Remote Sensing of the Lower Atmosphere: From Surface Concentration to Mixing Layer Height

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> Doctor of Philosophy in Electrical Engineering

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(ABSTRACT)

Differential Optical Absorption Spectroscopy (DOAS) is a remote sensing technique to detect different trace gas concentrations in the atmosphere. The Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) measurements by the Pandora instrument scan the sky at different elevation angles and main data products include near surface concentration, tropospheric column and vertical profile for different trace gases. It addresses an important gap in near surface air quality measurements that is difficult for in-situ, satellite and other remote sensing measurements to address. Different applications of the MAX-DOAS technique have been presented in this study for improving our understanding of tropospheric chemistry and near surface air quality monitoring.

Formaldehyde (HCHO) concentration retrieved from the DOAS technique exhibits significant variation depending on the fitting parameters used. This systematic variation stems from different factors such as uncertainty in molecular absorption cross section measurement, temperature dependence of trace gas absorption, correlation between trace gases and combination of absorbers used in the DOAS fitting. To investigate the sensitivity and systematic uncertainty of HCHO retrieval, different fitting scenarios were created where fitting parameters like wavelength range, polynomial order, offset order and molecular absorption cross section were varied. To minimize systematic uncertainty and provide steady variability, the fitting scenario that most closely resembles the median of the range is selected

and recommended as base fitting scenario. In addition, a real time analytical method to calculate *HCHO* near surface volume mixing ratio is presented where radiative transfer modelling is not required. The *HCHO* near surface volume mixing ratio calculated by MAX-DOAS is compared with surface *HCHO* measured by a ground in-situ instrument. The Pandora MAX-DOAS agrees very well with the ground in-situ instrument for the whole campaign $(R^2 = 0.83, \text{ slope} = 0.92)$ and provides excellent agreement for clear days $(R^2 =$ 0.88, slope=0.95). Additionally, a methodology is presented for detecting the mixing layer height (MLH) by using Pandora MAX-DOAS vertical water vapor distribution measurements. The wavelet method is applied to detect sharp gradients in the water vapor vertical profiles for estimation of mixing layer height. The Pandora derived mixing layer depth is compared to the estimations from the collocated Ceilometer (Vaisala CL51, EPA) measurements. Pandora MAX-DOAS agrees well with Ceilometer measurements for different time intervals during the day with a correlation coefficient of 0.68 to 0.76. Nitrogen Dioxide (NO_2) and Formaldehyde (HCHO) tropospheric columns and vertical profiles measured at the Hartsfield-Jackson Atlanta International Airport are also presented. Even though anthropogenic emissions decreased severely all over the United States due to Covid lockdown restrictions in 2020, trace gas levels at airports remained relatively same due to continuing air traffic. MAX-DOAS measurements are performed at different azimuth angles which gives a three dimensional representation of NO_2 and HCHO vertical profiles and enables to observe and distinguish air pollution at different directions. These measurements further show the potential of MAX-DOAS measurements for near surface air quality monitoring.

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(GENERAL AUDIENCE ABSTRACT)

MAX-DOAS is a ground based spectroscopic technique which can measure near surface concentration, tropospheric column and vertical distribution of different trace gases. Even though Satellite measurements can provide worldwide coverage, they generally measure only one time per day and have limited knowledge of near surface conditions. MAX-DOAS measurements performed by the NASA Pandora spectrometer systems can be used to provide near surface diurnal variation of different trace gas properties. In this work, different real-time applications of the MAX-DOAS technique are presented. At first, near surface concentration of Pandora MAX-DOAS Formaldehyde (HCHO) observations are validated by comparing with an in-situ instrument. Next, a methodology is presented for detecting the mixing layer height (MLH) by using Pandora MAX-DOAS vertical water vapor distribution measurements. Finally, MAX-DOAS measurements of Nitrogen Dioxide (NO_2) and Formaldehyde (HCHO) concentrations during the COVID-19 pandemic at The Hartsfield-Jackson Atlanta International Airport is presented. The measurements are done at different azimuth angles which produces three dimensional representations of NO_2 and HCHO vertical profiles. All these results prove that the NASA Pandora spectrometer systems have great potential for improving our understanding of tropospheric chemistry and air quality monitoring.

Dedication

Dedicated to my family and friends.

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List of Abbreviations

ΔS	Differential slant Column Density		
σ	Molecular absorption cross-section		
τ	Optical Depth		
BrO	Bromine Monoxide		
HCHO Formaldehyde			
HO_x	Combination of OH and HO_2		
NO_2	Nitrogen Dioxide		
NO_x	Combination of NO and NO_2		
O_2O_2	Oxygen collision complex		
O_3	Ozone		
AMF	Air Mass factor		
CCD	Charge-coupled device		
DOAS Differential Optical Absorption Spectroscopy			
EPA	Environmental Protection Agency		
ESA	European Space Agency		

FNR Formaldehyde to Nitrogen Dioxide ratio

FWHM Full Width at Half Maximum

- GEMS The Geostationary Environment Monitoring Spectrometer
- GeoTAso The Geostationary Trace gas and Aerosol Sensor Optimization aircraft
- LISTOS Long Island Sound Tropospheric Ozone Study
- MAX-DOAS Multi-Axis Differential Optical Absorption Spectroscopy
- MLH Mixing Layer Height
- NASA National Aeronautics and Space Administration
- OMI The ozone monitoring instrument
- OWLETS Ozone Water-Land Environmental Transition Study
- PAMS Photochemical Assessment Monitoring Stations
- PBL Planetary Boundary Layer
- PGN Pandonia Global Network
- RMS Root mean squared
- RT Radiative Transfer
- **TROPOMI** The TROPOspheric Monitoring Instrument
- U340 Ultraviolet filter with cutoff at 340 nm
- UV Ultraviolet
- VCD Vertical Column Density
- VOC Volatile Organic Compound

Chapter 1

Thesis Overview

1.1 Thesis goal and objectives

The main goal of this thesis is to advance our measurement capabilities to better characterize tropospheric photochemistry and vertical mixing in the lowest 2-3 km of the atmosphere.

Scattered sky UV-VIS differential optical absorption spectroscopy (MAX-DOAS) is a remote sensing technique that allows for measurements of near surface concentration and vertical profiles of multiple trace gases in the atmosphere including HCHO, NO_2 , O_3 and H_2O . As such, it provides a unique opportunity to gain insight into sources, transport and vertical mixing of air pollution. The DOAS technique is widely used across various ground-based networks, satellite and airborne platforms. This work focuses on the application of groundbased sky scanning MAX-DOAS measurements to achieve the following objectives:

- 1. Estimate the accuracy of atmospheric Formaldehyde (HCHO) measurements using differential optical absorption spectroscopy (DOAS). Formaldehyde serves as a proxy for photochemical oxidation of almost all Volatile Organic Compounds (VOC). It is a key indicator of near surface ozone production sensitivity and also a carcinogenic trace gas. On the other hand, it is one of the least measured species in the atmosphere.
- 2. Characterize vertical mixing within the lowest 2-3 km of the atmosphere by using water vapor vertical profiles from MAX-DOAS measurements to derive Mixing layer height

(MLH).

3. Evaluate the spatial heterogeneity of NO_2 and HCHO concentrations near one of the largest airports in the world (The Atlanta Hartsfield–Jackson International Airport).

Objective 1 is accomplished by (a) evaluating effect of systematic errors due to DOAS fitting on HCHO retrievals using most plausible combinations and (b) evaluating accuracy of spatially averaged near surface concentration measurements using MAX-DOAS technique against in-situ measurements at Westport, CT from July 19 to September 03, 2018 during the Long Island Sound Tropospheric Ozone Study (LISTOS) field campaign.

Objective 2 is accomplished by estimation of mixing layer heights from Pandora MAX-DOAS water vapor vertical profile measurements at the same location as objective 1. The wavelet method is applied to detect sharp gradients in the water vapor vertical profiles for estimation of mixing layer height. The MAX-DOAS MLH retrievals are then compared with MLH derived from collocated Ceilometer aerosol backscattered measurements.

Objective 3 is accomplished by using the MAX-DOAS technique to look at NO_2 and HCHO at different azimuth angles. One direction was used to measure the background pollution and the other directions were pointed at the airport. NO_2 and HCHO tropospheric column and vertical profiles at different directions were then compared to evaluate the spatial heterogeneity.

1.2 Thesis organization

This thesis has been organized as follows,

Chapter 2 introduces the concept of air pollution and the distribution of different trace gases in the atmosphere. Different radiative transfer processes in the atmosphere and the concept of the planetary boundary layer are discussed. Different processes for measuring trace gases in the atmosphere are also presented.

Chapter 3 describes principles of the Differential Optical Absorption Spectroscopy (DOAS) method and provides an introduction to the Multi-Axis DOAS (MAX-DOAS) technique, this is the methodology used for trace gas measurements in this thesis. It also explains different components of the NASA Pandora spectrometer system and data correction methods.

Chapter 4 presents analysis about the choice of DOAS fitting settings for HCHO sensitivity study and fitting evaluation, uncertainty estimation for ground-based HCHO measurements by MAX-DOAS and validation of HCHO near surface concentration.

Chapter 5 presents results about mixing layer height (MLH) evaluation using water vapor vertical profiles from Pandora MAX-DOAS measurements.

Chapter 6 presents NO_2 and HCHO tropospheric columns and vertical profiles measured at the Hartsfield-Jackson Atlanta International Airport for different viewing directions.

Chapter 7 presents the conclusion of the study.

Chapter 2

Introduction

This chapter gives a brief introduction about how air pollution is impacted by different trace gases in the atmosphere. It also describes different radiative transfer processes in the atmosphere. The concept of the planetary boundary layer is introduced and tropospheric chemistry of different air pollutants like O_3 , NO_x and HCHO are discussed. It also describes the importance of $HCHO/NO_2$ ratio for understanding tropospheric ozone production regimes. Finally, different measurement techniques for trace gases in the atmosphere are discussed.

This thesis addresses the question of monitoring of air pollution within the lowest 2-3 km using a passive remote sensing technique (DOAS). To understand the framework of the presented research, this section discusses atmospheric composition and chemistry that impact air quality and its measurements using solar radiation.

2.1 The Air Quality problem

Air pollution in urban and regional localities is one of the most challenging problems of the 21st century. Trace gases like ozone, nitrogen dioxide and particulate matters can cause harmful health effects to humans [Brunekreef and Holgate, 2002, Ritz et al., 2019, Li et al., 2021]. Even after implementing significant policies for air pollution control by law and also increasing public awareness, close to 135 million people still live in proximity to unhealthy air in the United States [American Lung Association, 2021]. Air pollution cost the United States

\$790 billion in economic damages for the year 2014, equating to 5% of it's gross domestic product (GDP) [Tschofen et al., 2019]. Globally the economic cost of air pollution is around \$2.9 trillion which is roughly 3.3% of the world's GDP [Myllyvirta, 2020]. The number of megacities are increasing worldwide and population increase in urban areas is exposing more people to air pollution [Molina and Molina, 2002]. It has been estimated that 3.3 million people die worldwide each year prematurely because of outdoor air pollution [Lelieveld et al., 2015]. Air quality issues are particularly bad in developing countries due to uncontrolled urbanization, overpopulation and rapid economic growth [Mannucci and Franchini, 2017].

2.2 Atmospheric Composition

Nitrogen (N_2) and Oxygen (O_2) are the two most abundant gas species in the atmosphere (78.08% and 20.95% respectively). The noble gas Argon (Ar) constitutes 0.95%, so together these three species makes up 99.9% of the atmosphere. The other main constituents are water vapor (H_2O) , Carbon Dioxide (CO_2) and the other noble gases. Some other gases are present in much lower amounts in the atmosphere, they are generally called trace gases. Aerosols are another important component of the atmosphere, which are tiny particles of solid or liquid suspended and disseminated in the air. The suspended solid or liquid particles (excluding the gaseous air) are known as particulate matters.

There are a large number of different trace gases in the atmosphere, only a few of them have amounts greater than one parts per million of air molecules. Trace species in the lower troposphere have a very important impact on human health and economy despite their small amounts.

Sources and sinks of trace gases

Trace gas emissions can be divided in two main categories, natural and anthropogenic. The following process are generally responsible for natural emissions [Seinfeld and Pandis, 2008]:

- Emission from vegetation (generally volatile organic compounds (VOCs))
- Emission from soil (NO, NO_2, N_2O, CH_4)
- Biomass burning (VOCS, CO, NO_x etc.)
- Emissions from volcano (SO₂, CO₂, HCl, BrO)
- Lightning (NO)

Different human activities like traffic, heating/cooling, industrial and agricultural processes are responsible for the primary anthropogenic sources [Platt and Stutz, 2008]:

- Emission from combustion (NO, NO₂, CO, CO₂, VOCs)
- Industrial activities (NO, NO₂, CO, CO₂, SO₂, VOCs)

There are some anthropogenic sources which produces trace gases in a similar way to natural processes. Examples include emission from agriculture, emission from biomass burning etc. Different trace gases have different sinks for removal from the atmosphere. Generally the main sinks for trace gas elimination [Ritchie, 2017] are oxidation by OH and O_3 , dry deposition, wet deposition, photolysis, transport to stratosphere, gas to particle conversion etc.

Majority of trace gases are found within the planetary boundary layer (PBL) and most human related activities happen within it. More details about PBL is discussed in the next section.

Free Atmosphere Capping Inversion Zi Boundary Layer Zi Boundary Layer Earth

2.3 The Planetary Boundary Layer (PBL)

Figure 2.1: The planetary boundary layer [Stull, 2006].

The atmospheric boundary layer is the lowest portion of the troposphere that is affected by the earth's surface. Figure 2.1 shows the structure of the planetary boundary layer in the atmosphere. The surface forcings that affect processes within the boundary layer (PBL) include frictional drag, terrain induced flow modification, heat transfer, evaporation, transpiration and pollutant emission [Stull, 2012]. PBL is often characterized by a uniform mixing of pollutants and is capped by the inversion layer above. Aerosol and water vapor concentration also has a sharp decrease across this boundary.

Figure 2.2 shows the planetary boundary layer for fair weather conditions throughout the day. Depending on the time of day, the boundary layer can have multiple layers within it. During the daytime, there is a mixed layer which is statically unstable. At night, a nocturnal stable boundary layer forms under the residual layer which is statically neutral. The residual layer, which is above the nocturnal stable boundary layer, can have impacts on air quality due to this layer containing the previous days mixed layer trace gas constituents [Morris et al., 2010, Sullivan et al., 2017], although it is not generally turbulent. The daytime mixed layer (ML) is responsible for the dispersion and transport of pollutants emitted from emission sources at



Figure 2.2: Diurnal evolution of the planetary boundary layer for fair weather conditions [Stull, 2006].

the surface. Diurnally, the ML grows throughout the day and reaches its maximum height during the mid afternoon. When a mixed layer has been fully developed, then temperature, humidity, and wind parameters are nearly constant with height. The growth of the ML is driven by convective processes such as thermals which are produced from solar heating of the surface and radiative cooling from the top of the cloud layer. A strongly stable entrainment zone with intermittent turbulence separates the mixed layer from the free atmosphere above it. Turbulence in the entrainment zone stops at night and converts into a nonturbulent layer called the capping inversion which is strongly stable statically.

2.4 MLH measurement methods

MLH is an important input parameter in boundary layer meteorological models which helps in optimizing the prediction of air pollutant concentrations in the boundary layer. That's why it is quite important to have continuous measurements of MLH by different instruments. Two main methods for determining the MLH are meteorological radiosondes and groundbased remote sensing. Radiosondes are one of the most useful approaches to observe MLH, they are launched from a large number of locations all around the world. The benefits of using radiosondes is their ability to provide high vertical resolution data of temperature, pressure, humidity, wind speed and wind direction. The mixing layer height is usually derived by detecting the maximum vertical gradient of potential temperature [Seidel et al., 2010]. Relative humidity profiles can also be used for MLH detection by locating the minimum vertical gradient because water vapor profiles are a good indicator of the mixing conditions of the atmosphere [Basha and Ratnam, 2009]. One drawback about this measurement method is that the full evolution of the ML can not be captured throughout the day as this becomes financially prohibitive. Only two observations at 00:00 and 12:00 UTC are available from most stations per day because of the high economic cost of launches [Seibert et al., 2000]. The MLH undergoes rapid growth in the morning due to solar heating, so even hourly measurements are not sufficient to capture the full diurnal evolution of the ML [Seibert et al., 2000]. For this reason, ground-based remote sensing has become the most regular approach to MLH measurements for continuous observations with high spatiotemporal resolution. Lidars utilize laser light to measure the amount of energy backscattered from cloud droplets and atmospheric aerosols. Ceilometers, which are a type of lidar, typically operate with lasers tuned in the infrared ranging from 900-1100 nm. These instruments are relatively low cost solutions for continuous monitoring of the boundary layer through the detection of aerosols [Compton et al., 2013, Caicedo et al., 2017, 2020]. The high vertical resolution, ranging from 5-10 meters, and high temporal resolution, ranging from 10-40 seconds, of most ceilometers can allow for detection of stratified layers that are not obvious in thermal profiles.

GPS radio occultation measurements can also be used for detecting PBL by estimating mini-

mum gradient in specific humidity profile [Ao et al., 2008]. Another method to detect specific humidity profile is to use a water vapor lidar such as the MPI-DIAL (Differential Absorption Lidar) [Hennemuth and Lammert, 2006]. Water vapor profiles can also be measured by ground based MAX-DOAS measurements [Irie et al., 2011, Wagner et al., 2013]. Airborne MAX-DOAS instruments also have the ability to detect water vapor profiles [Baidar et al., 2013]. Another study was recently published which showed good agreement between MAX-DOAS water vapor profiles with balloon-borne measurements and European Centre for Medium-range Weather Forecasts (ECMWF) ERA-interim dataset [Lin et al., 2020].

PBL detection using water vapor and aerosol backscatter profiles provided similar results in a study performed by [Lammert, 2004]. In a detailed sensitivity study, it has been showed that different methods (vertical gradients of temperature, potential temperature, relative humidity, refractivity etc.) produces different MLH height [Seidel et al., 2010]. Although the correlation coefficient for comparisons among different methods are statistically significant with a low value (around 0.5).

The creation and the diurnal evolution of the mixing layer is strongly dependent on the solar radiation that reaches the surface of the earth after traversing through the earth's atmosphere. A brief description of how radiation passes through different processes in the atmosphere are discussed in the next section.

2.5 Radiative Transfer processes in the atmosphere

The sun is the main source of most of earth's energy. It radiates over the entire electromagnetic spectrum, although all incident radiation smaller than 290 nm does not reach the earth's surface because of strong absorption by O_2 and O_3 in the atmosphere. Figure 2.3 shows the solar irradiance at the top of the atmosphere and at sea level. From 300 to 800 nm atmospheric absorption is not strong, the atmosphere can be considered transparent for this wavelength range. At infrared range ($\lambda > 700$ nm), radiation is again highly absorbed by water vapor and other greenhouse gases. Because of this phenomenon, almost half of the solar energy is in the visible wavelength region between 400 to 700 nm. Radiation reaching the earth's surface is also decreased because of reflection by clouds.



Figure 2.3: Solar spectral irradiance at the top of the atmosphere and at sea level [Wu et al., 2011].

The radiation that reaches the surface is absorbed and re-emitted. The emitted radiation from the earth no longer lies in the visible range, but rather in the infrared region of the electromagnetic spectrum because the earth is cooler than the sun. Many trace gases which are active in the infrared absorbs this radiation causing an increase in earth's temperature, this is commonly known as the greenhouse effect.

