ASSESSING THE SPATIO-TEMPORAL DISTRIBUTION OF OZONE OVER AN AGRICULTURE FIELD AND POTENTIAL IMPACTS ON CROP YIELD

MS THESIS

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Assessing the Spatio-Temporal Distribution of Ozone over an Agriculture Field and Potential Impacts on Crop Yield

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Be accepted in partial fulfillment of the requirements for the MS degree.

Dr. ABUBAKR MUHAMMAD _____________
Advisor (Chairperson of Defense Committee)

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Abstract

High concentrations of surface-level Ozone (O_3) are a risk to all vegetation including agricultural crops. Agricultural impacts of Ozone include yield reduction, effected quality of crops, increased susceptibility to disease and senescence. Ozone is the most damaging air pollutant to vegetation as compared to aerosols, particulate matter and trace gases. The season of high ozone concentration coincides with the growing season of crops. Ozone enters the cell during evapotranspiration and interferes with the ongoing processes inside the plant resulting in lower crop yields. Effects of crop exposure to ozone also appear in the soil as Ozone tends to suppress the phenomenon of nitrogen fixation. To reduce the negative vegetation impacts, it is of great importance to measure air pollution at a high spatial and temporal resolutions. In this thesis, Ozone trends were studied by using yearlong simulations of Community Multi-scale Air Quality Model coupled with Weather Research Forcast Model (CMAQ-WRF 3D model) and observational data from EPD Punjab for rural and urban areas. Bias correction method was applied to the modeled values for Nestle Farms. In order to comprehend the relative yield losses (RYL), for both the model-predicted and model-predicted adjusted values, concentration-response equations are used for different crops important to the agronomy of Pakistan. Both, mean and cumulative, metrics were used to analyze the total ozone-induced relative yield. We concluded that the RYL calculated for South Asia nearly matched with the ones calculated for Pakistan only using the CR equations.

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Chapter 1

INTRODUCTION

Air Pollution is defined as the presence of substances in the atmosphere at high concentration levels to effect life forms and materials. The substances may be in the form of a gas, solid or liquid particles either directly emitted or formed in the atmosphere by physical processes or chemical reactions. Some common air pollutants relevant to research include O_3, NO, NO_2,SO_2,CO, $PM_{2.5}$ and PM_{10} . The atmosphere is composed of various trace gases and particulate matter and there is a dire need to measure the amount of these species present in the atmosphere. Aerosols in the rural areas are mainly of natural origins with a moderate influence from anthropogenic sources [19].We will only be looking at the measurement techniques that are commercially used to monitor Ozone and particulate matter. The most generic form for measuring Ozone is that ambient air is continuously drawn into the monitor, pretreated and measured either directly or via chemical reaction [21]. Continuous and periodic measurement of Ozone can be done by using the principle of UV photometer and ozonesonde respectively.

In case of a UV Photometer, the ambient air is drawn in through an analyzer by a vacuum pump. Upon entering the analyzer, the sample is split into two flow paths. A scrubber is incorporated in one path that selectively removes Ozone from the air where as the air in the other path remains unchanged.These paths are connected via a solenoid valve which decides, based on a fixed interval, which air sample passes through the quartz tube. At the end of this quartz cell, a mercury vapor lamp is placed that produces a monochromatic beam of ultraviolet light at 254 nm. This wavelength is highly absorbable by Ozone. At the end of the instrument a vacuum diode measures the intensity of transmitted light. Where as, an ozonesonde is a basically a balloon-borne radiosonde. It is best for measuring the vertical profiles of Ozone. The radiative cooling of the ground during the night and its heating by solar radiation during the day cause diurnal changes in the stability of the lower atmosphere [19].

In accordance to The Clean Air Act, the Environment Protection Agency (EPA), US was advised to set certain National Ambient Air Quality Standards (NAAQS) for pollutants considered harmful to public health and the environment. The Clean Air Act identifies two types of national ambient air quality standards [2]. Primary standards provide public health protection which also includes the protection of human beings of all ages from pulmonary and cardio vascular diseases. Secondary standards provide public welfare protection, including protection against decreased visibility and damage to animals, crops, vegetation, and buildings [2]. National Ambient Air Quality Standards are set by the EPA for a total of six pollutants, that account for air pollution, in terms of their concentrations. Units of measure for the standards are parts per million (ppm) by volume, parts per billion (ppb) by volume, and micro grams per cubic meter of air (g/m^3) [2].

Atmosphere is considered to be polluted when concentration of gas and aerosol species reaches a certain value as recorded by instruments. The concentrations beyond which air is considered to be harmful for human health and averaging time are listed on the table 1-1. Air pollution has been effect human lives the most hazardous ways. Pollutants like Ozone and Particulate matter ($PM_{2.5}$) have been causing various pulmonary and lung diseases to humans of all age groups living in urban environments. The air we breathe in, has multiple pollutant particles and trace gases involved that results in cardiovascular diseases, heart diseases and in some severe cases stroke deaths. Air pollution was responsible for 6.4 million deaths worldwide in the year 2015, out of which 2.8 million occurred from household air pollution and the remaining 4.2 million from ambient air pollution.

Pollutant	Primary/Secondary	Averaging Time	Level	Form
Carbon Monoxide (CO)	Primary	8 hour	9 ppm	Not to be exceeded more than once
		1 hour	35 ppm	
Lead (Pb)	Primary & secondary	Rolling 3 month average	0.15ug/m^3	Not to be exceeded
Nitrogen Dioxide (NO_2)	Primary	1 hour	100 ppb	98th percentile of 1-hour daily maximum concentration, averaged over 3 years
	Primary & secondary	1 year	53 ppb	Annual mean
Ozone (O_3)	Primary & secondary	8 hour	70 ppb	Annual 4th highest daily maximum 8-hour concentration, averaged over 3 years
Particulate Matter ($PM_{2.5}$)	Primary	1 year	12ug/m^3	Annual mean, averaged over 3 years
	Secondary	1 year	15ug/m^3	Annual mean, averaged over 3 years
	Primary & secondary	24 hour	35ug/m^3	98th percentile, averaged over 3 years
Particulate Matter (PM_{10})	Primary & secondary	24 hour	150ug/m^3	Not to be exceeded more than once per year on average over 3 years
Sulphur dioxide (SO_2)	Primary	1 hour	75 ppb	99th percentile of 1-hour daily maximum concentration, averaged over 3 years
	Secondary	3 hour	0.5 ppm	Not to be exceeded more than once per year

Figure 1-1: National Ambient Air Quality Standards (NAAQS) Table - US EPA[2]

It is estimated that by the year 2060, in the absence of aggressive emission controls, ambient air pollution is increased by such a factor that it can cause between 6 million and 9 million deaths per year. In addition to it, ambient air pollution appears to be an important although not yet quantified risk factor for neuro-developmental disorders in children and neuro-degenerative diseases in adults.

Plants require water, sunlight and nutrients in order to grow properly. Ozone can cause substantial damage to most of the plants and vegetation crops in terms of low quality of the crop, increased inheritance to disease and reduction in plant growth. All these things directly impact the yield of any specific crop that then contribute to the overall loss in theoretical yield. Ozone enters the leaves through stomata when they inhale air and there it reacts with multiple compounds to yield reactive the odd-oxygen species that enable the oxidation of plant tissue and as a result the gene expression is altered. This causes an impairment in the process of photosynthesis and long with the degradation chlorophyll [8].

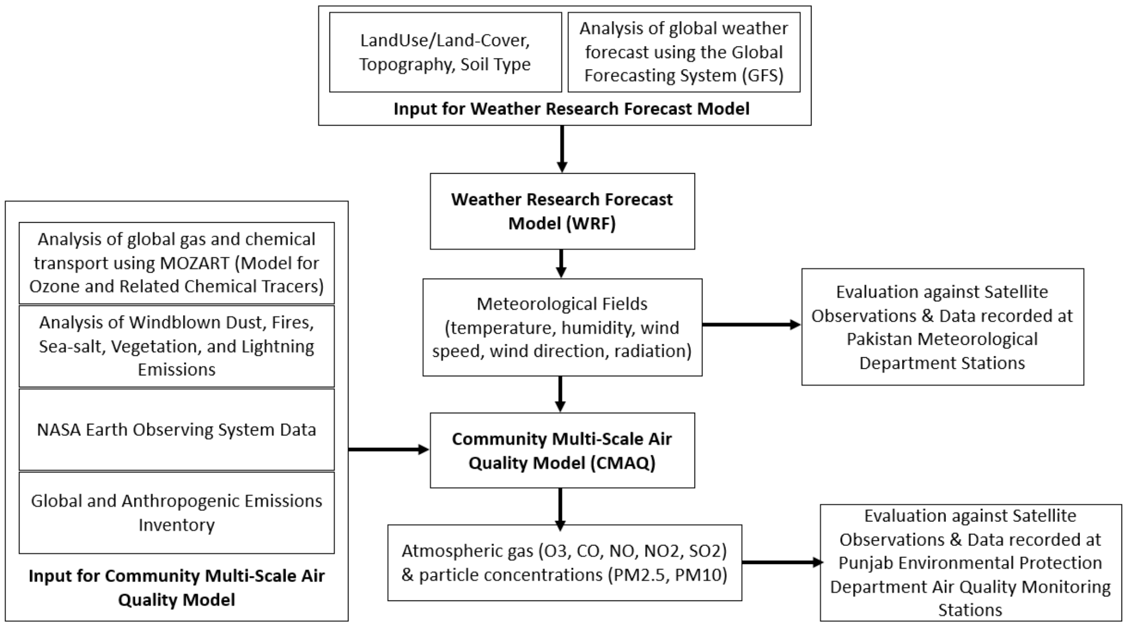

Figure 1-2: CMAQ-WRF 3d Model

Models are an efficient way to study the atmospheric process that govern the transport and transformation of trace gases and particles. Measurements are one way of gathering this information, but a more complete picture in space and time is often needed. Air quality models can provide this information for the past, present or future depending on how they are used[2]. Weather Research Forecast (WRF) is 3-d atmospheric dynamics modeling system that solves the equations of mass, energy and momentum. It not only serves as a tool for weather and climate researchers, but is also used for weather forecasting. Where as, Community Multiscale Air Quality (CMAQ) model is a 3-d chemical transport model that solves the atmospheric diffusion equation and is widely used to understand processes that govern the transport and transformation of atmospheric gases and particles and how it impacts society (public health, agriculture, climate change). By coupling these two models an Atmospheric Dynamics and Chemistry Transport Modeling (ADCTM) System is given shape as shown in figure (1-2). Such Decision Support Systems are used to understand sources, transport and transformation of pollution and its interaction with the physical atmosphere.

