate in the Level 2 OMI cloud algorithm described in Krotkov, 2011.

Finally, aerosols can cause problems for DOAS retrievals. However, the aerosol concentration here is expected to be small under background conditions, so the influences of aerosols are assumed to be negligible in the OMI NO$_2$ retrieval algorithm (Chance, 2002).

As noted above, OMI TCO$_3$ amounts can be retrieved with a DOAS algorithm. For our purposes, another ozone product, OMI-TOMS V8.5 (Anton et al., 2009), is used for TCO$_3$ comparisons (see Table 2). The OMI-TOMS V8.5 algorithm is a trusted retrieval method developed by scientists at NASA; earlier versions of the algorithm have been well tested in their use with the Total Ozone Mapping Spectrometer (TOMS).

The OMI-TOMS retrieval algorithm is described in the OMI Algorithm Theoretical Basis Document Volume II: OMI Ozone Products, edited by P. K. Bhartia in 2002, and available at http://eospso.gsfc.nasa.gov/eos_homepage/for_scientists/atbd/viewInstrument.php?instrument=13. The algorithm estimates the surface reflectivity and effective cloud fraction using the 331.2 nm wavelength. This information is combined with a two-step radiance computation; then \textit{a priori} profiles based on ozonesonde data are used to define a relationship between 317.5 nm top-
of-the-atmosphere (TOA) radiance and total ozone. Piece-wise linear interpolation estimates ozone corresponding to the measured radiance (Bhartia, 2002).

Sources of error, including cloud cover, aerosols, sea glint, and SO$_{2}$ absorption, are accounted for in the OMI-TOMS V8.5 algorithm in order to provide the most accurate TCO$_{3}$ retrievals. Clouds can cause retrieval difficulties for the OMI-TOMS TCO$_{3}$ product by obscuring the gas below the cloud cover, decreasing retrieval sensitivity to this part of the column. Radiative cloud pressure, inferred from Rotational Raman Scattering (RRS), is used as the cloud-top pressure below which climatology (based on ozonesonde measurements) must be used to estimate the “unmeasured” portion of the column. These estimates correct for cloud contamination in the OMI-TOMS TCO$_{3}$ retrieval algorithm (Yang, 2008).

Aerosols also present difficulties for the OMI-TOMS ozone retrieval. Absorbing aerosols interfere with retrieved ozone absorption, leading to overestimates of TCO$_{3}$. In order to eliminate this bias, absorbing aerosols are detected by the change in reflectivity at 331.2 nm and 360 nm wavelengths measured by OMI. A correction that uses a simple linear relationship that exists between this change and the ozone error is then incorporated into the algorithm. Non-absorbing aerosols can cause underestimates in TCO$_{3}$ and a correction similar to that for absorbing aerosols is applied in order to reduce this error. To correct for sea glint a similar method is also utilized.

In the case of a volcanic eruption, SO$_{2}$ amounts in the atmosphere can interfere with the retrieved ozone absorption. This error is corrected in the OMI-TOMS algorithm by using differences in the wavelength range of 305-310 nm to detect volcanic amounts of SO$_{2}$. Since there were no major volcanic eruptions during the DISCOVER-AQ field campaign from July 2011, this source of error was not a large factor in OMI TCO$_{3}$ retrievals. Table 2 provides a
summary of the OMI TCNO₂ and TCO₃ retrieval methods used in this study. OMI overpass data from both NASA and the Royal Netherlands Meteorological Institute (KNMI) isolate the OMI pixel nearest the ground stations of interest and provide the corresponding TCNO₂ and TCO₃ retrievals for direct comparisons. Figure 1 illustrates an example of TCNO₂ retrieved by OMI for the pixels containing and surrounding the Baltimore, Maryland, and Washington, D.C., DISCOVER-AQ region on July 2, 2011.

For this analysis most OMI NO₂ overpass data are obtained from the Aura Validation Data Center (AVDC) and NASA Goddard Space Flight Center (GSFC) website: http://avdc.gsfc.nasa.gov/index.php?site=666843934&id=13. For the ground station at GSFC,
the KNMI OMI overpass data are used in addition to the NASA OMI overpass data in order to obtain a comparison between the two products that use slightly different retrieval methods (Boersma et al., 2007). KNMI OMI NO2 overpass data are obtained from http://www.temis.nl/airpollution/no2col/overpass_no2.html. OMI ozone products are obtained from the AVDC and NASA GSFC website: http://avdc.gsfc.nasa.gov/index.php?site=1593048672&id=28.

2.3: Pandora

Pandora is a small spectrometer, weighing less than 15 kg (Brinksma et al., 2008). The spectrometer is connected to a sensor head by a fiber-optic cable, so that transmitted light fills the 50-µm-wide aperture. The fiber-optic cable allows the spectrometer, which is sensitive to temperature, to be stored in a temperature-controlled environment (Herman et al., 2009). Direct sun irradiances between 270 nm and 500 nm are measured by Pandora at a resolution of approximately 0.5 nm (Brinksma et al., 2008). Pandora has a 1.6° field of view and is mounted on a precision pan-tilt tracking device to follow the position of the center of the sun. The sun’s position is calculated throughout the day using ephemeris coordinates; this position is corrected as Pandora senses the sun’s edge and triangulates to the center (Herman et al., 2009).

In order to retrieve TCNO2, the DOAS method is used in the 400 nm to 440 nm window, with a fixed reference spectrum (Brinksma et al., 2008). The reference spectrum can be either a single measured spectrum taken around noon on a clear day at the measurement location or an average of many measured spectra. The logarithm of measured irradiance spectra is subtracted from the logarithm of the reference irradiance spectrum. A least-squares fit is then applied to the difference. From this fit, “relative slant columns”, which are the difference between the absolute
slant column at the time of retrieval and the reference slant column, can be determined. Calculated AMFs (air mass factors) are then used to convert the relative slant columns to vertical column amounts (Herman et al., 2009).

Clouds, temperature of the atmosphere, and NO₂ absorption cross sections can all introduce uncertainties into the Pandora TCNO₂ retrievals, and must be accounted for in order to provide the most accurate results from the instrument (Herman et al., 2009). Because Pandora is a direct-sun spectrometer, column retrievals from the instrument are adversely affected when there are clouds in the spectrometer’s field of view. To account for this, cloud filtering is applied to the data using the requirement that the DOAS-fitting RMS be less than 0.5%. Additionally, when there are clouds in Pandora’s field of view, the instrument is still able to follow the sun’s approximate position using only the position calculated from ephemeris coordinates, which come from a table of values that provide the positions of astronomical objects in the sky (Herman et al., 2009).

Differences between the actual and assumed temperature in the atmosphere can create inaccuracies in Pandora TCNO₂ retrievals by causing error in the relative slant column. Uncertainties in the laboratory absorption cross sections (Herman et al., 2009), also can cause inaccuracies in the relative slant column retrieved from Pandora. These sources of error are accounted for in a ±5% uncertainty associated with the relative slant column values from Pandora (Herman et al., 2009).

Through past experiments, Pandora has proven to provide reliable ground-based retrievals of TCNO₂. For example, as documented by Wang et al. (2010), an intercomparison field campaign was carried out in July 2007, in which a Pandora spectrometer and an MF-DOAS spectrometer were compared to a high-resolution Fourier Transform Ultraviolet Spectrometer
(FTUVS). Good agreement (to within 6.0 ± 6.0%) for TCNO$_2$ was found for the three instruments (Wang et al, 2010).

In our study, TCO$_3$ retrievals from Pandora are compared to OMI retrievals. In order to retrieve the TCO$_3$, the DOAS method is used in the 305 nm to 328.6 nm window, with a fixed reference spectrum (Cede, 2011). The retrieval method for Pandora TCO$_3$ is similar to that for Pandora TCNO$_2$, described above. Error in TCO$_3$ retrievals caused by clouds is similarly corrected as in the TCNO$_2$ retrievals.

In addition to the error corrections already provided, data from the Pandora spectrometers at the DISCOVER-AQ sites are further filtered by the instrument operators to improve accuracy. Retrievals of NO$_2$ and ozone by Pandora at DISCOVER-AQ sites are filtered for clouds and data with noise by including only those retrievals with a normalized RMS value of less than 0.05. Retrievals with error of greater than 0.05 DU for Pandora TCNO$_2$ are filtered out so that retrieval error is no greater than approximately 10%. For the Pandora TCO$_3$ retrievals, error of greater than 5 DU is filtered out so that retrieval error is no greater than approximately 1-2%.