Radiative transfer takes place in the atmosphere when radiation from the sun interacts with molecules and particles in the earth's atmosphere. The main interaction processes for radiation are,

- Absorption : Absorption is the process in which the radiation field loses some of it's radiation and it is collected by another substance in some other form of energy. Radiation is absorbed by aerosols and different molecules (ozone, water vapor, nitrogen dioxide, oxygen etc.) in the atmosphere. Absorption of solar UV rays below 300 nm produces the ozone layer in the stratosphere which provides protection to all life forms on earth from harmful solar UV radiation. Each molecule have unique absorption characteristics as a function of wavelength (also known as absorption cross-section) which can be used to identify and measure them.
- Elastic scattering : Elastic scattering is the process by which light or photons get deviated from it's original path because of collision with molecules or particles in the atmosphere, but it's energy remain unchanged. Due to exponential drop in pressure and air density with increasing altitude, most scattering takes place close to the earth's surface.

Elastic scattering can be further divided into two main categories, Rayleigh scattering and Mie scattering. Rayleigh scattering occurs when the the size of the scatterer, typically a molecule, is much smaller than the wavelength of the photon incident upon it [Rayleigh, 1899]. Mie scattering usually takes place when solar radiation is scattered on aerosol particles whose size is similar or larger than the wavelength of the radiation [Mie, 1908]. It exhibits a characteristics of strong forward scattering and the wavelength dependence is more weaker than Rayleigh scattering.

• Inelastic scattering : Inelastic scattering changes both the direction and energy of the photon. It is also known as Raman scattering where energy is transferred between the photon and the scattering particle [Raman, 1928]. The photon can either lose some of it's energy to the molecule (Stokes line scattering) or gain some of the molecule's excitation energy (anti-Stokes scattering).

- Thermal Emission : Thermal emission in the process by which air molecules or aerosol particles emit radiation due to thermal motion. It can be generally neglected for UV/visible wavelength range and only noticeable at infrared wavelengths longer than several microns.
- Aerosol Fluorescence : Radiating from aerosol particles because of excitation can generate Fluorescence.

2.6 Radiative Transfer Equation

The transport of radiation in the atmosphere is a complicated process due to scattering and absorption. The scattered photon can travel in any directions and get scattered more or be absorbed. So, analytical equations can be only be derived if simplifications are made. Generally, numerical techniques are used to get the solutions in two ways. For the first method, the resulting radiation field is calculated numerically. For the other method, paths of a collection of photons are statistically calculated for a particular condition. The radiation field can then be generated from the density of the photons.

After travelling through an absorbing layer of thickness ds, the radiance $I(\lambda)$ will be reduced by the amount $dI_a(\lambda)$,

$$dI_{\rm a} = \frac{d\Phi}{\Delta\Omega \cdot A_{\rm s}} = -I(\lambda) \cdot \varepsilon_{\rm a}(\lambda)ds = -I(\lambda) \cdot \sigma_{\rm a}(\lambda) \cdot Nds \tag{2.1}$$

Where the number of absorbing molecules per unit volume are expressed by N, the absorption coefficient is ϵ_a and the absorption cross-section is $\sigma_a(\lambda)$. If $I_0(\lambda)$ is the initial intensity then integrating the above equation produces:
$$\ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = \sigma_{\rm a}(\lambda) \cdot \int_0^L N ds = \sigma_{\rm a}(\lambda) \cdot S = \tau(\lambda)$$
(2.2)

Where S is the column density of the absorber with layer thickness L which the radiation is passing through. The optical density is expressed as D:

$$D = \int \varepsilon_{\mathbf{a}}(\lambda) ds \text{ or } dD = \varepsilon_{\mathbf{a}}(\lambda) ds$$
(2.3)

So, after passing through the absorbing layer, the radiance becomes:

$$I(\lambda)_L = I_0(\lambda) \cdot e^{-\sigma_a(\lambda) \cdot S} = I_0(\lambda) \cdot e^{-D}$$
(2.4)

This is also known as the Beer-Lambert law. It explains the attenuation of light due to absorption while traveling through a medium.

Similar to the absorption, the scattered radiation passing through an infinitesimal layer can be given by:

$$dI_{\rm s} = \frac{d\Phi_{\rm s}}{\Delta\Omega \cdot A_{\rm s}} = I(\lambda) \cdot \varepsilon_{\rm s}(\lambda) ds = I(\lambda) \cdot \frac{d\sigma_{\rm s}(\lambda)}{d\Omega} \cdot Nd\Omega ds$$
(2.5)

Where the number of scattering molecules or particles per unit volume are expressed by N, the scattering coefficient is ϵ_s and the scattering cross-section is $\sigma_s(\lambda)$. The scattered radiant flux is expressed by:

$$d\Phi_{\rm s} = I(\lambda) \cdot \Delta\Omega \cdot \frac{d\sigma_{\rm s}(\lambda)}{d\Omega} \cdot Nd\Omega dV$$
(2.6)

2.6. Radiative Transfer Equation

Where the differential scattering cross-section is $\frac{d\sigma_s(\lambda)}{d\Omega}$, it's value depends on the scattering angle ν and the polar angle ϕ . The total scattering cross section is:

$$\sigma_{\rm s}(\lambda) = \int_{4\pi} \frac{d\sigma_{\rm s}(\lambda)}{d\Omega} \cdot d\Omega \tag{2.7}$$

It can be useful to utilize a dimensionless scattering function:

$$S(\vartheta, \Phi) = \frac{4\pi}{\sigma_{\rm s}} \cdot \frac{d\sigma_{\rm s}(\lambda)}{d\Omega}$$
(2.8)

By summing up the effect of absorption and scattering for radiation passing through a layer of thickness ds, the total extinction can be expressed by:

$$dI = -dI_{\rm a} - dI_{\rm s} = -I(\lambda) \cdot (\varepsilon_{\rm a}(\lambda) + \varepsilon_{\rm s}(\lambda)) \, ds \tag{2.9}$$

The radiance added by scattering can be expresses as:

$$dI_{\rm S}^*(\lambda) = \varepsilon_{\rm s}(\lambda) ds \int_0^\pi \int_0^{2\pi} I^*(\lambda, \vartheta^*, \phi^*) \cdot \frac{S(\vartheta^*, \phi^*)}{4\pi} d\phi^* \cdot \sin \vartheta^* d\vartheta^*$$
(2.10)

For UV and visible wavelength range, the effect of thermal emission is negligible. So, the radiation transport equation can be written as:

$$\frac{dI(\lambda)}{ds} = -\left(\varepsilon_{\rm a}(\lambda) + \varepsilon_{\rm s}(\lambda)\right) \cdot I(\lambda) + \varepsilon_{\rm s}(\lambda) \int_0^\pi \int_0^{2\pi} I(\lambda,\vartheta,\phi) \cdot \frac{S(\vartheta,\phi)}{4\pi} d\phi \cdot \sin\vartheta d\vartheta \qquad (2.11)$$

2.7 Radiative Transfer Modeling

The radiative transfer equation (RTE) can provide the radiance measured by a instrument for a particular time and geometrical setup, this is generally achieved by running a radiative transfer model. The RTE can be solved analytically if simplifications are introduced and it is normally faster than numerical methods. Another method is statistical, which simulates individual photon path for a particular atmospheric setup. This provides better result because of conducting a lot of individual simulations but can be computationally expensive. Radiative transfer models solve the radiative transfer (RT) equation described in the previous section for direct and scattered radiation. Numerical methods solve the RT equation in a pseudo-spherical atmosphere in its integral form by using the characteristic method [Rozanov et al., 2001]. There are other models which uses the discrete ordinate method to solve the RT equation. The integrals in the RT equation is replaced with sums by using numerical quadrature. The RT equation is transformed to a set of linearly coupled differential equations which can then be solved [Stamnes et al., 1988, Spurr et al., 2001]. This method uses pseudospherical geometry for simulating multiple scattering in the atmosphere. Other RT models use the Monte Carlo technique which is based on statistical sampling. It simulates a group of photons as they transverse through the atmosphere and undergoes different processes such as Rayleigh scattering, Mie scattering, absorption and reflection. By assigning a probability for each of these processes, it can be determined if a photon undergoes a certain process. The statistical analysis of a group of photons produces the radiative transfer results [Lenoble et al., 1985]. By using the Monte Carlo method, precise simulation of RT can be done without complex numerical solutions. However, this method is generally slow due to large number of different photon simulations.

Generally, the following inputs are required for running the radiative transfer model,

2.8. Trace gas chemistry in PBL

- The vertical temperature profile.
- The vertical pressure profile.
- The vertical profile of ozone.
- The vertical aerosol extinction profile.

2.8 Trace gas chemistry in PBL

Sources and sinks of different trace gases were discussed briefly in section 2.2. In this section, the tropospheric chemistry of ozone, nitrogen dioxide and formaldehyde are discussed in details which are some of the the most important trace gases that contributes to air pollution in the planetary boundary layer.

2.8.1 Nitrogen Oxides (NO_x)

 $(NO + NO_2)$ is commonly known as NO_x , generally produced from a combination of human and natural activities. They can quickly convert into each other. Processes like forest fire, lightning and combustion is the main source of NO_x where air is heated to a very high temperature. The biggest natural sources are soil emissions, wildfires, lightning strikes and ammonia oxidation.

Fossil fuel combustion from power plants, industrial activities and home heating/cooling are the largest source of anthropogenic NO_x [Lee et al., 1997]. Emission from motor vehicles is also a growing source. The most anthropogenic sources are located in a very small area of the earth's surface, where as the natural sources are equally distributed. That's why NO_x is very abundant in urban areas compared to rural remote regions. NO_x strongly affects the availability and partitioning of HO_x radicals $(OH + HO_2)$, they have a strong influence on the oxidative power of the atmosphere. They also helps in the formation of ozone (O_3) in the troposphere. The main sink for NO_x is in the form of Nitric acid (HNO_3) .

High thermal energy is needed to dissociate molecular oxygen in to atomic oxygen, this generally happens when air is heated to a temperature of 2000 K. The atomic oxygen produced from high temperatures interact with molecular nitrogen to form NO.

$$O + N_2 \longrightarrow NO + N$$
 (2.12)

Ozone rapidly reacts with NO to generate NO_2 ,

$$O_3 + NO \longrightarrow NO_2 + O_2$$
 (2.13)

The main removal method of NO_2 from the atmosphere is mostly in the form of Nitric acid (HNO_3) by interaction with OH,

$$NO_2 + OH + M \longrightarrow HNO_3 + M$$
 (2.14)

So the reaction also removes OH from the atmosphere. So, NO_2 influences the removal of hydroxyl radical.

2.8.2 Ozone (O_3)

Ozone is produced in different ways in the troposphere and the stratosphere. In the stratosphere, short wave UV radiation split O_2 molecules into atomic oxygen which then interacts with O_2 to form O_3 , this is also known as the Chapman cycle [Chapman, 1930]. For troposphere, the combination of NO_x and volatile organic compounds (VOC) forms ozone in the presence of solar UV radiation. Tropospheric ozone is an air pollutant which has adverse health effects for plant and animal life forms, it is also an essential component of smog. In this section, we will mainly talk about tropospheric ozone chemistry for it's role in air pollution.

UV radiation below 420 nm photolyses NO_2 to create ozone. This happens rapidly at noontime, when the mean lifetime of NO_2 is only around 2 minutes [Junkermann et al., 1989].

$$NO_2 \xrightarrow{h\nu(\lambda < 420 \ nm)} NO + O(^3P)$$
(2.15)

The atomic oxygen $(O({}^{3}P))$ produced from equation (2.15) reacts rapidly with molecular oxygen to create O_{3} .

$$O(^{3}P) + O_{2} + M \longrightarrow O_{3} + M$$
(2.16)

Where, M is any atmospheric molecule (typically N_2 or O_2). An ozone and a NO molecule is produced for every photolysed NO_2 molecule. But as seen in equation 2.13, NO_2 is created again from NO and O_3 . So, a photostationary condition is formed among O_3 , NO and NO_2 which is known as the Leighton ratio [Leighton, 2012].

$$\frac{[\text{NO}]}{[\text{NO}_2]} = \frac{j_{\text{NO}_2}}{k_{\text{NO}} \cdot [\text{O}_3]}$$
(2.17)

Here, k_{NO} is the rate constant for the reaction of ozone and NO and j_{NO_2} is the NO_2 photolysis frequency. The rate constant k_{NO} is dependent on temperature where as the photolysis frequency j_{NO_2} depends on the solar radiation. This reaction cycle does not create any additional ozone creation. However, Net ozone production is achieved if NOconverts into NO_2 in a reaction without destroying an ozone molecule. So, the chemical conversion of NO to NO_2 is one of the most important factor for ozone formation in the troposphere. This can happen if there are a lot of NO_x in the atmosphere that can react with hydroxy and peroxy radicals (HO_2 and RO_2). Oxidation of volatile organic compounds (VOCs) is the main source for peroxy radical generation. HO_x radicals are always present during daytime, they are generally produced from the oxidation of ozone when water vapor is present in the atmosphere [Crutzen, 1970].

$$NO + HO_2 \longrightarrow NO_2 + OH$$
 (2.18)

The production of this additional ozone molecule can lead to conditions like smog which contains a large amount of oxidized VOC, ozone and organic aerosols. Peroxy radicals can also react with ozone but this only happens if NO_x concentrations are very low.

$$O_3 + HO_2 \longrightarrow 2O_2 + OH$$
 (2.19)

So, the the amount of ozone production depends on the concentrations of NO_x and VOCs in the atmosphere. Figure 2.4 shows a ozone isopleth diagram which indicates how the sensitivity of ozone production depends on NO_x and VOC concentrations.



Figure 2.4: Ozone isopleth diagram [Council et al., 1992]. In the top left, ozone production is limited by VOC concentration. In the bottom right, it is limited by NO_x concentrations.

In the top left of the diagram, ozone production is limited by VOC concentration (VOClimited). In the bottom right ozone production is limited by NO_x concentrations (NO_x limited). VOC-limited areas are typically urban centers with high pollution and NO_x -limited are typically rural or suburban areas.

2.8.3 Formaldehyde (HCHO)

Formaldehyde (HCHO) is primarily produced as an intermediate from the oxidation of hydrocarbons. Oxidation of methane (CH_4) is a global background source of HCHO, specially over ocean [Meller and Moortgat, 2000, Stavrakou et al., 2009b]. It is a carcinogenic trace gas which can cause irritation in respiratory tract and cancer. It also plays an important role in the formation of air toxic like surface ozone, which is designated as a criteria pollutant by The EPA. HCHO is present in both urban industrialized and rural remote areas. Photochemical oxidation of volatile organic compounds (VOC) is the primary source in the continental boundary layer [Carlier et al., 1986, Altshuller, 1993]. Other sources include:

- Biomass burning [Carlier et al., 1986].
- Fossil fuel combustion [Anderson et al., 1996, Altshuller, 1993].
- Photochemical oxidation of non-methane hydrocarbons (NMHCs) [Atkinson et al., 1995, Stavrakou et al., 2009a].
- by Ozonolysis in NO-rich environment [Slomp Jr and Johnson, 1958].

Since many hydrocarbons can form HCHO, it can be used as a marker for VOC production in the troposphere for different processes like anthropogenic emissions, photochemical reactions and smog [Chance et al., 2000]. The lifetime of Methane in the atmosphere is in the order of a decade, so it provides a stable source of HCHO in the troposphere [Finlayson-Pitts and Pitts Jr, 1999].

The main removal methods of HCHO from the atmosphere at daytime are photolysis and reaction with OH radical. The lifetime of HCHO is relatively short (around 5 hours) [Logan et al., 1981] during the day. At nighttime, reaction with the nitrate radical HNO_3 is the main elimination process. This is relatively slow, so the lifetime of HCHO is relatively longer at night [Altshuller, 1993].

2.8.4 $HCHO/NO_2$ Ratio

Column $HCHO/NO_2$ ratio (FNR) have long been used as a marker for O_3 sensitivity [Sillman and He, 2002]. The O_3 - NO_x -VOC photochemistry can be broadly defined in three categories, VOC-limited (where decrease in VOC quantity decreases O_3 production), NOxlimited (where decrease in NO_x quantity decreases O_3 production) and a transition regime

Study	Indicator	Location	O_3 transition regimes
[Tonnesen and Dennis, 2000]	Surface $HCHO/NO_2$	NYC	0.8-1.8
[Duncan et al., 2010]	Column $HCHO/NO_2$	US	1-2
[Choi et al., 2012]	Column $HCHO/NO_2$	US	1-2
[Chang et al., 2016]	Column $HCHO/NO_2$	Northeastern US	1.5 - 2.3
[Schroeder et al., 2017]	Column $HCHO/NO_2$	Colorado	1.1-3.3
		Houston	1.3-4.3
[Jin et al., 2020]	Column $HCHO/NO_2$	US	3.2-4.1
		LA	4.1-5
		Houston	2.6 - 3.5
		New York	2.9-3.8
		Atlanta	3.2 - 4.1

Table 2.1: Summary of O_3 Transitional regimes

in between where reduction in either VOC or NO_x can decrease O_3 production. The peak O_3 production usually lies in the middle of the transition regime. Table 2.1 gives a summary of O_3 production transition regimes based on satellite measurements and model simulations.

For VOC-limited regime, FNR is lower than the lower bound of the transition regime and for NO_x -limited regime, FNR is higher than the higher bound of the transition regime. O_3 production regimes vary depending on location, season, time of the day and ozone exceedance and non-exceedance days. The correct identification of the O_3 production regimes is very important to devise proper policy control for ozone reduction for a certain location.

Satellite *HCHO* measurements typically have very high uncertainty compared to NO_2 measurements and is the dominating factor in the uncertainty of determining Column *HCHO/NO*₂ ratio. HCHO satellite measurements from OMI and GOME-2 can have an uncertainty of 45-100% [González Abad et al., 2015] and 60% [De Smedt et al., 2012] respectively. HCHO vertical column uncertainty of ± 0.3 DU can increase the transitional regime by up to 37% [Schroeder et al., 2017].

Systematic uncertainty arises from different parameters used in the fitting like wavelength range, polynomial order, offset order, molecular absorption cross section etc [Pinardi et al.,

2013]. So this is why sensitivity studies are required to investigate the full range of HCHO slant columns that can be retrieved by varying different fitting parameters.

2.9 Trace Gas Measurement Techniques

Measurement of different meteorological properties like temperature, pressure, humidity, wind speed have enabled us to understand about different chemical and physical processes in the atmosphere. Similar to these quantities, measurement of trace gas quantities is also very important for improving our understanding of atmospheric physics and chemistry. Trace gases are generally present at the atmosphere at minute quantities which can present unique challenges to develop measurement methods.

Atmospheric measurement techniques can be performed in different ways based on the time scale or spatial scale of the investigation. They can be roughly divided in the following ways:

- Long term monitoring : Long term measurements are useful for tracking the changes in atmospheric composition for a long period of time. Examples include monitoring the rise of CO₂ in earth's atmosphere [Keeling and Whorf, 2005], thickness of the ozone layer [Molina and Molina, 1992, Tzortziou et al., 2012], trends of greenhouse gases [Hansen and Sato, 2004], halogen species in the stratosphere [Russell et al., 1977] etc.
- Regional and Episodic Investigation : Regional studies are generally performed to find out the cause, extent and effect of air pollution. Typical studies include monitoring of air pollutants (NO₂, O₃, NO, HCHO, SO₂) [Piters et al., 2012, Sullivan et al., 2019], plume evolution in urban areas [Brock et al., 2003, Dillon et al., 2002], antarctic ozone hole observation [Solomon, 1988, Kramarova et al., 2014] etc.

2.9.1 Requirements

Trace gas measurements techniques should have two important qualities. First of all, it should have the ability to detect the species at ambient concentration levels. This can be challenging because some trace gases can be present in the atmosphere at very low levels (around 0.1 parts per trillion). Secondly, it has to be specific technique, which means that the presence of another trace gas can not influence the result of the measurements. This is also a demanding criterion due to the presence of a large number of different gases present in the atmosphere at any given time. There are further optional qualities that might be desirable, such as simplicity of use, capability for real-time operation and portability.

2.9.2 In-situ vs Remote sensing

Trace gas measurement techniques can broadly be divided into two broad categories, insitu and remote sensing. In-situ instruments perform measurements at a location that is directly in the spot or very close to the subject of interest. On the other hand, remote sensing methods allow measurements from a large distance away, they are usually based on detection of electromagnetic radiation. By using remote sensing, trace gas concentrations can be measured at a location that is far away from the instrument.