The agricultural sector of Pakistan has always played in a vital role in the economy of the country as it contributes approximately 18.9-25.1% of the Gross Domestic Product (GDP) of the country. In addition to this, the agricultural sector cover up around 42.3% of the labor force of the country. The agricultural sector also accounts for food availability of both urban and rural population, as agriculture is the main source of income that mainly impacts the nutritional value by keeping in mind both food consumption and absorption. Agriculture also contributes towards for greater revenues of import and export of foreign exchange and contributes towards the growth of the economical sector.

Ozone has the ability to effect the entire plants photosynthesis process by directly targeting the photosynthetic components such as the chlorophyll content of a plant and Rubisco.[18] Ozone is also responsible for the reduction in leaf area index as it promotes increased senescence. The change in a plants stomatal conductance and altering the carbon allocated to each leaf ground level Ozone impacts the overall metabolism of the plant [18], also causing yellowing of the leaves most of the time. The impacts of high Ozone concentrations on the productivity of vegetation has dire consequences worldwide. Even though the mitigation effects of Ozone has resulted in lower peak concentrations of Ozone, both in rural and urban areas around the globe [14].

Chapter 2

CHEMISTRY OF OZONE PRODUCTION AND TRANSFORMATION

2.1 Introduction

Ozone, being one of the most crucial elements of the stratosphere, was explored in the nineteenth century. When the early quantitative measurements of the columns of ozone were performed in Europe during the beginning of the twentieth century, ozones significance as an atmospheric gas become quite evident. In order to measure the column of the ozone, Dobson, a British scientist, invented a spectro-photometer. The equipment is still used extensively. It is due to this that the standard unit for ozone measurement is Dobsun unit (DU) [19]. In 1930, another British scientist, Sydney Chapman proposed that in the stratosphere, the ozone is continuously formed by a sequence which has originated in the upper stratosphere during the photolysis of O2. The photo-chemical mechanism of the making of the ozone endures Chapmans name. The stratospheric ozone was not truly understood until the 1970s, in which Paul Crutzen clarified the functionality of the nitrogen oxide in the chemistry of the stratospheric ozone[19].This was keenly tracked by Harold Johnstons analysis of the stratospheric ozones likely depletion. Prevailing shortly, F. Sherwood Rowland and Mario Molina, foretold the effect of chlorine released by industries on stratospheric ozone.

2.2 Stratospheric Ozone

The atmosphere of the planet earth is depicted by a variety of different height pressures and temperatures. The foundation of differentiating the atmospheric layers is the distinction of the mean temperature profile, which are five in total. Stratosphere extends from the tropo-pause to the strato-pause where the increase in altitude rises the temperature, directing to a slow vertical mixing layer. [19].

About 90% of the atmosphere's ozone is found in the stratosphere, what is commonly known as the ozone layer. At the peak of the ozone layer the O_3 mixing ratio is about 12ppm. Stratospheric ozone is produced naturally as a result of the photolytic decomposition of O_2. The two oxygen atoms that result each react with another O_2 molecule to produce two molecules of O_3. Therefore, the overall process converts three molecules of O_2 to two O_3 molecules. The O_3 molecules produced themselves react with other stratospheric molecules, both natural and anthropogenic; the balance achieved between O_3 extinguished and created induces to a stable state abundance of O_3.

The creation of Ozone takes place in the stratosphere over an altitude of 30km, where the Ultra Violet (UV) solar radiation of wavelengths fewer than 242nm slowly dissociate molecular oxygen as follows:

$$\mathrm{O_2 + hv} \xrightarrow{1} \mathrm{O + O}$$

In the existence of a third molecule M (N_2 or O_2), the atoms of oxygen react with O_2 in order to produce O_3

$$\mathrm{O_2 + O + M} \xrightarrow{2} \mathrm{O_3 + M}$$

The reaction 2 is the only reaction that is responsible for the production of ozone in the atmosphere [19]. Sometimes, the molecule of O_3 created in that reaction powerfully absorb the emission itself in the wavelength span of 240-320nm. Thus, the photolytic lifetime of an O_3 molecule is on the order of 10 minutes at these altitudes. To summarize, at high altitudes the concentration of ozone decreases primarily as a result of a drop in the concentration of O_2, the photolysis of which initiates the formation of ozone.

The fact that stratospheric ozone concentrations are maximum in areas far removed from those whereO_3 is being produced suggests that the lifetime of O_3 in the stratosphere is longer than the time needed for the transport to occur.

2.3 Troposopheric Ozone

The lowermost layering of the atmosphere is the troposphere which spreads from the surface of the Earth up to the tropo-pause, experiencing rapid vertical mixing. Relatively different from the stratosphere, the troposphere serves as a chemical tank. The transportation of the species into the stratosphere from the troposphere is extremely slower as compared to the blending inside the troposphere. Light of adequately energetic wavelengths diffuses inside the troposphere in order to support the important photo-chemical reactions even after the removal of the energetic wavelengths in the stratosphere. The high water vapor content is quite a crucial factor in the chemistry of the troposphere. Tropospheres chemistry includes the reactions which creates and demolishes Ozone; the development and the deletion of Ozone, pretty similar to that of the stratosphere.

For the 1,000,000,000 molecules, around 35 of the total are typically O_3 in the troposphere. The Ground level O_3 blending ratios span between 20 to 60 ppb, in the troposphere. Quantities are expected to increase up to 100 ppb in the broad districts and also the urban areas. The levels of the Ozone surpassing 200 ppb is counted as a serious air pollution event. With the advent of Los Angeles photo-chemical smog which appeared during the late 1940s and the early 1950s along with the detection ofO_3 as its foremost primary element, an effort raised to study this new category of air pollution. The hydroxyl (OH) radicals react rapidly with the hydrocarbons this was known fact, but if the OH radicals performed any important part in the tropospheres chemistry was unknown.

Ozone in the troposphere is generated as a result of chemistry involving two major classes of precursors: volatile organic compounds ($VOCs$) and oxides of Nitrogen (NOx). But when it comes to the troposphere, ground-level Ozone is categorized as both, a health hazardous pollutant to all living things and an environment savior greenhouse gas that supports the cause of climate change along with global warming.The oxidization of the shorter-lived volatile organic compounds which happen to be radiated from biogenic and the anthropogenic sources steer the development of ozone in the regional and the urban atmosphere. The chemical reaction between the organic molecules and the OH radicals helps originates the method of the Ozone development. The ongoing reaction order is catalyzed by NOx, in a network of intricate free-radical reactions. The maximum of the NOx direct radiations is in the form of NO to the atmosphere. In reaction 1a, ground state (O) and excited singlet ($O(D^1)$) oxygen atoms are involved as both are equally important for troposphere and stratosphere.

Tropospheric O_3 is said to be vastly phytotoxic. Suitable exposure to O_3 can end up in chronic (variation in the yield, quality, growth and productivity) as well as in acute (symptomatic) effects. At low altitudes, the concentration of ozone decreases because of a decrease in the flux of photons at the UV wavelengths at which O_2 photo-dissociates

$$\mathrm{O_3 + hv \xrightarrow{1a} O_2 + O}$$

Also, the ground state O atom combines rapidly with O_2 to re-form O_3

$$\mathrm{\xrightarrow{1b} O_2 + O(D^1)}$$

The reaction 1a followed by 2 has no net chemical effect.

$$O_2 + O + M \xrightarrow{2} O_3 + M$$

2.4 Relationship with Atmospheric Physics

One of the physics applications is the atmospheric physics which includes the study of the atmosphere. It involves modeling of the atmosphere of the planet Earth as well as other planets atmospheres by means of radiation budget, fluid flow equations, energy transmission methods and chemical models in the atmosphere. It involves the pattern and the development of the equipment for learning the atmosphere along with the understanding of the information they offer with the inclusion of the remote sensing instruments. It also has very close relation with climatology as well as meteorology.

With a speed of 300,000 km/s, the electromagnetic radiations come from the sun, which then constitutes of the wavelengths that differ from the X-rays and gamma rays (which are very short) to microwaves (which are quite long). The visible spectrum constitutes wavelengths between the span of 400 and 700nm. The emissions of the wavelengths fewer than about 400 nm is ultraviolet (UV) and it credits for 7% of the whole of the solar emissions. We are only concerned with the emissions in the region of the ultraviolet wavelength of the electromagnetic spectrum for ozone. Other than the X-rays and gamma rays which get vastly absorbed by the atmosphere, the UV radiations are categorized into three spectras; UVa , UVb, and UVc. With the wavelengths ranging between 320 to 400 nm, the UVa appears right after the visible light but it is not absorbed by the ozone. The UVb emissions, which happen to span between the wavelengths from 280 to 320 nm is quite energetic and is widely absorbed by ozone. Being the extremely harmful yet energetic, the UVc, which spans between 200 to 280 nm is fully absorbed by the ozone and keeps the normal diatomic oxygen levels high in the atmosphere.

The presence of the Ozone is both in the stratosphere as well as the troposphere. The O_3 Troposphere is primarily created by the photo-chemical reactions which compromises of the originators produced by the natural methods and to an extremely highly degree by the activities of man. There is proof for a rising trend in the concentrations of the O_3 tropospheric. There are proofs to propose that the damages in the O_3 stratospheric are because of the increase in the O_3 degenerating pollutants which are produced by the activities of the human beings as well as the natural processes.

Chapter 3

DATA ANALYSIS AND 3-D MODELING

3.1 Introduction

The rapidly increasing environmental mortification at both global and national level has given rise to serious concerns. Environment Protection Department (EPD), Punjab launched an agency in authority of the protection, improvement and preservation of the environment throughout the province of Punjab known as the Environment Protection Agency (EPA). EPA has one mobile monitor and two stationary air quality monitors spread out through Lahore, at Jail Road and Walton Road, both being highly urbanized areas. These air quality monitors installed by Punjab government have now been operational since a year and measures the concentrations Ozone (O_3), $PM_2.5$, PM_10, Sulphur dioxide and Oxides of Nitrogen. Environment Protection Agency does not only sustains qualitative standards for the discharge of sewage and wastes but also takes in account the air emissions in terms of a specific area and a specific source.