A total of twelve Pandora spectrometers were placed at ground stations throughout the Baltimore, Maryland, and Washington, D.C., region for the DISCOVER-AQ campaign. We use retrievals of TCNO$_2$ and TCO$_3$ obtained by the Pandora spectrometers at eleven of these sites, for which collocated OMI overpass data were available for comparison during July 2011. Table 2 summarizes details of the Pandora data used in this study. Datasets of Pandora total column retrievals are acquired from the DISCOVER-AQ data archives.
2.4: Ozonesondes

An ozonesonde is a light-weight, balloon-borne instrument that uses chemical reactions to determine the amount of ozone present as it ascends through the atmosphere. An Electrochemical Concentration (ECC) ozonesonde transmits measurements back to a ground receiving station via an electronic coupler that connects the ozone sensor to a meteorological radiosonde as it ascends through the atmosphere (Komhyr et al., 1995). The radiosonde allows for measurement of pressure, temperature, relative humidity, wind speed, and wind direction in the troposphere and mid-stratosphere (Thompson et al., 2003). Balloons carrying ozonesondes typically rise to heights of approximately 35 km before bursting.

As noted by Thompson et al. (2003), balloon-borne ozonesondes are extremely useful in validating retrievals from space-borne instruments. In our study, we will compare TCO$_3$ measurements from ozonesondes at Edgewood and Beltsville, Maryland, to TCO$_3$ retrievals obtained from OMI and Pandora during July 2011. Ozonesondes were launched at least once a day on most days from Edgewood, Maryland, and several times a week from Beltsville, Maryland, throughout July 2011 for the DISCOVER-AQ campaign. Ozonesonde data are acquired from the DISCOVER-AQ archives for the Edgewood and Beltsville ground stations.

2.5: Moderate Resolution Imaging Spectroradiometer (MODIS) on Aqua

The Moderate Resolution Imaging Spectroradiometer (MODIS) was launched on NASA’s Aqua EOS satellite on May 4, 2002 (http://aqua.nasa.gov/). MODIS on Aqua crosses the equator at approximately 13:30 local time (Savtchenko, 2004) and provides data products
obtained at nearly the same time as Aura OMI data. MODIS products include aerosol optical and microphysical properties, as well as cloud optical and physical properties (Savtchenko, 2004).

For the purposes of this study, we analyze MODIS Aerosol Optical Depth (AOD) with Giovanni, a web-based application developed by the Goddard Earth Sciences Data and Information Services Center. Visible images from MODIS obtained from the DISCOVER-AQ archive also provide cloud cover over Maryland at the time of the OMI overpasses.

2.6: Micro Pulse Light Detection and Ranging (LIDAR) at Edgewood, MD

An automated Micro-pulse Light Detection and Ranging (LIDAR), or MPL instrument (courtesy Tim Berkoff, University of Maryland Baltimore County), was operated at Edgewood, Maryland, during the DISCOVER-AQ campaign. The MPL is a solid state, ground-based LIDAR instrument that can be used to profile scattering from clouds and aerosols in the atmosphere. The MPL operates by using a transmitter that is a “diode pumped μJ pulse energy, high repetition rate Nd:YLF laser” (Spinhirne, 1993). Using this transmitter, the MPL sends a signal out to the atmosphere, and then detects the strength of the return signal using a photodiode detector. In this way, the MPL is able to sense and profile significant cloud and aerosol scattering throughout the troposphere and even into the stratosphere (Spinhirne, 1993).

MPL observations are valuable when making comparisons between OMI and Pandora total column retrievals, since both instrument retrievals can experience errors when clouds or significant levels of aerosols are present in the atmosphere. MPL data used in this study are from the DISCOVER-AQ archives.
2.7: **HYSPLIT from NOAA**

The HYbrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model can estimate trajectories, dispersion, and deposition using either puff or particle approaches. Developed by NOAA, HYSPLIT contains a modular library structure with various programs for computing forward or backward trajectories (Draxler, 2012). For the purposes of this study, HYSPLIT is combined with gridded meteorological data files from the 12 km North American Mesoscale (NAM II) model to provide back trajectories for the DISCOVER-AQ sites at heights of 500 m and 1000 m on the dates of 8, 10, 13, 15, 16, 25, 26, and 29 July 2011.

2.8: **NATIVE at Edgewood, Maryland**

The Nittany Atmospheric Trailer and Integrated Validation Experiment (NATIVE), a mobile atmospheric research facility (Thompson and Taubman, 2007), was deployed to Edgewood, Maryland during July 2011 to obtain measurements for the DISCOVER-AQ campaign. Measurements taken with NATIVE instruments can be used to validate satellite data, monitor air quality, and investigate pollution transport and deposition. NATIVE has been deployed in a number of pollution-oriented field campaigns, including:

- **INtercontinental chemical Transport EXperiment/Megacity Initiative**: Local and Global Research Observations (INTEX-B/MILAGRO), Phases I and II, 2006 (http://www-air.larc.nasa.gov/missions/intex-b/intexb.html)
- **Water Vapor Validation Experiment—Satellite/Sondes** (WAVES), 2006 (http://ecotronics.com/lidar-misc/WAVES.htm)
Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS), 2008 (http://www.nasa.gov/mission_pages/arctas/)

Chemistry and Physics Atmospheric Boundary Layer Experiment (CAPABLE), 2009 and 2010 (http://capable.larc.nasa.gov/).

During July 2011, NATIVE was stationed at Edgewood to measure trace gas species and meteorological variables. For our purposes, we are particularly interested in measurements of surface nitrogen oxide (NO), total reactive nitrogen (NO\textsubscript{x}), and the photolysis rate of NO\textsubscript{2} (\textit{j}\textsubscript{NO2}).

Additionally, during the July 2011 portion of DISCOVER-AQ, the NATIVE payload at Edgewood was supplemented with a Teledyne Advanced Pollution Instrumentation (API) instrument that measures the concentration of NO\textsubscript{x} (NO and NO\textsubscript{2}) in the atmosphere. The instrument estimates the level of NO\textsubscript{2} as the difference between NO and NO\textsubscript{x} measurements (Lawson et al., 2011). The measurement of NO is accomplished when the instrument measures the light intensity of a gas-phase reaction of NO and ozone. This reaction produces oxygen as well as electronically excited NO\textsubscript{2} molecules. The intensity of the photons released by the electronically excited NO\textsubscript{2} molecules is directly proportional to the NO concentration in the sample (Lawson et al., 2011).

The Teledyne API 200 EU NO\textsubscript{x} Analyzer used at Edgewood, Maryland, during July 2011 was operated by Travis Knepp of NASA’s Langley Research Center. Data from the Teledyne API 200 EU NO\textsubscript{x} Analyzer are acquired from the DISCOVER-AQ archives for the Edgewood ground station.
2.9: The MERRA Model

The Modern Era Retrospective-analysis for Research and Applications (MERRA) model, developed by the Global Modeling and Assimilation Office at NASA’s GSFC, is designed to advance climate research by putting research satellites in a climate context and providing a better representation of the water cycle upon reanalyses of the satellite data. MERRA outputs are produced using the Goddard Earth Observing System version 5 (GEOS-5) data assimilation system. The MERRA model contains 540 x 361 grid points globally, and incorporates observational analyses every 6 hours. Included in the data assimilated in the MERRA model are satellite radiances and remotely sensed datasets from Television Infrared Observation Satellite (TIROS) Operational Vertical Sounder (TOVS), Advanced TIROS Operational Vertical Sounders (ATOVS), EOS Aqua, Geostationary Operational Environmental Satellite (GOES) Sounders, and Special Sensor Microwave/Imager (SSMI), as well as observational data from radiosondes, dropsondes, aircraft, and surface stations (Bosilovich, 2008).

In this work, MERRA model output from Giovanni provides cloud liquid water mixing ratio, cloud-top pressure, and cloud optical thickness. These images assist in studying cloud cover, which can cause retrieval errors in the TCO$_3$ and TCNO$_2$ amounts from the OMI and Pandora instruments.
Chapter 3: Results—OMI Ozone Validation

An OMI ozone validation is performed here for both the Pandora and the OMI TCO$_3$ instrument retrievals. By comparing the two instruments, as well as measurements from ozonesondes and NATIVE, we are able to gain an understanding of both the conditions for which the two instruments perform well and the conditions for which the instruments have difficulty making accurate retrievals.

3.1: OMI Overpass v. Pandora

Displaying daily Pandora and OMI TCO$_3$ retrievals on scatter plots, we find that some days during July experienced “good” agreement between TCO$_3$ retrievals from the two instruments, while other days during July experienced “poor” agreement. The percent differences between OMI and Pandora (Figure 2) quantify the agreement between Pandora and OMI TCO$_3$. Percent differences were calculated as

\[
\left( \frac{OMI_{TCO_3} - Pandora_{TCO_3}}{\frac{OMI_{TCO_3} + Pandora_{TCO_3}}{2}} \right) \times 100\%,
\]

where $OMI_{TCO_3}$ is the TCO$_3$ retrieval from OMI and $Pandora_{TCO_3}$ is a one hour average of the TCO$_3$ retrievals from Pandora centered on the time of the OMI overpass. The OMI-TOMS algorithm TCO$_3$ data are expected to have root mean square errors of about 1-2\% (Yang, 2008); Pandora TCO$_3$ data used from the DISCOVER-AQ archives also has errors of 1-2\%. Figures 2a-
c depict three days during July for which TCO$_3$ retrievals by Pandora and OMI at Edgewood were in agreement, while Figs. 2d-f depict three days during July for which TCO$_3$ retrievals by Pandora and OMI at Edgewood showed poor agreement.