Examples of trace gas measurement techniques from both these categories include gas chromatography, optical spectroscopy, mass spectroscopy, chemiluminescence and electrochemical techniques. In the next section, different spectroscopic methods are discussed which are universally usable, provides absolute results and can be used for both in-situ and remote sensing applications.

2.9.3 Spectroscopic Techniques

Spectroscopic methods can be very powerful because of it's high sensitivity and specificity. They can broadly be divided into two main branches, techniques that are based on the detection of absorption of radiation of a sample and techniques that rely on detecting the emission of radiation from a sample. A short description of different type of spectroscopic techniques based on wavelength range are described below:

- Microwave Spectroscopy : Spectroscopy in the microwave range can be used for determining atmospheric parameters such as clouds, precipitation and turbulence [Janssen, 1993].
- Infrared Spectroscopy : IR spectroscopy has been used widely in the past few decades for measuring species like CO₂, HNO₃, HCHO, HCOOH and many others [Pitts Jr et al., 1977, Tuazon et al., 1981]. They can be used in polluted air because of their ability for detection in the low ppb range. This technique can be employed by using an artificial broadband light source, tunable diode laser or thermal emission from trace gases.
- UV/Visible Absorption Spectroscopy : This technique utilizes the UV/visible wavelength range for trace gas measurements [Barth, 1969, Platt et al., 1980], and can be used in both active and passive modes. Active mode uses an artificial light source for providing radiation, where sun or stars are used for light source in passive mode.

Further divisions can be made for spectroscopic techniques based on different properties such as radiation transport, light path, light source and spectral resolution,

 Tunable Diode Laser Spectroscopy (TDLS) [Schiff et al., 1983, 1990, Grisar et al., 1987]

- Photo Acoustic Spectroscopy (PAS) [Rosencwaig, 1980, Sigrist, 1994]
- Light Detection And Ranging (LIDAR) [Rothe et al., 1974, Hinkley et al., 1976, Dong and Chen, 2017]
- Differential Absorption LIDAR (DIAL) [Remsberg and Gordley, 1978, Browell et al., 1998]
- Laser-Induced Fluorescence (LIF) [Kinsey, 1977, Sandholm et al., 1990]
- Cavity-Ringdown Spectroscopy (CRD) [Wheeler et al., 1998, Brown, 2003]
- Mask Correlation Spectroscopy [Giovanelli et al., 1979, Hoff, 1992]
- Differential Optical Absorption Spectroscopy (DOAS) [Platt, 1994, Platt and Stutz, 2008]

The work of this study is primarily based on the Differential Optical Absorption Spectroscopy (DOAS) technique which uses unique structural absorption characteristics of different trace gases for measurement purposes. More details about DOAS is described in chapter 3.

Chapter 3

Differential Optical Absorption Spectroscopy

This chapter discusses about the principles of the Differential Optical Absorption Spectroscopy (DOAS) method and introduces the sky scanning Multi-Axis DOAS (MAX-DOAS) technique. It also explains the basics of radiative transfer modeling and different trace gas vertical profile retrieval strategies. Different components of the NASA Pandora spectrometer system and it's data correction and processing steps are described.

DOAS was first used in 1976 for the measurement of OH [Perner et al., 1976]. Since then, more species such as HONO [Perner and Platt, 1979], NO_3 [Platt et al., 1980], IO [Platt and Hausmann, 1994], BrO [Platt and Hausmann, 1994] has been detected by this method. Different gases such as O_3 , NO_2 , HCHO, SO_2 , H_2O etc. which absorbs in the ultraviolet and visible wavelength range can be measured by this method [Platt, 1994]. It also has the ability to measure different trace gases concurrently, which makes it a time efficient technique and allows analysis of different species in the observed air mass. The basic principle of this technique is based on The Beer-Lambert law.

3.1 DOAS Principle

Differential Optical Absorption Spectroscopy (DOAS) is a UV/VIS spectroscopic remote sensing technique for measuring different trace gas amounts in the atmosphere [Platt, 1994, Platt and Stutz, 2008]. Figure 3.1 shows a sketch of a DOAS experiment for trace gas measurements. As solar radiation passes through the atmosphere, its intensity drops as it is subjected to trace gas absorptions and atmospheric scattering. The initial intensity $I_0(\lambda)$ is reduced by absorption by different trace gases and scattering by aerosols and air molecules.



Figure 3.1: Sketch of a DOAS experiment for trace gas measurements [Platt and Stutz, 2008]

The DOAS equation is based on the Beer-Lambart law (section 2.6) and can be expressed as follows [Platt, 1994],

$$log(\frac{I(\lambda)}{I_0(\lambda)}) = -L[(\sum \sigma_k(\lambda)c_k) + \epsilon_R(\lambda) + \epsilon_M(\lambda)]$$
(3.1)

Where,

- $I(\lambda)$ is attenuated solar irradiance.
- $I_0(\lambda)$ is reference solar irradiance.

- $\epsilon_R(\lambda)$ is the attenuation due to scattering by air molecules.
- $\epsilon_M(\lambda)$ is the attenuation due to scattering by aerosol.
- c_k is concentration of various trace gases.
- $\sigma_k(\lambda)$ is the molecular absorption cross-section. It is an unique characteristic property of every species as a function of wavelength (figure 3.2).

The attenuated light $I(\lambda)$ is collected by a telescope after traveling through earth's atmosphere. The light is focused to the entrance slit of a grating spectrometer which records the spectrum with a detector. Then the spectra data is transferred and stored in a PC. The mapping of pixels into appropriate wavelengths can be approximated by a polynomial. Different parts of the instrument also play a part in reducing the solar radiance further which can be summed up as transmissivity factor. The usefulness of DOAS lies in its ability to separate the broad band and narrow band extinctions. A polynomial can be used to approximate the broad band structure (Rayleigh and Mie scattering) and then the trace gas concentrations can be retrieved from the narrow band structures.

Based on light sources, DOAS systems can be classified as either active (artificial sources) or passive (natural sources). For passive sources, generally the sun is used, although the moon can also be used. Passive DOAS can be further divided into different viewing geometries, direct measurements where the telescope is pointed at the sun/moon or scattered light measurements where the instrument scan the horizon at different elevation and azimuth angles. For active DOAS measurements, lamps and LEDs are generally used as a source.



Figure 3.2: Molecular absorption cross section of different trace gases that can be retrieved by the DOAS method [Platt and Stutz, 2008].

3.2 DOAS Spectral Analysis

The goal of the spectral analysis is to retrieve slant column densities of different trace gases, which can be defined as the trace gas concentration integrated along the effective light path. For that, logarithm is applied on the modified Beer-Lambert law [Sinreich et al., 2005],

$$ln(I(\lambda)) = ln(I_0(\lambda)) - \int_0^L (\sum_{j=0}^n (\sigma'_j(\lambda, T, p) + \sigma^B_j(\lambda, T, p)) \cdot c_j(l) + \epsilon_R(\lambda, l) + \epsilon_M(\lambda, l)) dl \quad (3.2)$$

The narrow band and broad band extinction can be separated by combining all the broad band components $\sigma_j^B(\lambda, T, p)$ of trace gas molecular cross sections with Rayleigh scattering $\epsilon_R(\lambda, l)$ and Mie scattering $\epsilon_M(\lambda, l)$. After that equation (3.2) can be written as,

$$ln(I(\lambda)) = ln(I_0(\lambda)) - \left(\sum_{j=0}^n (\sigma'_j(\lambda, T, p) \cdot c_j(l) + \sum_{m=0}^p \alpha_m \cdot \lambda^m) dl\right)$$
(3.3)

Where $(\sum_{m=0}^{p} \alpha_m \cdot \lambda^m)$ is a polynomial of the order p, which can approximate the broad band absorption. Since the light path does not affect the differential trace gas cross section and the polynomial, equation (3.3) can be written as,

$$ln(I(\lambda)) = ln(I_0(\lambda)) - (\sum_{j=0}^{n} (\sigma'_j(\lambda, T, p)) \cdot \int_0^L c_j(l) + \sum_{m=0}^{p} \alpha_m \cdot \lambda^m)$$
(3.4)

$$ln(I(\lambda)) = ln(I_0(\lambda)) - \left(\sum_{j=0}^n (\sigma'_j(\lambda, T, p)) \cdot S_j + \sum_{m=0}^p \alpha_m \cdot \lambda^m\right)$$
(3.5)

By doing a least square fit, the solution of equation (3.5) can be derived by calculating S_j which are the slant column densities of different trace gases [Platt, 1994]. This can be a linear least squares fit [Albritton et al., 1977], non-linear least squares fit [Levenberg, 1944, Marquardt, 1963] or in most cases, a combination of both [Platt and Stutz, 2008].

The least squares fit produces slant column densities in such a way that the difference χ^2 between the observed measurements and the fit becomes as minimum as possible.

$$\chi^2 := \int_{\lambda_1}^{\lambda_2} \left(\ln(I(\lambda, L)) - \ln(I_0(\lambda)) + \sum_{j=0}^n \sigma'_j(\lambda, T, p) \cdot S_j + \sum_{m=0}^p \alpha_m \cdot \lambda^m \right)^2 d\lambda \xrightarrow{!} \min (3.6)$$

Here, λ_1 and λ_2 are respectively the lower bound and upper bound of the wavelength range for which the analysis is done. The range usually covers a wavelength window where strong absorption feature of that species is present. This can be represented by a sum since the measurements are done with discrete pixels at the detector.

$$\chi^{2} := \sum_{k=k_{\lambda_{1}}}^{k_{\lambda_{2}}} \left(\ln(I(k,L)) - \ln(I_{0}(k)) + \sum_{j=0}^{n} \sigma'_{j}(k,T,p) \cdot S_{j} + \sum_{m=0}^{p} \alpha_{m} \cdot k^{m} \right)^{2} \xrightarrow{!} \min \quad (3.7)$$

Where, k_{λ_1} and k_{λ_2} are respectively the lower bound and upper bound of the wavelength range for which the analysis is done. Because of noises and random errors during the measurement, this can not be reduced to zero. So, a residual is present which is the difference between the measured signal and the fitted signal.

$$R_k = \ln(I(k,L)) - \ln(I_0(k)) + \sum_{j=0}^n \sigma'_j(k,T,p) \cdot S_j + \sum_{m=0}^p \alpha_m \cdot k^m$$
(3.8)

The root mean square of the residual is usually considered as a marker for the quality of DOAS retrieval. Usually the smaller the residual RMS, the better the quality of the DOAS measurements. The residual usually comprises of unstructured signal. However, systematic error like inaccurate wavelength can cause systemic structures to appear in the residual.

3.2.1 Instrumental Effects

Wavelength Shift and Squeeze

Small wavelength shifts can lead to large systemic structures in the DOAS fitting residual. This is solved by introducing an additional shift/stretch polynomial to the original wavelength grid.

$$I(\lambda_k) \to I(\lambda'_k)$$
 with $\lambda'_k = \lambda_k + s_0 + s_1 (\lambda_k - \lambda_c) + s_2 (\lambda_k - \lambda_c)^2$ (3.9)

Here, s_0 is the shift parameter, s_1 is the squeeze parameter, s_2 is the stretch parameter and λ_c is the center wavelength of the original wavelength range. The original grid with wavelength λ_k transforms into a new wavelength grid with the wavelength λ'_k .

Offset Correction

Stray light in the spectrometer can introduce artificial signals to the measured spectrum. A polynomial can be added to correct for them since they vary slowly with wavelength. For UV measurements, low pass filters are often used to reduce visible light inside the spectrometer.

$$I(\lambda) \to I(\lambda') = I(\lambda) - P_{offset}$$
 (3.10)

Fraunhofer Lines

The sun has many strong absorption lines in it's spectrum, these lines are generally called Fraunhofer lines. The resolution of some DOAS instruments are larger than the width of these spectral structures. They are more common in the ultraviolet range with large optical densities which can be two to three orders higher than the trace gas optical densities. These lines has to be carefully removed or they will alter the measurement values. This is why a Fraunhofer reference spectrum (FRS) is used in DOAS analysis which acts as the I_0 spectrum. Commonly, FRS is selected from measurements with the lowest solar zenith angles and clean sky conditions.

The Ring effect

The Ring effect [Grainger and Ring, 1962] causes the reduction of the optical density of Fraunhofer lines. It is more prominent in large solar zenith angle observations. It takes place because of inelastic rotational raman scattering [Fish and Jones, 1995] of photons in air, which can change the wavelength of the photon. The atmospheric absorption of different trace gases can be one to two orders of magnitude smaller than the ring effect, so it has be corrected carefully.

The Ring spectrum can be constructed by either measurements or modelling. It can be measured by using the different polarization properties of scattering. Rayleigh scattering normally scatters light at 90°, while this happens very less for rotational Raman scattering. So a Ring spectrum can be measured by observing the spectrum at different polarization angles. Ring spectrum can also be modelled by using the rotational states of O_2 and N_2 , which makes up the majority of the atmosphere [Fish and Jones, 1995, Chance and Spurr, 1997]. This can be applied on measurement of solar spectrum or high resolution solar spectrum [Kurucz, 1984]. It does have to be convolved with the instrumental slit function before DOAS fitting.

The Solar I_0 Effect

The Fraunhofer lines can cause strong variation in intensity of the highly structured solar I_0 spectrum, this can affect the DOAS retrieval is generally known as the Solar I_0 effect [Platt et al., 1997]. Difference can arise between the convolved cross section which is generally measured with non structured light and the measured trace gas absorption from scattered sunlight. To compensate for the Solar I_0 effect, the absorption cross sections are corrected.

$$\sigma_{I_0}^*(\lambda, T, p, S) = -\ln\left(\frac{I^*(\lambda)}{I_0^*(\lambda)}\right) \cdot \frac{1}{S}$$
(3.11)

Here, S is the slant column density for the trace gas. $I^*(\lambda)$ is a convolution between the high resolution solar spectrum $I_0(\lambda)$ and the instrumental slit function H. $I_0^*(\lambda)$ is calculated as such,

$$I^*(\lambda) = H * I(\lambda) = H * (I_0(\lambda) \cdot e^{-\sigma(\lambda, T, p) \cdot S})$$
(3.12)

The Solar I_0 effect is negligible for weak absorbers and does not need to be included in the analysis. It's particularly high for strong absorbers like O_3 and NO_2 . For this work, only the absorption cross section of O_3 and NO_2 were corrected during the DOAS analysis.

3.3 Viewing Geometries

The primary quantity from DOAS measurements is the differential slant column density (dSCD). Depending on the viewing geometry, different data products can be derived from the measured dSCD. The two most commonly used viewing geometries are Direct sun and MAX-DOAS (figure 3.3).



Figure 3.3: Viewing geometry for MAX-DOAS and Direct sun [Pinardi et al., 2020].

Direct sun geometry follows the location of the sun in the sky and measures direct sunlight. On the other hand, MAX-DOAS measurements scan the sky at different elevation angles and measures scattered sunlight. Figure 3.4 shows DOAS Data Processing Procedure and respective data products for both geometries.



Figure 3.4: DOAS Data Processing Procedure for Direct sun and MAX-DOAS.

3.4 The MAX-DOAS Technique

MAX-DOAS (Multi Axis Differential Optical Absorption Spectroscopy) is a passive DOAS technique that has been widely used for trace gas and aerosol measurements [Hönninger et al., 2004, Sinreich et al., 2005, Wagner et al., 2004]. MAX-DOAS instruments scan the atmosphere from zenith to horizon in a set of consecutive elevation angles to measure scattered sunlight. For low elevation angles, the effective travel path of photons are longer in the troposphere compared to the zenith direction. This makes the MAX-DOAS technique to be more sensitive to tropospheric absorbers. MAX-DOAS has been very effectively used to measure HCHO in the atmosphere [Heckel et al., 2005, Li et al., 2013, Pinardi et al., 2013, Vigouroux et al., 2009]. It can provide information on tropospheric column, surface concentration, vertical trace gas aerosol extinction profiles. That makes it very well suited for validation of satellite observations, ground in-situ measurements and atmospheric models [Li et al., 2010, Peters et al., 2012, Vlemmix et al., 2015, Wang et al., 2017].



Figure 3.5: MAX-DOAS experimental setup for a simplified single scattering scenario [Sin-reich et al., 2013].

Figure 3.5 shows a MAX-DOAS experimental setup for a simplified single scattering scenario. In practice, multiple scattering can also happen (more details about multiple scattering provided in section 3.5 and 3.6.3). The sunlight passes through the atmosphere at different solar zenith angles (ν). The telescope of the instrument is pointed at different elevation angles (α), which receives the sunlight after it's scattered at different heights (red points). Atmospheric absorbers in troposphere and stratosphere is signified by green color. It can be seen that the stratospheric photon path is relatively short and the light passes through more tropospheric absorption as the elevation angles get lower.

For MAX-DOAS measurements, the reference spectrum is usually the zenith measurement for a particular scan. This is to ensure that the trace gas absorption in the reference spectrum becomes the lowest. The difference between the actual measurement at a certain elevation angle and the reference spectrum is defined as the differential slant column density (dSCD).

$$\Delta S(\vartheta, \alpha) = S(\vartheta, \alpha) - S(\vartheta, 90^{\circ})$$
(3.13)

We can further divide the slant column density into stratospheric portion and tropospheric portion,

$$\Delta S(\vartheta, \alpha) = (S_{\text{trop}}(\vartheta, \alpha) + S_{\text{strat}}(\vartheta, \alpha)) - (S_{\text{trop}}(\vartheta, 90^{\circ}) + S_{\text{strat}}(\vartheta, 90^{\circ}))$$
(3.14)

Atmospheric scattering takes place mostly in the lower atmosphere because most molecules and aerosols are located there. So it can be concluded that, independent of viewing direction and elevation angle, the path through the stratosphere is almost the same.

$$S_{\text{strat}}(\vartheta, \alpha) \approx S_{\text{strat}}(\vartheta, 90^{\circ})$$
 (3.15)

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$$\Delta S(\vartheta, \alpha) \approx S_{\text{trop}}(\vartheta, \alpha) - S_{\text{trop}}(\vartheta, 90^{\circ})$$
(3.16)

So MAX-DOAS is primarily sensitive to tropospheric absorption. Although the solar zenith angle changes between scanning different elevation angles, the change is quite small and has no major effect. Although this concept does not hold in early morning or late evening when the solar zenith angle changes quite rapidly (for solar zenith angle larger than 75°).

The vertical column density (VCD) can be defined as,

$$V = \int c(z)dz \tag{3.17}$$

It is the integrated concentration of a trace gas along the altitude z. The wavelength, the photon path, and the experimental geometry has no effect on VCD.

MAX-DOAS measurements can produce many useful trace gas properties such as the tropospheric column, near surface concentration, vertical profile etc. But atmospheric radiative transfer calculation is needed to derive these properties which can make the retrieval complicated. More details about radiative transfer modelling is explained in section 3.6.3.

3.5 Air Mass factor

Various different parameters can affect the slant column density measured by the DOAS method, such as the solar zenith angle, the viewing elevation angle, the relative azimuth angle and the wavelength. The integrated concentration along the altitude, also known as the vertical column density is independent of viewing geometry or wavelength. It only depends on the respective trace gas vertical profile. The slant column density and the vertical

3.5. Air Mass factor

column density can be expressed together via the concept of air mass factor (AMF) which is defined as [Noxon et al., 1979, Marquard et al., 2000],

$$A(\lambda, \theta, \alpha, \phi) := \frac{S(\lambda, \theta, \alpha, \phi)}{V}$$
(3.18)

The air mass factor is the integrated light path ratio between the slant column density and the vertical column density. It can also be explained by the optical depth (τ) when solar radiation passes through an absorbing material like the earth's atmosphere,

$$\tau(\lambda) = -\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = \sigma(\lambda) \cdot \int_0^L c(\mathbf{x})dl = \sigma(\lambda) \cdot S(\lambda)$$
(3.19)

From equation 3.18 and 3.19, the air mass factor can be written as,

$$A(\lambda) = \frac{\tau(\lambda)}{\sigma(\lambda) \cdot V}$$
(3.20)

So the air mass factor for MAX-DOAS measurements depend on the vertical dolumn density. $A(\lambda) = A(\lambda, V)$. The air mass factor also depends on the slant column density S and the molecular absorption cross section $\sigma(\lambda)$.

$$\tau(\lambda) = \sigma(\lambda) \cdot S(\lambda) = \sigma(\lambda) \cdot V \cdot A(\lambda, \sigma(\lambda) \cdot S)$$
(3.21)

Radiative transfer models can be used to calculate the air mass factors. Single scattering models are fast to use and easy to operate but it can also make significant errors. This is why multiple scattering models are used commonly which produces better results but can be computationally much more expensive. Different trace gas retrieval methods for MAX-DOAS measurements by using air mass factors from radiative transfer modelling are described in the following section.

