

**Monitoring of Glyoxal Column densities in different forest
type of Pakistan by using MAX-DOAS**



BY

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(2019)

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A thesis submitted in partial fulfillment of the requirements for the degree of
Master of Science in Environmental Science

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THESIS ACCEPTANCE CERTIFICATE

It is certified that the contents and forms of the thesis entitled
“Monitoring of Glyoxal Column densities in different Forest types of
Pakistan by using MAX-DOAS” submitted by Mr. Muhammad Ahmed
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DEDICATION

Every challenging work needs self-efforts as well as the guidance of elders especially those who were very close to our hearts.

My humble effort I dedicate to my sweet and lovely

Father Mother and Supervisor

Whose affection, love, encouragement and prays of day and night make me able to such success and honor

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ABBRIEATIONS

CHOCHO	Glyoxal
IESE	Institute of Environmental
NUST	Sciences and
	Engineering - National
	University of Sciences and
	Technology
MAX-DOAS	Multi Axis Differential
	Optical Absorption
	Spectroscopy
DOAS	Differential Optical
	Absorption Spectroscopy
DSCDs	Differential Slant Column
	Densities
VCDs	Vertical Column Densities
VOC	Volatile Organic Compound
SOA	Secondary Organic Aerosols

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ABSTRACT

Forests act as a contributor to the global emissions of biogenic volatile organic compounds (BVOCs). Measurements of their oxidation products, such as glyoxal (CHOCHO), provide useful indicators of fast photochemistry occurring in the lower troposphere. However, measurements of these species in forests location are extremely limited. Air pollution has become a serious issue in Pakistan and Forest also contribute in degrading the ambient air quality, therefore, air quality in forest ecosystem must be monitored continuously to understand the likely impacts of air pollutants on the atmosphere, environment and particularly human health. To address this, CHOCHO concentrations was measured using the multi-axis (MAX) differential optical absorption spectroscopy (DOAS) techniques in different Forest types, and Capital city of Pakistan.

Glyoxal being the tiniest α -dicarbonyl forms during VOC oxidation reactions. It has residence time of few hours determined by photolysis and hydroxyl radical reactions during day time. In the presence of NO_x, glyoxal photolysis results in the formation of secondary organic pollutants along with the tropospheric ozone. This is a pioneer study for glyoxal retrieval in Pakistan's Forest. It presents a comparison of glyoxal retrieval from mini MAX-DOAS measurements at different monitoring sites of Pakistan Forest which include, Sub-Tropical Chir-pine Forest, Himalayan Moist Temperate Forest, Himalayan Dry Temperate Forest, Sub-Alpine Pasture and Alpine Pasture.

At first CHOCHO data was obtained during Field campaigns. Next data set was generated from ground-based MAX-DOAS observations at IESE-NUST (Institute of Environmental Sciences and Engineering - National University of Sciences and Technology), Islamabad, Pakistan. Glyoxal differential slant column densities (DSCDs) were retrieved using DOAS (differential optical absorption spectroscopy) technique. And by using geometric air mass factor approach, tropospheric vertical column densities (VCDs) were derived from measured DSCDs. The retrieved glyoxal was compared over the all Forest sites in respective years. Diurnal, Weekly and Annual Seasonal cycle of glyoxal was investigated for data set of IESE from September-2016 to August-2018. Results showed that CHOCHO concentrations was higher in morning and evening but lower in the noon due to photolysis. It was also observed that CHOCHO was lowest on Friday, while annual seasonal cycle of CHOCHO shows

highest average concentrations in Summers and lowest in Winters over Islamabad. A considerably good correlation of 0.72 and 0.59 was found between MAX-DOAS observations of CHOCHO with temperature and GHI and a positive correlation of 0.44 was observed between MAX-DOAS measurements and NDVI. During field campaigns of different forest types, the CHOCHO concentrations were found to be maximum at Alpine Pasture and lowest at Chir-pine Forest. An anticorrelation of -0.11 was found between the CHOCHO concentration and average temperature and anticorrelation of 0.70 was found between relative humidity and CHOCHO concentrations.

1. Introduction

Human activities result into emission of chemical compounds which get accumulated into troposphere. Photochemical smog produced hinders the opportunities for better living style because of highly degraded air qualities (Finlayson-Pitts and Pitts Jr 1999), causing threat to health of living beings (Molina and Molina 2002)), agricultural yield (Dickens, Gregg et al. 2003) and local climate (Di Girolamo, Bond et al. 2004).

VOCs chemistry and the reactions taking place as a result of their oxidation in the air contributes in direct and indirect climate change (Ramanathan and Crutzen 2003), which also affects human health badly (Pope III and Dockery 2006). Therefore, it's necessary to explore VOCs sources and sinks and their oxidation phenomenon taking place in the atmosphere.

Earth's surface is accumulated by reactive organic compounds, and are released during a variety of processes occurring by Volatile Organic Compounds (VOCs) emissions some in the presence of light (photolysis) and others in the dark. VOCs exist in air in very large amount and their reactivity greatly affects the atmospheric chemistry. Under sunlight, VOCs react with nitrogen oxides emitted mainly from power plants, vehicles and industrial activities to form ozone and ground level particulates. The accumulation of ozone, fine particulates and other gaseous pollutants results in smog that reduces visibility and has other impacts on humans. VOCs acts as the predecessor of ozone and further they provide fuel for tropospheric ozone formation (Houweling, Dentener et al. 1998) (Jongbloed and Koole 2001) This also determines the tropospheric capacity of VOCs to get reduced. They also play crucial role in regulating the formation of second order pollutants (Kanakidou, Seinfeld et al. 2005); (Ramanathan and Crutzen 2003) (Tsigaridis and Kanakidou 2007) (Bianco, Kostarelos et al. 2005) (Volkamer, Jimenez et al. 2006)) and influence the CCN formation (cloud condensation nuclei) (Roberts, Artaxo et al. 2002) (Yu 2000)

1.1. Introduction

Earth's surface is rich in organic compounds which are highly reactive, and are involved in a variety of oxidation processes resulting in the emission of Volatile Organic Compounds (VOCs). As these reactions are continuously occurring, VOCs exist in air in very large amount and their reactivity greatly affects the atmospheric chemistry. VOCs are important pollutant because of its contribution in the production of ground level ozone, providing fuel for its formation. They also play crucial role in regulating the formation of second order pollutants (Bianco, Kostarelos et al. 2005, Kanakidou, Seinfeld et al. 2005, Volkamer, Jimenez et al. 2006, Tsigaridis and Kanakidou 2007) and influence the CCN formation (cloud condensation nuclei) (Yu 2000, Roberts, Artaxo et al. 2002). Tremendous climate change results in global warming, which is a serious hazard worldwide. Average temperature of the earth is increasing due to increased greenhouse gases resulting from man-made activities.

VOCs chemistry also contributes in direct and indirect climate changes (Ramanathan and Crutzen 2003), which in turn affects human health (Pope III and Dockery 2006). Therefore, VOCs sources and sinks and their oxidation phenomenon must be understood. Though volatile organic compounds (VOCs) are present only in trace amounts in the atmosphere, their presence can still drive the formation of air pollutants. As many as 105 different species of VOCs are estimated to have been measured in the atmosphere (Goldstein and Galbally 2007). Glyoxal is a volatile organic compound (VOC) in the atmosphere that is a precursor to tropospheric ozone and secondary organic aerosol. Glyoxal may enter the hydrosphere due to its production, use and application and can be formed by natural processes also thus degrading the life style for healthy living.

Among all the anthropogenic activities, industrialization is the leading cause to it. Human activities result into emission of chemical compounds which get accumulated into troposphere. Photochemical smog produced hinders the opportunities for better living style because of highly degraded air qualities (Finlayson-Pitts and Pitts Jr 1999) causing threat to health of living beings (Molina and Molina 2002), agricultural yield (Gregg, Jones et al. 2003) and local climate (Ramanathan, Crutzen et al. 2001).

1.2. State of forests in Pakistan

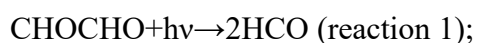
At present forests of Pakistan are suffering from large-scale deforestation and degradation. And it is continuing unprecedentedly by 0.75 per cent per year. In 1992 forested land was 4.242 million ha, which declined to 3.44 million hectares in 2001. Since independence in 1947 61,000 ha of forest land have been converted to some other land use type (Champion, Seth et al. 1965).

On the contrary government statistics show an increase in forest cover by 21.1 percent from 1947 to 1994. This increase is mainly attributed by afforestation and agro-forestry projects and strict control in illegal logging. Different forest types of Pakistan are;

- Alpine scrub
- Sub-alpine forests
- Himalayan dry temperate forests
- Himalayan moist temperate forests
- Temperate coniferous forests in Pakistan
- Sub-tropical Chir pine forest
- Tropical thorn forests
- Tropical dry deciduous forests
- Littoral and Swamp forests

1.3. Chemistry of Glyoxal in Air

Main products of oxidation reactions of BVOCs in the environment which serve as the air pollutants are secondary organic aerosols (SOA) and tropospheric ozone. Their intermediate products like formaldehyde and glyoxal are formed naturally (Volkamer, Platt et al. 2001, Calvert, Atkinson et al. 2002). Glyoxal is a tiniest α -dicarbonyl with mutagenic properties (Kielhorn, Pohlenz-Michel et al. 2004) and its residence time is dependents on their sinks. Photolysis is an important process in the removal of glyoxal from the atmosphere during day time. Glyoxal measurements in the atmosphere are possible by differential optical absorption spectrometry (DOAS). Elevated glyoxal levels will result into active VOC chemistry during that time of the day. The mean photolysis rate was measured under solar radiation as follows



$\text{CHOCHO} + h\nu \rightarrow \text{H}_2 + 2\text{CO}$ (reaction 2);

$\text{CHOCHO} + h\nu \rightarrow \text{H}_2\text{CO} + \text{CO}$ (reaction 3)

Artificially producing glyoxal sources also affect the atmospheric distribution of these species. Particularly, glyoxal (CHOCHO) is produced during oxidation reactions of aromatic hydrocarbons by hydroxyl radical. In these reactions, glyoxal is important ring cleavage specie.