The three days with poor agreement in Fig. 2 (8 July, 13 July, and 25 July) provide case studies for TCO$_3$ retrievals from OMI and Pandora. The retrieved TCO$_3$ amounts from the two instruments were drastically different at multiple sites in the DISCOVER-AQ region on these days. By examining cloud cover, local chemistry and transport, and aerosol amounts in the DISCOVER-AQ region on these days, we are able to gain understanding about the conditions that caused the poor agreement between the two TCO$_3$ retrievals.

Figure 3 portrays one-minute averages of the absolute difference between OMI and Pandora TCO$_3$ retrievals, |$OMI_{TCO_3} - Pandora_{TCO_3}$|, at Edgewood plotted against the absolute time from the OMI overpass in five minute steps. The difference between retrievals is greatest at times closest to the time of the OMI overpass. This indicates that for point comparisons of OMI and Pandora TCO$_3$ close in time, OMI is likely missing large variability (for example, plumes) in the column. At larger time differences, the absolute differences between the two TCO$_3$ amounts fade out at approximately 15-20 DU. Repeating this analysis at other DISCOVER-AQ sites revealed a similar pattern; thus retrievals with greater than a 20 DU difference between the OMI and Pandora TCO$_3$ amounts are considered to exhibit poor agreement.

A comparison of OMI TCO$_3$ versus one hour averages of Pandora TCO$_3$ centered on the time of the OMI overpass is shown in Figure 4. In addition to the TCO$_3$ amount, OMI overpass data files contain quality control information to flag for conditions that could cause erroneous retrievals. Included in this information is the UV aerosol index, which indicates the presence of either UV absorbing aerosols in the atmosphere (if it is a high positive value) or UV scattering
Figure 2: Daily plots of Pandora and OMI TCO$_3$ from Edgewood, Maryland on (a) 3 July 2011, DOY 184, (b) 6 July 2011, DOY 187, and (c) 29 July 2011, DOY 210. These are the three days for which Pandora and OMI exhibited the best agreement at Edgewood, Maryland. Percent differences are on the plot. Also shown are daily plots of Pandora and OMI TCO$_3$ from Edgewood, Maryland on (d) 8 July 2011, DOY 189, (e) 13 July 2011, DOY 194, and (f) 25 July 2011, DOY 206. These are the three days for which Pandora and OMI exhibited poor agreement at multiple sites throughout the DISCOVER-AQ region, including at Edgewood. Percent differences are on the plot. Day of Year (DOY) is given in local time.
Figure 3: Absolute difference between OMI and Pandora v. absolute time from the OMI overpass at Edgewood, Maryland.

aerosols or clouds (if it is a small or negative value). Both the distance from the center of the OMI pixel to the ground site and the cloud fraction retrieved by OMI are included in the overpass data files as well. High UV aerosol index values, large distances from the center of the OMI pixel to the site, and large cloud fractions are indicated on Figure 4. Pandora averages that contain less than one-third of the retrievals expected in an hour are displayed too. Points outside of the ±20 DU bounds on either side of the one-to-one line are considered to exhibit significantly poor agreement between OMI and Pandora TCO$_3$ retrievals.

There are several noteworthy features in Figure 4. First, on days for which OMI indicates a cloud fraction $\geq 0.2$, Pandora tends to retrieve a higher TCO$_3$ amount than OMI. Also, with the exception of a few days with high cloud fractions, the Aldino, Fairhill, and SERC sites exhibit good agreement between OMI and Pandora TCO$_3$ retrievals, though SERC OMI TCO$_3$ is more consistently biased high. The agreement between Pandora and OMI TCO$_3$
retrievals can be attributed to the location of these sites. Fairhill and Aldino are 101 km and 54 km northeast of Baltimore, respectively, in relatively rural locations. Fairhill is the most rural site in the campaign. Though SERC is only about 42 km from Washington, D.C., it is rural and wooded area along the Chesapeake Bay containing 2650 acres of forest.

As indicated by several of the studies discussed in Chapter 1, the relatively coarse resolution of OMI can lead to averaging of pollutants in adjacent rural and urban locations, which can cause poor agreement between ground- and satellite-based total column retrievals. It is plausible that Fairhill and Aldino are far enough away from major urban areas to prevent such averaging. In the case of SERC, the site is likely contained within a large enough rural area that such averaging within the OMI pixel is ameliorated. Almost all TCO$_3$ retrievals from OMI at SERC are higher than the corresponding Pandora TCO$_3$ retrievals, and further study and measurements may be needed to understand the results at this particular site.

Comparisons in Fig. 4 indicate that on some days, multiple sites exhibit similar large differences in the TCO$_3$ retrievals from OMI and Pandora. This holds true for 8 July (DOY 189), 13 July (DOY 194), and 25 July (DOY 206). The average percent difference between retrievals from Pandora and OMI at sites with poor agreement on case study days was 22%, with percent differences calculated as in Eqn. 4; the average percent difference between retrievals at the eleven sites on all other days during July was 1.6%. Case studies are analyzed for the DISCOVER-AQ region on 8, 13, and 25 July to determine the conditions that cause the poor agreement observed between the TCO$_3$ retrievals at multiple locations. In the next section, the local conditions for this poor agreement will be addressed for each case study.
Figure 4: OMI versus Pandora TCO$_3$ for July 2011 at (a) Edgewood, (b) Aldino, (c) Beltsville, (d) Essex, (e) Fairhill, (f) GSFC, (g) Padonia, (h) SERC, (i) UMBC, (j) UMD, and (k) USNA. 8 July, 13 July, and 25 July were recurring outliers at many sites and are marked on the figure. Points are flagged for potential problems due to (red) high cloud cover, (green) number of Pandora points, (black) distance, and (cyan) UV Aerosol Index. To make each plot as easy to read as possible axes are not uniform throughout the figure.
3.2: Case Studies of Days with Poor Agreement at Multiple Sites

In the previous section, we saw that 8 July, 13 July, and 25 July all exhibited poor agreement between Pandora and OMI TCO$_3$ retrievals at multiple sites. The following case studies reveal that the cause of this poor agreement is varying cloud cover over the region, although aerosols and transport were also considered as error sources. As noted in Chapter 2, significant cloud cover can cause TCO$_3$ retrieval errors for both Pandora and OMI; in these three cases, the retrieval errors seem to be derived from cloud contamination.

Map 2: Map of the July 2011 DISCOVER-AQ region. Sites that saw poor agreement between Pandora and OMI TCO$_3$ on 8 July 2011 are indicated by green. Sites that saw poor agreement between Pandora and OMI TCO$_3$ on 13 July 2011 are indicated by orange.
3.2.1: 8 July 2011 and 13 July 2011

Figure 4 illustrates that Edgewood, Essex, Fairhill, GSFC, Padonia, UMBC, and UMD all showed poor agreement between Pandora and OMI TCO\textsubscript{3} retrievals on 8 and 13 July 2011. Additionally, Aldino and Beltsville showed poor agreement between Pandora and OMI TCO\textsubscript{3} retrievals on 8 and 13 July 2011, respectively. (See Map 2 for the locations of these sites.) Cloud cover, local chemistry and transport, and aerosols are considered as possible origins of the poor agreement between TCO\textsubscript{3} retrievals.

Figure 5 provides an overview of clouds and moisture in the atmosphere in the DISCOVER-AQ region on 8 and 13 July 2011. The visible image from MODIS Aqua (Fig. 5a) is from 8 July 2011, and indicates that there was heavy cloud cover in the region at the time of the OMI overpass; visible images from 13 July (not shown) indicate similar cloud cover. As indicated in Fig. 4, sites with poor agreement on these two dates had cloud cover \( \geq 0.20 \) and the visible images (Fig. 5a) show the vast coverage of clouds in the region at the time of the overpass. Information provided by the MERRA Model output furthers our insight into the cloud cover on 8 and 13 July 2011, though it should be noted that MERRA Model output is from approximately 10-11 hours before the OMI overpass. Cloud liquid water mixing ratio from MERRA on 8 July (Fig. 5b) shows that there were significant levels of moisture throughout the atmosphere. Cloud-top pressure from the MERRA model on 13 July (Fig. 6) shows that clouds were distributed at varying levels throughout the atmosphere on this date as well, with cloud-top heights ranging from approximately 200 hPa to 700 hPa. Varying cloud-top heights may cause inaccurate TCO\textsubscript{3} retrievals, particularly for OMI. Since OMI must estimate ozone levels below clouds (see Chapter 2), if cloud top heights within a pixel are not uniform, estimates of ozone become complicated.
In addition to cloud cover, local chemistry and transport are taken into account. Figure 7 shows the OMI-TOMS Level 3 global 0.25° gridded TCO₃ and the HYSPLIT back trajectories in and surrounding the DISCOVER-AQ region on 8 July 2011. Based on these results, winds for the DISCOVER-AQ site originated in areas that had higher levels of ozone than the DISCOVER-AQ region. If elevated levels or precursors of ozone were transported to the DISCOVER-AQ region on these winds, ozone levels below cloud heights could increase. This would contribute to Pandora TCO₃ amounts greater than TCO₃ amounts retrieved by OMI, since in the presence of such heavy clouds, OMI must estimate the column amounts below the cloud. A similar analysis revealed that transport was an unimportant source in causing retrieval errors for either instrument on 13 July 2011.