3.6 Trace Gas Vertical Profile Retrieval Methods

3.6.1 Optimal Estimation

Optimal estimation method (OEM) is a common and widely used strategy for atmospheric retrieval applications to solve inverse problems [Rodgers, 2000]. It has been used in many studies for trace gas and aerosol property retrievals by using the MAX-DOAS technique [Tirpitz et al., 2021]. In optical estimation theory, a forward model F(x) is used such as,

$$y = F(x) + \epsilon \tag{3.22}$$

Where, y is a measurement vector containing a finite number of variables (for example, slant column densities at different elevation angles), x signifies the atmospheric state (for example, number densities at different heights) and ϵ is the error from the measurements. Another parameter b can be introduced which is not known yet but can be calculated (for example, atmospheric pressure, temperature etc.).

$$y = F(x, b) + \epsilon \tag{3.23}$$

For MAX-DOAS measurements, the vector y contains differential slant column densities for different elevation angles and the vector x contains trace gas concentrations or aerosol extinction coefficients at different layers. The target of the inverse method is to calculate atmospheric properties x given measurements y.

$$x = F^{-1}(y) (3.24)$$

The problem of this straightforward approach is that the solution does not exist often and unstable results can occur due to large measurement error ϵ . That's why an a priori state vector x_a is used where a least squares method is used to minimize the difference between the retrieved value and the a priori state.

$$\chi^{2}(x) = (y - F(x, b))^{T} \mathbf{S}_{\epsilon}^{-1} (y - F(x, b)) + (x - x_{a})^{T} \mathbf{S}_{a}^{-1} (x - x_{a})$$
(3.25)

Here, S_a is the a priori covariance matrix and S_{ϵ} is the measurement covariance matrix. S_{ϵ} contains the squares of the measurement error at diagonal locations and zero everywhere else. The estimate for most probable value of \hat{x} (maximum a posteriori, MAP) that minimizes the difference between the retrieved value and the a priori state is retrieved by,

$$\hat{x} = \arg\min\chi^2(x) \tag{3.26}$$

The Gauss-Newton method can be used to provide solution for linear case where K is the weighting function matrix,

$$\hat{\mathbf{x}} = \left(\mathbf{S}_a^{-1} + \mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K}\right)^{-1} \left(\mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{y} + \mathbf{S}_a^{-1} \mathbf{x}_a\right)$$
(3.27)

The solution for the non-linear case can be derived linearly with $K_i = K(x_i)$,

$$\mathbf{x}_{i+1} = \mathbf{x}_i + \left(\mathbf{S}_a^{-1} + \mathbf{K}_i^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K}_i\right)^{-1} \left[\mathbf{K}_i^T \mathbf{S}_{\epsilon}^{-1} \left(\mathbf{y} - \mathbf{F}\left(\mathbf{x}_i\right)\right) - \mathbf{S}_a^{-1} \left(\mathbf{x}_i - \mathbf{x}_a\right)\right]$$
(3.28)

 \hat{x} is the covariance matrix for error during the retrieval. it excludes model parameter errors and forward model errors.

$$\hat{\mathbf{S}} = \left(\mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K} + \mathbf{S}_a^{-1}\right)^{-1}$$
(3.29)

The parameters x_a and S_a can be derived from atmospheric observations at a particular site or from historical climatological data. It contains the best approximation of the atmospheric state before measurement have begun. The ratio of the retrieved state \hat{x} to true state x is called the averaging kernel matrix A which signifies the sensitivity between them.

$$\mathbf{A} = \frac{\partial \hat{\mathbf{x}}}{\partial \mathbf{x}} = \left(\mathbf{S}_a^{-1} + \mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K}\right)^{-1} \mathbf{K}^T \mathbf{S}_{\epsilon}^{-1} \mathbf{K}$$
(3.30)

The degrees of freedom d_s contains the number of independent variables that can be derived,

$$d_s = tr(A) \tag{3.31}$$

If there are no noise, then the retrieved atmospheric state \hat{x} can be expressed in terms of the true state,

$$\hat{x} = x_a + A(x - x_a) \tag{3.32}$$

So the averaging kernel A expresses a benchmark about how to get a particular retrieval at a certain height by averaging the true profile. It denotes the sensitivity of the retrieval to the true state. For a perfect retrieval, $\hat{x} = x$, the unit matrix will be equal to the averaging kernel matrix, A = I.

3.6.2 Parameterized Retrieval

Parameterized retrieval methods (PAR) share a lot of commonalities with the optimal estimation method, with one of the main difference being it does not constraint a priori values [Sinreich et al., 2013, Frieß et al., 2019]. It uses a few number of parameters to represent the state vector, x = x(p). These parameters include quantities like profile shape, vertical column density, layer number and layer thickness.

Optimal estimation methods usually perform radiative transfer calculations concurrently which can be time consuming. The calculation of the weighting matrix for cost function minimization can be computationally expensive. On the other hand, parameterized models use precalculated look up tables because it only has a few number of parameters. So this method is faster although this has the disadvantage that by choosing only a few parameters, it limits the state vector possibilities. Optimal estimation on the other hand, can be biased toward a priori state vector, specially in clean conditions.

3.6.3 Application of Radiative Transfer Modeling for MAX-DOAS

Air mass factors can be calculated from the radiances calculated by radiative transfer models (section 2.7). Here, a short description is provided about the procedures and input data needed for running the radiative transfer models for DOAS applications [Frank, 1991, Perliski and Solomon, 1993, Platt and Stutz, 2008].

• The radiative transfer model calculates radiances for two different scenario: a simula-

tion where the absorber is absent from the atmosphere and another simulation where the absorber is present.

- By using the DOAS method, slant column density S is calculated.
- By integrating the concentration of the absorber, the vertical column density is calculated.
- The air mass factor is derived.

This steps are used to calculate air mass factors in most multiple scattering models and in some few single scattering models. This is generally referred as the traditional AMF computation method. Existing models that use this includes,

- Discrete ordinates radiative transfer (DISORT) model [Stamnes et al., 1988].
- GOMETRAN/SCIATRAN [Rozanov et al., 1997].
- AMFTRAN [Marquard et al., 2000].
- Integral equation method [Anderson Jr and Lloyd, 1990].
- Backward Monte Carlo [Perliski and Solomon, 1993, Marquard et al., 2000].

3.6.4 Real time analysis

The real-time algorithm is an analytical approach based on trigonometric setup which uses look up table for radiative transfer calculations [Spinei, 2022]. It is based on the fact that O_2O_2 absorption strongly affects scattering processes in the atmosphere. It is computationally very efficient since the look up tables can be computed beforehand. The aerosol and trace gas profiles are determined by comparing O_2O_2 air mass factor with aerosol and no aerosol (pure Rayleigh scattering) conditions. By using radiative transfer models like VLIDORT [Spurr, 2008], air mass factors for the Rayleigh case (no aerosols) are calculated.

The number of elevation angles used in the measurements provides the maximum number of vertical layer that can be retrieved by this method. The height grid is later interpolated linearly from ground to 2.5 km. The trace gas retrieval method is describe in the following section.

3.6.5 Trace Gas Vertical profile Estimation using Real Time Analysis

The inputs for the trace gas profile estimation algorithms are described below [Spinei, 2022],

- Viewing elevation angles of the max-doas scan.
- Relative azimuth angles for each elevation angles in the scan.
- Differential slant column density of the trace gas for corresponding elevation angles ΔS_{qas}^{VEA} .
- Differential slant column density of O_2O_2 for corresponding elevation angles $(\Delta S_{O_2O_2}^{VEA})$.
- Simulated Air mass factors for O_2O_2 at 477 nm for Rayleigh scattering for the same viewing elevation angles and relative azimuth angles.
- O_2O_2 vertical column density estimated from the nearest radiosondes launch $(VCD_{O_2O_2})$.
- Surface O_2O_2 number density estimated from in-situ meteorological measurements $(n_{O_2O_2})$.

The layer center for O_2O_2 measurements can be approximated as,

$$Height_{Layer_center}^{VEA} = \frac{\Delta S_{O_2O_2}^{VEA} + VCD_{O_2O_2}}{n_{O_2O_2}} \frac{Sin(90^{\circ} - VEA)}{2}$$
(3.33)

If we assume that the trace gas has the same profile as O_2O_2 ,

$$\Delta S_{gas_O_2O_2profile}^{VEA} = \frac{\Delta S_{O_2O_2}^{VEA}}{VCD_{O_2O_2}} VCD_{gas}$$
(3.34)

Then the partial columns of gas can be estimated as,

$$\Delta S_{gas}^{VEA} = \frac{\Delta S_{gas}^{VEA} - \Delta S_{gas}^{VEA} - 0.5VCD_{gas}}{VCD_{O_2O_2} + \Delta S_{O_2O_2}^{VEA}} VCD_{O_2O_2}$$
(3.35)

The profile shape is then normalized by the maximum slant column density,

$$Normalized_S_{gas}^{VEA} = \frac{\Delta S_{gas}^{VEA}}{max(\Delta S_{gas}^{VEA})}$$
(3.36)

This profile shape needs to be corrected for the effect of aerosol optical depth (AOD). The estimated ΔS_{gas} decrease due to scattering with aerosols can be written by,

$$\Delta S_{gas_O_2O_2profile_aod}^{VEA} = \frac{\Delta S_{O_2O_2_rayleigh}^{VEA} - \Delta S_{O_2O_2}^{VEA}}{VCD_{O_2O_2}} VCD_{gas}$$
(3.37)

The number density can be calculated as a function of the viewing elevation angles (VEA),

$$n_{gas}^{VEA} = \frac{0.5\Delta S_{gas_O_2O_2profile_aod}^{VEA} - \Delta S_{gas_O_2O_2profile}^{VEA} + 2\Delta S_{gas}^{VEA}}{VCD_{O_2O_2} + \Delta S_{O_2O_2}^{VEA}} n_{O_2O_2} Normalized_S_{gas}^{VEA}$$

$$(3.38)$$

The profile is further corrected,

$$nC_{gas}^{VEA} = nS_{gas}^{VEA} - \frac{n_{gas}^{VEA}}{max(n_{gas}^{VEA})}$$
(3.39)

If nC < 0: nC = 1 + nC, else nC = 1. Finally,

$$n_{gas}^{VEA} = n C_{gas}^{VEA} \, n_{gas}^{VEA} \tag{3.40}$$

After that, the trace gas concentrations are again recalculated,

$$n_{gas}^{VEA} = \frac{n_{gas_i}^{VEA} \Delta h_i}{\sum n_{gas_i}^{VEA} \Delta h_i} \frac{VCD_{gas}}{\Delta h_i}$$
(3.41)

3.6.6 Comparison of Computational Performance

Table 3.1: MAX-DOAS	retrieval	strategies	from	different	${ m institutions}$	[Frieß	et al.	, 2019]

Algorithm	Institute	Method	Forward Model
bePRO	BIRA-IASB	OEM	LIDORT
BOREAS	IUP Bremen	OEM	SCIATRAN
HEIPRO	IUP Heidelberg	OEM	SCIATRAN
MMF	BIRA-IASB	OEM	VLIDORT
PRIAM	MPIC	OEM	SCIATRAN
MAPA	MPIC	PAR	McARTIM
DARK	KNMI	PAR	DAK
Realtime	NASA	ANA	N/A
A MAX-DOAS comparison study was conducted by [Frieß et al., 2019], where the accuracy, performance and the time required for a single profile retrieval was compared between different algorithms. A list of different MAX-DOAS retrieval strategies are mentioned in table 3.1. It can be seen that most institution still use the optimal estimation method (OEM) for MAX-DOAS retrieval. Some institutions are switching to parameterized algorithm (PAR) because of simplistic approach and faster run time. Currently, only NASA uses the Real time algorithm which does not use any forward model and provides the fastest result.



Figure 3.6: Time required for a single profile retrieval for different species [Frieß et al., 2019].

All the different approaches such as the optimal estimation method, the parameterized algorithm and the Real time algorithm provides good results. OEM algorithm perform well in polluted areas, but demonstrates large bias towards a priori conditions, which can produce large errors in clean environments. This bias can also be found in high altitudes, where the sensitivity is low. Parameterized algorithms do not have this disadvantage, but it can produce a wide variation of results when the sensitivity to true atmospheric state is low. Figure 3.6 shows the the comparison of computational performance between different algorithms, by showing the time required for a single profile retrieval for different species. The Real time algorithm is the fastest among all the approaches. Not only that, it is 3000 time faster than the second fastest MAPA algorithm [Beirle et al., 2019] in the study. In terms of accuracy, despite having a simplified radiative transfer approach, it provides satisfactory results for trace gas retrievals with excellent computational performance [Tirpitz et al., 2021].

3.7 The Pandora Spectrometer System

This section describes the different components of the NASA Pandora spectrometer system. It also provides an introduction to the Pandonia Global Network. The correction methods for Pandora measurements are also discussed.

3.7.1 The Pandonia Global Network



Figure 3.7: Pandonia network locations around the world.

The Pandonia Global Network is a joint venture of NASA and ESA which uses the Pandora

spectrometer system at different locations around the world to provide total columns and vertically resolved concentrations of a range of trace gases. Near real time O_3 and NO_2 total vertical column density (VCD) data products are available on the website. SO_2 and HCHO are currently experimental data products. Figure 3.7 shows the Pandonia network locations around the world.

One of the main objective is to provide assistance for validation and verification of satellite measurements [Cede et al., 2021]. Pandora provides support for satellites such as the Ozone Monitoring Instrument (OMI) [Herman et al., 2009, Tzortziou et al., 2012] and the Sentinel-5P TROPOMI instrument [Griffin et al., 2019, Ialongo et al., 2020, Verhoelst et al., 2021]. Future satellites such as TEMPO will also be supported [Chance et al., 2019]. Pandora has also been used to validate airborne measurements such as GeoTASO [Nowlan et al., 2016, Judd et al., 2019] and DC-8 [Spinei et al., 2018]. Air quality model simulations are also compared with Pandora observations [Zhao et al., 2019, Kollonige et al., 2018].

The Pandora spectrometer systems are being integrated into the Environmental Protection Agency (EPA) network under the Photochemical Assessment Monitoring Stations (PAMS) to improve our understanding of tropospheric ozone chemistry in highly polluted areas [Swap et al., 2019].

3.7.2 Components of the Pandora Spectrometer System

The major components of the Pandora spectrometer system are (figure 3.8),

- Telescope
- Tracker
- Optical fiber

3.7. The Pandora Spectrometer System



Figure 3.8: The Pandora spectrometer system.

- Spectrometer
- PC

The Pandora spectrometer system has an operating wavelength range of 280-530 nm with 0.6 nm resolution. The optical head sensor is attached on top of a sky and sun scanner, a fiber optic cable is used to connect the head sensor to the spectrometer. It is a single strand fused silica fiber with a 400 μm core and 440 μm clad diameter and silicone jacket. The numerical aperture is 0.22 and the fiber length can be from 3 m to 20 m, usually 10 m. The spectrometer is housed inside a temperature-controlled box for operational stability. The

spectrometer model is AvaSpec-ULS 2048x64, it has an un-cooled back-thinned CCD with 2048 x 64 effective pixels and a total size of 29 mm wide and 1 mm high. It is connected to a Cincoze DC-1100-R10 computer which collects the raw spectra data from the spectrometer inside the box. Due to it's small and compact size, the Pandora spectrometer system can be deployed easily at different locations for validation and air quality monitoring purposes. After the measurements are done, the raw data are uploaded online where it is processed by a central system for the correction of dark current, stray light, wavelength shift, temperature, non-linearity, latency, flat field etc [Cede, 2017].

3.7.3 Instrumental Calibration

Each Pandora instrument is calibrated and characterized in the laboratory for wavelength calibration, radiometric calibration, temperature sensitivity, slit function etc. Wavelength calibration is the process by which wavelengths are assigned to the measurements from individual pixels of the detector. The slit function of the instrument is also determined through this process. The slit function and wavelength calibration are performed by using atomic emission lines (Hg, Zn, Ne, Kr, Xe etc.). Then pixels are assigned for a range of emission lines and a polynomial is fitted through those pixel-wavelength pairs.

Radiometric calibrations are also performed by scanning a spectral lamp for a range of different temperatures by varying the instrument temperature. The field of view (FOV) of the instrument can also be characterized in the calibration process by scanning a point source. Stray light inside an optical instrument is another major source of systematic error. It is usually characterized by a matrix correction method where a set of monochromatic optical sources is used and then interpolated to compute the correction matrix. After applying the correction, the stray light error is generally reduced by one to two orders of magnitude. To characterize the stray light response of an instrument, the spectral line spread function (LSF) needs to be measured by illuminating it with a monochromatic light source. The LSF is normalized by the maximum signal within the bandpass of the spectrometer which produces the stray light distribution function (SDF) of the instrument. Within the bandpass, the value of the bandpass signal is set to zero. For an ideal characterization, the stray light response for every pixel of the detector should be known. In practice, this is sometimes hard to achieve, so the monochromatic light source is tuned for about N lines over the spectral band and the rest of the stray light response is calculated by interpolation between these N lines.

3.7.4 Data Processing



Figure 3.9: Data processing steps by the blick software.

Table 3.2 shows the different data file types and contents for Pandora data processing and figure 3.9 shows the data processing steps by the Blick software.

More details about each data type and conversion are explained below:

• L0 data: The L0 file contains the meta data, data column descriptions and raw measurement data for the Pandora instrument. every time the spectrometer does a new measurement, a line or comment is added.

Data file type	Content		
LO	Raw field spectra		
L1	Data after applying instrumental corrections		
L2Fit	Data after spectral fitting is applied		
L2	Total Columns (Direct sun)		
	Tropospheric Columns (MAX-DOAS		
	Near surface concentrations (MAX-DOAS)		
	Vertical profiles (MAX-DOAS)		

Table 3.2: Data file types and contents

- L1 data: The L0 data is converted into L1 data after applying instrumental corrections. The L1 file contains meta data, data column descriptions and the L1 data. The following instrumental corrections are applied to the L0 data.
 - Dark Current: Pandora measures the dark current by blocking the light input using a opaque filter. The dark current is the summation of dark offset and dark slope. There are two main methods of dark corrections, immediate and dark mapping. For immediate dark correction, dark counts are measured right after bright count measurements and then subtracted from bright count. Dark map is a more advanced method where DC measurements are taken for a range of different temperature and integration times to create a dark map, the resultant dark map is used in conjunction with immediate measurements to correct the bright count. The immediate dark correction method is more simple to use and hence used in most Pandora dark count corrections.
 - Offset Correction: In most Pandora instruments, there are blind pixels which do not receive any light when the detector is fully illuminated. The blind pixels can be used to estimate the offset for the pixels. The average of blind pixels is subtracted from both dark count and bright count measurements before calculating the corrected count. For simplicity, it is assumed that the offset is same for every pixel when in reality this is not the case.