1.4. Sources of Human and Environmental Exposure

1.4.1. Natural Sources

Environmental sources of glyoxal could be natural and man-made. Natural sources include the production of glyoxal by photochemical reactions in the air. Glyoxal can also be produced biologically as a by-product (i.e., for the generation of hydrogen peroxide (Kersten 1990) or by auto-oxidation of lipids (Hirayama 1984). Formation of glyoxal by photochemical reactions from humic acid has also been detected in sea water (Mopper and Stahovec 1986).

1.4.2. Artificial Sources

Man-made sources include cigarette smoke, residential log fire smoke, vehicle exhaust, fog, smog and some household cleaning products. It may also be introduced into the air during combustion of fossil fuel and various other materials (Underwood and Weed 1956).

1.5. Emission of Glyoxal in the Forest

Open burning of biomass is the main source of biogenic emissions which contribute about 55% of global glyoxal concentration. Anthropogenic is 27% while 18% is caused by pyrogenic emissions. Photolysis (51%) is considered as major glyoxal sink, followed by secondary organic aerosol (SOA) formation (22%), oxidation of OH radical (18%) and wet and dry deposition (8%). 6 Important process in removal of glyoxal from atmosphere is photolysis during daytime, while hydroxyl radicals also contribute to a minor extent. Atmospheric residence time is described to be only a few hours (Fu, Jacob et al. 2008). Globally glyoxal concentrations are reported to be 56 Tg annually with the lifetime of about 2.5 h which is agreed with literature studies such as 45 Tg annually

with 2.9 h lifetime (Knipping, Lakin et al. 2000) and 56 Tg annually with 3 h lifetime (Myriokefalitakis, Vrekoussis et al. 2008). The annual global burden of glyoxal is assessed as 15.8 Gg annually (Fu, Jacob et al. 2008). Another study carried out at global scale, estimations are found to be low with a difference of 20% and are mainly due to SOA sinks which are not defined (Myriokefalitakis, Vrekoussis et al. 2008). Total pyrogenic emissions increased by fire emissions contribute about 60% in global glyoxal concentrations, while remaining is subsidized by secondary productions, such as acetylene oxidation, aromatics, glycoaldehyde and ethylene with contribution percentages of 24%, 5%, 4% and 7% respectively.

1.6. Pakistan and Air Pollution Issues

Among the most popular issues, air pollution is predominant, especially in the major cities of Pakistan due to rapid urbanization and vehicular exhausts. This causes several health impacts such as eye infections, reduced lung functions, skin irritations and transmission of infectious diseases. It is of great concern as the retarded lung function due to air pollution can result into lung cancer. During last few years, alarming increase in Asthmatic patients has also been observed due to outdoor air pollution. And studies prove that consistent intake of polluted air makes the diseases more complex (Qureshi, Awan et al. 2016).

Urban air pollution causes 80,000 hospital cases annually. In year 2005 outdoor air pollution alone caused more than 22,600 deaths in adults. Approximately 8,000 chronic bronchitis cases, and nearly 5 million respiratory infections cases in children with age under 5 are reported. Pak-EPA (Pakistan Environmental Protection Agency) has conducted a number of studies to explore the root causes and pollutant concentrations in different regions of Pakistan. Which indicates that concentrations of various pollutants are above Pak NEQS. No relevant study is found on atmospheric glyoxal over South Asia especially 7 in Pakistan. This study will provide a baseline for the atmospheric glyoxal because it plays vital role in atmospheric chemistry as source, intermediate and as a sink specie. Present Study It's a comparative study, conducted for the retrieval of glyoxal, at different Forest types of Pakistan and Islamabad, Pakistan. Data for different forest was collected in a campaign name Forest Campaign and for Islamabad at ARL-IESE-NUST (Atmospheric Research Lab, Institute of Environmental Sciences and Engineering, National University of Sciences and Technology). Two

different data sets were run in QDOAS software to obtain DSCDs (Diffraction Slant Column Densities) of glyoxal.

1.7. Importance of the Study/Research

Glyoxal is considered as one of the major and most prevailing dicarbonyls existing in the atmosphere. Mostly, high concentrations of aromatic and living species suggest that glyoxal distributions in atmosphere could be a great contributor to SOA. Further, it has been detected as a compound which produce higher glyoxal yields, referring to air hydration and polymerization(Jang and Kamens 2001). Health impact of glyoxal on animals has been reported by many researchers but no research has been conducted on humans. Mainly water and food possessing glyoxal concentrations are the contributing routes to human population, whereas air also plays a major role as reported in literature that almost 20 m³ air contain about 4 µg glyoxal/m³(Leblanc, Morales et al. 2000). So, for better understanding of atmospheric chemistry and air quality, it is necessary to have estimates about the actual concentration of glyoxal as its Major portion is emitted from biogenic therefore the proposed methodology has been supported by many scientists and gives direct measurement with accurate result. This study can help us in following perspectives;

Contribution in International database
Baseline for future research in Pakistan
Establishing a relationship between glyoxal, and anthropogenic activities

1.8. Objectives of the Study

1. Ground based monitoring of CHOCHO column densities by using Max-DOAS at IESE-NUST monitoring site.
2. To compare the result of CHOCHO column densities retrieved from stationary MAX-DOAS from areas with different Forest types of Pakistan.

2. Literature Review

Climate change is considered one of the most pressing issue worldwide. World average temperature is increasing due to increased greenhouse gas emissions. Rapid industrialization among all the anthropogenic activities is the leading cause to it. Carbon dioxide contributes a major portion in elevating surface temperature (Laurance 1999, Nath, Bora et al. 2012). The concentration of CO₂ is on a constant rise since 1950's. Its quantity has increased from 315 ppm to 399.89 from 1959 until 2013(Bond, Doherty et al. 2013). This rapid increase is attributed to burning of fossil fuel, production of cement (67%) and shift in land use patterns (33%). Two major sinks namely marine and forest tends to take in about 60% of these emissions while the rest of the 40% are recorded as an increase that has resulted from anthropogenic activities. Forests play a recurring role in minimizing and stabilizing CO₂ concentrations. They are considered as natural sinks as about 60 to 70% of carbon is trapped in the form of organic material in the soil(Clay, Chang et al. 2012). In order to reduce the rising speed of climate change these sinks needs to be protected and enhanced(Lal 2007).

The rising concern of greenhouse gases have forced international organizations to come into an agreement in 1997 in Kyoto (also known as Kyoto Protocol). The signatory states are dedicated to reducing their GHG emissions into the atmosphere. Under this framework new guidelines and strategies have been devised for effective forestry and agricultural practices and their management of carbon sequestration in all types of soils.

The rapid changes in lifestyle have given rise to drastic land use change which is becoming a leading source of man-made emissions after the combustion of fossil fuels. The shift in land use patterns largely effects the storage forms of carbon and biomass in soil.(Chrsquo, Ahmed et al. 2011)

2.1. Climate Change and Global Warming

Climate change is the name of statistical changes in weather distribution patterns, when the changes last for extended time period (i.e., decades to centuries). Climate theory of Earth is constructed on the hypothesis that a balance is maintained between the amounts of energy that it absorbs in the form of UV/visible light coming from sun and the amount

of heat it radiates back to the space in the form of infrared radiation. Variables responsible for change in energy balance and affecting the average temperature of the globe are called forcings since they force the temperature to rise or fall. This includes variations in sun's brightness cycles, particulate matters and aerosols deriving from volcanic eruptions, oceans, anthropogenic sources and changes in amount of heat trapping greenhouse gases in the atmosphere. GHGs include CO₂, CO, NO_x, CH₄, O₃, CFCs and HCFCs. Among all forcings, CO₂ is playing a key role in global warming being the only variable that changes significantly by amount. CO₂ concentrations are increasing continually, reaching up to 400 ppm today, since the last recorded as 280 ppm in 1750 whereas, according to (Change 2007) IPCC CO₂ range of natural emissions are 180 to 300 ppm. Recent oceanic studies states that, Earth's capability to sequester CO₂ naturally is decreasing, and presently the nature is sequestering almost half of the anthropogenic CO₂ being produced.

2.2. Trace Gases and its Effect on Global Warming

Human activities have caused a prominent increase in emission concentrations of trace gases in atmosphere that has triggered the global surface temperature to rise. Variations in natural climate are concealing this continual increase in temperature, but this effect could be doubled or quadrupled, if the trace gas emissions continued, with the present rate, for next 65 years. Climate effects caused by trace gases depend upon the interactions between radiations, atmospheric chemistry and dynamics. These chemical species include CFCs, HCFCs, CH₄, tropospheric O₃, N₂O, and stratospheric H₂O. Trace gases are driving temperature increase by direct and indirect effects in troposphere as well as in stratosphere. CFCs and HCFCs are indirectly affecting the global temperature balance by destroying stratospheric O₃ and allowing the UV radiations to enter in the troposphere. CH₄, NO_x, and CO are the driver of tropospheric O₃ production that has radiative properties in this layer. Tropospheric H₂O can trouble the tropospheric chemistry and promotes the CH₄ and O₃ production. Collectively it can be stated that indirect effects of trace gases can be as important as direct ones (Ramanathan and Crutzen 2003).