3.2 Why Diurnal Profiles?

In general terms, a diurnal cycle represents a recursive pattern that occurs every twenty four hours as the Earth completes one full rotation around its own axis. As long as environmental chemistry is concerned, a diurnal cycle is the most basic form to represent climatic patterns, let it be meteorological variables or air quality components. Diurnal profiles of any air quality specie represent their averaged concentrations at each hour of the day, more precisely a temporal (hourly) distribution of that specie.

3.3 Strong Correlation:Temperature and Ozone

It is obvious from the 2018 monthly plots of ozone displayed in figures (3-1) till (3-12) that ozone concentrations are relatively higher during the day time as compared to prior the sunrise and post sunset hours. This fact justifies the there is a strong correlation between ozone and temperature. Ozone production speeds up at higher temperature levels as production of the natural constituents of ozone escalate. Weaker winds coincide with higher levels of temperature which in turn causes the atmosphere to become stationary. As a result, the air keeps on cooking and ozone concentration levels keep on increasing. Temperature has been categorized as a key component whenever high ozone episodes occur, there is still a whole new chapter on how these high temperatures will impact the brutality that surface level ozone has to offer.

3.4 EPD Data Analysis

Yearlong data for 2018 was available for the EPD Jail Road monitor, a ground based remote-sensing, which included data of concentrations for air quality species, both gases and aerosols, such as O_3, $PM_{2.5}$,PM_{10} and So_2. We evaluate the performance of the air quality monitor in capturing the temporal distribution of ozone in an urban environment in figure (3-1) till (3-12).