- Stray Light Correction: For Pandora instruments, the stray light is characterized by using a laser source, six different wavelengths are measured and then interpolated to produce the correction matrix. After that, that the stray light correction matrix is multiplied with the measured signal to produce the stray light corrected signal.
- Non-Linearity Correction: Charge-coupled device (CCD) sensors are nonlinear generally. For Pandora detector, the non-linearity is normally a few percent for high counts and also very low counts. So the instrument returns more signal for low counts than it should. The non-linearity is characterized during the calibration procedure in the laboratory. Generally, a first or second order polynomial is used to estimate the non-linearity.
- **Pixel Response Non Uniformity:** The pixels returns slightly different signal even if every pixel is illuminated by the same amount of light. The is behavior is known as pixel response non uniformity. The PNRU is characterized during the instrumental calibration is typically in the amount of $\pm 1\%$. This is also known as flat field correction.
- L2Fit data: The L2fit data is generated from L1 data by applying DOAS spectral fitting algorithm. The L2Fit file contains meta data, data column descriptions and the L2Fit data.
- L2 data: The L1 data is converted into L2 data after applying applying L2 algorithm which creates atmospheric data products like, total or tropospheric column, near surface concentration and vertical profiles for different trace gases.

3.7.5 Data Quality Assurance

Data quality flags for Pandora measurements are based on signal to noise ratio, threshold uncertainty and air mass factor. These parameters can vary depending on processing codes and output trace gas.

Quality flag	Definition	
0 Assured high quality		
1	Assured medium quality	
2	Assured low quality	
10	Preliminary high quality	
11	Preliminary medium quality	
12	Preliminary low quality	

Table 3.3: Data quality flags.

Chapter 4

Atmospheric Formaldehyde Column and Surface Concentration Accuracy Characterization.

4.1 Goals and Motivation

HCHO is mainly generated as a secondary product of the oxidation of volatile organic compounds (VOCs). It has a relatively short lifetime (5 hours) in the atmosphere. Since surface ozone is formed in the lower troposphere by photochemical oxidation of VOC and NOx, HCHO can be used as an indicator of VOC abundance. Accurate and consistent monitoring of VOC production is necessary for control and mitigation of tropospheric ozone pollution and HCHO has been widely used recently for this purpose. By providing accurate measurements of near surface concentration of HCHO, the Pandora MAX-DOAS technique can contribute significantly in air quality monitoring. However, there still remains significant systematic uncertainty about the retrieval of HCHO by using the DOAS method.

The main goals of this analysis are to: (1) characterize systematic fitting errors and identify DOAS fitting settings for MAX-DOAS analysis that produce the closest to the median HCHO columns from most reasonable DOAS fitting scenarios; (2) compare near surface HCHO Chapter 4. Atmospheric Formaldehyde Column and Surface Concentration Accuracy 60 Characterization. concentrations derived from Pandora observations (using the median DOAS settings) with the in-situ surface HCHO concentration measurements.

4.2 Overview of The LISTOS Field Study



Figure 4.1: The LISTOS 2018 Campaign.

The New York City metropolitan area continues to experience high concentrations of ground level ozone (O_3) exceeding the federal air quality standards [US EPA, 2015] despite decreasing air pollution over the rest of the United States [de Foy et al., 2016, Tong et al., 2015]. High levels of ozone are also observed downwind of New York City [Kleinman et al., 2000, Castellanos et al., 2009] where sea-land interactions play an important role in air pollution distribution along the coastal regions. In the mornings the New York City air pollution is transported northeast to Long Island Sound where a shallow and stable marine boundary layer is present over the relatively cold waters [Lee et al., 2011]. Later, photo-chemically modified air pollution is carried inland by the afternoon sea breeze [Goldberg et al., 2014]. The Long Island Sound Tropospheric Ozone Study (LISTOS), a multi-agency multi-platform campaign, was designed to characterize the sources and processes causing poor air quality associated with the land-water circulation and photochemistry (figure 4.1). Ground-based, balloon borne and aircraft measurements were conducted during June-September 2018 within Long Island Sound and the surrounding coastlines [Judd et al., 2020, Wu et al., 2021].

4.3 Observations

MAX-DOAS measurements by Pandora 60 at Westport, CT (41.1183°, -73.3367°, 4 m a.s.l.) during the LISTOS 2018 campaign have been presented here from 19 July to 03 September 2018 (figure 4.2). The measurements included the following viewing elevation angles: 1°, 2°, 3°, 4°, 5°, 6°, 7°, 8°, 9°, 10°, 15°, 20°, 30°, 88° at azimuth angle of 212.8° from north. Integration time at each elevation angle was 20 seconds accept for the lowest angle (1°) where it was 30 seconds. Measurements were taken in a "V" pattern from 88° to 1° and back to 88° elevation angles. The total scan time was about 9 minutes. MAX-DOAS measurements were interspersed with target measurements (total 5 min pointing at a bright house, 266.5° from N, 518 m away, 24 m wide and 9 m tall) and direct sun measurements (2 min). All measurements were taken sequentially with and without U340 filter.

4.4 Choice of DOAS fitting settings for HCHO sensitivity study

HCHO has multiple molecular absorption bands between 290 and 360 nm suitable for passive DOAS measurements [Meller and Moortgat, 2000]. In addition to HCHO, ozone (O_3) , Chapter 4. Atmospheric Formaldehyde Column and Surface Concentration Accuracy Characterization.



Figure 4.2: Pandora 60 MAX-DOAS (212.5°, blue) and target (266.5°, red) directions at Westport, CT during LISTOS 2018. White building serving as a target is 518 m away, 24 m wide and 9 m tall. Pandora field of view is 1.5° circular and corresponds to a projection of about 13.6 m in diameter at the target distance.

bromine monoxide (BrO), oxygen collision complex (O_2O_2) , and potentially water vapor (H_2O) also absorb in the same wavelength window and need to be accounted for in solving Eq. (3.2). The DOAS fitting settings (fitting window, broadband polynomial order, offset polynomial order, molecular cross-section of absorbing species) to retrieve HCHO are typically selected by minimizing fitting optical depth residuals and maximizing measurements precision [Pinardi et al., 2013]. DOAS fitting accuracy depends on instrumental errors in measuring intensities, wavelength calibration, instrument transfer function, etc. Therefore, the DOAS fitting settings choice is potentially instrument dependent. Since currently there

is no way to absolutely calibrate the atmospheric ΔS_{HCHO} measurements the question remains whether the selected settings represent the most accurate results and what is the true spread of the comparable solutions. To answer the question of spread (ΔS_{HCHO} systematic fitting errors) for Pandora instruments, we performed sensitivity studies accounting for most plausible retrieval scenarios reported in literature [Pinardi et al., 2013, Hak et al., 2005]. Total number of evaluated DOAS fitting scenarios for ΔS_{HCHO} analysis was 5184. The different fitting parameters varied in this study include:

- Wavelength window (4 scenarios): 324.5-359 nm, 328.5-359 nm, 332-359 nm, 336-359 nm;
- Broad band polynomial order $(P_L, 3 \text{ scenarios}): 3, 4, 5;$
- Offset polynomial order (3 scenarios): 0, 1, 2;
- σ_{HCHO} (2 scenarios): [Meller and Moortgat, 2000] at 298K, [Chance and Orphal, 2011] at 298K;
- σ_{O_3} (6 scenarios): [Malicet et al., 1995] and [Serdyuchenko et al., 2014] at 223/243K, 223/243/293K, quadratic in temperature model;
- $\sigma_{O_2O_2}$ (3 scenarios): [Hermans et al., 2003] at 262 K; [Thalman and Volkamer, 2013] at 262 K, 294 K;
- + σ_{BrO} (2 scenarios): [Wilmouth et al., 1999] and [Fleischmann et al., 2004] at 221 K;
- Ring pseudo-absorption cross-section (2 scenarios): [Cede, 2017] and [Chance and Spurr, 1997].

To reduce computational time, a single reference spectrum was created to process the last 10 mostly cloud-free days of the campaign from August 24 to September 3, 2018. The reference

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spectrum was generated by averaging 2-hours of zenith spectra around noon on August 24, 2018 (one for spectra with and one without U340 filter). DOAS fitting was performed using the QDOAS software v.3.2 [Danckaert et al., 2012b]. Measurements with solar zenith angle greater than 75° were excluded from the analysis.

4.5 DOAS fitting evaluation

4.5.1 Effect of fitting parameters on ΔS_{HCHO}

For the sensitivity study regarding variation in ΔS_{HCHO} , separate analysis have been conducted for two different viewing elevation angles (15° and 2°). 15° measurements are the sole angles used for calculating HCHO tropospheric column and 2° measurements are used to estimate HCHO near surface volume mixing ratio. Both elevation angles produce similar results, here we will just discuss in details about 2° measurements.

The measurements that produce successful retrievals for all 5184 fitting scenarios were first selected from the dataset for 2° viewing elevation angle measurements. Since MAX-DOAS retrieval errors depend on the solar zenith angle, so in order to make a proper comparison between U340 filter and without filter measurements, coinciding measurements need to be compared. So the dataset was again filtered and only measurements that fall within 30 minutes of one another from U340 filter and without filter measurements for the 10 day period of the sensitivity study. After this, we have 89 measurements for the 10 day period of the sensitivity study for 5184 fitting scenarios. Then the median value for every measurement is calculated and the root mean square distance for every fitting scenario is calculated from the median. The root mean square distance from the median is a indicator of which fitting scenario resembles the median the best and which fitting scenarios will produce values that are far



Figure 4.3: (a) Scatter plot of ΔS_{HCHO} retrieved from various fitting settings with respect to the data set median for U340 Filter (VEA = 15°),(b) Scatter plot of ΔS_{HCHO} retrieved from various fitting settings with respect to the data set median for without Filter (VEA = 15°), (c) Scatter plot of ΔS_{HCHO} retrieved from various fitting settings with respect to the data set median for U340 Filter (VEA = 2°),(d) Scatter plot of ΔS_{HCHO} retrieved from various fitting settings with respect to the data set median for without Filter (VEA = 2°),(e) histogram of ΔS_{HCHO} deviation from the fitting scenario closest to median for U340 Filter (VEA = 15°), (f) histogram of ΔS_{HCHO} deviation from the fitting scenario closest to median for without Filter (VEA = 15°), (g) histogram of ΔS_{HCHO} deviation from the fitting scenario closest to median for U340 Filter (VEA = 2°), (h) histogram of ΔS_{HCHO} deviation from the fitting scenario closest to median for the fitting scenario closest to median for the fitting scenario closest to median for the fitting scenario from the fitting scenario closest to median for U340 Filter (VEA = 2°), (h) histogram of ΔS_{HCHO} deviation from the fitting scenario closest to median for without Filter (VEA = 2°)

higher or lower than the median. Since the fitting scenario that most closely resembles the median is preferred, so the fitting scenario with the lowest root mean square distance from the median is selected as the recommended fitting scenario. This evaluation is done separately for U340 filter and without filter measurements for 2° viewing elevation angle measurements. The the same analysis is also performed on 15° viewing elevation angle measurements. Then the distribution of ΔS_{HCHO} deviation is generated by subtracting every fitting scenario from the fitting scenario closest to the median and calculating the percentage deviation. While some individual settings can lead to a large deviation from the median (> 80%), 95% of all





Figure 4.4: (a) Scatter plot of Residual optical depth RMS retrieved from various fitting settings with respect to the data set median for U340 Filter (VEA = 15°),(b) Scatter plot of Residual optical depth RMS retrieved from various fitting settings with respect to the data set median for without Filter (VEA = 15°), (c) Scatter plot of Residual optical depth RMS retrieved from various fitting settings with respect to the data set median for U340 Filter (VEA = 2°),(d) Scatter plot of Residual optical depth RMS retrieved from various fitting settings with respect to the data set median for U340 Filter (VEA = 2°),(d) Scatter plot of Residual optical depth RMS retrieved from various fitting settings with respect to the data set median for without Filter (VEA = 2°),(e) histogram of Residual optical depth RMS deviation from the fitting scenario closest to median for U340 Filter (VEA = 15°), (f) histogram of Residual optical depth RMS deviation from the fitting scenario closest to median for without Filter (VEA = 15°), (g) histogram of Residual optical depth RMS deviation from the fitting scenario closest to median for U340 Filter (VEA = 2°), (h) histogram of Residual optical depth RMS deviation from the fitting scenario closest to median for WEA = 2°), (h) histogram of Residual optical depth RMS deviation from the fitting scenario closest to median for U340 Filter (VEA = 2°), (h) histogram of Residual optical depth RMS deviation from the fitting scenario closest to median for U340 Filter (VEA = 2°), (h) histogram of Residual optical depth RMS deviation from the fitting scenario closest to median for WEA = 2°), (h) histogram of Residual optical depth RMS deviation from the fitting scenario closest to median for WIA0 Filter (VEA = 2°)

scenarios resulted in a ΔS_{HCHO} range of about $\pm 20\%$. Figure 4.3 and 4.4 show retrieved ΔS_{HCHO} and residual optical depth RMS from all tested fitting settings relative to the selected scenario.

Figure 4.3 (a,b,c,d) shows comparison of ΔS_{HCHO} retrieved from various fitting settings with respect to the fitting scenario closest to the median with U340 and without filter (5184 fitting scenarios) for 15° and 2° viewing elevation angles. Figure 4.3 (e,f,g,h) shows the corresponding distribution of ΔS_{HCHO} deviation from fitting scenario closest to the median for spectra collected with and without filter. The ΔS_{HCHO} distribution follows a Gaussian pattern. The majority of ΔS_{HCHO} measurements can be found within ±10% from the median. The closest to the median fitting scenarios are described in table 4.1 for the four different groups (*HCHO* 15° spectra without filter, *HCHO* 15° spectra with U340 filter, *HCHO* 2° spectra without filter and *HCHO* 2° spectra with U340 filter). Wavelength window is the main parameter that influences ΔS_{HCHO} retrieval and it is same (328.5-359 nm) for the four different analysis. This indicated that choosing 328.5-359 nm wavelength range for DOAS fitting will produce values that will be closer to the median for all possible combinations.

Figure 4.4 (a,b,c,d) shows comparison of residual optical depth RMS retrieved from various fitting settings with respect to the residual optical depth of the fitting scenario closest to the data set median with U340 and without filter (5184 fitting scenarios) for 15° and 2° viewing elevation angles. Figure 4.4 (e,f,g,h) shows the corresponding distribution of residual optical depth RMS deviation fitting scenario closest to the median for spectra collected with and without filter. It is evident that the distribution of residual optical depth RMS deviation from the median approximates a normal distribution. Although the residual optical depth RMS deviation is not as larges as the ΔS_{HCHO} deviation. So it can be surmised that while some settings can produce very high or large ΔS_{HCHO} value compared to the median, the residual does not increase in proportional order. Also the residual optical depth RMS of the RMS distribution.

Chapter 4. Atmospheric Formaldehyde Column and Surface Concentration Accuracy

Characterization.

	HCHO 15 degree	HCHO 15 degree	HCHO 2 degree	HCHO 2 degree
Parameters	Spectra without filter	Spectra with U340	Spectra without filter	Spectra with U340
Fitting Wavelength window	328.5 - 359 nm			
Polynomial order	4	4	4	4
Offset order	0	1	2	1
Temperature of the high-resolution σ of O_3	223 and 243 K	223, 243 and 293 K	223 and 243 K	223, 243 and 293 K
High-resolution σ of HCHO	[Chance and Or- phal, 2011], 298 K	[Meller and Moortgat, 2000], 298 K	[Chance and Or- phal, 2011], 298 K	[Meller and Moortgat, 2000], 298 K
High-resolution σ of O_3	[Malicet et al., 1995]	Malicet et al. [1995]	[Malicet et al., 1995]	[Malicet et al., 1995]
High-resolution σ of O_2O_2	[Thalman and Volkamer, 2013], 294 K			
High-resolution pseudo Rotational Raman (Ring) absorption cross- section	CINDI-2	CINDI-2	CINDI-2	Pandora Ring 1
High-resolution σ of BrO	[Wilmouth et al., 1999]	[Wilmouth et al., 1999]	[Fleischmann et al., 2004]	[Wilmouth et al., 1999]

Table 4.1: DOAS fitting scenario for deriving ΔS_{HCHO} closest to the median of all scenarios (spectra collected with and without U340 filter)

4.5.2 Effect of fitting parameters on $\Delta S_{O_2O_2}$

A sensitivity study has also been performed for $\Delta S_{O_2O_2}$ retrieval, since it is a important parameter that is used in tropospheric column and near surface concentration calculations for *HCHO*. A total of 1284 fitting scenarios were analyzed in the sensitivity study and all the different elevation angles were included. Figure 4.5 (a) shows a scatter plot of $\Delta S_{O_2O_2}$ retrieved from various fitting settings with respect to the data set median for U340 Filter and without filter. Figure 4.5 (b) shows histogram of $\Delta S_{O_2O_2}$ deviation from the fitting scenario closest to median for U340 Filter and figure 4.5 (c) shows histogram of $\Delta S_{O_2O_2}$ deviation

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Figure 4.5: (a) Scatter plot of $\Delta S_{O_2O_2}$ retrieved from various fitting settings with respect to the data set median for U340 Filter and without filter, (b) histogram of $\Delta S_{O_2O_2}$ deviation from the fitting scenario closest to median for U340 Filter, (c) histogram of $\Delta S_{O_2O_2}$ deviation from the fitting scenario closest to median for without Filter.

from the fitting scenario closest to median for without Filter. The gaussian fit demonstrates that 95% of retrievals fall within $\pm 4.5\%$ of median for U340 filters and $\pm 3.92\%$ of median for without filter measurements. This variation is very small compared to the variations observed for ΔS_{HCHO} retrievals (section 4.5.1).

4.6 Ground based In-situ Surface HCHO measurements

In-situ formaldehyde concentrations were measured using an Aerodyne Research, Inc. formaldehyde analyzer. Figure 4.7 shows the in-situ surface volume mixing ratio (ppb) of HCHO during the LISTOS campaign. The average vmr during the campaign was 2.65 ppb (standard deviation = 1.57 ppb, minimum = 0.54 ppb, maximum = 9.24 ppb, Q25 = 1.45 ppb, Q75 = 3.46 ppb). It also shows in-situ measurements of other trace gases like O_3 , NO_2 and meteorological properties such as temperature, pressure and wind speed.



Figure 4.6: $\Delta S_{O_2O_2}$ retrieved from the scenario closest to the median for U340 vs open spectra for 15° elevation angle.

4.7 HCHO Tropospheric columns

Tropospheric columns from ground-based multi-axis measurements are very important for satellite validation and also for connecting satellite measurements with the surface in-situ



Figure 4.7: In situ measurements at Westport, CT (July 01 to September 03, 2018): (a) HCHO vmr (blue line) and O_3 vmr (red line) (1 hour running average); (b) NO_2 vmr (1 hour running average); (c) $HCHO/NO_2$ ratio (solid line represents hourly running average); (d) Temperature ; (e) Pressure and (f) Wind speed.

observations. HCHO columns in this study were calculated using a semi-geometrical approximation from ΔS_{HCHO} and ΔS_{O2O2} measured at 15° and 90° elevation angles according to equation 4.1. Figure 4.8 shows ΔS_{HCHO} retrieved from the scenario closest to the median for U340 vs open spectra for 15° elevation angle.

Since O_2O_2 vertical mixing ratio is considered constant (at a given temperature, pressure and relative humidity), O_2O_2 can be used to correct for scattering conditions due to molecules, aerosols and solar position. Vertical column density $VCD_{O_2O_2}$ is calculated based on meteorological data from radiosondes launches.

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$$VCD_{HCHO} = \frac{\Delta S_{HCHO}^{15^{\circ}-90^{\circ}}}{\Delta AMF_{O_2O_2}^{15^{\circ}-90^{\circ}}+1} = \frac{\Delta S_{HCHO}^{15^{\circ}-90^{\circ}}}{\frac{\Delta S_{O_2O_2}^{15^{\circ}-90^{\circ}}}{VCD_{O_2O_2}}+1}$$
(4.1)



Figure 4.8: ΔS_{HCHO} retrieved from the scenario closest to the median for U340 vs open spectra for 15° elevation angle.