2.3. Forest types

Forest includes natural forests and forest plantations. It is used to refer to land with a tree canopy cover of more than 10 percent and area of more than 0.5 ha. Forests are determined both by the presence of trees and the absence of other predominant land uses. FAO 2000a (FRA 2000)

2.3.1. Sub-tropical Chir pine forest

These are inflammable pine forests with, or often without, a dry evergreen shrub layer and no underwood. This main type exists here is Chir pine (*Pinus roxburghii*). Found between 900 m and 1700 m elevation in the Western Himalayas in the range of the south-west summer monsoon. It is the only pine of these forests although there is a minor overlap with *Pinus wallichiana* (Kail, Biar) at the upper limit.

2.3.2. Himalayan moist temperate forests

These forests, with limited undergrowth, includes evergreen and deciduous species. They grow at elevations between 1500 and 3000. Specie distribution is based on lower and uper zone these forest. Dominant species in the lower zone are Cedrusdeodara, *Pinus wallichiana*, *Piceasmithiana* and *Abiespindrow* (Partal) while *Abiespindrow* and *Q. semecarpifolia* are overriding in higher region.

2.3.3. Himalayan dry temperate forests

These types of forest consist of evergreen forest including open scrub brushwood, while some of area also show presence of coniferous and broad-leaved species. This kind of species are most common at North West side of the study area and extended though the length of the area. Main Species are dry zone deodar, *Pinus gerardiana* (Chalghoza) and/or *Quercus ilex*. Blue pine is mostly dominated at inner 12 Trak region of the forest while locally found species also exist there which are; *Juniperusmacropoda* (Abhal, Shupa, Shur) and some *Piceasmithiana*.

2.3.4. Sub-alpine forests

Sub alpine forest species like evergreen conifers and broad-leaved trees mostly found in lower canopy side, typically along with deciduous shrubby undergrowth of *Viburnum* (Guch), *Salix* (Willow, Bed). Such type of forest almost found in throughout Himalayas

range at range of 3350 meter. Common species of these forest types are; *Abies spectabilis* and *Betula utilis* (Birch, Bhuj). High level pine are mostly occurred at burnt sides and landslips.

2.3.5. Alpine scrub

This category mainly includes shrub formations 1 to 2-meter-high but extending up to 150 meters. These forests are characterized by *Salix*, *Lonicera* (Phut), *Berberis* (Sumbul, Sumbul), *Cotoneaster* with *Juniperus* and occasionally *Rhododendron* or *Ephedra* (*Asmania*). With high solar irradiance and low humidity level.

2.4. Earth's Atmosphere

Atmosphere of any planet is defined as a layer of gases surrounding the planet and other material bodies of adequate masses that are detained in place by the gravitational force of the planet. The modern atmospheric state and composition is the result of evolutionary processes starting 4.5 billion years ago. Resilient volcanic eruptions caused the outgassing of water vapor and carbon dioxide that initially formed a gaseous layer around the planet. Afterwards on cooling, these water vapors formed seas and oceans. Different photochemical reactions resulted in accumulation of carbon dioxide and oxides of nitrogen. This accumulated carbon dioxide was then used by the micro-organisms in the oceans to form oxygen. Lately in Early Proterozoic era oxygen started building up in the atmosphere and ozone layer was formed (about 2.4 billion years ago) to support the appearance of first multicellular cellular life on the planet. (Sharp 2017)

2.5. Atmospheric Boundaries

Even though air seems as a well-mixed composite that forms our atmosphere, but physically it is not as uniform as it seems to be. It has number of layers, separated by boundaries, depending upon the varying temperature and pressure with altitude.

Include;

- Troposphere
- stratosphere
- Mesosphere
- Thermosphere

- Ionosphere
- Exosphere

2.6. Air Pollution

Depending upon the nature and its role in atmospheric chemistry, every pollutant has a fate that lies somewhere in the cycle of “emission – chemical transformation - transport - deposition”, this process is schematically described in Figure 2.1. It shows the atmospheric phases of natural and anthropogenic emissions as how they are transformed chemically in presence of day light (and in absence of light as well) and at the end the left overs are deposited either through the process of wet deposition or dry deposition. Sources of these pollutants mainly lie near the ground surface but after being emitted they are chemically transported and distorted vertically and horizontally by wind currents. The ability of any pollutant to affect our health or materials in any way lies in its composition and life time. In this context short lived pollutants principally have local impacts, for example triggering atmospheric pollution issues in industrialized and urban regions, while pollutants with longer life time are transported to the larger distances and altitudes, causing global impacts.

Pollutants are generally in the form of solid particles (i.e., aerosols), chemicals or fumes. Their sources can be anthropogenic as well as natural for instance volcanic\ emissions, biodegradation and gaseous emissions from plants accounts for natural volatile organic emissions. But we are more concerned about anthropogenic sources as we may manage to control them. For instance, CO₂, CO, SO₂, NO_x, and VOCs emissions from fossil fuel combustion (including gas, oil and coal) at domestic and commercial scale. Pollutants are either primary or secondary, depending upon the pathways of their formation. Primary pollutants are emitted directly into the air, for example exhaust from an industry or a car while secondary pollutants are produced as a result of chemical reactions among primary pollutants, for example ozone formation in troposphere (Burn, Henk et al. 1993).

2.7. Glyoxal

Carbonyl compounds are subsets of highly reactive VOCs that significantly contributes in the formation of secondary organic aerosols (SOA) (Finlayson-Pitts and Pitts Jr 1999, Jang, Czoschke et al. 2002). Carbonyls are directly released during incomplete burning

of fossil fuel and biomass, or formed during photochemical oxidation of VOCs (Possanzini, Tagliacozzo et al. 2007). Some of the carbonyls like acetaldehyde and formaldehyde are found to have toxic and carcinogenic nature (Partridge, Shala et al. 1987). Glyoxal, one of the smallest α -dicarbonyl, was found as an important precursor for SOA formation through heterogeneous and homogeneous reactions (Liggio, Li et al. 2005, Fu, Jacob et al. 2008). It is among the most predominant dicarbonyls in contaminated ambient air with 45 Tg/yr as global source (Fu, Jacob et al. 2008). Glyoxal is a mutagenic product formed as secondary pollutant, through oxidation of hydrocarbons (Calvert, Atkinson et al. 2002) (Volkamer, Platt et al. 2001, Volkamer, Molina et al. 2005) and directly emitted from biomass burning and tailpipe emissions (Grosjean, Grosjean et al. 2001, Kean, Grosjean et al. 2001, Hays, Geron et al. 2002, Ban-Weiss, McLaughlin et al. 2008), however when compared with secondary formation pathways, contribution from direct emissions were observed as minor (Volkamer, Molina et al. 2005, Fu, Jacob et al. 2008).

2.8. Glyoxal in Atmosphere

Glyoxal is precursor of formaldehyde that has carcinogenic nature. Many studies have reported tropospheric glyoxal. For example, (Munger, Jacob et al. 1995), reported the mean mixing ratios for glyoxal of 0.04 ppbV and 0.07 ppbV order respectively, in a rural site's boundary layer, originating from biogenic sources, i.e. isoprene (Munger, Jacob et al. 1995, Lee, Zhou et al. 1998). Lower glyoxal values of 0.03 ppbV were reported over pine farm in California (Spaulding, Schade et al. 2003). Glyoxal along with other aldehydes were detected in the air affected by burning of biomass, residential and domestic log fires (Ho and Yu 2002).

2.9. Sources of Glyoxal

Glyoxal have 45 Tg a^{-1} of emissions globally, among these biogenic hydrocarbon's oxidation is responsible for 55%, burning of biomass for 20%, emissions from biofuel burning for 17%, and solely anthropogenic pollution sources for 8%, respectively (Fu, Jacob et al. 2008). From biogenic sources of glyoxal, primarily isoprene and up to some extent monoterpenes dominate. Isoprene is released during photosynthesis to release heat stress. Rate of isoprene emissions is directly dependent on the external temperature. Isoprene, being the most dominant source of most of existing NMVOC (non-methane VOC), accounts for about 65-70% of total glyoxal emissions (Fu, Jacob et al. 2008,

Myriokefalitakis, Vrekoussis et al. 2008, Vrekoussis, Wittrock et al. 2009) and 44% of total VOC flux in the troposphere (Guenther, Hewitt et al. 1995).

2.9.1. Biogenic Sources

Most important precursor of glyoxal is isoprene, contributing up to 47% of glyoxal globally. Oxidation by NO^3 yields large quantities of glyoxal at cost of fractional loss of isoprene itself. Oxidation by OH radical produces glyoxal as secondary pollutant and also tertiary pollutant via glycolaldehyde (HOCH_2CHO) as intermediate. Globally glycolaldehyde contributes for 9.9% molar yield of glyoxal. During the periods when NO_x concentrations are low, glyoxal production process can be delayed even for days. Global isoprene emissions from biogenic sources assessed by MEGAN are 410 Tg a⁻¹, generating about 21 Tg a⁻¹ of glyoxal (Guenther, Karl et al. 2006). Glyoxal is also produced during oxidation of numerous monoterpenes with ozone, including geraniol, citral, D3-carene and α -pinene (Fick, Pommer et al. 2003, Fick, Nilsson et al. 2004, Nunes, Veloso et al. 2005). α -pinene accounts for glyoxal molar yield of about 4%-9%, this production is found to be sensitive to relative humidity and temperature (Fick, Pommer et al. 2003, Fick, Nilsson et al. 2004). According to GEIA inventory global monoterpene emissions are 160 Tg a⁻¹ and on average global glyoxal molar yield from monoterpene oxidation is 2.8%, generating 1.8 Tg a⁻¹ of glyoxal (Guenther, Hewitt et al. 1995). Glyoxal is also produced when aromatic compounds react in abiotic conditions in the presence of hydroxyl and ozone. Photochemical reactions of humic acids in sea water also results in glyoxal production (Mopper and Stahovec 1986).