The diurnal averages for each month were calculated for the year 2018 along with

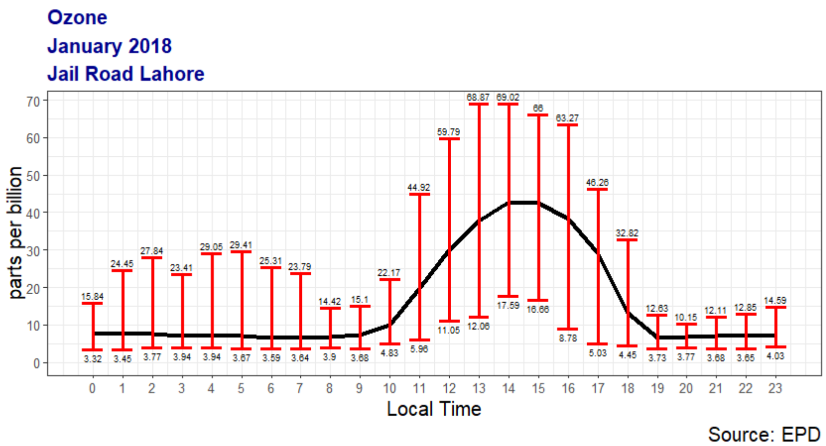

Figure 3-1: Observed Ozone concentrations by EPD data in January 2018

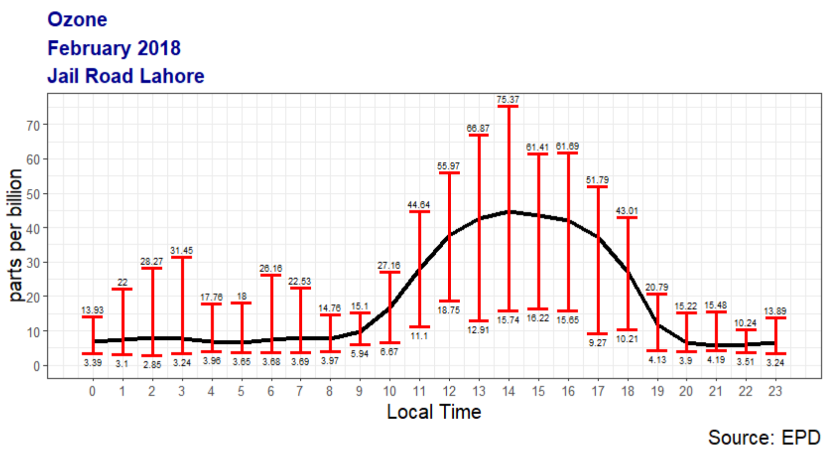

Figure 3-2: Observed Ozone concentrations by EPD data in February 2018

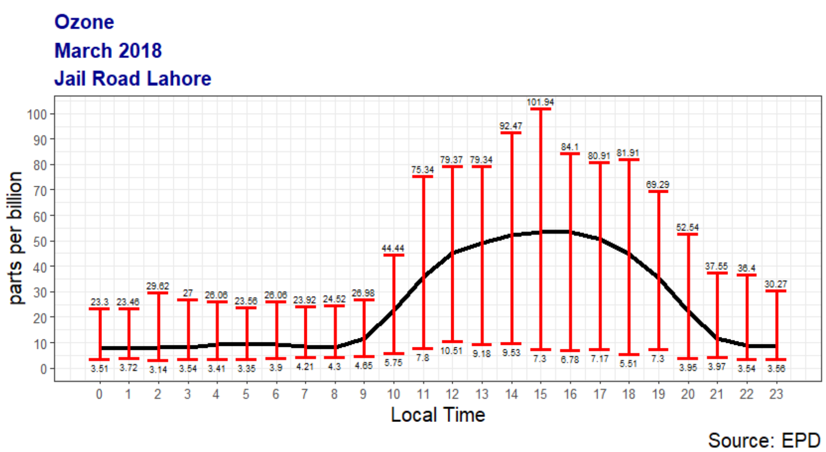

Figure 3-3: Observed Ozone concentrations by EPD data in March 2018

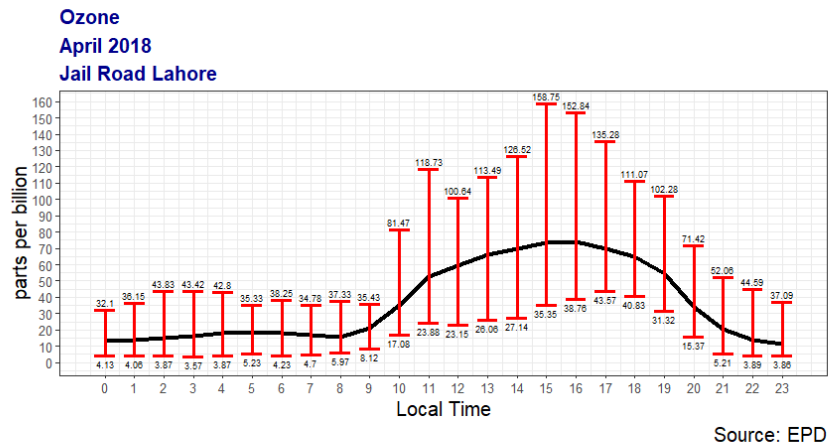

Figure 3-4: Observed Ozone concentrations by EPD data in April 2018

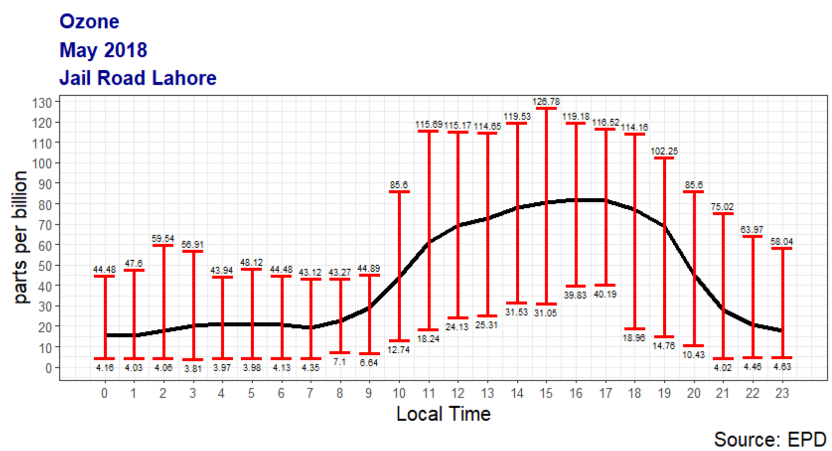

Figure 3-5: Observed Ozone concentrations by EPD data in May 2018

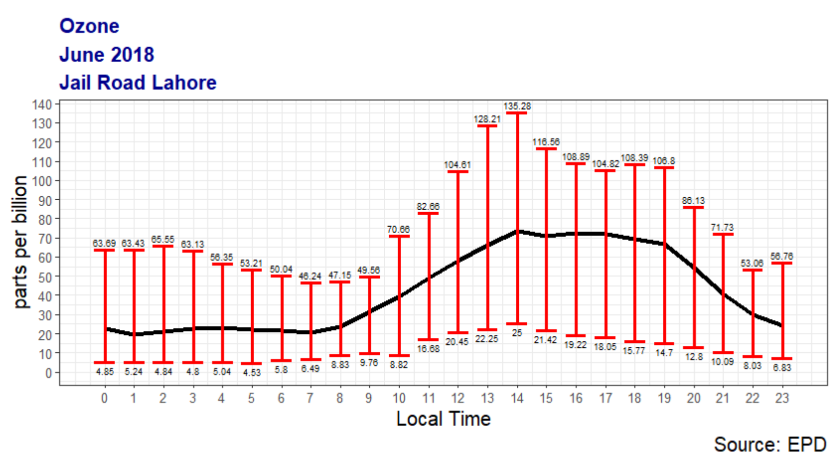

Figure 3-6: Observed Ozone concentrations by EPD data in June 2018

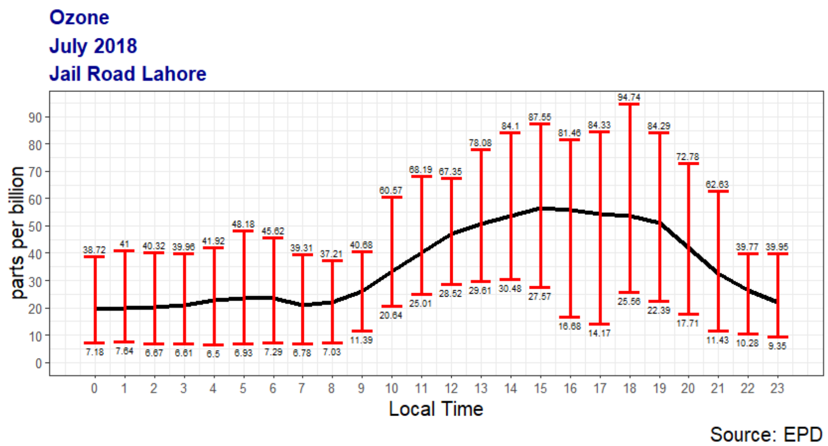

Figure 3-7: Observed Ozone concentrations by EPD data in July 2018

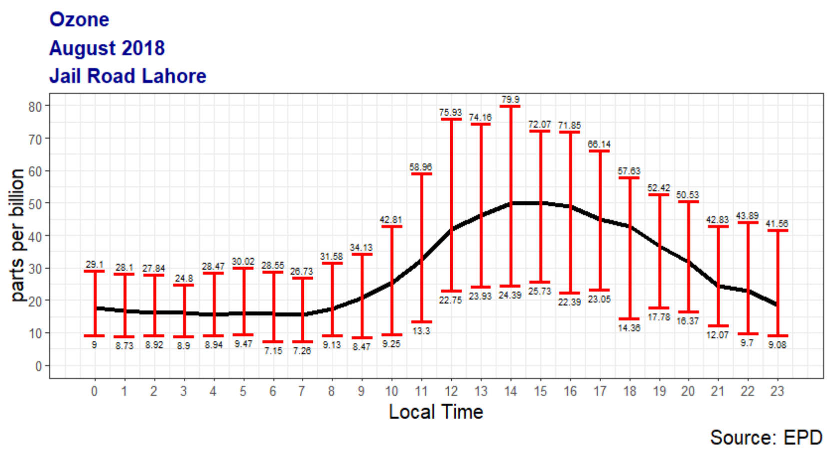

Figure 3-8: Observed Ozone concentrations by EPD data in August 2018

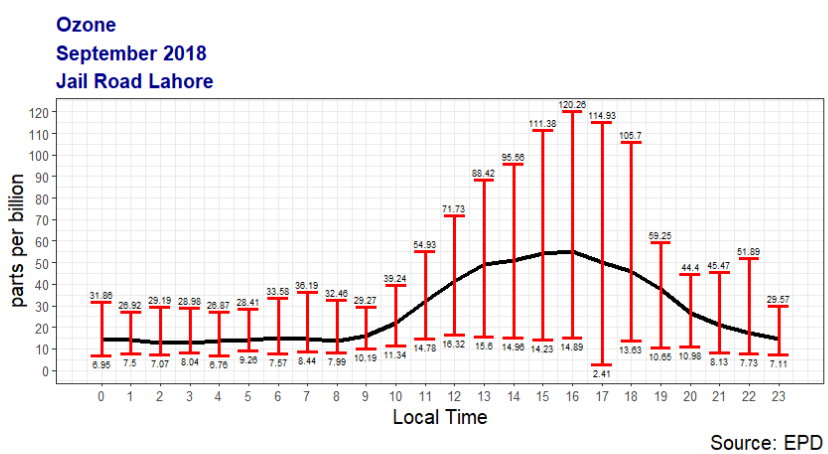

Figure 3-9: Observed Ozone concentrations by EPD data in September 2018

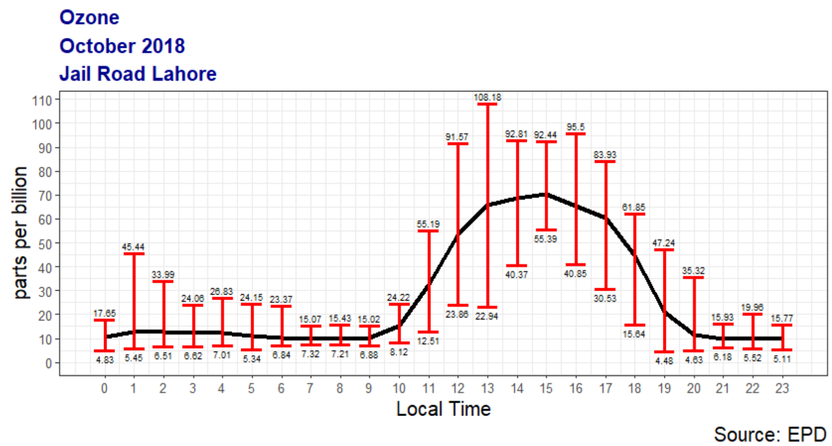

Figure 3-10: Observed Ozone concentrations by EPD data in October 2018

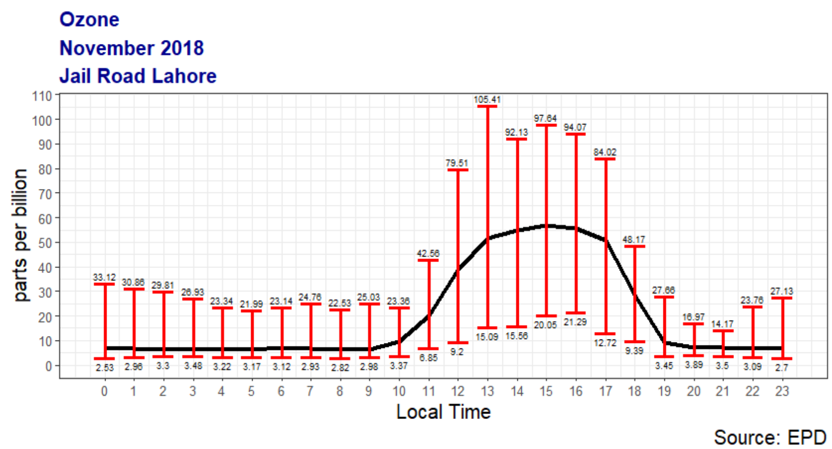

Figure 3-11: Observed Ozone concentrations by EPD data in November 2018

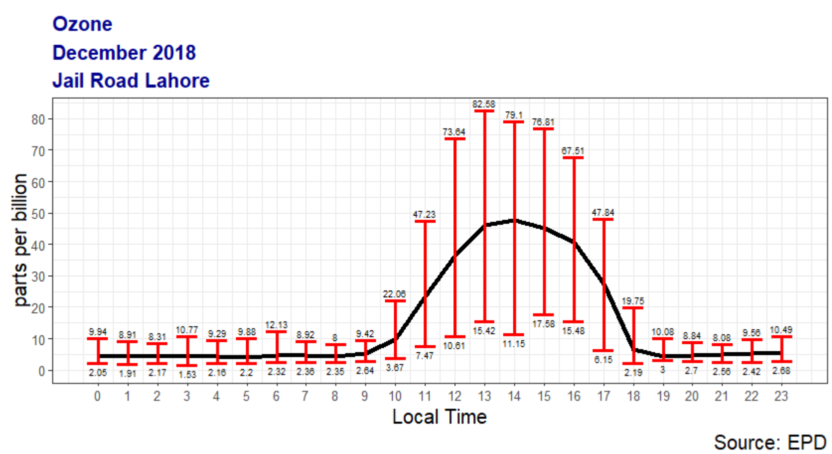

Figure 3-12: Observed Ozone concentrations by EPD data in December 2018

error bars that represent the maximum and minimum at every hour of the day. In addition to this, an overall diurnal plot was also calculated for concentrations over the entire year, that is shown in figure (3-13). Similarly, the average frequency of Ozone occurrence on monthly basis is displayed in the form of bar plot in figure (3-14).

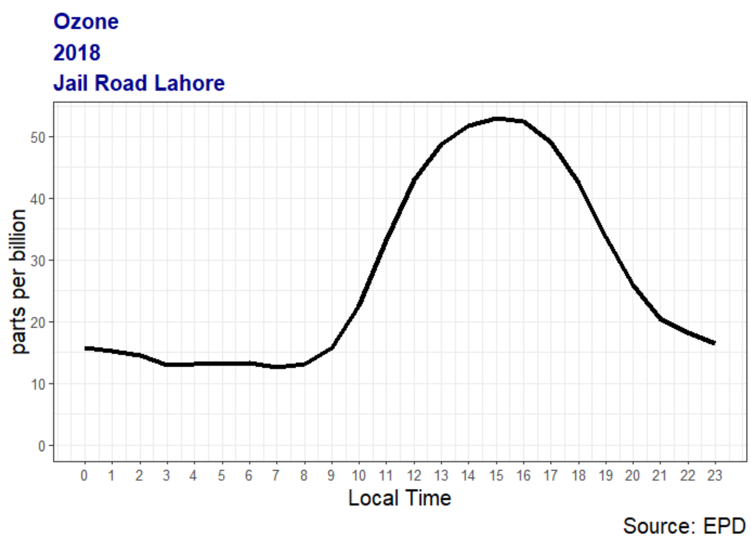

Figure 3-13: Yearly diurnal averaged profile for Ozone at Jail Road Station Lahore

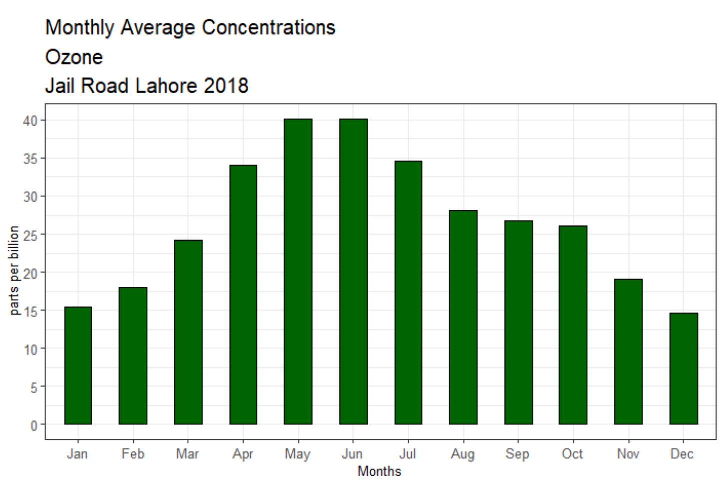

Figure 3-14: Monthly averaged frequency of Ozone in 2018 at Jail Road Station Lahore

3.5 ADCTM Data Analysis

Models are a way to study the atmospheric process that govern the transport and transformation of trace gases and particles. The Community Multi-scale Air Quality model (CMAQ) is a 3-dimensional chemical transport model that solves the atmospheric diffusion equation and is widely used to understand processes that govern the transport and transformation of atmospheric gases and particles and how it impacts society in terms of public health, agriculture and climate change. The atmospheric diffusion equation is a modification of the continuity equation that also includes initial conditions and boundary conditions, a numeric equation that has the turbulent flux terms that are expressed with eddy diffusion theory. The numerical solution to the advection diffusion equation requires initial and boundary conditions.