Figure 5: (a) Visible satellite image from MODIS Aqua showing cloud cover over the DISCOVER-AQ region on 8 July 2011 near the time of the OMI overpass. (b) MERRA Model outputs of cloud liquid water mixing ratio in the region on 8 July 2011. Red boxes indicate the region of interest.
Figure 6: MERRA Model output showing the cloud-top pressure in the region on 13 July 2011. Red boxes indicate the region of interest.

Figure 7: (a) Ozone throughout the region: Level 3 data from OMI; (b) 24-h Back Trajectories at Edgewood, Maryland, from HYSPLIT. Back trajectories are at heights of (red) 500 m and (blue) 1000 m, ending at 13:30 local time. Back trajectories were similar for other DISCOVER-AQ sites on 8 July 2011.

The presence of aerosols in the DISCOVER-AQ region on 8 and 13 July 2011 must also be considered when attempting to determine why these dates were outliers in TCO$_3$ retrieval comparisons at so many sites. Figure 8a shows the AOD at 550 nm from MODIS Aqua on 13 July 2011. The AOD image indicates moderate scattering of light throughout the atmosphere, with optical depths ranging between 0.42 and 0.5; this scattering may be due to both aerosols as well as the extensive cloud cover, such as that seen in Fig. 5a. The UV Aerosol Index from OMI...
on 13 July is presented in Figure 8b, and shows that there were not significant levels of UV-absorbing aerosols present in the atmosphere on 13 July 2011. Analysis was similar for the case of 8 July.

Aerosol LIDAR shown in Figure 9 from 8 July 2011 indicates that there was both a great deal of backscatter from the cloud base during the time of the OMI overpass, as well as some backscatter near the surface, possibly from low aerosols. Additionally, there was rain at Edgewood, Maryland, during the afternoon of 8 July 2011, evidence of which is visible in the LIDAR image. Rain in the region confirms cloudy conditions, and would likely have further hindered retrievals of the TCO$_3$.

Based on this study, it can be concluded that the primary source of poor agreement between OMI and Pandora TCO$_3$ amounts on 8 and 13 July was from the vast cloud cover. On 8 July 2011, precipitation in the region may also have contributed to inaccurate TCO$_3$ retrievals.
3.2.2: 25 July 2011

Figure 4 shows poor agreement between TCO$_3$ retrievals on 25 July 2011, a date for which Edgewood, Aldino, Beltsville, Essex, Fairhill, GSFC, UMBC, UMD, and USNA all experienced poor agreement between Pandora and OMI TCO$_3$ retrievals. Map 3 shows the locations of these sites. As in the previous case study, cloud cover, local chemistry and transport, and aerosols are considered as possible causes of poor agreement between TCO$_3$ retrievals at these sites.

An overview of clouds and moisture in the atmosphere in the DISCOVER-AQ region on 25 July 2011 is shown in Figure 10. The visible image from MODIS Aqua (Fig. 10a) shows that there was patchy cloud cover in the region at the time of the OMI overpass. Figure 4 indicates that the sites with poor agreement on 25 July 2011 had cloud cover $\geq 0.20$, but the visible image clarifies the extent of the cloud cover in the region at the time of the overpass. The MERRA model cloud liquid water mixing ratio (Fig. 10b) suggests that there were significant levels of...
moisture throughout the atmosphere, reaching throughout the troposphere up to 200 hPa. Figure 10c also indicates that there were varying cloud-top heights in the DISCOVER-AQ region during this time period. Should the cloud-top heights within an OMI pixel be varied in this way, a retrieval error could result from the necessary estimation of ozone below the non-uniform cloud-top height. MERRA model outputs are from approximately 9 hours before the OMI overpass.

Local chemistry and transport on 25 July are also considered as causes for the different TCO$_3$ retrievals obtained by Pandora and OMI at DISCOVER-AQ stations. OMI-TOMS Level 3 global 0.25° gridded TCO$_3$ retrievals and HYSPLIT back trajectories in and around the DISCOVER-AQ region imply that transport did not play a significant role in the large discrepancies between TCO$_3$ retrievals from Pandora and OMI on this day.
Figure 10: (a) Visible satellite image from MODIS Aqua showing clouds over the DISCOVER-AQ region on 25 July 2011 near the time of the OMI overpass. (b) MERRA Model output of cloud liquid water mixing ratio in the region on 25 July 2011. (c) MERRA Model output showing the cloud-top pressure in the region on 25 July 2011. Red boxes indicate the region of interest.

Considering the effects of aerosols on TCO$_3$ retrievals on 25 July 2011, the AOD from MODIS Aqua (Fig. 11) indicates that light extinction did occur to some extent in the atmosphere, with optical depths between 0.42 and 0.5; this is likely due to cloud cover (see Fig. 10a), as well
as aerosols that may have been in the region (See Figure 12 below). The UV Aerosol Index map from OMI was unavailable for 25 July. Aerosol LIDAR shown in Fig. 12 from 25 July 2011 at Edgewood, Maryland indicates that there was a great deal of backscatter low in the atmosphere. This backscatter, located at approximately 1 km, may have been due to a low aerosol layer at the time of the OMI overpass. The low aerosol layer that is apparent in Fig. 12 could have resulted in retrieval errors for both OMI and Pandora TCO₃. Also during this time, there is backscatter higher in the atmosphere, which is a likely indicator of cloud bases.

![Figure 11: Aerosol Optical Depth at 550 nm from MODIS Aqua on 25 July 2011. Latitude (degrees) is given on the y-axis; longitude (degrees) is given on the x-axis. Aerosol Optical Depth is unitless.](image)

![Figure 12: Backscatter measurements from Berkoff’s Micropulse Lidar instrument at Edgewood, Maryland on 25 July 2011. Backscatter is unitless, ranging from 0 to 1, as indicated by the color bar. The purple box indicates the approximate time period of the OMI overpass. Time is in local time.](image)
Considering the cloud cover, local chemistry and transport, and aerosols in the DISCOVER-AQ region on 25 July 2011, it seems that cloud cover played an important role in causing poor agreement between the Pandora and OMI TCO$_3$ retrievals. However, unlike the cases of 8 July and 13 July, it appears that a low aerosol layer also contributed to error in the TCO$_3$ retrievals on 25 July 2011.

3.2.3: Conclusions: TCO$_3$ Retrieval Differences between Pandora and OMI

Based on the above case studies, factors such as aerosols (25 July) and below-cloud transport (8 July) may contribute to poor agreement between TCO$_3$ retrievals from Pandora and OMI. However, the overwhelming similarity between all three cases, and the largest cause of poor agreement between TCO$_3$ retrievals, is cloud cover. On days with extensive cloud cover, the Pandora TCO$_3$ retrieval is consistently higher than the OMI TCO$_3$ retrieval. Though the clouds in the region can create retrieval difficulties for both instruments, Pandora retrievals of TCO$_3$ are biased high on days that have significant cloud cover.

In Figure 13 we see that the diurnal averages of TCO$_3$ from the Pandora instruments on 8, 13, and 25 July are generally higher than the monthly diurnal average of TCO$_3$ from the Pandora instruments. This especially holds true during the approximate time of the OMI overpass.

Using data from the Edgewood, Maryland site, it is seen that the unusual rises in Pandora TCO$_3$ on 8 and 25 July correspond to drastic drops in $j_{\text{NO}_2}$, the photolysis rate of NO$_2$. This rate is essentially an actinic flux measurement, and is directly proportional to the number of UV photons in the atmosphere. As the amount of UV radiation in the atmosphere drops due to cloud cover, Pandora TCO$_3$ retrievals become unusually high, as seen in Fig. 14. The high TCO$_3$
retrievals from Pandora in these cases are likely erroneous. Because Pandora is a direct sun spectrometer, the diminished UV radiation during these time periods prevents Pandora from performing optimally and retrieving accurate ozone levels.

Figure 13: Mean diurnal ozone during July 2011 from Pandora (black) plotted with diurnal ozone from Pandora on 8 July 2011 (cyan), 13 July 2011 (dark blue), and 25 July 2011 (green). Pandora values are averages based on Pandora retrievals from all sites. The approximate time of the OMI overpass is indicated by the purple box.
Figure 14: (a) $j_{NO2}$ and (b) TCO$_3$ retrievals from OMI (black) and Pandora (cyan) at Edgewood, Maryland, on 8 July 2011, and (c) $j_{NO2}$ and (d) TCO$_3$ retrievals from OMI (black) and Pandora (cyan) at Edgewood, Maryland, on 25 July 2011. Green and red lines on plots (a) and (b) represent the same starting and ending times, respectively. Blue and orange lines on plots (c) and (d) represent the same starting and ending times, respectively. DOY is given in local time.
3.3: Ozonesonde Comparisons

As noted in Chapter 2, ozonesondes are useful instruments for validating retrieved column data. Here we will use ozonesondes as a standard to compare with both Pandora and OMI TCO$_3$ at Edgewood and Beltsville.