2.9.2. Anthropogenic Sources of Glyoxal

Among the anthropogenic emission sources acetylene (HC-CH) is the most important precursor and second major glyoxal source (Xiao, Jacob et al. 2007). It is released during combustion activity and against OH oxidation it has mean global lifetime of 18 days. Since acetylene has longer lifetime, it provides free sources of glyoxal and SOA in troposphere, accounting for 20% of the total sources of glyoxal (Bohn and Zetzsch 1998). Aromatic compounds also produce glyoxal during first stages of OH oxidation in ring cleavage reactions (Volkamer, Platt et al. 2001). Several studies have reported that direct biomass and biofuel burning emissions produces glyoxal and its precursor glycolaldehyde (Christian, Kleiss et al. 2003, Greenberg, Friedli et al. 2006). Automotive emissions and successively formed photochemical smog results in the

formation of tropospheric glyoxal (Pitts, Atkinson et al. 1985). In addition, Residential and domestic log fires are among the potential sources of glyoxal (Kleindienst, Shepson et al. 1986, MacDonald, Oetjen et al. 2012). Cigarette smoke emissions have been found to contain traces of glyoxal (Moree-Testa and Saint-Jalm 1981). Ozone when used as water disinfectant reacts with organic carbon in the water to produce glyoxal (Lopez, Ricco et al. 1999). Total anthropogenic glyoxal concentrations of 60% are produced by oxidation of acetylene driven by primary glyoxal concentrations of 20% and aromatic contributing about 15%. Glyoxal concentrations emitted by biogenic sources are considered secondary sources, where isoprene oxidation is responsible for 90% of total emission and remaining is contributed by monoterpenes and ethene. Sinks of glyoxal associated with in cloud SOA formation (4.7 Tg annually) are reported as in fair agreement with literature studies with the preceding estimate (Fu, Jacob et al. 2008). Though aerosols with irretrievable uptake, accounting for 5.9 Tg annually of organic carbon and black carbon and 1.8 Tg annually on sulfates, are found to be much higher than studies conducted by Fu and his coworkers on global budgets of Glyoxal (Stavrakou, Müller et al. 2009). The resulting average lifetime opposite to SOA conversion (ca. 11 h), is found to be two times less than in comparison to the study reported by (Fu, Jacob et al. 2008). Lifetimes in contradiction of photolysis and hydroxyl oxidation are found to be 4.8 h and 14 h, respectively, which are in fair agreement with (Myriokefalitakis, Vrekoussis et al. 2008). It was testified that sinks of glyoxal aerosol are significantly higher when the uptake coefficient from study conducted by (Volkamer, San Martini et al. 2007), taken as 3.7×10^{-3} and total annual estimated concentrations are 9.2 Tg.

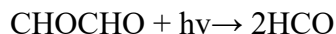
2.10. Removal Processes of Glyoxal

Several processes help to remove glyoxal from air naturally. Photolysis acts as the most prominent sink (Tadić, Moortgat et al. 2006). Other sinks include SOA formation (Volkamer, San Martini et al. 2007), dry and wet deposition (Fu, Jacob et al. 2008), and oxidation mechanisms driven by OH radical (Setokuchi 2011).

2.10.1. Photolysis

Photolysis is the most important removal process of a variety of carbonyls and other pollutants during day time. Atmospheric residence time with respect to photolysis is of

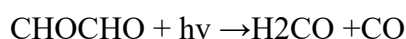
few hours (Tadić, Moortgat et al. 2006). Theoretically photolysis of glyoxal can be shown as follows;



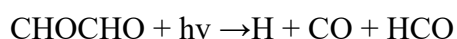
$\Delta H^\circ_{298} = 68.5 \text{ kcal/mol}$; $\lambda \text{ threshold} \leq 417 \text{ nm}$



$\Delta H^\circ_{298} = -2.1 \text{ kcal/mol}$; all λ



$\Delta H^\circ_{298} = -1.7 \text{ kcal/mol}$; all λ



$\Delta H^\circ_{298} = 85.4 \text{ kcal/mol}$; $\lambda \text{ threshold} \leq 334 \text{ nm}$

2.10.2. Wet and Dry Deposition

Due to higher water solubility potential, glyoxal may also be engaged by cloud droplets and aqueous aerosols, resulting in deposition (Betterton and Hoffmann 1988, Zhou and Mopper 1990)

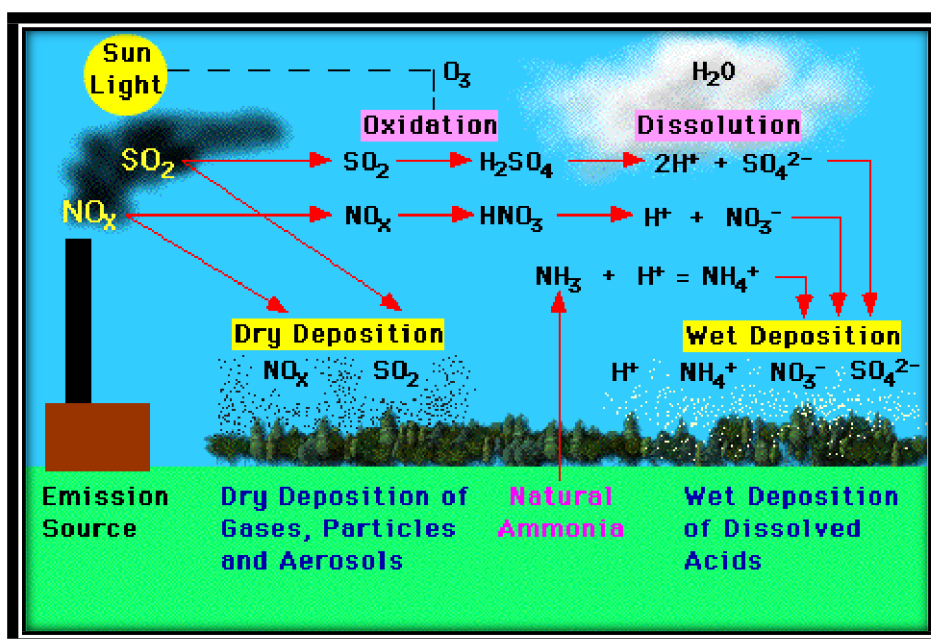


Figure 1 Dry and Wet Deposition of Glyoxal

2.10.3. SOA Formation

Glyoxal potentially contributes for SOA formation as a precursor. It is found as an in-cloud precursor of carboxylic acids formation in atmosphere (Chebbi and Carlier 1996). C-C bonds of carbonyls breaks in gas phase oxidation to yield, more volatile, smaller chemical species (Atkinson, Baulch et al. 2006).

2.11. Atmospheric Residence Time

Glyoxal has short chemical life time depending upon photolysis and reaction with OH radical (Atkinson 2000, MacDonald, Oetjen et al. 2012), it has average life time of 1-2 hours in troposphere and boundary layer, determined by the brightness of overhead sun (Volkamer, Molina et al. 2005), and 2–3 hours worldwide (Fu, Jacob et al. 2008, Myriokefalitakis, Vrekoussis et al. 2008).

2.12. Health Effects of Glyoxal

Glyoxal is a skin irritant, eye irritant and sensitizer as well. Direct contact with chemicals containing glyoxal can cause contact dermatitis (Kielhorn, Pohlenz-Michel et al. 2004).

2.12.1. Carcinogen potential of Glyoxal

Glyoxal is found as direct genotoxic in vitro in mammalian and bacterial cells, it is also found to form DNA adducts, causing mutations, DNA repair, DNA single strand breakings, chromosomal aberrations and sister chromatid exchanges (Kielhorn, Pohlenz-Michel et al. 2004).

2.13. DOAS Technique

DOAS (Differential Optical Absorption Spectroscopy) being a remote sensing measurement is used for the monitoring of trace gas species in atmosphere by using the absorption bands in visible and UV regions. Using this method, trace gas species are recognized by absorption in their visible/Ultra Violet absorption band range. Few of relevant species include NO₂, O₄, CHOCHO, HCHO, H₂O, BrO, IO, O₃, and SO₂.

$$I(\lambda) = I_0(\lambda) e^{-aLC}$$

Lambert-Beer law is the ultimate principle for measurement of absorption cross-section, which states as; the decrease in EM radiation can be related with number of radiations absorbing molecules in optical path length,

Where,

I : measured flux

I_0 : incident flux

α : absorption cross section of the targeted species

L : Length of optical path

C : concentration of the absorbing trace gas (optical density).

Few of the limitations to Lambert Beer law are the presence of numerous gases, scattering phenomena and aerosols (including Rayleigh, Raman and Mie scattering). But still DOAS allows us to overcome these limitations partially, if not fully, particularly the scattering phenomenon and few instrumental impacts. Figure 2.6.1 illustrates the DOAS Principle.

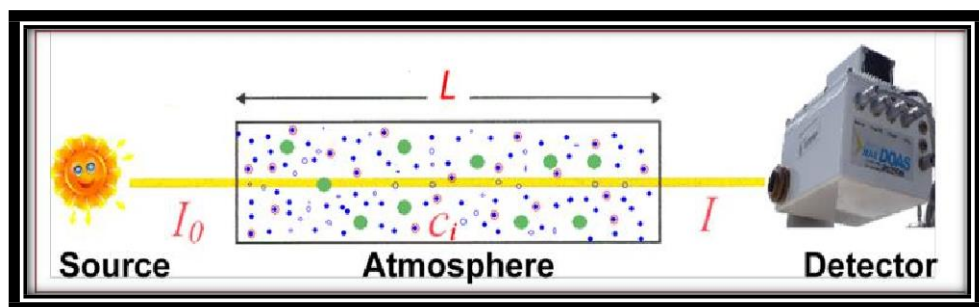


Figure 2: Pictorial view showing DOAS working Principle

3. Methodology

Pakistan having different forest types which are Littoral and Swamp forests: Tropical dry deciduous forests: Tropical thorn forests: Sub-tropical pine forests: Himalayan moist temperate forests: Himalayan dry temperate forests: Sub-alpine forests: Alpine scrub: due to which the emission of glyoxal will be different in all types.