WRF is 3-d atmospheric dynamics modeling system that solves the equations of mass, energy and momentum. It not only serves as a tool for weather and climate researchers, but is also used for weather forecasting. Comparison of monthly-averaged surface ozone concentrations for Jail Road monitoring station is done by using model predicted values in the figures (3-15) till (3-26). Hourly model predicted values for each day are averaged over each month of the year. Data source for all these plots is the Community Multi-scale Air Quality Model coupled with Weather Research Forecast Model Simulations for the year 2018.

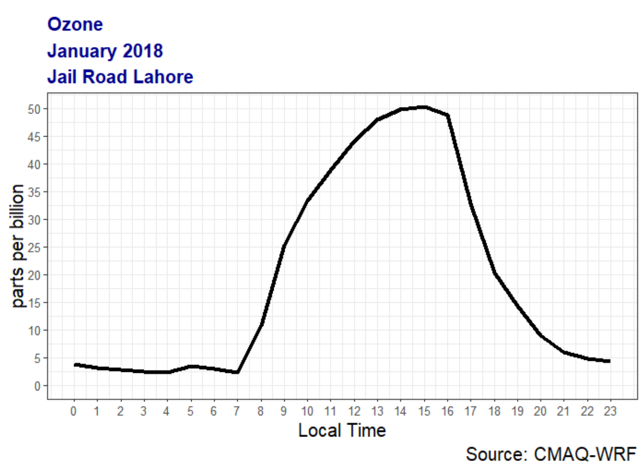

Figure 3-15: Predicted Ozone concentration by 3D model in January 2018

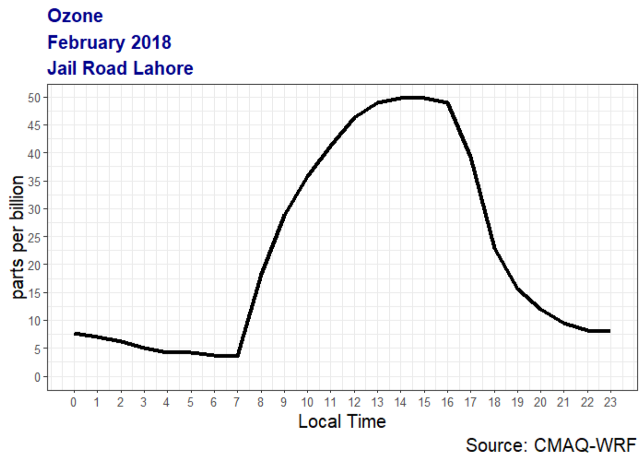

Figure 3-16: Predicted Ozone concentration by 3D model in February 2018

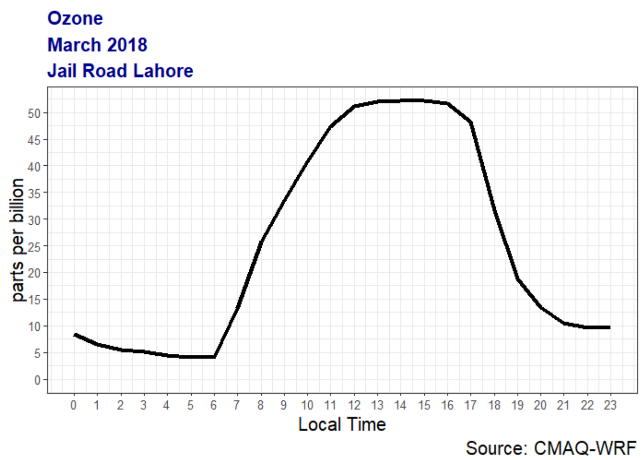

Figure 3-17: Predicted Ozone concentration by 3D model in March 2018

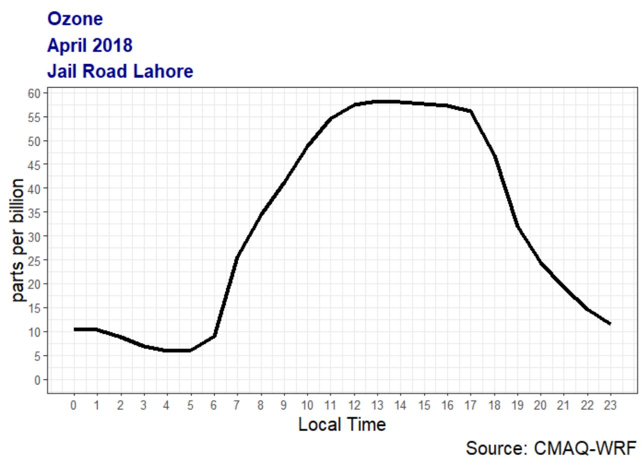

Figure 3-18: Predicted Ozone concentration by 3D model in April 2018

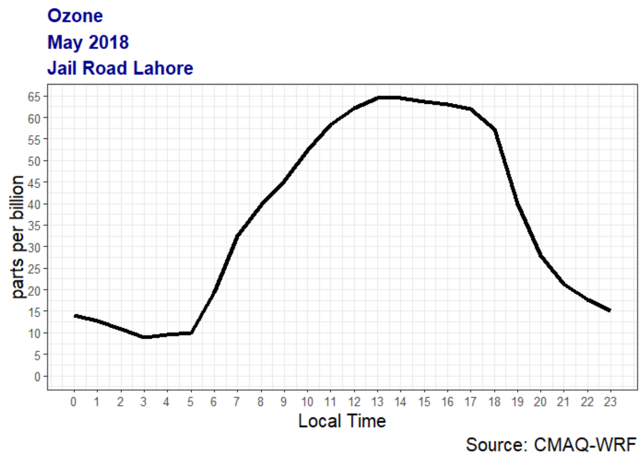

Figure 3-19: Predicted Ozone concentration by 3D model in May 2018

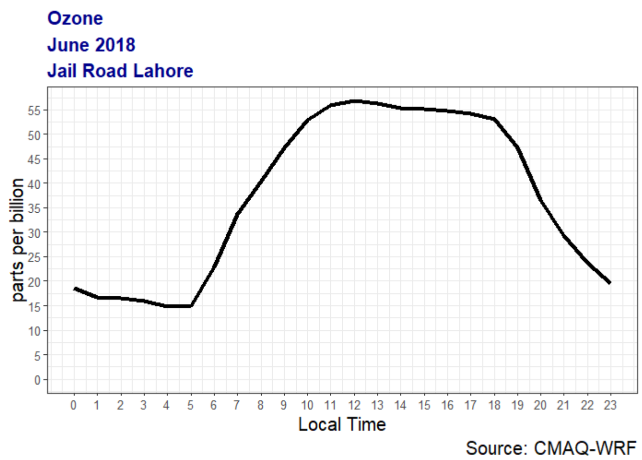

Figure 3-20: Predicted Ozone concentration by 3D model in June 2018

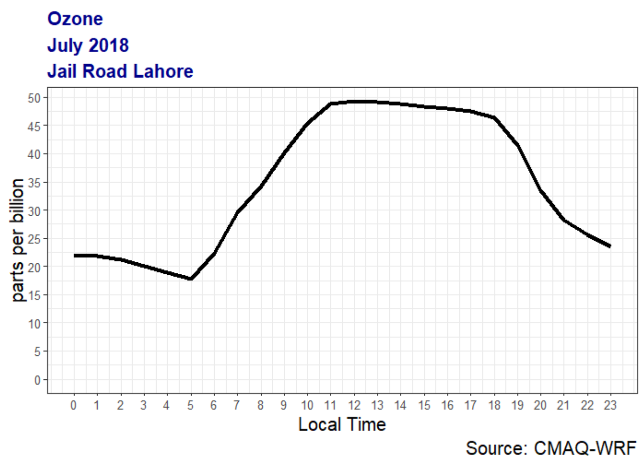

Figure 3-21: Predicted Ozone concentration by 3D model in July 2018

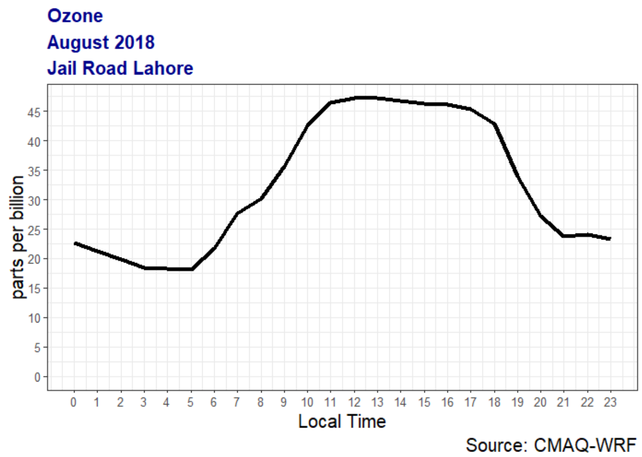

Figure 3-22: Predicted Ozone concentration by 3D model in August 2018

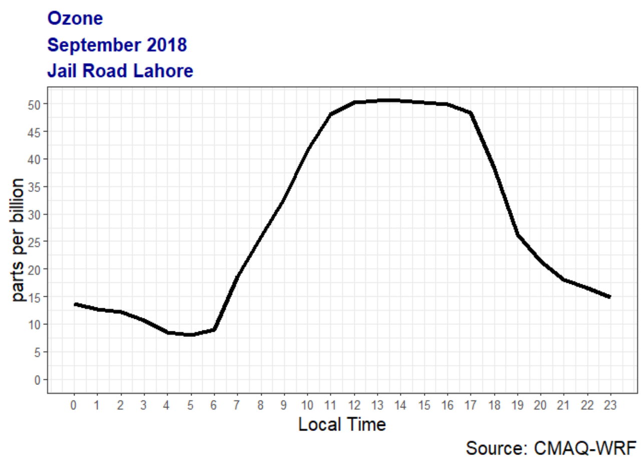

Figure 3-23: Predicted Ozone concentration by 3D model in September 2018

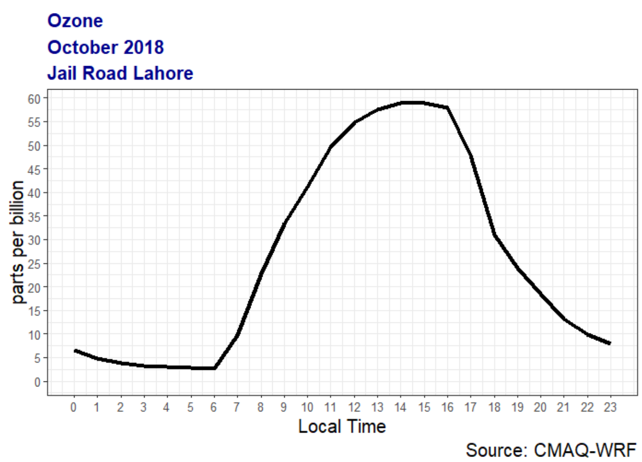

Figure 3-24: Predicted Ozone concentration by 3D model in October 2018

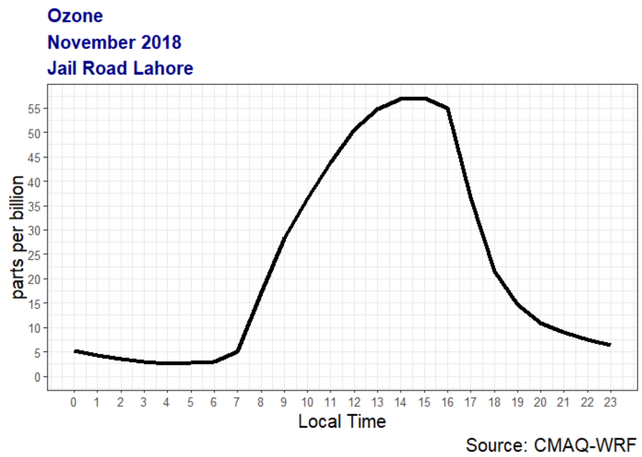

Figure 3-25: Predicted Ozone concentration by 3D model in November 2018

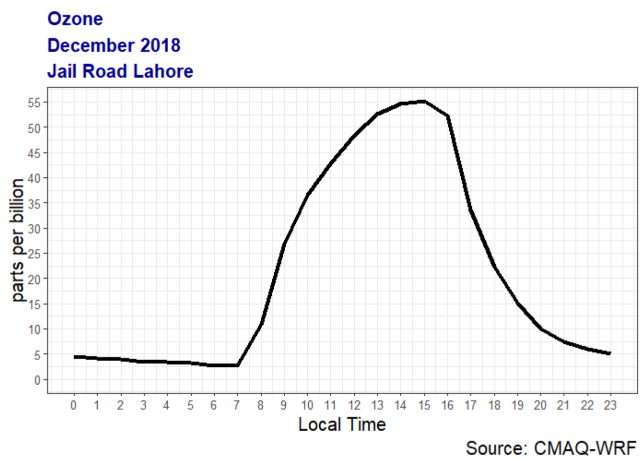

Figure 3-26: Predicted Ozone concentration by 3D model in December 2018

Models are run in grid based horizontal resolution, the minimum of which is 4km horizontal resolution, which means each grid cell is of 4x4. We compare the point measurements, from Punjab Environment Protection Department monitor, with the average of these 3-D model grid cells. Vertical exchange is what we are most interested in when it comes to ozone. Whether the model is 1-D or 3-D, the vertical exchange and the interpretation of the vertical profile of ozone remains same in both of them.

The atmospheric models fail to capture the early and late hours of the day as it is the time when the mixing of the atmosphere is at its peak. CMAQ model simulations tend to over estimate the early and late hour concentrations of ozone, may be because the emissions estimate are too high and we are giving the same amount of emissions for every hour, mainly because the emissions inventory for Pakistan is not updated periodically.