3.3.1: Ozone sondes at Edgewood

At Edgewood, ozonesondes were launched almost on a daily basis during July 2011, with two ozonesondes occasionally being launched on the same day. Figure 15 compares TCO$_3$ from the Edgewood OMI overpass to TCO$_3$ from the July 2011 Edgewood ozonesondes. There is relatively good agreement between OMI and the ozonesonde TCO$_3$; the equation of the best fit line and the $R^2$ value are given on the figure. Figure 16 compares TCO$_3$ from Pandora at Edgewood to the July 2011 ozonesondes launched from Edgewood. Pandora data points are one-hour averages of TCO$_3$ retrievals centered on the mid-point of the ozonesonde flight time. It is evident from $R^2$ values and best fit lines (see equations on figures) that Edgewood ozonesondes were in better agreement with OMI data from the site than with Pandora data from the site. Both Pandora and OMI retrievals behaved poorly at times based on our case studies, and both instruments also experience errors with respect to ozonesonde TCO$_3$. 

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Figure 15: OMI TCO$_3$ versus ozonesonde TCO$_3$ at Edgewood, Maryland, during July 2011. Included on the plot are a black one-to-one line and a red best-fit line, as well as the equation of the best-fit line. Comparisons to launches on the 8 and 13 of July are indicated; there was no launch on 25 July.

Figure 16: TCO$_3$ from Pandora versus TCO$_3$ from ozonesondes at Edgewood, Maryland, during July 2011. Included on the plot are a black one-to-one line and a red best-fit line, as well as the equation of the best-fit line. Comparisons to launches on the 8 and 13 of July are indicated; there was no launch on 25 July.
3.3.2: Ozone sondes at Beltsville

Far fewer ozone sondes were launched from Beltsville than were launched from Edgewood during July 2011, but data from ozone sondes at this site are nevertheless still useful. Considering Figs. 15-18, there is a notable difference in TCO$_3$ amounts between the Edgewood and Beltsville sites; TCO$_3$ is tends to be 25-50 DU higher at Edgewood than at Beltsville. This is probably due to unique meteorological conditions at Edgewood that favor bay breeze events, which can cause high levels of ozone for the site. As seen in Fig. 4, Edgewood is also the site that has the most days that exhibit poor agreement between Pandora and OMI TCO$_3$ retrievals. The conditions at Edgewood which contribute to the unusually high ozone levels seen here likely make obtaining accurate column retrievals more complicated. Particularly in the case of bay breeze events, OMI may not pick up ozone increases in the column below the boundary layer as easily as Pandora. Further data and investigation is warranted to more fully understand the air quality and local chemistry at Edgewood, Maryland.

Beltsville ozone sondes data are also useful for comparing to TCO$_3$ retrievals from both OMI and Pandora. Figure 17 compares TCO$_3$ from the Beltsville OMI overpass to TCO$_3$ from the July 2011 Beltsville ozone sondes. Even though there are a limited number of ozone sondes available for comparison, there is relatively good agreement between OMI and ozone sondes TCO$_3$. Figure 18 compares TCO$_3$ from Pandora at Beltsville to the July 2011 Beltsville ozone sondes. Pandora data points are one-hour averages of TCO$_3$ retrievals centered on the midpoint of the ozonesonde flight time. Based on Figs. 17 and 18, Beltsville ozone sondes were in better agreement with OMI data from the site than with Pandora data from the site. Though there are too few ozonesonde launches to calculate valid R$^2$ values, best fit lines (see equations on figures) and spread of the data points on the two figures indicate that Pandora retrievals of TCO$_3$
in the DISCOVER-AQ region during July 2011 were less accurate than OMI retrievals with respect to ozonesonde TCO$_3$.

Figure 17: OMI total TCO$_3$ versus ozonesonde TCO$_3$ at Beltsville, Maryland during July 2011. Included on the plot are a black one-to-one line and a red best-fit line, as well as the equation of the best-fit line.

Figure 18: TCO$_3$ from Pandora versus TCO$_3$ from ozonesondes at Beltsville, Maryland during July 2011. Included on the plot are a black one-to-one line and a red best-fit line, as well as the equation of the best-fit line.
Chapter 4: Results—OMI NO₂ Validation

4.1: Relationships Between Pandora TCNO₂ and Ground-based Measurements

We begin our study of TCNO₂ retrievals by making comparisons between Pandora TCNO₂ retrievals and ground-based NOₓ products measured at Edgewood, MD. These comparisons confirm that the Pandora spectrometer is retrieving TCNO₂ amounts that are consistent with ground observations.

During the DISCOVER-AQ campaign, NATIVE measured jNO₂ at Edgewood. Because jNO₂ is the photolysis rate of NO₂, we expect that as jNO₂ increases, TCNO₂ from Pandora will decrease. Figure 19 verifies that this was usually the case at Edgewood during July 2011.

We also see the expected relationship between NO and NO₂, as illustrated in Figure 20a. NOₓ is a product of combustion, so we expect both NO and NO₂ to reach a peak during the
morning rush hour as people commute to work and industry begins for the day. Figure 20a clearly shows this peak around fraction of day 0.3, which corresponds to approximately 7:30-9:00 am local time.

Figure 20b shows the diurnal patterns of Pandora TCNO$_2$ and ground NO$_2$ at Edgewood, Maryland. The two patterns share similar rises and falls, though there are some differences in the data, including a time lag between the diurnal pattern of ground NO$_2$ and diurnal pattern of Pandora TCNO$_2$. These differences are not surprising since Pandora retrieves TCNO$_2$ but the Teledyne API 200 EU NO$_x$ Analyzer measures only the NO$_2$ found at the surface. The expected relationships between Pandora TCNO$_2$ retrievals and ground-based measurements of j$_{NO2}$, NO, and NO$_2$ depicted in Figures 19 and 20 imply value in Pandora TCNO$_2$ retrievals.
4.2: Comparison of KNMI Dutch OMI NO\textsubscript{2} product and NASA Standard Product OMI NO\textsubscript{2} Retrievals

In this work, the standard product (SP) OMI NO\textsubscript{2} retrievals from NASA are used. However, it is of note that the Dutch OMI NO\textsubscript{2} (DOMINO) product is also widely used and accepted. The DOMINO retrieval method is slightly different than the retrieval method for NASA’s SP. Both products use the DOAS method to retrieve TCNO\textsubscript{2}, but their methods of determining slant column abundances are slightly dissimilar. While the SP uses spectral fitting to determine the stratospheric slant column (Boersma, et al., 2007), the DOMINO product uses the TM4 global chemistry transport model (CTM) and data assimilation techniques to determine the stratospheric slant column (Boersma, et al., 2007). There are further differences between the two products in the way that air mass factors are calculated. In the SP, surface albedo fields for use in the AMF are taken from the Global Ozone Monitoring Experiment (GOME) satellite; in the DOMINO product, they are obtained from both TOMS and GOME. A priori profile shapes for use in the SP AMFs are taken from yearly averages of profile shapes from GEOS-Chem; a priori profile shapes for use in the DOMINO AMFs are taken from collocated daily output at the overpass time from the TM4 CTM. The ghost column for use in the AMF is not included in the SP, but it is implicit in the AMF definition for the DOMINO product. Finally, an across track variability correction factors are based on 24-hour data in the SP, but they are computed per-orbit in the DOMINO product (Boersma, et al., 2007).

Despite differences in retrieval algorithms, the SP and the DOMINO product compared similarly with Pandora TCNO\textsubscript{2} retrievals at GSFC, as seen in Figure 21a-b. Figure 21c shows how the two overpass products compare during July 2011. Hereafter it can be assumed that OMI TCNO\textsubscript{2} retrievals are from the NASA SP.
Figure 21: (a) NASA retrieval of OMI Overpass TCNO₂ versus Pandora TCNO₂ and (b) KNMI retrieval of OMI Overpass TCNO₂ versus Pandora TCNO₂ at Goddard Space Flight Center in Greenbelt, Maryland. Pandora values are 1 hour averages centered on the time of the OMI overpass. (c) NASA retrieval of OMI Overpass TCNO₂ versus KNMI retrieval of OMI Overpass TCNO₂ at Goddard Space Flight Center in Greenbelt, Maryland. A red best-fit line and its equation are included on the plot.
4.3: Comparison of OMI Overpass TCNO$_2$ and Pandora TCNO$_2$

As illustrated in section 4.1, Pandora TCNO$_2$ patterns relate approximately as expected with ground-based NO$_x$ measurements, indicating that Pandora is performing as expected with respect to TCNO$_2$. Figure 22 shows the diurnal pattern of Pandora TCNO$_2$ from Edgewood, and further confirms this performance. In Fig. 22, data for the month is placed into 30-minute bins throughout the day and averaged. “Error” bars indicate one standard deviation of the bin average. Because NO$_x$ is a product of combustion, we expect a bimodal diurnal pattern in the TCNO$_2$. The diurnal pattern shown in Fig. 22 indicates a morning peak during the rush hour. The afternoon peak is less prominent, due to a combination of factors. The afternoon rush hour is generally less precise (the time at which people leave work is less standardized than the time at which people go to work) and the boundary layer is better mixed in the afternoon, which allows for a more uniform profile of chemical pollutants.