Figure 4.9 shows the comparison between HCHO VCD calculated from open and U340



Figure 4.9: HCHO tropospheric vertical column retrieved from Pandora multi-axis spectra collected with and without U340 filter data using the DOAS fitting scenario closest to the median.

measurements according to equation 4.1. Measurements without and with U340 filter agrees with each other very well. The open and U340 measurements were interpolated on a common time grid for a linear regression analysis as shown in fig 4.10 (b). The comparison shows

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Figure 4.10: (a) Linear regression analysis of ΔS_{HCHO} retrieved from the scenario closest to the median for U340 vs open spectra for 15° elevation angle, (b) Linear regression analysis of HCHO VCD retrieved from the scenario closest to the median for U340 vs open spectra

strong linear agreement between HCHO tropospheric column measured by without and with U340 filter ($R^2 = 0.98$, slope = 0.93). This indicates that HCHO tropospheric column measured by without and with U340 filter delivers the same results, so it is not necessary to do measurements of both kinds for HCHO tropospheric column retrieval.

4.8 HCHO near surface concentrations

Near surface volume mixing ratios of HCHO (χ^{surf}_{HCHO}) using real time algorithm are determined from spectra measured at 1°, 2° and 90° elevation angles of a single scan (equation 4.2). Reference spectrum is created by averaging zenith measurements at the beginning and end of the scan. Even though Pandora 60 head sensor contained Delrin plastic parts [Spinei et al., 2021], the amount of HCHO emitted due to their heating is smaller than 0.05 DU. This is because the reference spectrum and the rest of the spectra were measured within less

4.8. HCHO near surface concentrations

than 10 min with similar head sensor temperatures.

$$\chi_{HCHO}^{surf} \approx \Delta S R^n \frac{P_{surface} \cdot N_A}{R_g \cdot T_{surface}} \cdot \chi_{O_2}^2 \cdot 10^9 \ [ppb] \tag{4.2}$$

Where, $P_{surface}$ is the measured surface pressure, $T_{surface}$ is surface temperature, R_g is a gas constant, N_A is the Avogadro number, χ_{O_2} is oxygen volume mixing ratio (0.2095). The main assumption in deriving Eq. (4.2) is that both gases have the same effective height. Since HCHO and O_2O_2 have different profiles and we have no prior information about them we calculate two different cases and select the largest one for vmr estimation:

$$\Delta SR^{1} = \frac{\Delta S_{HCHO}(\lambda_{HCHO}, 1^{\circ})}{\Delta S_{O_{2}O_{2}}(\lambda_{HCHO}, 1^{\circ})}$$

$$(4.3)$$

$$\Delta SR^{0} = \frac{\Delta S_{HCHO}(\lambda_{HCHO}, 0^{\circ})}{\Delta S_{O_{2}O_{2}}(\lambda_{HCHO}, 0^{\circ})} = \frac{2 \cdot \Delta S_{HCHO}(\lambda_{HCHO}, 1^{\circ}) - \Delta S_{HCHO}(\lambda_{HCHO}, 2^{\circ})}{2 \cdot \Delta S_{O_{2}O_{2}}(\lambda_{HCHO}, 1^{\circ}) - \Delta S_{O_{2}O_{2}}(\lambda_{HCHO}, 2^{\circ})}$$
(4.4)

Where $\Delta S_{gas}(\lambda_{gas}, 0^{\circ})$ is ΔS linearly extrapolated to the surface from measurements at 1° and 2° elevation angles.

Since effective wavelengths of *HCHO* and O_2O_2 are not the same due to Rayleigh scattering at their molecular absorption cross section bands (340 nm for *HCHO* versus 360 nm for O_2O_2), absorption from O_2O_2 has to be corrected. For spectra collected with no filters this can be done by linear extrapolation from $\Delta S_{O_2O_2}$ at 360 nm (retrieved from 350-370 nm) and 477 nm (retrieved from 435-490 nm) to 340 nm: Chapter 4. Atmospheric Formaldehyde Column and Surface Concentration Accuracy 76 Characterization.

$$\Delta S_{O_2O_2}(\lambda_{HCHO}, VEA) = \Delta S_{O_2O_2}(360, VEA) - \frac{\Delta S_{O_2O_2}(477, VEA) - \Delta S_{O_2O_2}(360, VEA)}{477 - 360} \cdot (360 - \lambda_{HCHO})$$
(4.5)

Figure 4.11 shows time series of HCHO surface in-situ and Pandora MAX-DOAS near surface volume mixing ratios at Westport, CT during the LISTOS 2018 campaign. Due to some issues with Pandora positioner data gaps are present during several campaign days. Both data sets have similar diurnal trends.

Since MAX-DOAS measurements are impacted by the clouds it is important to check for cloud presence during the measurements. Figure 4.12 shows the ceilometer aerosol backscattered observations for the entire measurement period from which the cloud presence for selected days can be determined. Since the ceilometer was pointing straight up this does not guarantee that there were no clouds on the horizon in the pointing direction. The accuracy of MAX-DOAS measurements generally degrade in high cloud conditions. However it can be observed from the ceilometer plots that even in some high cloud days, the MAX-DOAS near surface volume mixing ratio closely resembles the ground in-situ measurements.

Figure 4.13 (a) shows the linear regression plot between Pandora and in-situ HCHO surface vmr for the entire LISTOS campaign (258 measurements), with a slope of 0.92 and R^2 value of 0.83. The slope indicates that the Pandora is underestimating the in-situ data by around 10%. The last 10 days of Pandora measurements (August 24 to September 3, 2018) were mostly cloud free and had favorable conditions for MAX-DOAS measurements. Figure 4.13 (b) also shows linear regression analysis for the cloud free days (148 measurements). Strong linear correlation was observed for cloud free days with a slope of 0.95 and R^2 of 0.88 [Nowak et al., 2019].



Figure 4.11: HCHO surface volume mixing ratios measured by Aerodyne QCL and Pandora 60 MAX-DOAS at Westport, CT during the LISTOS 2018 campaign.

4.9 Uncertainty Estimation for HCHO retrieval

We assume that the DOAS fitting uncertainties of ΔS_{HCHO} and $\Delta S_{O_2O_2}$ are independent of each other since they are retrieved in different fitting windows. To calculate the total Chapter 4. Atmospheric Formaldehyde Column and Surface Concentration Accuracy Characterization.



Figure 4.12: HCHO surface volume mixing ratios measured by Aerodyne QCL and Pandora 60 MAX-DOAS (left) and ceilometer aerosol backscattered profile (right) at Westport, CT during the LISTOS 2018 campaign.

uncertainty, we propagate the DOAS fitting and measurement uncertainties into the HCHO tropospheric column and near surface concentration error budget. Technically, this is not correct since the true HCHO AMF depends on the atmospheric scattering conditions (e.g. aerosols, HCHO profile). There are two main types of errors in HCHO tropospheric column and near surface concentration retrieval, (1) random error and (2) systematic error. They are described in details below.

4.9.1 Random Error

The random error originates from uncertainty in DOAS fitting due to instrumental error and atmospheric conditions. Low signal to noise ratio, photon shot noise and other detector properties are common sources of random error. The slant column fitting error from DOAS least squares fit algorithm can sufficiently represent all different sources of random error [Stutz and Platt, 1996]. In this analysis, the slant column fit error is divided by the slant



Figure 4.13: HCHO surface volume mixing ratios measured by Aerodyne QCL and Pandora 60 (MAX-DOAS) at Westport, CT during the LISTOS 2018 campaign for (a) all days and (b) August 24 to September 03, 2018.

column density to calculate the amount of error in percentage points. ΔS_{HCHO} has a random error of 9% ± 6.5% for VEA = 15° and 8% ± 7% for VEA = 1°. $\Delta S_{O_2O_2}$ has a statistical error of 2% ± 0.75% for VEA = 15° and 1% ± 0.5% for VEA = 1°. The O_2O_2 VCD from radiosondes measurements has a statistical error of ±1.15%. Total random error and it's different sources are described in details in table 4.2. The total random error for HCHO tropospheric column calculation can be calculated by combining all the different errors in quadrature. After adding the individual errors in quadrature, the total error for HCHO near surface vmr estimation is calculated.

4.9.2 Systematic error

The systematic error originates from choice of wavelength window, polynomial order, offset order and molecular absorption cross section. Correlation between trace gases and combinaChapter 4. Atmospheric Formaldehyde Column and Surface Concentration Accuracy
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tion of absorbers used in the DOAS fitting also affects the systematic error. One of the main motivation behind the sensitivity study was to get an approximation of the systematic error in ΔS_{HCHO} calculation. Figure 4.3 (e,f,g,h) shows distribution of ΔS_{HCHO} deviation from the median case for spectra collected with and without filter. The distribution is similar to a gaussian function but it's not exactly a gaussian distribution. Since this distribution is produced entirely from varying different systematic parameters, the range of systematic error from the median can be calculated by determining the 5th and 95th percentile of distribution of the ΔS_{HCHO} deviation from the median. The 5th percentile denotes the maximum negative error from the median and the 95th percentile denotes the maximum positive error from the median. Individual 5th and 95th percentile deviation from the median were calculated for the open and u340 distribution for each viewing elevation angle displayed in Figure 4.3 (a,b,c,d), then an average was taken to calculate the overall 5th and 95th percentile deviation for the two different viewing elevation angles. By this approximation, the systematic error for ΔS_{HCHO} measurements is 22% for VEA = 15° and 20% for VEA = 1°. For $\Delta S_{O_2O_2}$, the systematic error is 4%.

4.9.3 Overall Error

Uncertainty Source	Tropospheric column (VEA = 15°)	Near surface vmr (VEA = 1° and 2°)
ΔS_{HCHO} random error [%]	9 ± 6.5	8±7
$\Delta S_{O_2O_2}$ random error [%]	2 ± 0.75	1 ± 0.5
ΔS_{HCHO} systematic error [%]	22	20
$\Delta S_{O_2O_2}$ systematic error [%]	4	4
$VCD_{O_2O_2}$ random error [%]	1.15	N/A
Overall random error [%]	9 ± 6.5	8 ± 7
Overall systematic error [%]	22	20

Table 4.2: Summary of different error sources in HCHO MAX-DOAS retrieval

The statistical error and systematic error are calculated separately and rounded to the nearest integer for simplification. The individual error sources are added in quadrature to calculate the overall random and systematic error. The total error for HCHO tropospheric column is estimated to be $9\% \pm 6.5\%$ for random error and 22% for systematic error. The error for surface pressure and temperature measurements in equation 4.2 is considered to be minimal and can be ignored. The total error for HCHO near surface concentration estimation is $8\% \pm 7\%$ for random error and 20% for systematic error. As commonly seen in error propagation , if one error is significantly larger than other sources of error, then that error dominates the overall error and the smaller errors make very little contribution to the the total error. That same principle can also be seen here. ΔS_{HCHO} errors are relatively large compared to the other sources of error and the overall error is essentially the error in ΔS_{HCHO} retrieval.

4.10 Summary of HCHO sensitivity study

- 1. ΔS_{HCHO} calculated using the DOAS technique were varied depending on polynomial order, offset order, molecular absorption cross sections and fitting window. Total 5184 cases were evaluated and the closest to the median case was identified. The distribution of ΔS_{HCHO} for U340 filter and without filter follows a gaussian pattern. This illustrates that ΔS_{HCHO} calculated by the DOAS technique can vary widely depending on the fitting parameter used. To reduce uncertainty and provide steady variability, the case that most closely resembles the median of the range is selected and recommended as base case. We recommend a base case with wavelength range of 328.5-359 nm based on the sensitivity study.
- 2. $\Delta S_{O_2O_2}$ calculated using the DOAS technique were varied depending on polynomial

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order, offset order, molecular absorption cross sections in 328.5 - 375 nm fitting window. Total 1296 cases were evaluated and a gaussian fit demonstrated the distribution for U340 filter and without filter from the median fitting scenario.

- 3. Excellent linear agreement were found between spectra collected without filter and with an U340 filter for HCHO differential slant column density ($R^2 = 0.96$, slope = 0.96) and HCHO tropospheric column ($R^2 = 0.98$, slope = 0.93). This indicates that for HCHO measurements, it is not necessary to do measurements with an U340 filter since measurements without filter performs the same way.
- 4. Strong linear correlation between the near surface HCHO vmr derived from MAX-DOAS spectra and in situ surface vmr was observed during the cloud-free days ($R^2 = 0.88$, slope=0.95), with slightly lower correlation for the entire measurement period ($R^2 = 0.83$, slope= 0.92).
- 5. The total error for HCHO tropospheric column calculation is estimated to be $9 \pm 6.5\%$ for random error and 22% for systematic error. The total error for HCHO near surface concentration estimation from Pandora MAX-DOAS measurements is $8 \pm 7\%$ for random error 20% for systematic error.
- 6. The systematic error depends on different fitting parameters like polynomial order, offset order, molecular absorption cross sections and fitting window. The systematic error of 22% for HCHO tropospheric column and 20% for HCHO near surface concentration signifies how ΔS_{HCHO} can vary widely just because of the combination of different fitting parameters used in the retrieval.



Figure 4.14: *HCHO* vertical profiles at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign.

4.11 HCHO profiles

HCHO vertical profiles were also generated from MAX-DOAS measurements by using the real-time algorithm [Frieß et al., 2019, Tirpitz et al., 2021]. Figure 4.14 shows *HCHO* vertical profiles at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign. concentration of *HCHO* in ambient air is relatively low. So a clear variation can only be seen in high concentration days like August 08, August 28 and September 03.

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4.12 $HCHO/NO_2$ Ratio from MAX-DOAS

4.12.1 Tropospheric Column

HCHO and NO_2 tropospheric columns were derived from Pandora MAX-DOAS measurements at Westport, CT. As we can see in figure 4.15, NO_2 tropospheric column is quite low compared to HCHO. This is because NO_2 concentrations are generally low in suburban or rural areas where there are not a lot of anthropogenic emission sources.

In the last decade, a lot of studies have used satellite measurements of $HCHO/NO_2$ tropospheric column ratio to designate near surface O_3 sensitivity regime [Duncan et al., 2010, Choi et al., 2012, Chang et al., 2016, Jin et al., 2017, 2020]. It is argued that in heavily polluted areas, the tropospheric column of HCHO and NO_2 are significantly weighted toward the surface, so the tropospheric column of these gases are a reasonable approximation for their near surface concentrations.

It was pointed out by [Schroeder et al., 2017] that satellite measurements of $HCHO/NO_2$ tropospheric column ratio might not be sufficient for near surface O_3 sensitivity classification. This is because the vertical distribution of HCHO and NO_2 are quite different. Though HCHO column is more weighted towards the surface, it is more distributed vertically in the atmosphere. On the other hand, NO_2 column is heavily weighted towards the surface and drops heavily with increasing altitude. So the tropospheric column $HCHO/NO_2$ ratio might not accurately reflect the condition at the ground.

Figure 4.16 shows the ratio of $HCHO/NO_2$ tropospheric columns (blue dot) and in-situ concentration (red line) at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign. It can be observed that the column $HCHO/NO_2$ ratio and in-situ surface $HCHO/NO_2$ ratio does not always follow the same pattern.



HCHO and NO₂ Tropospheric Column at Westport, CT (LISTOS, 2018)

Figure 4.15: HCHO and NO_2 tropospheric columns at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign.
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HCHO/NO₂ Ratio (In-situ and Column) at Westport, CT (LISTOS, 2018)

Figure 4.16: Ratio of $HCHO/NO_2$ tropospheric columns (blue dot) and in-situ concentration (red line) at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign.

4.12.2 Vertical Profile

Figure 4.17 shows the vertical profile of *HCHO* differential slant column density at Westport,

CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign. This is



HCHO Vertical Profiles at Westport, CT (LISTOS, 2018)

Figure 4.17: Vertical profile of HCHO differential slant column density at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign.

an useful way to observe the vertical distribution of HCHO in the atmosphere. Similarly, figure 4.18 shows the vertical profile of NO_2 differential slant column density at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign.



*NO*₂ Vertical Profiles at Westport, CT (LISTOS, 2018)

Figure 4.18: Vertical profile of NO_2 differential slant column density at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign.

Since, the vertical differential slant column density profile of both HCHO and NO_2 is available, we can combine both of them into a vertical profile of the ratio of $HCHO/NO_2$ differential slant column density. Since they were both retrieved in nearby wavelegnth ranges, (328-359) nm for HCHO and (336-370) nm for NO_2 , it is a reasonable assumption of their



HCHO/NO₂ dSCD Ratio at Westport, CT (LISTOS, 2018)

Figure 4.19: Vertical profile of $HCHO/NO_2$ differential slant column density ratio at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign.

ratio in the vertical scale.

Figure 4.19 shows the vertical profile of $HCHO/NO_2$ differential slant column density ratio at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 cam90 Chapter 4. Atmospheric Formaldehyde Column and Surface Concentration Accuracy Characterization.

paign. It can be seen that in general, the magnitude of the ratio increases with increase in altitude. This affirms the notion that the vertical distribution of HCHO and NO_2 in the lower atmosphere is different, NO_2 tends to stay close to the surface but HCHO is mixed more in the free troposphere.

4.13 Discussion

Pandora MAX-DOAS measurements can perform accurate estimation of HCHO near surface concentration. It was validated by comparing Pandora HCHO near surface measurements with collocated in-situ observations. The Pandora MAX-DOAS agrees very well with the ground in-situ instrument for the whole campaign $(R^2 = 0.83, \text{ slope} = 0.92)$ and provides excellent agreement for clear days ($R^2 = 0.88$, slope=0.95). However, large systematic uncertainty in HCHO spectral retrieval does introduce a source of error in HCHO measurements. The systematic error depends on different fitting parameters like polynomial order, offset order, molecular absorption cross sections and fitting window. The systematic error of $\pm 22\%$ for HCHO tropospheric column and $\pm 20\%$ for HCHO near surface concentration signifies how *HCHO* differential slant column density can vary widely just because of the combination of different fitting parameters used in the retrieval. To reduce uncertainty and provide steady variability, the case that most closely resembles the median of the range is selected and recommended as base case. A base case with a wavelength range of 328.5-359 nm has been recommended based on the sensitivity study. HCHO tropospheric column derived from spectra collected without filter and spectra collected with an U340 filter were found to be strongly in agreement with each other $(R^2 = 0.98, \text{ slope} = 0.93)$. The excellent agreement suggests that using an U340 filter does not provide any added benefit for HCHO retrieval.

Because of it's ability to scan the sky at different elevation angles, Pandora MAX-DOAS

4.13. Discussion

technique can provide information about the vertical distribution of different trace gases in the atmosphere. By using the Real time method, NO_2 , HCHO and H_2O vertical profiles were derived. The vertical profile of this different trace gases provide important information about how meteorology changes with increase in altitude. They are also a very useful input in air quality models.

Satellite measurements of $HCHO/NO_2$ tropospheric column ratio has been used widely in the last decade to designate near surface O_3 sensitivity regime, because the tropospheric column of HCHO and NO_2 are significantly weighted toward the surface, so the tropospheric column of these gases are a reasonable approximation for their near surface concentrations. However in our analysis, it is observed that although HCHO column is more weighted towards the surface, it is more distributed vertically in the atmosphere. On the other hand, NO_2 column is heavily weighted towards the surface and drops heavily with increasing altitude. So the tropospheric column $HCHO/NO_2$ ratio might not accurately reflect the condition at the ground. This shows that while satellite measurements have wide global coverage, for accurate air quality policy panning in the local level, near surface trace gas measurements are required to report the conditions on the ground. The MAX-DOAS technique and the Pandonia Global Network can be very useful for that purpose.