The data is collected in summer by stationary MAX-DOAS as glyoxal concentration are maximum in summer through the oxidation of a number of volatile organic compounds (VOCs). In order to investigate glyoxal emission from different forest type we design this experiment to monitor glyoxal column densities in areas having different forest type of Pakistan.

Table 1: Different forest types where data was collected

Sr. #	Forest Type	Monitoring Duration
01	Sub-tropical chir pine forest	3 days
02	Himalayan moist temperate forest	3 days
03	Himalayan dry temperate forest	1 day
04	Sub-alpine Pasture	1 day
05	Alpine Pasture	1 day

3.1. Site Description

3.1.1. Site A: IESE-NUST

Site A in this study shown by red balloon in Figure 3.1 on which the instrument was placed as fixed measurement at the top of the two-story building (referred as Air Research Lab, IESE-NUST,) pointing towards the South, on Institute of Environmental Sciences and Engineering (IESE), which is located at Islamabad (33.6416° N, 72.9835°

E), Pakistan. On the north side of the site A there is Kashmir highway, on the south west side there is grand trunk (GT) road and IJP road on its south side. All of these roads carry major transportation load of both light and heavy vehicles passing through and within the twin cities of Islamabad and Rawalpindi. On the southeast side of the IESE-NUST – the fourth most populated city (population of 2.16 million) of Pakistan, Rawalpindi city is situated with poor air quality as compared to Islamabad (population of 0.9 million).

3.1.2. Measurements at IESE-NUST Site

The time period for measurement was from September 2016 to August 2018. The angle used for the data collection were (2, 4, 5, 6, 10, 15, 30, 45 and 90). Having interval of about one minute per angle and it almost take 9 minutes to complete the cycle.

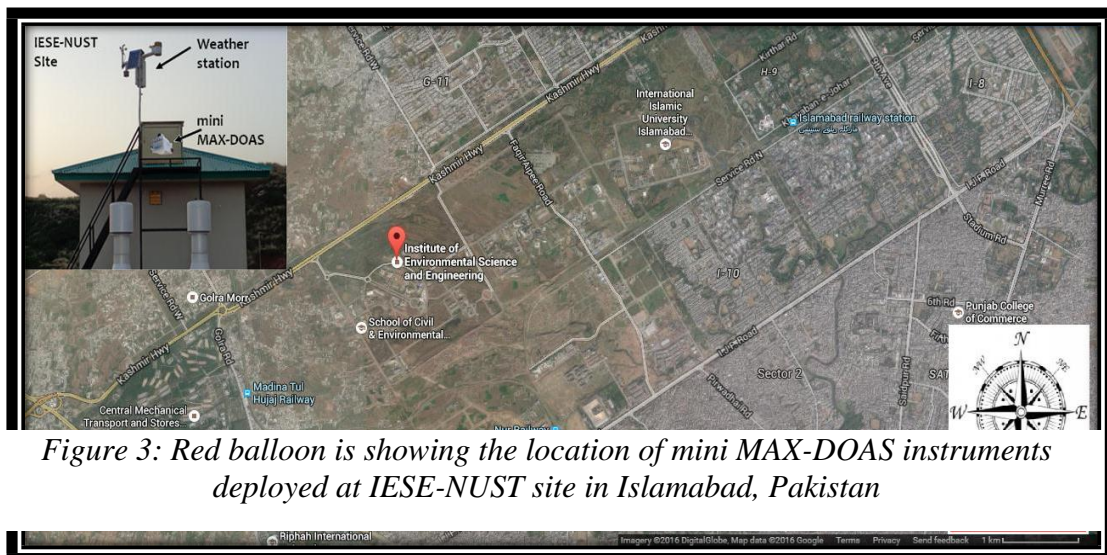


Figure 3: Red balloon is showing the location of mini MAX-DOAS instruments deployed at IESE-NUST site in Islamabad, Pakistan

3.1.3. Site B: Different Forest Types of Pakistan

Site B contain different forest types which are shown in table 2. The instrument was mounted on all mentioned forest types at their top looking above the canopy cover.

Table 2: *Enlisted is the detailed schedule for fixed ground monitoring and Field campaigns*

Activity Details	Location	Dates
**GM: Continuous Ground Monitoring	Islamabad	8th September 2017 – 31 th August 2018
*FC-1: MAX-DOAS field campaign	Shinkiari(Sub-Tropical Chir-Pine Forest)	12 th July 2018
*FC-2: MAX-DOAS field campaign	Shinkiari(Sub-Tropical Chir-Pine Forest)	13 th July 2018
*FC-3: MAX-DOAS field campaign	National Tea Garden-Shinkiari	14 th July 2018
*FC-4: MAX-DOAS field campaign	Pine Park Hotel, Shogran(Moist Temperate Forest)	16 th July 2018
*FC-5: MAX-DOAS field campaign	Pine Park Hotel, Shogran(Moist Temperate Forest)	17 th July 2018
*FC-5: MAX-DOAS field campaign	Pine Park Hotel, Shogran(Moist Temperate Forest)	18 th July 2018
*FC-6: MAX-DOAS field campaign	Rama-Astore(Dry Temperate Forest)	21 th July 2018
*FC-7: MAX-DOAS field campaign	Deosai National Park(Alpine Pasture)	22 th July 2018
*FC-8: MAX-DOAS field campaign	Naran-Batakundi (Sub-Alpine Pasture)	25 th July 2018

*FC=Field campaigns, **GM=Ground Monitoring

The spectra will be acquired for a time period of two year. Analysis will be performed to retrieve CHOCHO Differential Slant Column Densities (DSCD). Then tropospheric vertical column densities (VCD) of CHOCHO will be derived from measured DSCD by using geometric air mass factor approach. Furthermore, ground-based mini MAX-DOAS observations will be compared among different forest types of Pakistan.

3.2. The instrument Mini MAX-DOAS

The Instrument which is used for this research is Mini MAX-DOAS (Multi Axis – Differential Optical Absorption Spectroscopy) instrument which is a fully automated, light weight spectrophotometer with dimensions of 13cm × 19cm × 14cm it is used to perform ground-based measurements and can also use for field campaigns, as it can scan air while tied up on moveable and fixed platform..

It contains electronically controlled spectrograph with optical fibers. The Viewing angle elevation is being controlled by using a stepper motor which rotate the instrument between the horizontal and vertical.

The Spectral range of the instrument is 320 nm to 460 nm with 0.5 nm resolution. Mini-MAX-DOAS is operated on desktop or laptop having XP Window and window 7 operating system, installed with DOASIS software having a script in which all detail of operation is given.

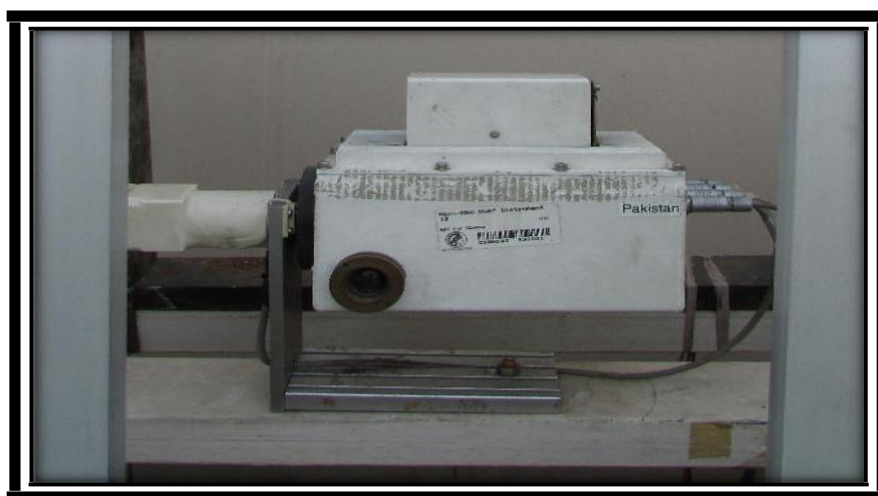


Figure 4: Mini-MAX-DOAS instrument mounted at roof top of IESE-NUST building in Atmospheric Research Laboratory

3.3. Software/Tools

Software which were used for the analysis of glyoxal from data are listed in table 3.