![Diurnal Pattern of Pandora TCNO$_2$ at Edgewood, MD](image)

*Figure 22: Diurnal pattern of Pandora TCNO$_2$ at Edgewood throughout July 2011, beginning at 0600 LT and ending at 1800 LT.*
The total expected error in OMI TCNO\textsubscript{2} retrievals is about 5\% in clear unpolluted conditions, but can be as large as 20-50\% in polluted or cloudy conditions (Chance, 2011); error in Pandora TCNO\textsubscript{2} retrievals is \leq 10\%. By plotting daily Pandora and OMI TCNO\textsubscript{2} retrievals on the same axes, it is clear that some days during July experienced good agreement between TCNO\textsubscript{2} retrievals from the two instruments, while other days during July experienced poor agreement between TCNO\textsubscript{2} retrievals from the two instruments. The percent differences between OMI and Pandora in Figure 23 provide good indications of agreement between Pandora and OMI TCNO\textsubscript{2}. Percent differences were calculated as:

\[
\left( \frac{OMI_{TCNO_2} - Pandora_{TCNO_2}}{OMI_{TCNO_2} + Pandora_{TCNO_2}} \right) \times 100\% , \quad [5]
\]

where \( OMI_{TCNO_2} \) is the TCNO\textsubscript{2} retrieval from OMI and \( Pandora_{TCNO_2} \) is a 1-hour average of the TCNO\textsubscript{2} retrievals from Pandora centered on the time of the OMI overpass. Figures 23a-c depict three days during July for which TCNO\textsubscript{2} retrievals by Pandora and OMI at Edgewood were in good agreement, while Figs. 23d-f depict three days during July for which TCNO\textsubscript{2} retrievals by Pandora and OMI at Edgewood were in poor agreement.

The three days showing poor agreement at Edgewood in Fig. 23 (15 July, 26 July, and 29 July) coincide with case studies presented here of poor agreement between OMI and Pandora TCNO\textsubscript{2} retrievals throughout the DISCOVER-AQ region.
Figure 23: Daily plots of Pandora and OMI TCNO$_2$ from Edgewood, Maryland on (a) 9 July 2011, DOY 190, (b) 10 July 2011, DOY 191, and (c) 11 July 2011, DOY 192. These are the three days for which Pandora and OMI exhibited the best agreement at Edgewood, Maryland. Plots from (d) 15 July 2011, DOY 196, (e) 26 July 2011, DOY 207, and (f) 29 July 2011, DOY 210, represent three of the days for which Pandora and OMI TCNO$_2$ retrievals showed poor agreement at multiple sites, including Edgewood. Percent differences are included on the plot.
Figure 24 portrays 1-minute averages of the absolute difference between OMI and Pandora TCNO$_2$ retrievals at Edgewood plotted against the absolute time from the OMI overpass in five minute intervals. The difference between retrievals has the greatest variability at times closest to the time of the OMI overpass. This indicates that for point comparisons of OMI TCNO$_2$ to Pandora TCNO$_2$ close in time, OMI is missing large variability in the column. At larger time differences the absolute difference between the two TCNO$_2$ amounts levels out at approximately 0.06 DU, which is about $1.6 \times 10^{15}$ molecules/cm$^2$. Repeating this analysis at other DISCOVER-AQ sites revealed similar patterns; thus retrievals with greater than a $1.6 \times 10^{15}$ molecules/cm$^2$ difference between the OMI and Pandora TCNO$_2$ amounts are considered to exhibit poor agreement.

Figure 25 shows a comparison of OMI TCNO$_2$ and 1-hour averages of Pandora TCNO$_2$ centered on the time of the OMI overpass. In addition to the TCNO$_2$, OMI overpass data files contain quality control information to flag for conditions that could result in erroneous TCNO$_2$. 

![Figure 24: Absolute difference between OMI and Pandora TCNO$_2$ retrievals versus absolute time from the overpass.](image-url)
retrievals. Included in this information is the OMI CTP (which identifies the location of the OMI pixel in the instrument’s swath), the distance from the center of the OMI pixel to the ground site, and the cloud fraction retrieved by OMI. Retrievals from pixels on the ends of the OMI swath, large distances from the center of the OMI pixel to the site, and large cloud fractions are indicated on Fig. 25. Pandora averages that contain less than one-third of the expected retrievals in an hour are also shown by colored dots. Following the implications from Fig. 24, points outside of the $\pm 1.6 \times 10^{15}$ molecules/cm$^2$ bounds on either side of the one-to-one line are considered to exhibit poor agreement between OMI and Pandora TCNO$_2$ retrievals.

Several features of Fig. 25 should be discussed. First, many of the comparisons indicate that the OMI pixel over the location was in one of the pixels closest to the end of the swath. These pixels have a resolution that is not as fine as those at nadir; thus less accurate TCNO$_2$ retrievals result. Second, the agreement between Pandora and OMI TCNO$_2$ is generally poorer than the agreement between Pandora and OMI TCO$_3$. Many of the OMI retrievals available for comparisons were from pixels near the edge of the swath. The coarse resolution in these pixels is likely to create more error in retrievals for the highly variable NO$_2$ columns than for the more regional ozone columns.

As in the TCO$_3$ retrieval comparisons, SERC seems to have one of the best agreements between Pandora and OMI TCNO$_2$. This agreement points to the rural environment in which SERC is located. Because SERC is such a large forested region, pixels over SERC encounter less averaging of NO$_2$ and other pollutants than other sites. In addition to SERC, USNA exhibits relatively good agreement between Pandora and OMI TCNO$_2$. Though there are not as many retrievals available for comparison at USNA as at SERC, it is interesting that these two sites, within close proximity to one another, experience some of the best agreement between TCNO$_2$
Figure 25: OMI versus Pandora TCNO₂ for July 2011 at a) Edgewood, (b) Aldino, (c) Beltsville, (d) Essex, (e) Fairhill, (f) GSFC, (g) Padonia, (h) SERC, (i) UMBC, (j) UMD, and (k) USNA. 10 July, 15 July, 16 July, 26 July, and 29 July were recurring outliers at many sites, and are marked on the figure. Points are flagged for high cloud cover (red), number of Pandora points (cyan), distance (black), and OMI Cross Track Position (CTP) (magenta).
retrievals. Further measurements and study are necessary to reveal features of this region that may be conducive to good TCNO$_2$ retrievals from OMI and Pandora.

The comparisons that are illustrated in Fig. 25 indicate that on some days, multiple sites exhibit large differences in the TCNO$_2$ retrievals from OMI and Pandora. This holds true for 10 July (DOY 191), 15 July (DOY 196), 16 July (DOY 197), 26 July (DOY 207), and 29 July (DOY 210). The average percent difference between retrievals that saw poor agreement between Pandora and OMI TCNO$_2$ on these days was 60%, with percent differences calculated as in Eqn. [5]; the average percent difference between retrievals at the eleven sites on other days during July was 23%. Case studies are performed for the DISCOVER-AQ region on 10, 15, 16, 26, and 29 July to determine the cause of the disagreement between TCNO$_2$ retrievals at multiple locations.

4.4: Case Studies of Days with Poor Agreement at Multiple Sites during Fair Weather

Five different days during July 2011 exhibited particularly poor agreement between the Pandora and OMI TCNO$_2$ retrievals at multiple sites. Four of these days—10 July, 15 July, 16 July, and 29 July—suffered retrieval errors caused by small, passing cumulus clouds. These clouds, typical of fair weather on a summer day, can block the field of view for Pandora, but are not usually substantial enough to cause OMI to register a high cloud fraction. The scattering of light by these clouds can cause retrieval errors for both instruments.
4.4.1: 10, 15, and 16 July 2011

Figure 25 illustrates that Aldino, Essex, Fairhill, GSFC, Padonia, and SERC all had poor agreement between Pandora and OMI TCNO\textsubscript{2} retrievals on 10 July 2011. Beltsville, Edgewood, GSFC, and UMD all showed disagreement between Pandora and OMI TCNO\textsubscript{2} retrievals on 15 July 2011. Beltsville, Essex, GSFC, SERC, UMBC, UMD, and USNA all exhibited poor comparisons between Pandora and OMI TCNO\textsubscript{2} retrievals on 16 July 2011. Map 4 shows the locations of these sites. Cloud cover, local chemistry and transport, and aerosols are considered as causes of the disagreement between TCNO\textsubscript{2} retrievals at these sites on the dates of interest.