3.6 Summer versus Winter Season

We are well aware that ozone is a photo-chemical process, which means ozone is created in the presence of sunlight. In winters days are shorter and nights are long, thus hours with higher ozone concentrations will be less as compared to the number of hours with high ozone concentration during summer months. Ozone concentrations during night time are low where there is no photo-chemistry and in winters when it is cold.

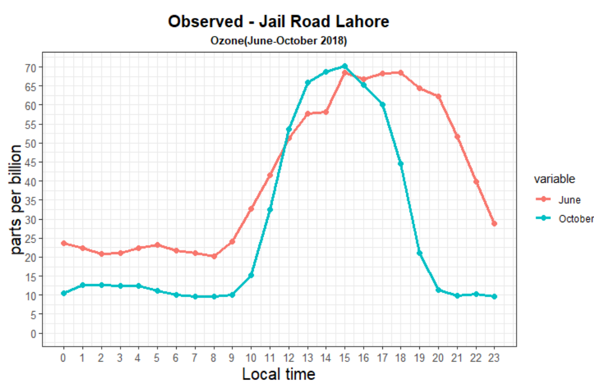

Figure 3-27: Observed Ozone concentrations by EPD data in June and October 2018

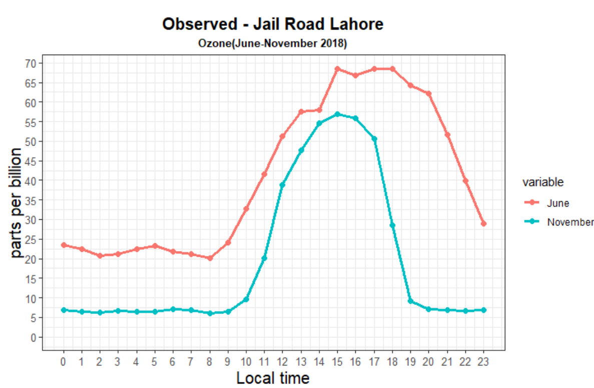

Figure 3-28: Observed Ozone concentrations by EPD data in June and November 2018

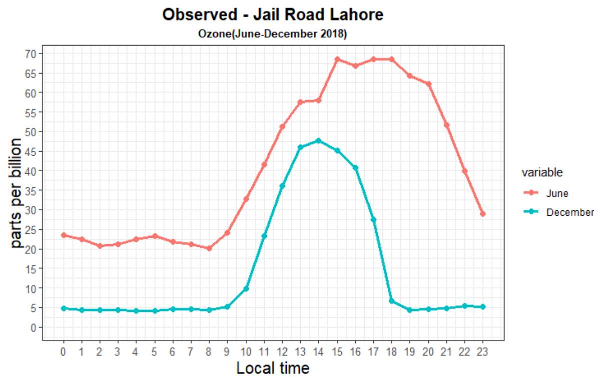

Figure 3-29: Observed Ozone concentrations by EPD data in June and December 2018

This phenomenon can be clearly seen in figure (3-27), (3-28) and (3-29) where the concentrations of ozone for winter months (October, November and December) are compared with the concentrations for the month of June. It is obvious from figure (3-29) that as cold weather prevails the ozone peak becomes shorter yet in the harmful range, that is for October the peak value was 70 ppb, 57 ppb for November and 45 ppb in December at 15^{th} hour of the day.

3.7 Observed versus Predicted

Once the monthly diurnal trends of Ozone were calculated along with the seasonal trends for winter and summer. Now we need to analyze the ability of the 3D atmosphere model in capturing or predicting the concentrations on Ozone at an urban site. For that purpose, we used the Ozone concentrations recorded at the Jail Road Station by Punjab Environment Protection Department Air Quality Monitor along with the 3D model simulations for the month of June, October, November and December. Figure (3-30), (3-31), (3-32) and (3-33) shows the comparison of observed Ozone concentrations against the predicted ones for summer and winter months.

Looking at the aforementioned figures, if we observe the 10^{th} hour of the day for each of the graphs, a prominent difference of approximately 20 ppb is seen between the observed and predicted concentration. This means that daytime concentrations are over-predicted by a significant amount. As for the night-time concentrations, if we look at the before sunrise hours for figures (3-30) and (3-31), we depict that there is a minor underprediction. However, this is not he case for the December profile (figure (3-33)) where the predicted concentrations are almost inline with the observed ones.

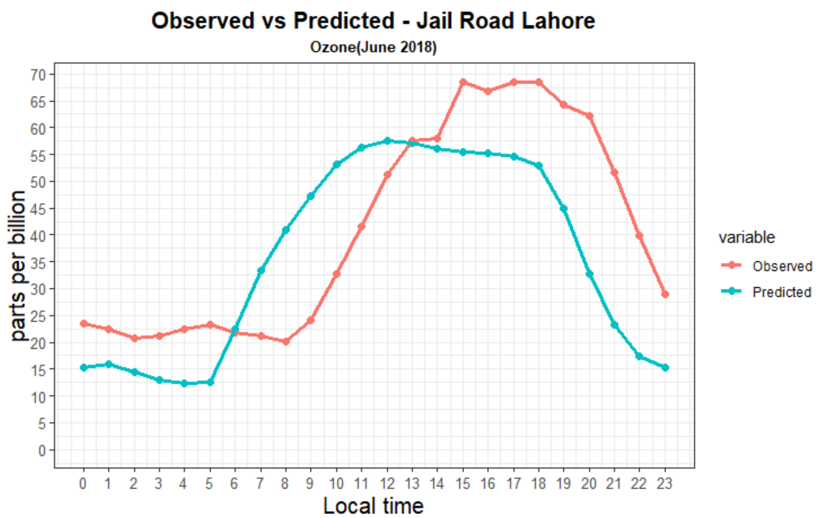

Figure 3-30: Observed Ozone concentrations by EPD data and model predicted Ozone concentrations at Jail Road in June 2018

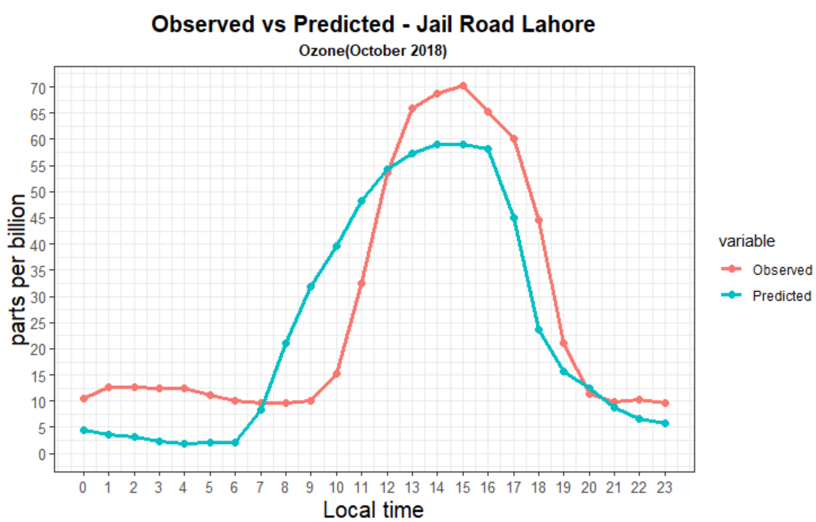

Figure 3-31: Observed Ozone concentrations by EPD data and model predicted Ozone concentrations at Jail Road in October 2018