Table 3: Software used, their versions and respective Tasks

Sr no.	Software	Version	Tasks
1	DOASIS (differential optical absorption spectroscopy intelligent system)	3.2.350	Operating software for MAX-DOAS
2	WinDOAS (Windows differential optical absorption spectroscopy)	2.1	Calibration
3	QDOAS (Q differential optical absorption spectroscopy)	2.110.1	Retrieve DSCDs
4	Microsoft Excel	Microsoft office 16	VCD extraction and graphical representation

3.4. Software required for the analysis

- 1 DOASIS
- 2 WinDOAS
- 3 QDOAS
- 4 Excel

3.4.1. DOASIS

DOASIS (Differential Optical Absorption Spectroscopy Intelligent System) is the simple and sensitive software required for running the MAXDOAS. MAX-DOAS is a powerful remote sensing measurement technique which provides valuable vertical

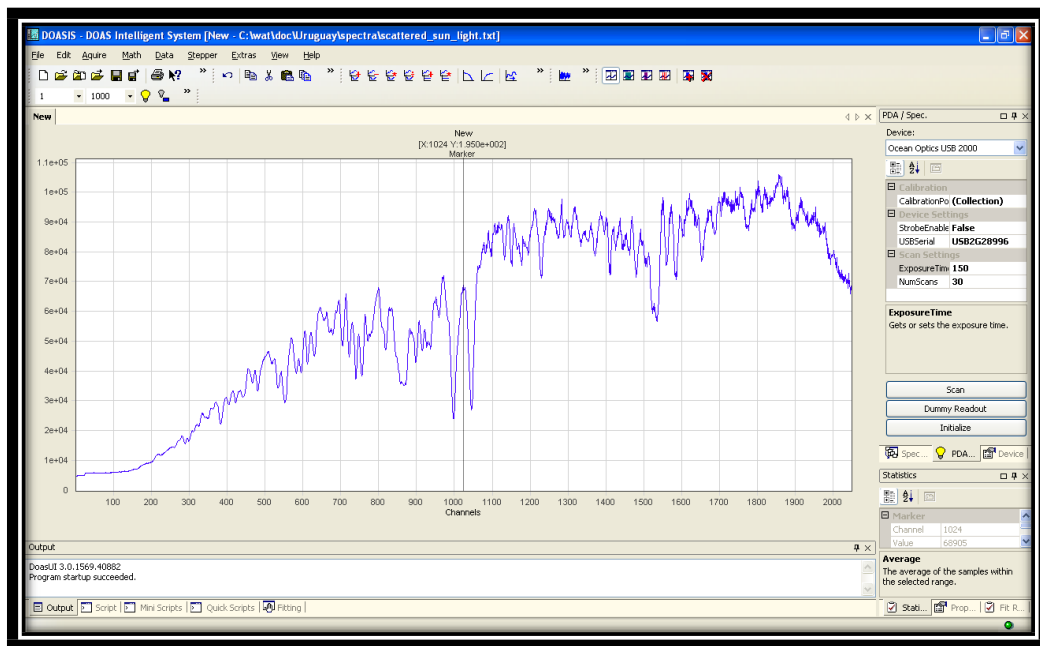


Figure 5: Pictorial view of DOASIS Window

distribution information on atmospheric aerosols and trace gases (Platt and Stutz 2008). It works on the manuscript of which all the details about instrumentation and command are given. Its main functions are to measure spectra and control spectrometer temperature, stepper motor and integration time per spectrum. Figure 5 is showing pictorial view of DOASIS while taking spectrum.

DOASIS is used to calculate dark current, offset and Ring spectrum for spectrometer, all of these are used in DOAS fit analysis in further steps. Dark current and offset is used for zero correction of measured spectra.

Measurement of spectrum in “No photons” condition called Offset; it is measured in dark in other words. A smaller integration time and large number of scans are used for measuring Offset spectra as enlisted in table 3.2. Whereas, Dark current is the smaller electric current flowing through DOAS spectrometer and to measure it, small scan number with moderate integration time must be used shown in table 4.

Table 4: For dark current and offset measurements usually used Values

Parameter	Integration/Exposure time (milliseconds)	Scan numbers
Offset Measurement	~10-100	~1000-10000
Dark current	~10000	1

Slant column densities of glyoxal were retrieved from measured spectra using QDOAS software (Q Differential Optical Absorption Spectroscopy) (Danckaert, Fayt et al. 2017). A high-resolution solar spectrum was used for wavelength calibration in WinDOAS (Kurucz 1984). For glyoxal, 434-460 nm wavelength analysis window was chosen. For DOAS fit absorption trace gas cross section used were;

Glyoxal(Volkamer, Molina et al. 2005),

NO₂ (1×10^{17} molecules/cm², 298 K) and

NO₂ (220K) (Vandaele, Hermans et al. 1998),

O₃ (223K) (Serdyuchenko, Gorshchev et al. 2014)

O₄ (293K) (Thalman and Volkamer 2013),

H₂O (296K, HITEMP)(Rothman 2010),

Ring (Ring_NDSC2003)

and online convolution of these cross-sections were done with constant offset and fifth order polynomial degree in the fitting process of QDOAS. For glyoxal analysis, WinDOAS and QDOAS were used in the following three major steps:

▪	Wavelength Calibration
▪	Wavelength Convolution
▪	Glyoxal Analysis

3.4.2. WinDOAS

3.4.2.1. Wavelength Calibration

The calibration process is done using a measured spectrum fitted to a convoluted solar spectrum. The WinDOAS (Windows Differential optical absorption spectroscopy) was used for calibration of wavelength a high intensity spectrum of noon is used for this purpose.

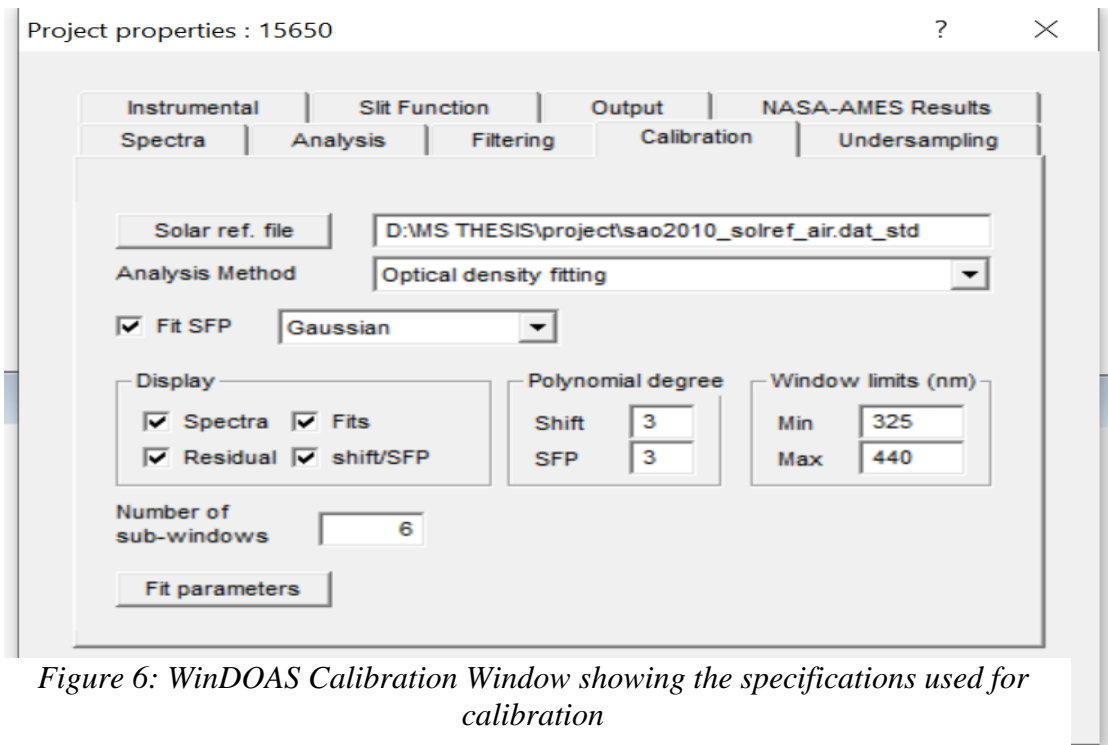


Figure 6: WinDOAS Calibration Window showing the specifications used for calibration

Calibration fit is often referred as “Kurucz-fit” since high resolution spectrum is used as input and convolutes it accordingly as per the spatial resolution of mini-MAX DOAS the spectrum (usually taken at 90° of noon time/with least SZA) taken at noon was used as it has high intensity. Whole wavelength is split up into innumerable sub-windows. The residual error in the calibration process could be reduced by repeating the calibration twice. At the end this calibrated spectrum is used for the analysis of all measured spectra in QDOAS.

3.4.3. QDOAS

3.4.3.1. Wavelength Convolution

The convolution was performed in QDOAS software by using “Convolution tool”, as Convolution is a mathematical process vital for wavelength processing operations. In this case, online convolution was performed. Additionally, Gaussian shape as slit function with 0.5 nm FWHM was used.