Map 4: The July 2011 DISCOVER-AQ region. Sites that saw poor agreement between the Pandora and OMI TCNO\textsubscript{2} on 10 July 2011 are indicated by orange. Sites that saw poor agreement between the Pandora and OMI TCNO\textsubscript{2} on 15 July 2011 are indicated by green. Sites that saw poor agreement between the Pandora and OMI TCNO\textsubscript{2} on 16 July 2011 are indicated by blue.
Figure 26 provides an overview of clouds and moisture in the atmosphere in the DISCOVER-AQ region on 10 July 2011. The visible image from MODIS-Aqua (Fig. 26a) presents small, scattered clouds in the region during the OMI overpass. These clouds were small enough to avoid causing OMI to detect a large cloud fraction in most cases (see Fig. 25), but likely still caused enough scattering and interference with the TCNO₂ retrievals from the two instruments to contribute to the poor agreement between OMI and Pandora that is illustrated in Fig. 25. Information provided by the MERRA model outputs furthers our insight into the cloud cover on 10 July 2011. Cloud liquid water mixing ratio from MERRA approximately one hour after the OMI overpass shows that there were significant levels of moisture throughout the atmosphere, reaching from the lower troposphere to between 300 hPa and 200 hPa. The MERRA model data from about 10 hours before the overpass shows that cloud-top pressures ranged between 400 hPa and 800 hPa, an indication of the varied cloud cover in the region on 10 July 2011. Varying cloud-top heights within an OMI pixel could result in a retrieval error by OMI due to the necessary estimation of NO₂ below the non-uniform cloud-top height. Also, low-level clouds are problematic for both OMI and Pandora, particularly if a majority of the polluted air in the column is below the cloud height. This general pattern of scattered clouds at varying heights prevailed on 15 and 16 July 2011 as well.

In addition to cloud cover, local chemistry and transport on 10, 15, and 16 July are considered. Figure 27 shows the OMI Level 3 global gridded 0.25° TCNO₂ retrievals and the HYSPLIT back trajectories in and surrounding the DISCOVER-AQ region on 15 July 2011. Winds were from regions with TCNO₂ amounts slightly lower than those retrieved in the DISCOVER-AQ region. This transport could have contributed to the poor agreement between Pandora and OMI TCNO₂ amounts. If air with less NO₂ moved into the more polluted
Figure 26: (a) Visible satellite image from MODIS Aqua showing cloud cover over the DISCOVER-AQ region on 10 July 2011 near the time of the OMI overpass. (b) MERRA Model output of cloud liquid water mixing ratio in the region on 10 July 2011. (c) MERRA Model output showing the cloud-top pressure in the region on 10 July 2011. Red boxes indicate the region of interest.

DISCOVER-AQ region, passing clouds would have prevented OMI from getting an accurate TCNO$_2$ retrieval. For example, if NO$_2$ levels above the passing clouds were still high, NO$_2$
levels below cloud height could have been overestimated by OMI. Local chemistry and transport were similar on 10 and 16 July 2011.

The presence of aerosols in the DISCOVER-AQ region on 10, 15, and 16 July 2011 must also be considered when determining why these days were outliers in TCNO$_2$ retrieval comparisons. According to the MODIS Aqua image in Figure 28, there was some low-level light extinction in the atmosphere on 15 July 2011, with aerosol optical depths between 0.18 and 0.26. AOD from MODIS-Aqua was similar for 10 July 2011 (0.26-0.34) and 16 July 2011 (0.02-0.18). The UV Aerosol Index from OMI on 15 July 2011 (Figure 28b) indicates that there were not significant levels of UV-absorbing aerosols present in the atmosphere. These data were not available for 16 July 2011, but were similar for 10 July 2011. Finally, the aerosol LIDAR shown in Figure 29 from 16 July 2011 is representative of LIDAR images for all three days.

Figure 27: (a) NO$_2$ throughout the region on 15 July 2011: Level 3 data from OMI. (b) 24-h Back trajectories at Edgewood, Maryland from HYSPLIT. Back trajectories are at heights of (red) 500 m and (blue) 1000 m, ending at 13:30 local time. Back trajectories were similar for other DISCOVER-AQ sites on 15 July 2011.
Some backscatter from aerosols is indicated in the boundary layer (below the red line) during the time of the OMI overpass. However, it is unlikely that this backscatter caused large errors for OMI or Pandora retrievals. Figures 28 and 29 imply that aerosols were not a major factor contributing to poor agreement between TCNO$_2$ retrievals from Pandora and OMI on 10, 15, or 16 July 2011.

We conclude that scattered, passing clouds in the DISCOVER-AQ region on 10, 15, and 16 July were the major source of poor agreement in TCNO$_2$ retrievals from OMI and Pandora.

Figure 28: (a) Aerosol Optical Depth (unitless) at 550 nm from MODIS Aqua on 15 July 2011. (b) Aerosol UV Index (unitless) from OMI on 15 July 2011. Latitude (degrees) is given on the y-axis; longitude (degrees) is given on the x-axis.

Figure 29: Backscattering measurements (unitless) from Berkoff’s Micropulse Lidar instrument at Edgewood, Maryland on 16 July 2011. Time is in local time. The purple box indicates the approximate time period of the OMI overpass.
According to Nader Abuhassan, one of the DISCOVER-AQ contacts for the Pandora instruments, moving clouds can cause saturation to occur during the 20-second measurement window used to retrieve NO$_2$. If this occurs, Pandora data are not saved. Thus, the passing cumulus clouds could have resulted in fewer Pandora retrievals available to average for comparison with the OMI TCNO$_2$ retrieval.

Figure 30 compares Pandora TCNO$_2$ retrievals at Edgewood, Maryland to ground measurements of NO$_2$ at Edgewood, Maryland. It is clear that Pandora retrievals were consistent with ground-based NO$_2$ observations on 10 July 2011, with both instruments indicating a plume around mid-day. Though it is encouraging that Pandora makes this correct observation, we cannot confirm that the magnitudes of Pandora retrievals were correct. This type of agreement in diurnal patterns was typical for the three days in this case study.

Figure 30 leads to the conclusion that poor agreement between Pandora and OMI TCNO$_2$ retrievals on 10, 15, and 16 July is due to inaccurate retrievals by both OMI and Pandora. Retrieval errors were caused by a combination of clouds in the area (particularly problematic for Pandora) and transport of less polluted air to the region. Features such as the plume shown in

![Figure 30](image-url): (a) Pandora TCNO$_2$ at Edgewood, Maryland, on 10 July. Hour of the day is in local time. (b) Ground NO$_2$ measured at Edgewood, Maryland, on 10 July 2011. Hour of the day is in local time.
Fig. 30 can also cause retrieval difficulties for the satellite, as these phenomena are likely to have been related to emissions near the ground. Satellites have difficulty making observations within the boundary layer, and such dynamics near the surface create variations in the column that OMI is not always able to detect, particularly in cloudy conditions.

**4.4.2: 29 July 2011**

Figure 25 illustrates that Beltsville, Edgewood, Essex, GSFC, Fairhill, Padonia and UMD all showed significantly poor agreement between Pandora and OMI TCNO$_2$ retrievals on 29 July 2011. Map 5 gives the locations of these sites. To determine the cause of the poor agreement at these sites on 29 July, we consider cloud cover, local chemistry and transport, and aerosols in the DISCOVER-AQ region.

![Map 5: The July 2011 DISCOVER-AQ region. Sites that saw poor agreement between the Pandora and OMI TCNO$_2$ on 29 July 2011 are indicated by pink.](image)
An overview of clouds and moisture in the atmosphere in the DISCOVER-AQ region on 29 July 2011 is provided in Figure 31. The visible image from MODIS Aqua (Fig. 31a) shows that there were many small cumulus clouds in the area during the OMI overpass, as well as thin clouds or haze. Figure 25 indicates that OMI did not detect a large cloud fraction for the sites with poor agreement; however, the small passing clouds likely still caused enough scattering and interference with the TCNO$_2$ retrievals from OMI and Pandora to contribute to the poor agreement between the two retrievals. Cloud liquid water mixing ratio from the MERRA model shows that there were significant levels of moisture as high in the atmosphere as 200 hPa shortly after the OMI overpass (see Figure 31). The MERRA model cloud-top pressure from about 10 hours before the OMI overpass confirms that cloud-tops did in some cases reach as high as approximately 200 hPa, but were also as low as 900 hPa on 29 July 2011.

Local chemistry and transport on 29 July must also be investigated. OMI Level 3 TCNO$_2$ retrievals in and surrounding the DISCOVER-AQ region are depicted in Figure 32a, and Figure 32b shows the HYSPLIT back trajectories in the region. Winds on 29 July 2011 were from areas with TCNO$_2$ amounts slightly lower than those retrieved in the DISCOVER-AQ region. As air with less NO$_2$ moved into the more polluted DISCOVER-AQ region, it is possible that the broken cloud cover prevented OMI from attaining an accurate TCNO$_2$ retrieval.