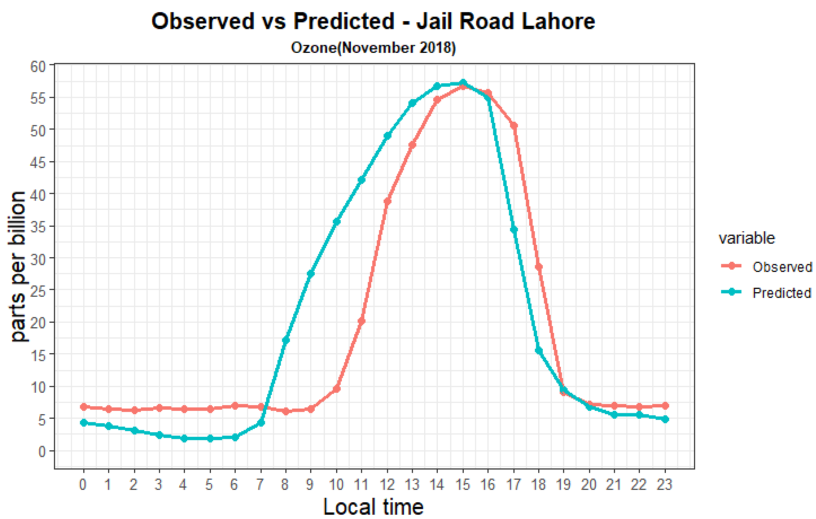

Figure 3-32: Observed Ozone concentrations by EPD data and model predicted Ozone concentrations at Jail Road in November 2018

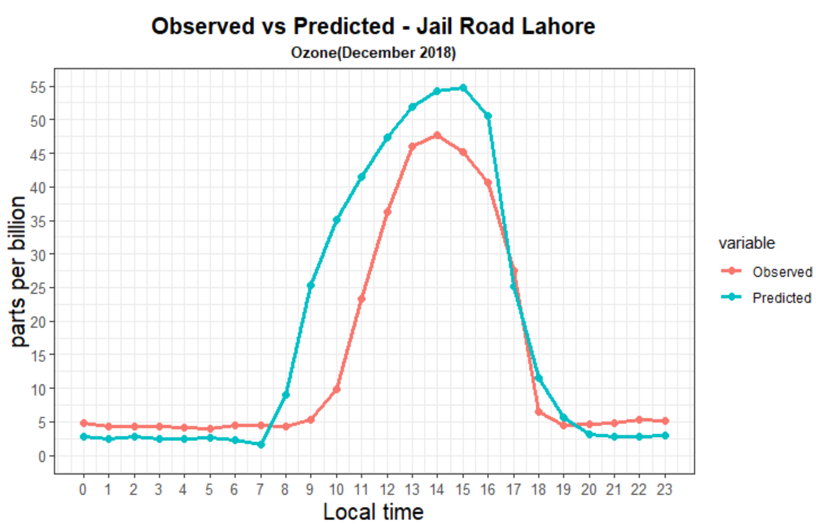

Figure 3-33: Observed Ozone concentrations by EPD data and model predicted Ozone concentrations at Jail Road in December 2018

Chapter 4

DEVELOPMENT OF INSTRUMENT SUITE

4.1 Introduction

In order to study trends of Ozone in a rural environment, there was a necessity to build an instrument suite that would be able to capture the atmospheric dynamics in a rural setup. As per the fact that our interest lies in the vertical profile of ozone and we are more concerned with the vertical mixing of the atmosphere over space and time, we have developed a pole mounted instrument suite. It consists of various sensors installed at different height and depths in order to successfully capture the dynamics of ozone over space and time at a rural site.

4.2 Components

The components used in building the instrument suite included soil moisture sensors shown in figure (4-1) installed at four different depths, 10,40,100 and 200 centimeters. The next sensor was temperature and humidity sensor installed at a height of 5 meters, shown in figure (4-1). Lastly, a Personal Ozone Monitor was integrated and installed at 10 meters height shown in figure (4-2).

4.2.1 Capacitive Soil Moisture Sensor

The soil moisture sensor measures the moisture content in soil by capacitive sensing rather than resistive. The manufacturing of this sensor is done by corrosion resistive material and can measure the soil moisture by submergence into soil. The sensor has an operating voltage of around 3.3V-5V DC. The soil moisture sensor is a three pin interface being ground, Vcc and the analogue data pin.

4.2.2 SHT11 Temperature and Humidity Sensor

The SHT11 is a two wire digital serial interface that involves a simple offset and scaling factor. The temperature is measured in Celsius and the relative humidity is measured with a resolution of 0.03 percent.The sensor provides a digital output with a accuracy of upto +/- 2 degree accuracy for temperature and +/-3.5% accuracy for relative humidity. SHT 11 sensor is an extremely low power sensor that has a DC input voltage of 2.4V-5.5V.

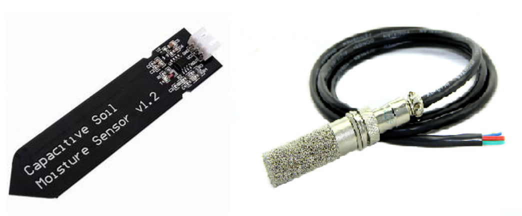

Figure 4-1: Capacitive Soil Moisture sensor (left) and SHT11 temperature and humidity sensor (right)

4.2.3 Personal Ozone Monitor

The Personal Ozone Monitor by 2B Technologies, which is certified by the US EPA as a Federal Equivalent Method (FEM: EQOA-0815-227), works on the principle of UV photometer that is the ambient air is passed through a light of 254nm, which is highly absorbent by Ozone, and the amount of Ozone present in the air depends upon the amount of light absorbed.

Figure 4-2: 2B Technologies Personal Ozone Monitor

4.2.4 Printed Circuit Board (PCB)

The printed circuit board used to interface the soil moisture and temperature sensors was the one used in [4]. The micro-controller embedded on this PCB is PIC17F26K20 that works as the main brain on the integrated circuitry. Along with the micro-

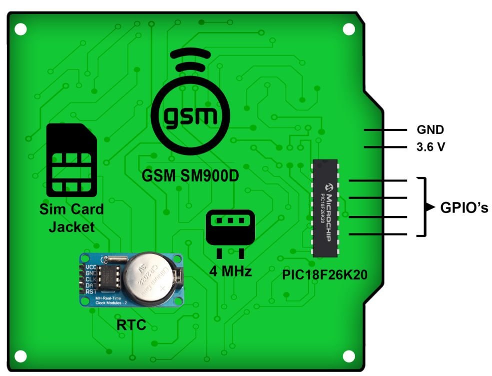

Figure 4-3: Printed Circuit Board

controller the other components that are embedded on the board include GSM module, an RTC clock, sim card jacket and a 4MHz oscillating frequency crystal as shown in figure (4-3). A 3.3V DC input voltage was given to the Printed Circuit Board and a total of four GPIOs were used to connect the soil moisture and SHT11 sensors. DC battery was directed connected to the GSM module that is being used to switch on and off the SIM900D module in order to transmit and receive data string of the sensors data according to the sampling time set in the firmware.[4] Battery is directly connected to GPRS module, but we

4.3 Data Transfer on Server

The data transfer hierarchy, from a remote site to the smart water-grids portal is shown in (4-4). In the most qualitative manner, TCP/IP protocols are followed to transmit data between the sensor node and server. TCP/IP protocol is one of the most basic protocols to move data, both transmission and receiving. Data is sent in the form of packets to the server. The server then processes the received data string and gathers relevant information from it such as date, time stamp, temperature reading, humidity reading and soil moisture level. All these data readings are stored with respect to the date and time that are then extracted in the form of a .csv file and used to calculate monthly and diurnal trends according to the requirement. The number of packets solely depend on the size of each data packet.

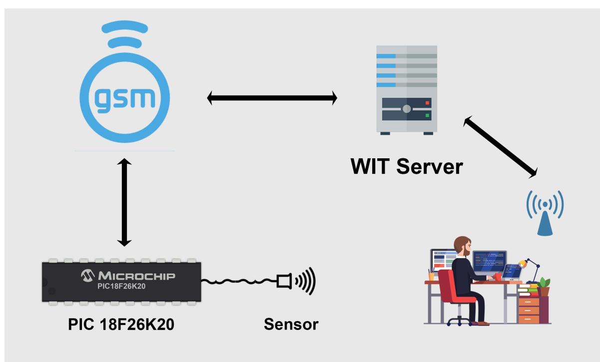

Figure 4-4: Data Transfer on the Server

Chapter 5

CROP YIELD REDUCTION

5.1 Introduction

By now, we have build up a strong argument of how Ozone tends to effect the growth and quality of vegetation. Having said that and understood the physiology behind it, now we need to figure out to what extent Ozone tends to damage a plant. In this chapter we will be defining the crops whose yield is effected by Ozone exposure and will apply two different exposure based metrics for those crops that will then be used to solve the concentration response equations in order to get an idea on how much relative yield loss each crop is experiencing on account of increased Ozone concentrations in the atmosphere.

5.2 Crops of Importance

Pakistan is a country that experiences all four seasons which opens the opportunity to grow multiple types of crops. The type of soil that Pakistan has favors the cultivation and results in greater yields for most of the crops. There are two cropping seasons in Pakistan:

1. **Kharif** season sowing starts from April and goes till June and the harvesting is done from October to December. The crops that lie under the Kharif season include Rice, Sugarcane, Maize, Pulses and Bajra.

2. **Rabi** season sowing starts in October and goes up to December and the harvesting in done in April and May. Crops like Tobacco, Barley, Wheat and Mustard are grown in Rabi season.

Being an agrarian economy, a lot of crops are economically important to Pakistan, in terms of the import export revenue earned through them which include Cotton, Wheat, Rice, Maize and Soybean. Its not necessary that the crops which account for the highest economic revenue are the ones being produced in greater amount. Talking in terms of production, the crops that are being produced in greater amounts include Sugarcane , Wheat, Cotton, Rice and Maize.

The statistics shown in table 5.1 are taken from the latest economic survey of Pakistan on Agriculture that summarize the production, in tons, of various crops along with the area, in acres, that has been designated for their cultivation through out Pakistan.Table 5.2 shows the list of the crops that we will be focusing on in terms of relative yield losses along with there growing seasons.