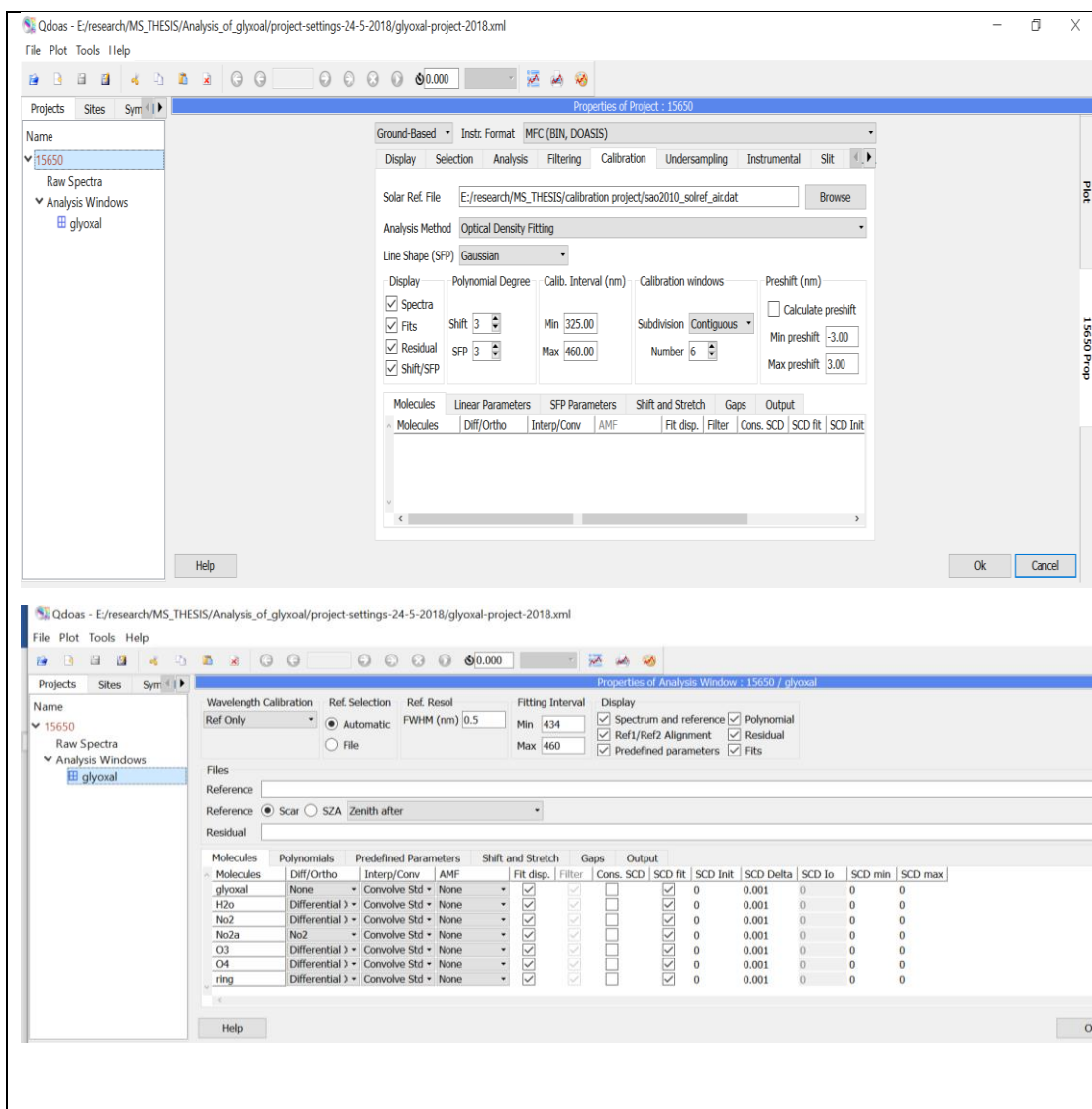


Figure 7: QDOAS windows showing specifications used for online convolution

3.4.3.2. Glyoxal Analysis Window

For glyoxal, wavelength range of 434 - 460 nm was used after various run and the lowest permissible fit error residual. The formerly created calibrated spectrum is the reference spectrum used here for analysis. DOAS is generally used technique for the retrieval of trace gases in troposphere and boundary layer (Platt and Stutz 2008). As a self-calibrating technique, it identifies the structure of absorption molecules allowing the various trace gas retrievals simultaneously within designated wavelength interval. Taking in account the related absorption cross sections of each trace gas, retrieved spectral signature of the gas are then transformed to SCDs (slant column densities). MAX-DOAS technique was specifically developed for the retrieval of information about trace gases having shorter life time, from the observations accompanied for the lower angles of elevation (Leser, Hönninger et al. 2003, Hönninger, Friedeburg et al. 2004, Wittrock, Oetjen et al. 2004, Heckel, Richter et al. 2005, Frieß, Monks et al. 2006, Sinreich, Volkamer et al. 2007).

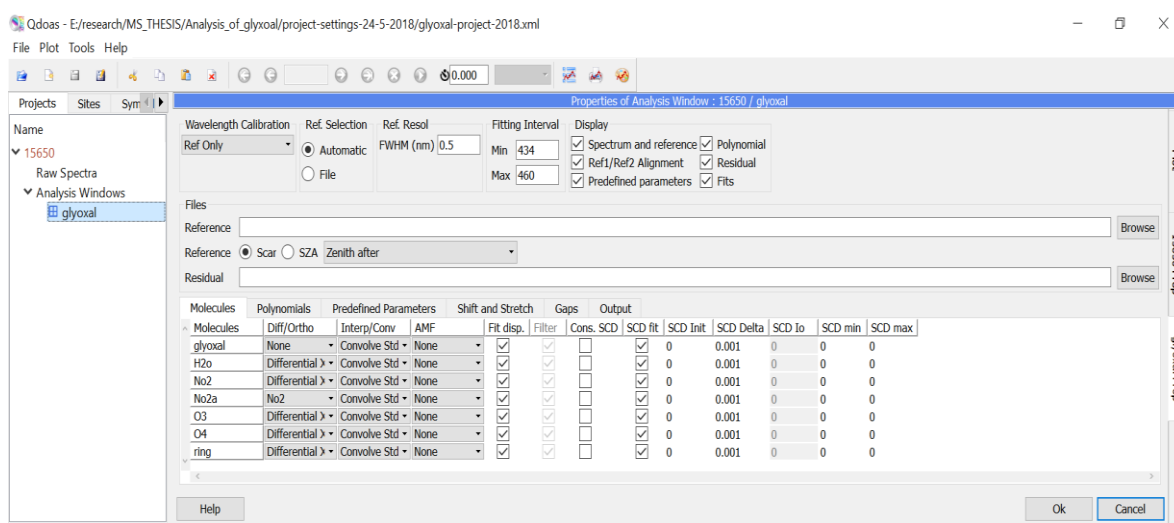


Figure 8: QDOAS Analysis Window showing specifications used for analysis

3.4.4. Microsoft Excel

The results of QDOAS are automatically saved on the pre-assigned path in computer as ASCII file and later on those files are opened as Delimited; Space; General file in MS Excel. An example of MS Excel type, QDOAS output file is shown in fig. 9.

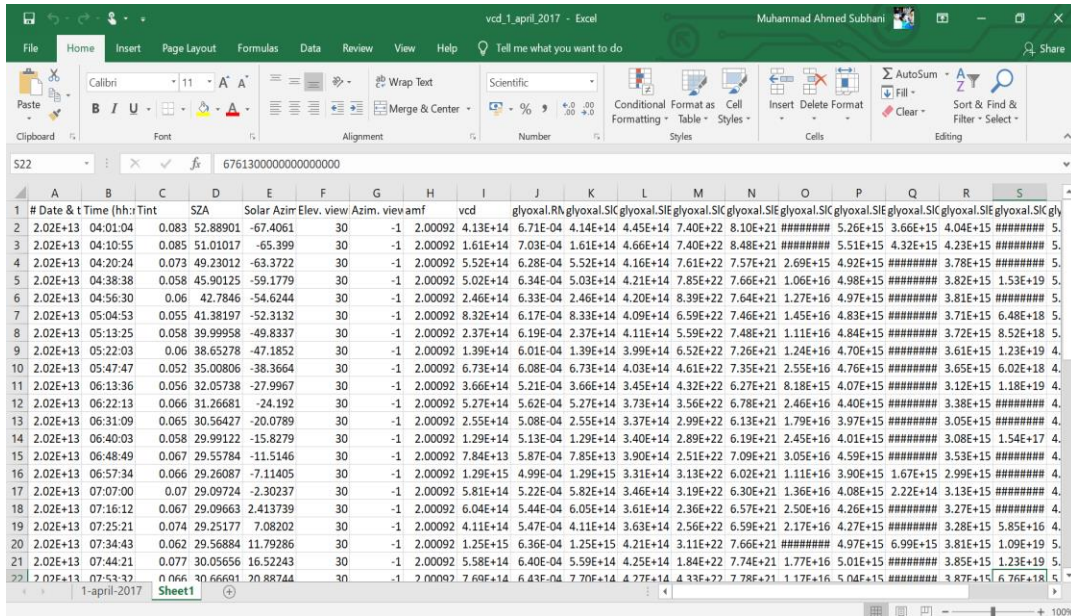


Figure 9: Microsoft Excel Window showing glyoxal Root Mean Squares (RMS) and glyoxal (DSCD) values

3.5. Glyoxal Retrieval Process

The glyoxal DSCDs were obtained by applying DOAS fitting method (Sinreich, Volkamer et al. 2007, Platt and Stutz 2008) to the retrieved spectra (Fayt and Van Roozendaal 2001). DSCDs retrieved as output in the form of ASCII files are basically the difference between SCDs (measured at 30° elevation angle) and the selected reference spectrum (it is a Fraunhofer reference spectrum acquired at minimum SZA; $\alpha = 90^\circ$). By applying shift and stretch, measured spectra were then adjusted against the selected Fraunhofer reference spectrum and fitted cross sections.

Table 5: Details of cross-sections used with convolution specifications

Sr.#	Cross-sections	Convolution
1	Glyoxal (Volkamer, Molina et al. 2005)	Standard Convolution
2	NO ₂ at 298K (Vandaele, Hermans et al. 1998)	Standard Convolution
3	NO ₂ at 220K (Vandaele, Hermans et al. 1998)	Standard Convolution
4	O ₃ at 223K (Serdyuchenko, Gorshchev et al. 2014)	Standard Convolution
5	O ₄ at 293K (Thalman and Volkamer 2013)	Standard Convolution
6	H ₂ O (296K, HITEMP)(Rothman 2010)	Standard Convolution
7	Ring (Ring_NDSC2003)	Standard Convolution

Two different NO₂ absorption cross-sections were used to avoid any error in glyoxal DOAS fit, which was primarily caused by inadequate removal of NO₂ absorptions. NO₂ surely acts as a strong absorber in the selected wavelength interval. Due to its ill-defined wavelength calibration and temperature dependency of its absorption cross-sections, it can give biased results.

The optimal settings used for glyoxal DOAS fit are enlisted in Table 3.4., Quantitative filtering of retrieved DSCDs was done by applying filter of 2.0×10⁻³ on RMS (root mean square) column in the excel sheet. An example of retrieved glyoxal DOAS fit is shown in Fig. 3.6.2. The spectrum was measured on 26th June 2013 at 2:17 PM at 5° elevation angle. The reference absorption cross sections used are glyoxal (Vandaele, Hermans et al. 1998, Bogumil, Orphal et al. 2003, Volkamer, Molina et al. 2005, Thalman and Volkamer 2013), water vapor (Rothman 2010). Using the suggested settings, analysis was performed. For each day an automatic reference was used to run analysis in QDOAS. From the retrieved DSCDs tropospheric glyoxal VCDs were calculated using the differential air mass factor method. AMF calculation using radiative transfer modeling is dependent upon several factors like, viewing geometry, cloud fraction, surface albedo, aerosol loading and previous profile of trace gas absorber (Hendrick, Roozendael et al. 2006, Wagner, Burrows et al. 2007).