Finally, we consider the presence of aerosols in the DISCOVER-AQ region on 29 July 2011. According to the MODIS-Aqua image in Figure 33, aerosols in the atmosphere were at a middle level, with optical depths between 0.42 and 0.58. Figure 33b shows the UV Aerosol Index from OMI, and indicates that there were not significant levels of UV-absorbing aerosols present in the DISCOVER-AQ region on 29 July 2011. The aerosol LIDAR shown in Figure 34 from 29 July 2011 indicates a great deal of backscatter in the bottom 2 km of the atmosphere.
Figure 31: (a) Visible satellite image from MODIS Aqua showing cloud cover over the DISCOVER-AQ region on 29 July 2011 near the time of the OMI overpass. (b) MERRA Model output of cloud liquid water mixing ratio in the region on 29 July 2011 and (c) MERRA Model output showing the cloud-top pressure in the region on 29 July 2011. Red boxes indicate the region of interest.
Figure 32: (a) NO$_2$ throughout the region: Level 3 data from OMI. (b) 24-h Back trajectories at Edgewood, Maryland, from HYSPLIT. Back trajectories are at heights of (red) 500 m and (blue) 1000 m, ending at 13:30 local time. Back trajectories were similar for other DISCOVER-AQ sites on 29 July 2011.

during the approximate time of the OMI overpass. These light-scattering aerosols are likely the apparent haze seen in Fig. 31a. Although the cloud-cover on 29 July is similar to the previous case studies in this section and contributes to the poor agreement between OMI and Pandora TCNO$_2$ retrievals, the high backscatter from aerosols also contributes to poor agreement between the OMI and Pandora TCNO$_2$ retrievals on 29 July. It appears that this aerosol layer was particularly problematic at Edgewood, MD, where the LIDAR was located. In Fig. 25, we see that the Pandora TCNO$_2$ column is far lower than the OMI TCNO$_2$ column. If the aerosol layer at Edgewood caused retrieval error for Pandora, but was not as dense over other sites, this explains why Edgewood showed poorer agreement between TCNO$_2$ retrievals relative to other sites on this date. In section 4.5 we will consider a case in which aerosols are the primary cause of poor TCNO$_2$ retrieval agreement between Pandora and OMI.
4.4.3: Conclusions: Poor Agreement of TCNO$_2$ Retrievals during Fair Weather

The case studies for 10 July, 15 July, 16 July, and 29 July indicate that small passing cumulus clouds cause TCNO$_2$ retrieval errors for both Pandora and OMI. Pandora error likely results from the fact that small, passing clouds can cause fewer retrievals to be retained. OMI errors are due to the estimation of the column below clouds, even though OMI does not flag the pixel as having a high cloud fraction. OMI does not always estimate the column amounts below
the small clouds accurately, particularly if cloud-top heights are varied or winds near the ground are transporting cleaner or more polluted air to the region where the retrieval is being made. Also, albedo of the clouds can cause OMI to have an increased sensitivity to the part of the NO$_2$ column above cloud height (see Chapter 2). The indication that small passing clouds cause retrieval difficulties for OMI TCNO$_2$ is further supported by the fact that none of the OMI level 3 data over the DISCOVER-AQ region on these days is flagged out due to clouds (see Figs 27a and 32a), though we know small clouds were present. (See Figs. 26a and 31a.)

Passing clouds are problematic for both OMI and Pandora TCNO$_2$ retrievals, but they seem to pose the greatest difficulty for TCNO$_2$ retrievals from OMI. We now turn our attention to aerosols, and the way in which an aerosol layer can affect TCNO$_2$ retrievals from the two instruments.

### 4.5: Case Study of 26 July 2011: Clear Skies, Low Aerosol Layer

The final day for which we perform a case study to determine the source of poor agreement between OMI and Pandora TCNO$_2$ retrievals is 26 July 2011. Unlike our previous case studies, this day had mainly clear skies in the DISCOVER-AQ region. In spite of clear skies, the agreement between Pandora and OMI TCNO$_2$ retrievals was poor at multiple sites (see Fig. 25). Our case study reveals that the cause of this poor agreement was a low aerosol layer in the 2011 DISCOVER-AQ region.

Figure 25 illustrates that Aldino, Beltsville, Edgewood, Essex, Fairhill, GSFC, Padonia, UMBC, and UMD all exhibited poor agreement between Pandora and OMI TCNO$_2$ retrievals on 26 July 2011. Map 6 gives the locations of these sites. Cloud cover, local chemistry and
transport, and aerosols in the DISCOVER-AQ region are considered as causes of the poor agreement between Pandora and OMI TCNO$_2$ retrievals on this date.

An overview of the clouds and moisture in the atmosphere in the DISCOVER-AQ region on 26 July 2011 is provided in Figure 35. The visible image from MODIS Aqua (Fig. 35a) shows that skies in the area during the OMI overpass were mainly clear. This assessment agrees well with Fig. 25, in which none of the sites were flagged as having a high cloud fraction on 26 July. MERRA model cloud liquid water mixing ratio from about an hour after the OMI overpass indicates that some clouds may have entered the region afterwards.

Local chemistry and transport on 26 July are also considered. OMI Level 3 TCNO$_2$ retrievals in and surrounding the DISCOVER-AQ region and HYSPLIT back trajectories from the region specify that local chemistry and transport were not major causes of the poor agreement between OMI and Pandora TCNO$_2$ retrievals in the DISCOVER-AQ region on 26 July 2011.
Finally, we consider the presence of aerosols in the DISCOVER-AQ region on 26 July 2011. According to the relatively low AOD (between approximately 0.02 and 0.1) over the DISCOVER-AQ region in the MODIS-Aqua image in Figure 36a there was minimal light extinction due to scattering or absorption throughout most of the atmosphere on this date. Figure 36b shows the UV Aerosol Index from OMI, and indicates that there were not significant levels of UV-absorbing aerosols present in the DISCOVER-AQ region on 26 July 2011. The aerosol LIDAR shown in Figure 37 from 26 July 2011, however, measured a great deal of backscatter in the boundary layer during the approximate time of the OMI overpass. Given the clear skies shown in Fig. 35a, this backscatter is almost certainly caused by aerosols. The high backscatter
from aerosols in the boundary layer contributes to the poor agreement between the OMI and Pandora TCNO$_2$ retrievals on 26 July. Considering the height of the backscatter, it is likely that Pandora retrieval errors are greater than OMI retrieval errors in the presence of this aerosol layer because OMI likely experiences very little impact from scattering so low in the atmosphere.

Figure 36: (a) Aerosol Optical Depth (unitless) at 550 nm from MODIS Aqua on 26 July 2011. (b) Aerosol UV Index (unitless) from OMI on 26 July 2011. Latitude (degrees) is given on the y-axis; longitude (degrees) is given on the x-axis.

Figure 37: Backscattering measurements (unitless) from Berkoff’s Micropulse Lidar instrument at Edgewood, Maryland on 26 July 2011. Time is in local time. The purple box indicates the approximate time period of the OMI overpass.
Chapter 5: Conclusions

A study of Pandora and OMI TCO\(_3\) and TCNO\(_2\) retrievals from both the Washington, D.C., and Baltimore, Maryland, areas during the NASA-sponsored July 2011 DISCOVER-AQ campaign reveals that substantially cloudy conditions cause retrieval errors for TCO\(_3\), while scattered cloud cover and aerosol layers cause retrieval errors for TCNO\(_2\). It should be noted that because different conditions lead to poor agreement for TCO\(_3\) and TCNO\(_2\) retrievals, days that show poor agreement between TCO\(_3\) retrievals are not the same as days that show poor agreement between TCNO\(_2\) retrievals. In other circumstances, OMI and Pandora perform well, and show good agreement to within ±1.6% for TCO\(_3\) retrievals, and to within ±23% for TCNO\(_2\) retrievals.

TCO\(_3\) retrievals for the two instruments generally agree well on days for which the cloud fraction at the time of the OMI overpass is ≤ 0.20 (see Fig. 4). Additionally, TCO\(_3\) retrievals from OMI and Pandora exhibit better agreement at rural locations, such as Fairhill, MD, than at the more urban sampling sites in the 2011 DISCOVER-AQ campaign. Retrievals of TCNO\(_2\) from Pandora and OMI at the locations of SERC and USNA exhibited the best agreement among sites included in this study. These two sites are closely located, indicating that the region is favorable for accurate retrievals of TCNO\(_2\) from both instruments. Further data and studies are necessary to determine the specific reasons for the agreement exhibited between Pandora and OMI TCNO\(_2\) retrievals at these two locations.

In-depth case studies have revealed that TCO\(_3\) retrievals from OMI and Pandora are adversely affected by cloud cover of a fraction > 0.20, resulting in an average percent difference of 22% between retrievals. TCNO\(_2\) retrievals from OMI and Pandora are hindered by both small passing cumulus clouds and the presence of aerosol layers in the atmosphere, with an average
percent difference of 60% between retrievals in such conditions. Further comparisons of total column retrievals with ozonesondes and a Teledyne API 200 EU NOx Analyzer expose the shortcomings of OMI and Pandora in these three specific sets of conditions.


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