Crops Grown in Pakistan		
Crops	Area(acres)	Production(tons)
Sugarcane	3,244	81,108
Wheat	21,582	25,492
Fruits(Punjab)	9,816,76	4,368,125
Maize	3,209	5,702
Rice	7,163	7,442
Cotton	6,669	11,935
Soybean	2,471	260

Table 5.1: Different crops grown in Pakistan along with there Production in tons and area of cultivation in acres [1]

Crop Name	Growing Season
Wheat	Nov-Feb
Maize	Jan-Apr
Soybean	Aug-Oct

Table 5.2: Different crops and there growing season

5.3 Exposure Based Metrics

To get and estimate of the crops yield losses due to exposure of crops to Ozone we have used the knowledge of the important crops for Pakistan. The next thing we had to do was to use the 3D model simulations for Ozone concentrations for growing season of each crop. As we are looking for ozone exposure on vegetation, we will be using certain concentration response equations that can relate to a specific level of ozone to a predicted yield reduction [8].

5.3.1 M12-Mean Metric

M12 is a mean exposure based metric which is represented by equation (5.1) in which the hourly concentrations of Ozone are taking into account for the three month growing season of a specific crop and n represents the number of hours in that three month growing season. As the name suggest, M12, this metric takes into account on the Ozone concentrations of 12 hours of a day that is from 0800-19-59.

$$M12(ppbv) = \frac{1}{n} \sum_{i=1}^{n} \left[O3_i \right] \tag{5.1}$$

A substitute to the M12 metric is M7 and the only difference in between them is the number of hours, that is in case of M7 the concentrations of Ozone taken into account are from 0900-1559.

5.3.2 AOT40-Cumulative Metric

The AOT40 metric is a cumulative metric which takes into account the hourly concentrations of Ozone for the three month growing season, prior the harvest, as given in equation (5.2). AOT40 metric only takes into account the concentrations of Ozone greater than 40 ppb and is considered to be more accurate exposure metric to calculate relative yield.

$$AOT40(ppmh) = \sum_{i=1}^{n} \left[O3_i - 0.04\right] \quad where \quad O3_i > 0.04 \tag{5.2}$$

5.4 Concentration Response Equations and Relative Yield Loss

To assess the recent and future possibility of the impacts on Ozone exposure to vegetation, numerous Open Top Chamber (OTC) field studies were predominantly conducted in the North America and Europe to develop the specific Concentration Response functions for specific crops through which we are able to predict the relative yield response for a specific crop to high Ozone concentrations [10] [11] [12]. The two exposure based metrics that we have defined previously were used by [3], [15] and [16] in there research to create the crop specific Concentration Response Equations. In Table 5.3 shows the CR equations for Soybean, Wheat and Maize using the AOT40 metric as calculated by [16]. In addition to it, Table 5.4 shows the CR equations for

Concentration Response Equations - AOT40		
1	Wheat	$RY = \quad -\left(0.0161 \times AOT40\right) + 0.99$
2	Soybean	$RY = \quad -\left(0.0116 \times AOT40\right) + 1.02$
3	Maize	$RY = \quad -\left(0.0036 \times AOT40\right) + 1.02$

Table 5.3: Concentration Response Equations using AOT40 Exposure Metric

Soybean, Wheat and Maize using the M12/M7 metric as calculated by [3] and [15]. By using these CR equations Relative Yields (RY) were calculated fr each crop, Relative Yield being the crop yield under ozone exposure. Theoretical yield was assumed to

Concentration Response Equations - M12/M7		
1	Wheat (Spring)	$RY = \frac{e^{\left(-\frac{M7}{186}\right)^{3.2}}}{e^{\left(-\frac{25}{186}\right)^{3.2}}}$
2	Wheat (Winter)	$RY = \frac{e^{\left(-\frac{M7}{137}\right)^{2.34}}}{e^{\left(-\frac{25}{137}\right)^{2.34}}}$
3	Soybean	$RY = \frac{e^{\left(-\frac{M12}{107}\right)^{1.58}}}{e^{\left(-\frac{20}{107}\right)^{1.58}}}$
4	Maize	$RY = \frac{e^{\left(-\frac{M12}{124}\right)^{2.83}}}{e^{\left(-\frac{20}{124}\right)^{2.83}}}$

Table 5.4: Concentration Response Equations using M12/M7 Exposure Metric

be 1, that is 100%. Relative Yield was subtracted from theoretical yield for each crop and metric in order to calculate Relative Yield Loss (RYL) as shown in equation 5.3.

$$RYL(\%) = \left(1 - RY\right) \times 100 \tag{5.3}$$

Along with these CR equations, the Ozone concentrations used were of two types:

1. **Predicted :** Ozone concentrations predicted by 3D model at the rural site of Sarsabz and Mustapha Farms

2. **Adjusted :** Ozone concentrations that were corrected for Sarsabz and Mustapha Farms by adding bias correction error to them. The bias error was calculated by subtracting the observed concentrations at Jail Road Station from the model predicted concentrations. We assumed that the error at a rural site will be equal

to that at an urban site for this bias correction application.

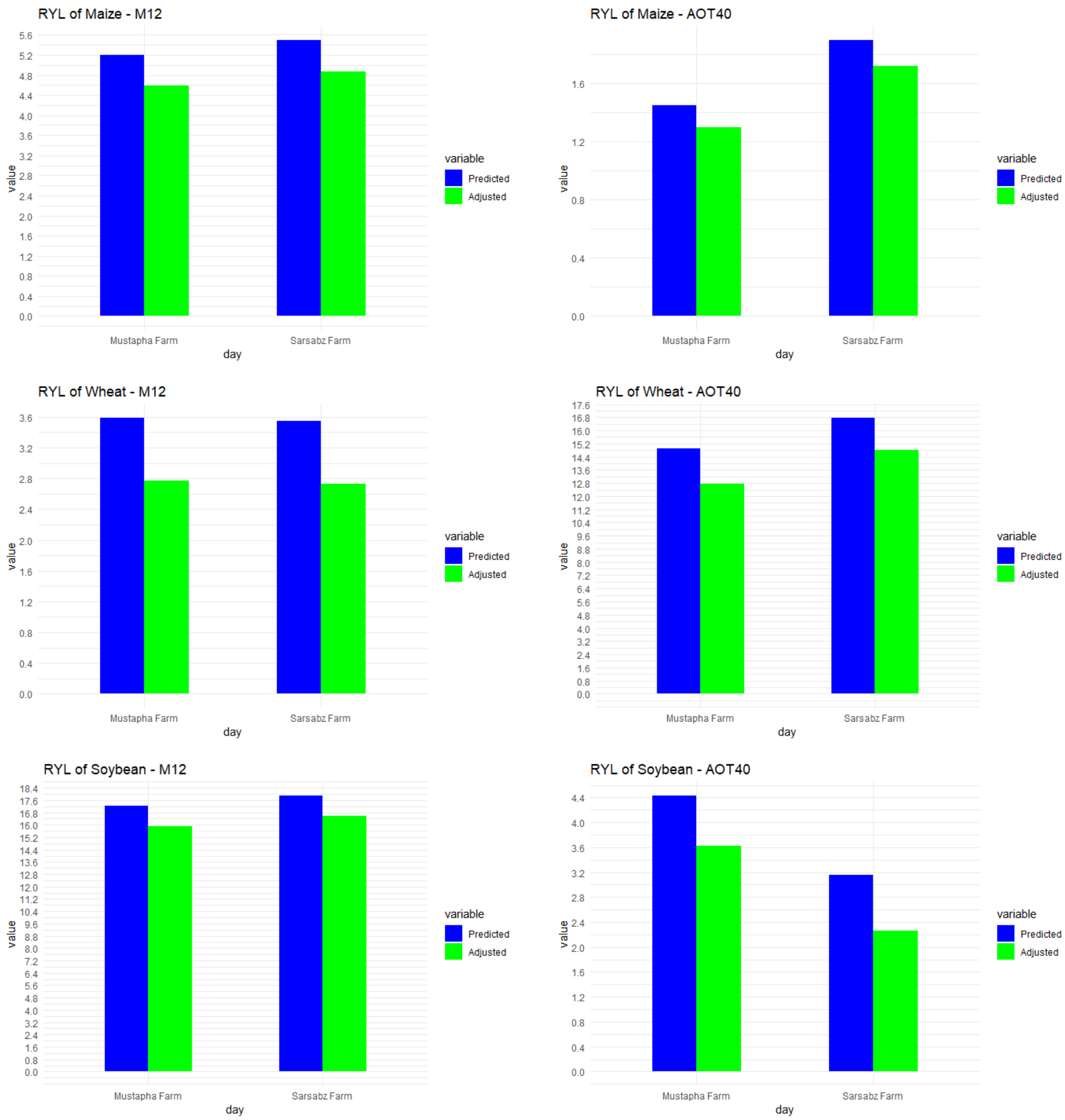

Figure 5-1: Relative Yield Loss (%) of Soybean, Wheat and Maize

Figure (5-1) shows the Relative Yield Loss in % for the three crops and in reference to both the metrics. RYL is calculated for both, model predicted and adjusted concentrations of Ozone for the growing season of each of the three crops When these calculated RYL were compared with the published values in [8] and [9], our yield losses were justified.

Chapter 6

CONCLUSION AND FUTURE WORK

During this research we predicted the risk to the yield of three staple crops (soybean, wheat and maize) by using CR equations that incorporated two Ozone exposure based metrics (M12 and AOT40). We concluded that the relative yield loss for the year 2018 fluctuate between 1.7-5.8% for maize, 5.6-17.6% for wheat and 6.6-18.4% for Soybean depending on the metric we have used. Our results assent with the previous studies done for global crop losses[8], verifying the fact that Ozone does have a strong influence on vegetation. While the emission sources that cause buildup of pollution are located in densely populated urban areas or from industrial zones, the impacts are more widespread, impacting agriculture production. Expansion of the monitoring networks that acquires consistent, long term measurements and the capability to accurate model these phenomena is essential to our understanding of pollution its impacts on human health, agriculture and sensitive ecosystems

The future aspects of this research includes the installation and operation of an instrument suite to monitor the air quality and weather at both the rural sites (Sarsabz and Mustapha Farms) mentioned in this research. The instrument suite to be installed should include sensors for solar radiation and particulate matter. In addition to it, the model simulation can should be conducted on a multi-year scale at a higher spatial resolution along with a detailed comparison against satellite. Lastly, a better correction technique should be applied to adjust the Ozone concentrations that are used to calculate the Relative Yield Losses for key species of crops.

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