Chapter 5

Vertical Mixing Layer Height Estimation using Water Vapor Vertical Profiles from MAX-DOAS Measurements

5.1 Goals and Motivation

Air pollution has become one of the major environmental issues in urban areas because of it's detrimental effects on human health [Rückerl et al., 2011, Lelieveld et al., 2015]. Large emissions from industry, traffic and heating can rapidly increase air pollution. This is especially problematic when the emitted gases are trapped below the mixing layer. That's why MLH is considered to be an important parameter for air pollution characterization along with different emission sources, meteorological conditions, transport and deposition. Several studies have been carried out to investigate the relationship between the mixing layer height (MLH) and air quality and especially about it's impact on public health [Schäfer et al., 2006, Geiß et al., 2017]. The height of the boundary layer has been shown to be correlated with trace gas and aerosol concentrations, especially ozone [Geiß et al., 2017]. In this study, we measure vertical profiles of water vapor mixing ratio by using Pandora MAX-DOAS measurements [Nowak et al., 2020]. Then the vertical profiles are analyzed for sharp gradients which signifies the mixing layer height. Finally, The MAX-DOAS MLH retrievals are compared with MLH derived from co-located Ceilometer aerosol backscattered measurements.

The main goals of this study are to (1) develop a methodology for estimating Mixing layer heights (MLH) from water vapor vertical profiles and (2) validate Pandora MAX-DOAS measured MLH with collocated ceilometer measurements.

5.2 Water vapor (H_2O) near surface concentrations

Water vapor near surface concentrations have been derived from Pandora MAX-DOAS measurements by using equation 4.2. The DOAS fitting parameters for H_2O retrieval are,

- Wavelength window: 425-497 nm
- Polynomial Order: 5
- Offset order: 1
- O_3 cross-section: [Serdyuchenko et al., 2014], quadratic temperature model.
- O_2O_2 cross-section: [Thalman and Volkamer, 2013], 293K.
- NO_2 cross-section: [Vandaele et al., 1998], 298K.
- H_2O cross-section: [Rothman et al., 2010], 296K.
- Ring cross-section: [Chance and Spurr, 1997]

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Figure 5.1: H_2O surface volume mixing ratios measured by Aerodyne QCL and Pandora 60 (MAX-DOAS) at Westport, CT during the LISTOS 2018 campaign for August 24 to September 03, 2018.

Figure 5.2 shows H_2O surface volume mixing ratios measured by Aerodyne QCL and Pandora 60 MAX-DOAS at Westport, CT during the LISTOS 2018 campaign. Figure 5.1 shows the correlation between Aerodyne QCL and Pandora 60 MAX-DOAS measurements. Strong linear correlation was observed with a slope of 0.95 and R^2 of 0.74, although the MAX-DOAS systematically underestimates the in-situ measurements by around 3.5 parts per thousand.

MAX-DOAS measurements generally show the averaged concentration over a certain height



Comparison of In-situ and MAX-DOAS measurements at Westport,CT (LISTOS, 2018)

Figure 5.2: H_2O surface volume mixing ratios measured by Aerodyne QCL and Pandora 60 MAX-DOAS at Westport, CT during the LISTOS 2018 campaign.

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in the boundary layer, where the in-situ measurements represent a point at the ground. This is one of the potential reasons for the systematic underestimation. The method also assumes similar O_4 and H_2O profile shape in the boundary layer which might not always be the case. This can also contribute to the systematic underestimation of MAX-DOAS H_2O measurements.

The good linear correlation between in-situ and Pandora MAX-DOAS Water vapor near surface concentration provides confidence in it's ability to measure water vapor concentrations properly. This is particularly important because water vapor vertical profiles measured by the MAX-DOAS technique are used to estimate Mixing layer heights (MLH).

5.3 Water vapor (H_2O) profiles

 H_2O vertical profiles were generated from MAX-DOAS measurements by using the realtime algorithm [Frieß et al., 2019, Tirpitz et al., 2021]. The zenith measurements at the beginning and the end of a scan is averaged and used as a reference spectrum for that particular scan. The number of vertical layers is same as the number of elevation angles. The measured vertical profiles are then linearly interpolated from 100 m to 2.5 km and temporally interpolated on a 30 minute time grid. Measurements with solar zenith angle larger than 75 degrees were excluded from the analysis because of high measurement uncertainties. The QDOAS software [Danckaert et al., 2012a] was used for DOAS fitting.

The QDOAS software analyzes the measured spectra and then produces the O_2O_2 and H_2O differential slant column densities (ΔSCD) for different elevation angles. then the Real time algorithm is used to convert water vapor differential slant column densities ΔSCD_{H_2O} into vertical profiles with units of volume mixing ratio (parts per thousand). Because water vapor is abundant in the lower troposphere, a very detailed profile can be measured. Figure



Figure 5.3: H_2O vertical profiles at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign.

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5.3 shows H_2O vertical profiles at Westport, CT from Pandora MAX-DOAS measurements during the LISTOS 2018 campaign. Additional data products used in retrieval are,

- Ground in-situ meteorological data (temperature, pressure etc.).
- Vertical temperature and pressure profiles from radiosondes.
- O₂O₂ air mass factors (AMF) were pre-computed by using a radiative transport model called VLIDORT [Spurr, 2008] for pure Rayleigh atmosphere (No aerosols).

In early morning hours, the mixing layer is relatively shallow which is a remains of the nocturnal stable layer from the previous night. This is quite evident in the H_2O vertical profiles generated from Pandora MAX-DOAS measurements (figure 5.3). There is also a residual layer just above the mixing layer in the early morning hours. As the day progresses, heating due to solar radiation produces convection and mixing and the mixing layer starts to rise. From MAX-DOAS profiles, two distinct boundaries can be observed (figure 5.3). The first one is close to the ground where water vapor mixing ratio is large (greater than 20 parts per thousand) and this first gradient is generally considered as the mixing layer height where equal mixing take place. The water vapor mixing ratio keep decreasing as height increases and there is another gradient where it again drops sharply (lower than 10 parts per thousand) and this boundary can be considered as the planetary boundary layer height. Because water vapor mixing ratio decreases sharply at the mixing layer height, the H_2O vertical profile can be analyzed to identify that height. The water vapor vertical profile can also be compared to aerosol backscattered profiles measured by the Ceilometer. There should be similarities between them since both aerosol and water vapor take a sharp decrease at the mixing layer boundary. Although this technique may face limitations for detecting mixing layer in polar or desert conditions, where the amount of water vapor present in the atmosphere is low.

There are different methods for estimating MLH by analysing the vertical water vapor profiles such as location of minimum vertical gradient of specific humidity, minimum vertical gradient of relative humidity [Seidel et al., 2010]. The gradient method and the variance method provides the same result for water vapor profiles according to a study by [Lammert and Bösenberg, 2006]. In this study, the wavelet method [Gamage and Hagelberg, 1993] has been used which is one of the most widely used method for MLH determination. More details about the wavelet method is described in section 5.4.

5.4 Wavelet Covariance Transform

The wavelet covariance transform is a method that can be used to detect sharp gradients in atmospheric profiles [Davis et al., 2000]. It has been applied extensively to lidar backscattered profiles to detect mixing layer height [Cohn and Angevine, 2000, Brooks, 2003]. The haar step function can be defined as,

$$h(\frac{z-b}{a}) = 1; \quad b - \frac{a}{2} \le z \le b$$
 (5.1)

$$h(\frac{z-b}{a}) = -1; \quad b \ge z \le b + \frac{a}{2}$$
 (5.2)

$$h(\frac{z-b}{a}) = 0; \quad elsewhere \tag{5.3}$$

Then a wavelet covariance transform is used to convolute the haar wavelet function with the atmospheric profile [Gamage and Hagelberg, 1993],

$$W_f(a,b) = \frac{1}{a} \int_{z_{bottom}}^{z_{top}} f(z) h(\frac{z-b}{a}) dz$$
 (5.4)

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Here, f(z) is the atmospheric profile, *a* is dilation, *b* is the translation and *z* is the altitude. z_{top} and z_{bottom} signifies the top and the bottom of the atmospheric profile. By applying a fixed dilation on different translation points along the atmospheric profile, a covariance transform profile is generated. Using a small dilation length can produce a disordered covariance transform profile because of errors in the measurements. Here, an iterative algorithm is used to determine dilation length which was first proposed by [Brooks, 2003] and later updated by [Grabon et al., 2010]. The wavelet method is generally applied on a regular equispaced grid and that's why water vapor vertical profiles have been linearly interpolated from the altitude of 100 m to 2.5 km.

5.5 Application of Wavelet Method on MAX-DOAS derived H_2O profiles

The choice of dilation length (denoted by a) and translation (denoted by b) are one of the most important parameters in wavelet method. The choice of be determines the range where the wavelet covariance transform is applied in the vertical profile. The dilation length is the length of the haar wavelet function that is applied on the atmospheric vertical profile. A small dilation length can produce a lot of local minimums as it picks up small differences in the profile. A large dilation length produces local minimums at the largest gradients in the profile. For our analysis, b ranges from 100m to 1800 m. The dilation length is varied depending on the time of the day.

The morning PBL is highly stratified, this happens because at night a nocturnal stable layer forms close to the ground and another residual layer forms which is the remains from the PBL from the previous day. To correctly determine the stable layer in the early morning hours, it is important to limit the maximum height up to which the wavelet algorithm is applied [Caicedo et al., 2020]. From 0700 to 1000 local time, the maximum height for the retrieval is 500 m and the dilation length is 100 m. There is a rapid growth period after that when the stable layer begins to rise rapidly due convection [Stull, 2012]. From 1000 to 1200 local time, the the maximum height for the retrieval is increased to 1000 m and the dilation length is raised to 200 m. From 1200 to sunset, the atmosphere should be well-mixed and the maximum height for the retrieval is raised to 1600 m which is close to the typical highest range for Pandora MAX-DOAS trace gas profile measurements. For this range a dilation length of 300 m is used.

5.6 Sensitivity Study for Uncertainty Estimation

The uncertainty for this method can be estimated by using a range of dilations for the haar covariance transform. If the profile contains a lot of variations, the a low dilation value will be able to locate that variation. On the other hand, a large dilation value will only locate the major variations in the profile. By using a range of different dilation values, different MLH can be calculated for each dilation and finally a mean and standard deviation can be determined. If the standard deviation is high, then that will mean that there are a lot of variations in the atmospheric profile. The standard deviation is a good metric for MLH uncertainty and can be used for filtering the data.

Table 5.1 shows the parameters used for sensitivity study regarding dilation length. In addition to the center dilation, a range of other dilations both smaller and larger are used to calculate the mixing layer height for each different dilation. Using different dilation produces a range of individual mixing layer height. The variation is this range is a good indicator of the uncertainty that comes from choosing a dilation length. The mean from this range

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Time Period	Maximum Height	Center Dilation	Range of Dilation
(local time)	(m)	(m)	(m)
0700-1000	600	100	$60,\!80,\!100,\!120,\!140$
1000-1200	900	100	$60,\!80,\!100,\!120,\!140$
1200-1700	1600	300	200, 220, 240, 260, 280, 300
			$320,\!340,\!360,\!380,\!400$

Table 5.1: Sensitivity study parameters for different dilation.

of MLH is chosen as the mixing layer height and the uncertainty is given by the standard deviation from this range.

5.7 MLH derived from Pandora MAX-DOAS H_2O pro-



files

Figure 5.4: H_2O vertical profiles (left) and Ceilometer aerosol backscattered profiles (right) at Westport, CT from Pandora MAX-DOAS measurements on August 08, 2018. Ceilometer detected MLH is indicated by white dots and MLH detected by wavelet covariance method is shown in black dots with error bars.

The Vaisala CL51 ceilometer were used to measure aerosol backcattered signal at Westport, CT during the LISTOS campaign. It uses 910 nm wavelength for measurements, the vertical resolution is 10 m and temporal resolution is 36 seconds. It can measure up to 15 km



Figure 5.5: H_2O vertical profiles (left) and Ceilometer aerosol backscattered profiles (right) at Westport, CT from Pandora MAX-DOAS measurements on September 03, 2018. Ceilometer detected MLH is indicated by white dots and MLH detected by wavelet co-variance method is shown in black dots with error bars.



Figure 5.6: H_2O vertical profiles (left) and Ceilometer aerosol backscattered profiles (right) at Westport, CT from Pandora MAX-DOAS measurements on August 06, 2018. Ceilometer detected MLH is indicated by white dots and MLH detected by wavelet covariance method is shown in black dots with error bars.

vertically [Knepp et al., 2017]. Aerosol backscatter lidars typically have a vertical height resolution of 10 m whereas MAX-DOAS measurements typically have 100-200 m resolution depending on the atmospheric conditions. LIDARs can take a measurement in 30s, but MAX-DOAS usually takes around 9 minutes for a full profile scan. Which mean that it takes 9 minutes to produce a full water vapor profile. Chapter 5. Vertical Mixing Layer Height Estimation using Water Vapor Vertical Profiles 104 from MAX-DOAS Measurements



Figure 5.7: H_2O vertical profiles (left) and Ceilometer aerosol backscattered profiles (right) at Westport, CT from Pandora MAX-DOAS measurements on August 24, 2018. Ceilometer detected MLH is indicated by white dots and MLH detected by wavelet covariance method is shown in black dots with error bars.



Figure 5.8: H_2O vertical profiles (left) and Ceilometer aerosol backscattered profiles (right) at Westport, CT from Pandora MAX-DOAS measurements on July 31, 2018. Ceilometer detected MLH is indicated by white dots and MLH detected by wavelet covariance method is shown in black dots with error bars.

Figure 5.4 shows H_2O vertical profiles and Ceilometer aerosol backscattered profiles at Westport, CT. Ceilometer detected MLH is indicated by black dots with error bars and MLH detected by wavelet covariance method is shown in red open circles. The PBL is stratified for August 08. In the morning, a sharp gradient can be shown close to the ground at 300 - 400 m and the wavelet method detects it as the mixing layer height. This is typically a shallow



Figure 5.9: H_2O vertical profiles (left) and Ceilometer aerosol backscattered profiles (right) at Westport, CT from Pandora MAX-DOAS measurements on August 25, 2018. Ceilometer detected MLH is indicated by white dots and MLH detected by wavelet covariance method is shown in black dots with error bars.



Figure 5.10: H_2O vertical profiles (left) and Ceilometer aerosol backscattered profiles (right) at Westport, CT from Pandora MAX-DOAS measurements on September 01, 2018. Ceilometer detected MLH is indicated by white dots and MLH detected by wavelet covariance method is shown in black dots with error bars.

layer which is a remnant of the nocturnal stable layer from previous night. Another final gradient can be noticed at 1000 m which is the residual of the mixing layer from previous day and it forms the boundary with the free troposphere. As mixing conditions increases due to solar heating, the mixing layer increases to 800 m at late afternoon. The final gradient and the boundary with free troposphere rises to 1500 m. Similar pattern can also be seen

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Figure 5.11: H_2O vertical profiles (left) and Ceilometer aerosol backscattered profiles (right) at Westport, CT from Pandora MAX-DOAS measurements on September 02, 2018. Ceilometer detected MLH is indicated by white dots and MLH detected by wavelet covariance method is shown in black dots with error bars.

in figure 5.5 for September 03 and figure 5.6 for August 6. The mixing layer is low in the morning and rises as the day progresses with another gradient at the top. For September 03, the ceilometer and Pandora agrees well with each other from 0700 - 1500 local time. After that, Pandora detected MLH is higher than Ceilometer MLH, potentially due to measuring an elevated layer.

On the other hand, August 24 (figure 5.7) shows only a single sharp gradient close to the ground around 200 m. July 31 (figure 5.8) also shows the same pattern of a single gradient but at a little bit higher around 500 m at the morning and then rising. This behavior can generally be seen at days when the water vapor concentration is lower than general.

Ceilometer has the ability to detect lower near surface layers more effectively than MAX-DOAS measurements. Figure 5.9 shows measurements for August 25 where Ceilometer and MAX-DOAS agrees well with each other in the morning. But after that Pandora MAX-DOAS measurements detect an elevated layer whereas the Ceilometer detects a layer that is further close to the ground. MAX-DOAS measurements are susceptible to high levels of uncertainty in cloudy or rainy conditions. This happens because the presence of cloud changes the scattering conditions in the atmosphere. Figure 5.10 and 5.11 shows two days with cloudy conditions. The presence of cloud can be determined here by looking at the Ceilometer aerosol backscattered profiles, dark red values indicates cloud presence in these profiles. The agreement between Pandora and Ceilometer is generally not good for cloudy conditions. For September 01, Pandora underestimates the MLH all throughout the day. Same pattern can also be seen in the morning of September 02, although later in the day after the mixing layer gets elevated, it does agree reasonably with Ceilometer measurements.

In these figures, there are a few points with large error bars for MAX-DOAS derived MLH. It indicates the presence of multiple layers for those water vapor profiles. In that case, different dilation values produce a range of possible MLH values which increases the uncertainty of the derived mean MLH. For majority of the MAX-DOAS MLH retrievals, the error bars are quite small to notice in the plots, which indicates a single gradient for most of the MAX-DOAS water vapor vertical profiles.

5.8 Comparison with water vapor profiles from Ozonesondes

An Ozonesonde is a balloon-borne instrument which is launched from the ground. As it rises up through the atmosphere, it performs in-situ measurements of ozone concentration and different meteorological properties like, temperature, pressure and humidity. Water vapor profile can be derived from the different meteorological properties measured by the Ozonesonde. There were a few Ozonesondes launch at Westport, CT during the LISTOS Chapter 5. Vertical Mixing Layer Height Estimation using Water Vapor Vertical Profiles 108 from MAX-DOAS Measurements

2018 campaign. The instrument were launched on July 16, July 19, August 05, August 06 and August 07. So, there are only three days in common (August 05-07) between the Pandora MAX-DOAS measurements and Ozonesonde launches.



Figure 5.12: Comparison of water vapor vertical profiles from Pandora MAX-DOAS and Ozonesondes (the green dashed line indicates MLH detected from MAX-DOAS measurements and the blue dashed line indicates the largest gradient of the Ozonesondes water vapor profile.)

Figure 5.12 and 5.13 shows several water vapor profiles derived from Ozonesonde launches from four different instances on August 05, 06 and 07. It is compared with the nearest water vapor vertical profile measurements from Pandora MAX-DOAS measurements, the blue dashed line indicates the MLH detected by the wavelet covariance transform method. Pandora MAX-DOAS water vapor profiles generally underestimates the Ozonesondes observations by around 20% - 40%. The sensitivity of MAX-DOAS measurements decrease with increase in altitude, so the gap between Pandora and Ozonesondes water vapor concentrations also increases with height. Even if the amount is lower, there are similarities between the characteristics of water vapor profiles measured by these two methods, both generally



Figure 5.13: Comparison of water vapor vertical profiles from Pandora MAX-DOAS and Ozonesondes (the green dashed line indicates MLH detected from MAX-DOAS measurements and the blue dashed line indicates the largest gradient of the Ozonesondes water vapor profile.)

follow the same pattern. Since the wavelet method detects gradients in the water vapor profiles, so even if water vapor concentrations from Pandora are lower, it is able to detect MLH from the water vapor profiles since the characteristics are alike.

5.9 Comparison between Pandora MAX-DOAS MLH and Ceilometer MLH

A linear regression analysis was performed between MLH retrieved by Pandora MAX-DOAS measurements and MLH retrieved by Ceilometer measurements. For quality purposes, only those Ceilometer data were included for which the uncertainty is less then 10 percent of the MLH value for both Ceilometer and Pandora measurements. Figure 5.14 (a) shows the

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comparison between the two methods for 0700 to 1700 local time (eastern standard time). They agree reasonably with each other with a slope of 0.64 and a r (correlation coefficient) value of 0.68 and a median difference of 29.73%. The histogram shows the difference from Ceilometer measurements in figure 5.14 (b), 50% of MAX-DOAS MLH retrievals fall within $\pm 25\%$ of Ceilometer retrievals and about 72% Pandora measurements are within $\pm 50\%$ of the Ceilometer measurements.



Figure 5.14: Comparison of mixing layer height (MLH) derived by Ceilometer and Pandora MAX-DOAS at Westport, CT for cloud free days for 0700-1700 local standard time, (a) linear regression analysis, (b) histogram of difference from Ceilometer measurements.

Figure 5.15, 5.16 and 5.17 shows further comparisons for 0800-1600, 0900-1500 and 1000-1400 local standard time. It can be observed that the correlation coefficient improves to 0.73, 0.75 and 0.76 for these time periods and the median difference decreases to 21.96%, 17.29% and 19.7%. For 0900-1500 local standard time, 65% of MAX-DOAS MLH retrievals fall within $\pm 25\%$ of Ceilometer retrievals and about 75% Pandora measurements are within $\pm 50\%$ of the Ceilometer measurements. So the agreement between these two methods get better as the solar zenith angle gets lower. In a few cases, MAX-DOAS measurements detect



Figure 5.15: Comparison of mixing layer height (MLH) derived by Ceilometer and Pandora MAX-DOAS at Westport, CT for cloud free days for 0800-1600 local standard time, (a) linear regression analysis, (b) histogram of difference from Ceilometer measurements.



Figure 5.16: Comparison of mixing layer height (MLH) derived by Ceilometer and Pandora MAX-DOAS at Westport, CT for cloud free days for 0900-1500 local standard time, (a) linear regression analysis, (b) histogram of difference from Ceilometer measurements.

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Figure 5.17: Comparison of mixing layer height (MLH) derived by Ceilometer and Pandora MAX-DOAS at Westport, CT for cloud free days for 1000-1400 local standard time, (a) linear regression analysis, (b) histogram of difference from Ceilometer measurements.

an elevated layer whereas the Ceilometer detects a layer that is further close to the ground, which produces some large negative differences in the histogram plots of figure 5.14 to 5.17.

Table 5.2: Results of linear regression analysis between Pandora MAX-DOAS and Ceilometer measurements for different time intervals (local standard time)

Parameters	0700-1700	0800-1600	0900-1500	1000-1400
Number of points	68	57	42	30
r	0.68	0.73	0.75	0.76
Slope	0.64	0.65	0.61	0.59
Median Absolute Difference [%]	29.73	21.96	17.29	19.7

Table 5.2 summarizes the linear regression analysis between Pandora MAX-DOAS and Ceilometer for different time intervals. It indicates that measurements performed during high solar zenith angle have less agreement than measurements having shorter solar zenith angles. The correlation coefficient increases and median absolute difference decreases between these two methods as the solar zenith angle is decreased. It can be explained by the fact that the error for MAX-DOAS measurements increases with increase in solar zenith angle. So early morning and late afternoon observations are more prone to higher errors.

The histogram of all the different time periods shows outliers skewed predominantly negatively compared to Ceilometer MLH measurements. This indicates that for these values, Pandora MAX-DOAS derived MLH values are quite higher than Ceilometer MLH. Since Ceilometer have better spatial resolution, it's able to pick up shallow near surface layers more effectively. Sometime Pandora MLH retrieval are unable to detect those shallow layers and picks up an elevated layer causing the outliers. The outliers also reduce with solar zenith angle decrease.

The Ceilometer is pointed vertically straight at the zenith directions whereas the Pandora MAX-DOAS instrument is pointed diagonally at the horizon at different elevation angles. So even though both instruments are at the same location, they are pointed at the same direction. Also as discussed earlier, MAX-DOAS instruments have different vertical and temporal resolution than aerosol backscatter lidar measurements. A Ceilometer typically have a height resolution of 10 m where as MAX-DOAS measurements typically have 100-200 m resolution. Ceilometer can take a measurement in 30 seconds which are usually averaged for a 15 minute interval. On the other hand, MAX-DOAS usually takes around 9-10 minutes for a full profile scan. Even with this difference, the agreement is quite good between both methods.

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5.10 Discussion

Gradients in water vapor profile is a widely used indicator of MLH height and used in other instruments such as radiosondes and lidar. The haar wavelet covariance transform method were applied on the water vapor vertical profiles which detects the MLH height by estimating the location of the sharpest gradient in the water vapor vertical profiles. The MLH product derived from MAX-DOAS is consistent with boundary layer meteorology. It can detect the trace of nocturnal stable layer from previous night at early morning hours. As solar heating creates convection, The MLH rises up as the day progresses.

MLH retrieved from Pandora MAX-DOAS measurements were then compared with collocated Ceilometer aerosol backscaterred MLH for different time intervals during the day. In a detailed comparison study among different MLH measurment methods, it was observed that different methods can produce different MLH heights [Seidel et al., 2010] with a low but statistically significant correlation coefficient (around 0.5). For this study, the correlation coefficient varies from 0.68 - 0.76 with a median absolute difference of 17.29% - 29.73%, which indicates reasonable agreement between these two methods. The Ceilometer points straight at the zenith, but the MAX-DOAS method scan the horizon at different elevation angles, which means sometimes they are observing different air masses which introduces more disagreement. Different spatial and temporal resolution are some other potential reasons for disagreement between these two methods.

Using a Pandora spectrometer system for MLH detection provides a huge advantage in scalability and deployment. There are hundreds of Pandora spectrometer systems located around the world which can use this method for detecting the mixing layer height concurrently with trace gas measurements. It can also be used as a comparison tool for MLH detection for other instruments.

Chapter 6

Spatial Trace Gas Distribution Heterogeneity Near a Major Airport(ATL)

6.1 Goals and Motivation

Airports are one of the major sources of air pollution at major cities because of their close distance from city centers [Ratliff et al., 2009]. Although aircraft exhaust emissions are generally the primary focus for airport pollution controls, there are several other major sources such as the auxiliary power units, equipment for ground operation, airport transportation systems and vehicular traffic [Masiol and Harrison, 2014] that contributes to air pollution at the airport. Majority of aircraft exhaust emissions are actually emitted at the cruising altitude. Direct emissions from aircraft exhausts generally consists of Carbon Dioxide (CO_2), Carbon Monoxide (CO), Water vapor (H_2O), Oxides of Nitrogen (NO_x), Hydrocarbons, particulate matters, Sulfur Dioxide (SO_2) and Soot.

Since most major airports are located close to cities, it can be difficult to distinguish pollution coming from different sources like industry and traffic. High levels of NO_2 is a particular concern for airport air quality because it has a lot of different sources at the urban envi116 Chapter 6. Spatial Trace Gas Distribution Heterogeneity Near a Major Airport(ATL)

ronment.Vehicular traffic were found to be the dominant source for NO_x emissions at Los Angeles airport [Yu et al., 2004] and Berlin airport [Suppan and Graf, 2000].

The main goal of this study is to evaluate the spatial heterogeneity of NO_2 and HCHO at the Atlanta Hartsfield–Jackson International Airport.

6.2 Observations

This experiment focuses on the city of Atlanta, which has the busiest airport in the world [Kaiser et al., 2020]. The airport is located 11 km south from the Atlanta downtown area.

The Pandora 168 instrument was located at a branch of Georgia Environmental Protection Division, about 1 km east of the airport (33.7790° N, -84.3958° W, 291 meter above sea level). Figure 6.1 shows the location of the instrument compared to the Atlanta downtown and the airport. Pandora 168 performed MAX-DOAS measurements at different azimuth angles for comparing between the pollution at the airport and background direction. The instrument was pointed at 20° azimuth angle to look at the background. Then the airport was scanned at four different azimuth angles (262°, 267°, 273° and 278°) to observe pollutions from the airport.

6.3 Cloud Screening

Passive DOAS measurements are impacted by the presence of clouds in the sky. This is especially a hindrance for MAX-DOAS measurements where the presence of clouds can change the scattering conditions of the atmosphere which can be hard to quantify [Hönninger et al., 2004, Platt and Stutz, 2008]. This is why an ALL Sky Imager (ASI-16) was installed



Figure 6.1: Pandora 168 instrument location compared to the background and the airport.

at Atlanta. It has a fish-eye lens which has a field of view of 180° .

The camera comes with the Findclouds software package which calculates the cloud fraction of the image. The parameter cloudiness covers a range from 0 to 1, where 0 is cloudless





Figure 6.2: Full sky image taken by the all sky imager, (a) camera image (10 May, 2020), (b) software evaluated image (10 May, 2020), (c) camera image (16 May, 2020), (d) software evaluated image (16 May, 2020).

sky and 1 is for completely covered sky. The BRBG algorithm is used for this retrieval, which takes the blue/red and blue/green ratio of the observation. The presence of clouds and aerosols increase the blue/red difference [Ghonima et al., 2012]. Then the cloudiness is assigned based on a RGB threshold [Feng et al., 2019]. It also creates a sunmask to cover the position of the sun which is calculated from image time and location coordinates of the instrument. Figure 6.2 shows two examples of an image taken by camera (left) and the software evaluated image (right) for cloudiness calculation.



Figure 6.3: Cloud fraction calculated by the Findclouds software from May 10-16, 2020 (0800-2000 local standard time).

Images were taken by the all sky imager from May 04,2020 to May 16, 2021. The images were then processed with the findclouds software to generate the cloudiness of each image. The cloud fraction database will be used to subset the data into various cloud conditions to evaluate the Pandora measurements based on cloud level. Figure 6.3 shows cloud fraction calculated by the software from May 10-16, 2020. The software faces difficulty to distinguish between the trees on the horizon and the clouds. So, generally an offset of 0.1 is added to the cloudiness fraction because of tree coverings in the images.

6.4 BlickP Processing

The raw measurements data (L0) have been processed by using the Blick processing software (BlickP). It converts the L0 file to L1 file after applying all instrumental corrections. Then

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the L1 file is converted into L2fit file which contains slant column densities for different elevation angle measurements. The "s-code" signifies the "L1 configuration" which consists of a series of different parameters. The "qs-code" refers to how the data quality flag is produced for the L1 data. The "f-code" describes the fitting setup for the retrieval of L2Fit data by the Blick software. The "qf-code" refers to how the data quality flag is produced for the L2Fit data. The settings used for data processing is described below,

Type	Name	Description
<u>1</u>		
s-code	mca0	All corrections applied
qs-code	st00	Original standard L1 correction quality limits
f-code	fuh5	Sky U340 HCHO setup referencing to smallest viewing
		zenith angle, O_2O_2 cross-section changed
f-code	nuh1	Sky U340 NO2 setup referencing to smallest viewing
		zenith angle, O_2O_2 cross-section changed
qf-code	fuh0	Sky HCHO setup referencing to smallest viewing zenith
		angle quality limits
qf-code	nvh00	Sky NO2 setup referencing to smallest viewing zenith
		angle quality limits

Table 6.1: Codes and Description for BlickP

6.5 NO₂ and HCHO profiles in Atlanta during the COVID19 pandemic

For airports located in major cities, one of the main challenge is to distinguish between city background pollution and emissions generated from the airport. MAX-DOAS measurements have an advantage in this regard, since it can perform measurements at different azimuth angles which provides a three dimensional spatiotemporal representation. Here, when the instrument is pointed at three different directions, at the background (20° azimuth angle), at airport north side (273° azimuth angle) and at the airport south side (262° azimuth angle). Then measurements at different azimuth angles are compared to find spatial differences.



Figure 6.4: NO_2 vertical profiles at the Atlanta airport for 20° azimuth angle (background), 262° azimuth angle (airport south) and 273° azimuth angle (airport north).



Figure 6.5: NO_2 vertical profiles at the Atlanta airport for 20° azimuth angle (background), 262° azimuth angle (airport south) and 273° azimuth angle (airport north).

Figure 6.4 and 6.5 shows two days with high levels of NO_2 at Atlanta. It is quite clear that the amounts of NO_2 is much higher in the airport direction than the background. This could be due to anthropogenic emissions from aircraft exhausts, airport activities and vehicular traffic to and from the airport. This illustrates that it is possible to differentiate between
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NO_2 concentrations at the airport and the background.

Figure 6.6: HCHO vertical profiles at the Atlanta airport for 20° azimuth angle (background) and 262° azimuth angle (airport south).





The same kind of analysis can also be done on HCHO vertical profiles. Figure 6.6 and 6.7 shows HCHO vertical profiles at the background and at the airport. Interestingly, no difference is observed in HCHO amounts between them. This happens due to the difference

of production regimes of these two different trace gases. Since the primary source of NO_2 is anthropogenic, it is elevated in the airport direction due to increased transportation activities such as aircraft and on road vehicular emissions in that area. On the other hand, *HCHO* is mainly produced photochemically, so since the airport is fairly closed to the background, it can be assumed that the photochemical conditions are nearly the same, so amount of *HCHO* production is also quite identical.

6.6 NO₂ and HCHO columns in Atlanta during the COVID-19 pandemic

The difference between the airport and the background concentration can further be investigated by looking at the tropospheric column of NO_2 and HCHO. For identifying the time periods when there were low horizontal atmospheric transport, the data has been filtered for low wind speed (< 1.5 m/s). Also since MAX-DOAS measurements are sensitive to clouds, the data is further filtered for low cloudiness fraction (< 25%) measured by an all-sky camera.

The hourly mean column for NO_2 (June 01 - December 31, 2020) is shown in figure 6.8 for the background and the airport. It is observed that NO_2 tropospheric column at the airport is constantly elevated throughout the day compared to the background. There is also a good correlation between the diurnal pattern at both these locations.

Figure 6.9 shows the hourly mean column for HCHO (June 01 - December 31, 2020) is shown in figure 6.8 at the background and the airport. HCHO tropospheric column is nearly the same in both locations during the middle of the day. In early morning and late afternoon hours, HCHO is slightly elevated in the background.



Figure 6.8: Hourly mean of NO_2 tropospheric column at the airport and the background (June - December, 2020).



Figure 6.9: Hourly mean of *HCHO* tropospheric column at the airport and the background (June - December, 2020).



Figure 6.10: Histogram of NO_2 tropospheric column difference between the airport and the background (June - December, 2020).



Figure 6.11: Histogram of HCHO tropospheric column difference between the airport and the background (June - December, 2020).

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Figure 6.10 shows a histogram of NO_2 tropospheric column difference between the airport and the background (June - December, 2020). The distribution is skewed in the right direction which indicates that NO_2 concentrations are higher in the airport direction than in the background. From June 01 - December 31 2020, the NO_2 tropospheric column at the direction of the airport were 51% higher than the city background on average. On the other hand, figure 6.11 shows a histogram of HCHO tropospheric column for the same time period. The distribution looks is symmetric and the HCHO tropospheric column at the airport direction were 7% lower than the background on average.

The difference between NO_2 and HCHO levels at the airport can be explained by the production regime of these two gases. The main source of NO_2 in anthropogenic emissions, so it is higher at the airport where a lot of emission sources are present including aircraft exhaust, ground support equipment, airport traffic etc. On the other hand, HCHO is driven by photochemistry and since the background and the airport is close, it can be assumed that they have the same photochemical conditions, so HCHO concentrations are also roughly the same. Because of the presence of high biogenic VOCs (specially isoprene) in southeastern USA, Atlanta has one of the highest HCHO levels in the country [Palmer et al., 2001]. This could be another factor behind why it's hard to distinguish HCHO amounts between the background and the airport.

6.7 Discussion

MAX-DOAS measurements at different azimuth angles provides a three dimensional representation of trace gas concentrations and can be used to observe and compare air pollution at different directions. This method was applied at The Hartsfield-Jackson Atlanta International Airport to observe NO_2 and HCHO tropospheric column and vertical profiles at different directions. One direction was used to measure the background pollution and the other directions were pointed at the airport. It was observed that NO_2 tropospheric columns at the direction of the airport were in average 51% higher than the background showing the effect of different anthropogenic sources surrounding the airport. However, HCHO tropospheric column, which is also a marker for VOC production, was almost same at both the background and the airport. This provides a unique insight into the difference between these two precursors of near surface ozone production. Because of similar photochemical conditions at both the background and the airport, HCHO tropospheric columns is also roughly the same. But the impact of anthropogenic emissions can be seen by looking at NO_2 tropospheric columns at the direction of the airport. Further works need to be performed by analyzing meteorological conditions and traffic volume for full characterization and quantification of different emission sources.

Chapter 7

Conclusions

Different applications of the MAX-DOAS technique have been presented in this thesis for better characterizing tropospheric chemistry and to improve near surface air quality monitoring. As an indicator of VOC oxidation, HCHO is an important trace species in the troposphere which can be used to improve characterization of tropospheric ozone production regimes. However, there are significant systematic uncertainties about HCHO measurements in the atmosphere by using the DOAS method. A detailed sensitivity study was conducted where HCHO slant columns calculated using the DOAS technique were varied depending on polynomial order, offset order, molecular absorption cross sections and fitting window. The systematic error of 22% for HCHO tropospheric column and 20% for HCHO near surface concentration illustrates that HCHO measurements by the DOAS technique can vary widely depending on the fitting parameter used. To reduce uncertainty and provide steady variability, the case that most closely resembles the median of the range is selected and recommended as base case. A base case with the wavelength range of 328.5 - 359 nm has been recommended based on the sensitivity study. In addition, a real time analytical method to calculate HCHO near surface volume mixing ratio is presented where radiative transfer modelling is not required. The HCHO near surface volume mixing ratio calculated by MAX-DOAS is compared with surface HCHO measured by the ground in-situ instrument. The Pandora MAX-DOAS agrees very well with the ground in-situ instrument for the whole campaign $(R^2 = 0.83, \text{ slope} = 0.92)$ and provides excellent agreement for clear days $(R^2 =$ 0.88, slope=0.95). This fulfils the first objective of this thesis by estimating the accuracy of *HCHO* MAX-DOAS measurements and validating near surface concentration measurements.

A methodology is presented for calculating Mixing Layer Heights (MLH) from water vapor profiles measured by the Pandora MAX-DOAS measurements. By using the wavelet covariance transform method, the sharpest gradient in the water vapor profiles are calculated to estimate the MLH. The results were compared with a collocated Ceilometer retrievals which uses gradients in the aerosol profile to detect MLH. Pandora MAX-DOAS agrees well with Ceilometer measurements for different time intervals during the day with a correlation coefficient of 0.68 to 0.76 and a median absolute difference of 17.29% to 29.73%. This achieves the second objective of this thesis by characterizing the vertical mixing in the lowest portion of the atmosphere. Although MAX-DOAS can not perform measurements at night and Pandora MLH retrievals have lower spatial and temporal resolution than Ceilometer measurements, using a Pandora spectrometer system for MLH detection provides a huge advantage in scalability and deployment. There are hundreds of Pandora spectrometer systems located around the world which can use this method for detecting the mixing layer height concurrently with trace gas measurements, without any additional instrumentation.

 NO_2 and *HCHO* tropospheric columns and vertical profiles measured at the Hartsfield-Jackson Atlanta International Airport were also presented. Airports are a major source of near surface air pollution in a lot of major cities around the world. By using the ability to scan at different azimuth angles, Pandora MAX-DOAS can distinguish between air pollution from different directions. It also provides useful information about the vertical distribution of different trace gases. It was observed that NO_2 tropospheric columns are 51% higher at the direction of the airport compared to the background, but the *HCHO* tropospheric column is almost the same at both locations. This indicates the difference in the production regime of these two species, NO_2 is produced primarily from human activities, so it is elevated at the direction of the airport due to increased anthropogenic emissions. But *HCHO* is mainly produced from photochemical conditions, so it is same in both the background and the airport direction due to close proximity with each other. It demonstrates further about the capability of the MAX-DOAS technique to better understand tropospheric chemistry by looking at air pollution at different directions and thus fulfilling the final objective of this thesis.

Although Pandora instruments are primarily used for satellite product validation, this study shows potential for using Pandora MAX-DOAS measurements for near surface air quality monitoring. More field studies over various seasons and different locations are needed for further analysis. HCHO in-situ instruments at more Pandora locations can provide validation for near surface concentrations for different meteorological conditions. Airborne HCHO and NO_2 vertical profile observations can be performed to compare with Pandora vertical profile measurements and capture the altitudinal variation of $HCHO/NO_2$ ratio. For MLH retrievals, half-hourly launches of Ozonesondes over a couple weeks are needed to fully capture the diurnal evolution of MLH consistently, which can then be used to provide validation for Pandora MAX-DOAS water vapor profiles and MLH measurements. For HCHO and NO_2 spatial heterogeneity evaluation, in-situ instruments and traffic counters need to be placed precisely at different Pandora viewing directions for corroborating Pandora measurements, it would also be useful to have some modelling simulations to quantify different emission sources. These analyses will enable the full evaluation of Pandora's capabilities as a surface air quality monitoring instrument.

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