Usually for the conversion of SCDs (Slant column densities) to VCDs (Vertical column densities) the AMF calculations are used.

The VCDs (VCD_{trop}) in troposphere is equal to the ratio of SCDs and AMF as shown in the equation 1:

$$\text{Equation 1} \quad \text{VCD}_{\text{trop}} = \frac{\text{SCD}_{\text{trop}(\alpha)}}{\text{AMF}_{\text{trop}(\alpha)}}$$

By using the geometric approximation, the AMF can be assessed as shown in the equation 2:

$$\text{Equation 2} \quad \text{AMF}_{\text{trop}} = \frac{1}{\sin \alpha}$$

For the derivations of VCDs from field campaign data and ground monitoring data elevation angle of 30° was selected. Practically we often do not have information about

all these parameters. Still, this can be done using geometric approximation (Sinreich, Volkamer et al. 2007) given by following equation.

$$\text{VCD}_{\text{geo}} = \frac{\text{DSCD}_{(\alpha)}}{\text{DAMF}_{(\alpha)}} = \frac{\text{DSCD}_{(\alpha)}}{(1/\sin_{(\alpha)} - 1)}$$

Where;

α : Elevation angle

and the indecisions (mostly introduced by spatial inhomogeneity of the absorber, aerosol load etc.) presented for NO₂ by this method are up to 20% (Pikelnaya, Hurlock et al. 2007) and might not outstrip in the case of glyoxal retrieval as well (and we assume that due to shorter time span, it mostly exists in the boundary layer of troposphere and its concentrations in the semi-urban environments are found nearly homogeneously dispersed).

4. Results and Discussion

4.1. Concentrations of CHOCHO during Field Campaigns

MAX-DOAS measurements for CHOCHO VCDs were performed from 12th July 2018 to 25th July 2018 in the Northern Areas of Pakistan as shown in the table 6.

Table 6: Maximum and average Concentrations of CHOCHO observed during Field Campaigns

Location	Date	Avg._CHOCHO VCDs (molec/cm ²)	MAX_CHOCHO VCDs (molec/cm ²)	CHOCHO Mixing ratios (ppbv)
Shinkiari(Sub-Tropical Chir-Pine Forest)	7/12/2018	3.30887E+14	1.55817E+15	0.281
Shinkiari(Sub-Tropical Chir-Pine Forest)	7/13/2018	4.90304E+14	1.93852E+15	0.417
Tea Garden-Shinkiari	7/14/2018	4.1492E+14	1.51421E+15	0.353
Shogran(Moist Temperate Forest)	7/16/2018	3.69195E+14	1.0919E+15	0.314
Shogran(Moist Temperate Forest)	7/17/2018	4.23586E+14	2.15771E+15	0.361
Shogran(Moist Temperate Forest)	7/18/2018	5.3329E+14	2.32596E+15	0.454

Rama-Astore(Dry Temperate Forest)	7/21/2018	5.14003E+14	2.31847E+15	0.437
Deosai(Alpine Pasture)	7/22/2018	6.50532E+14	4.97352E+15	0.554
Naran-Batakundi(Sub-Alpine Pasture)	7/25/2018	5.9333E+14	2.64906E+15	0.505

Maximum average concentration (0.554 ppbv) of CHOCHO was found on July 22, 2018 in Alpine pasture (Deosai, Gilgit Baltistan) followed by Sub-Alpine pasture in Naran, Khyber Pakhtunkhwa where an average concentration of 0.505 ppbv was recorded.

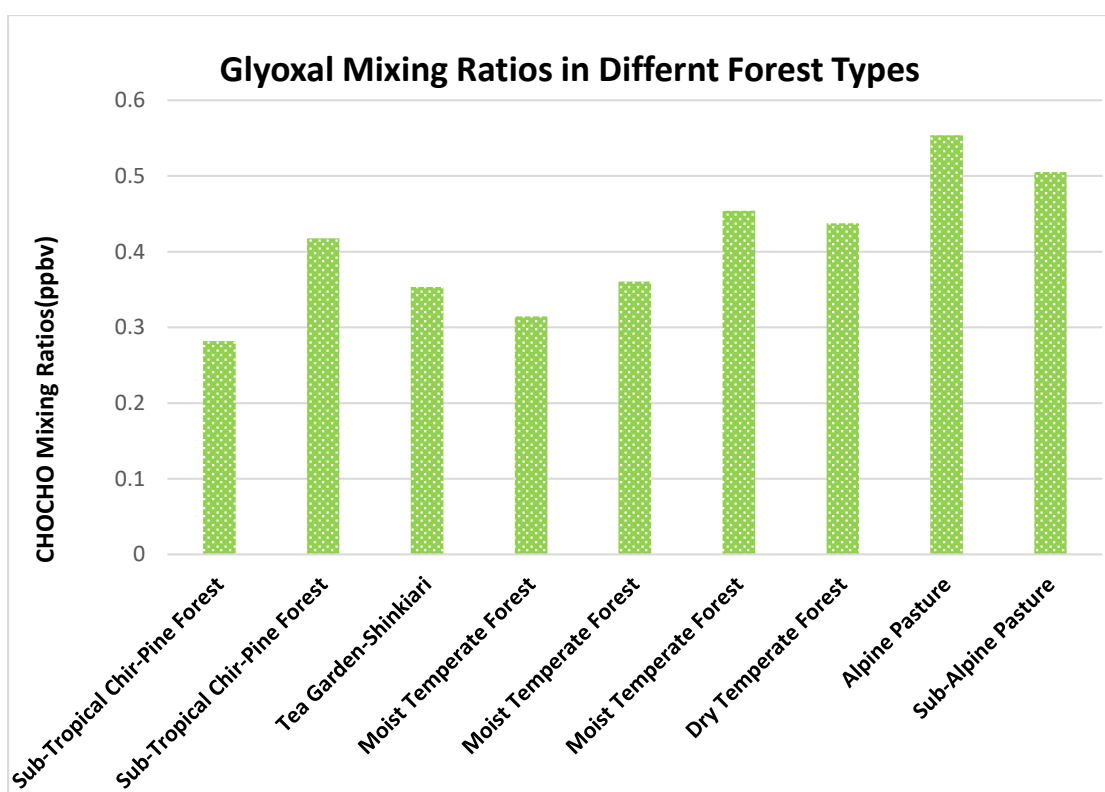


Figure 10: CHOCHO conc. (ppbv.) for Field campaigns in different forest types of Pakistan

The CHOCHO concentrations in different forest types of Pakistan were compared with the average temperature in the respective areas of field campaigns (figure 11). An anticorrelation of -0.11 was found between the CHOCHO concentration and average temperature (figure 12).

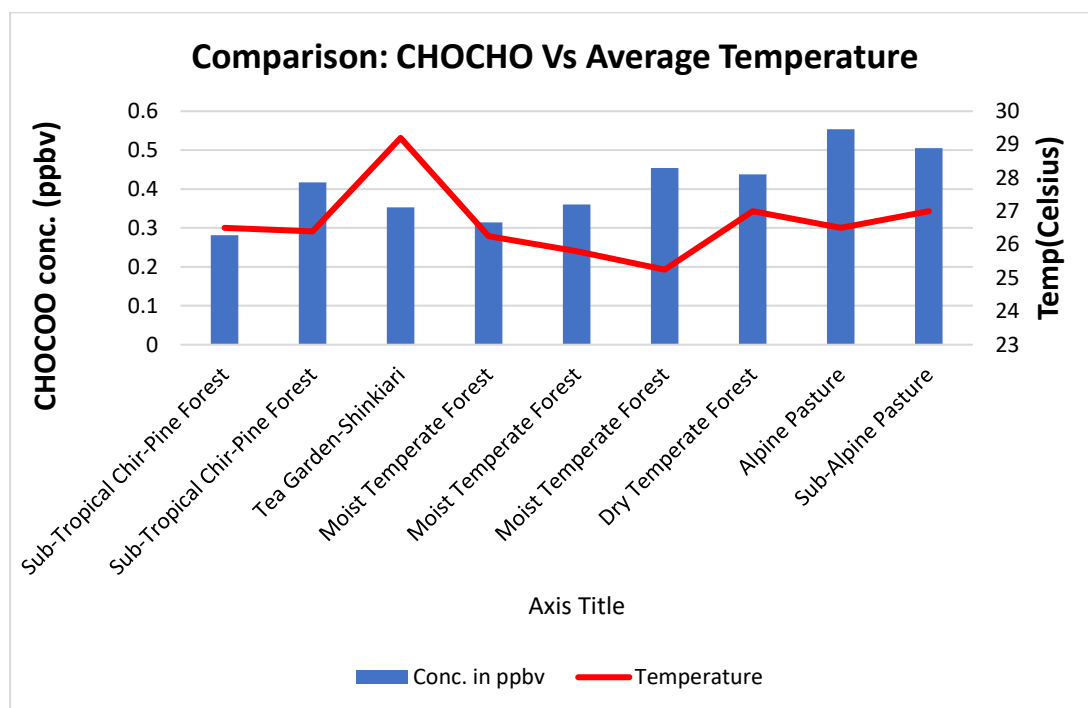


Figure 11: Comparison of CHOCHO concentration in different forest types of Pakistan with the average temperature in these areas

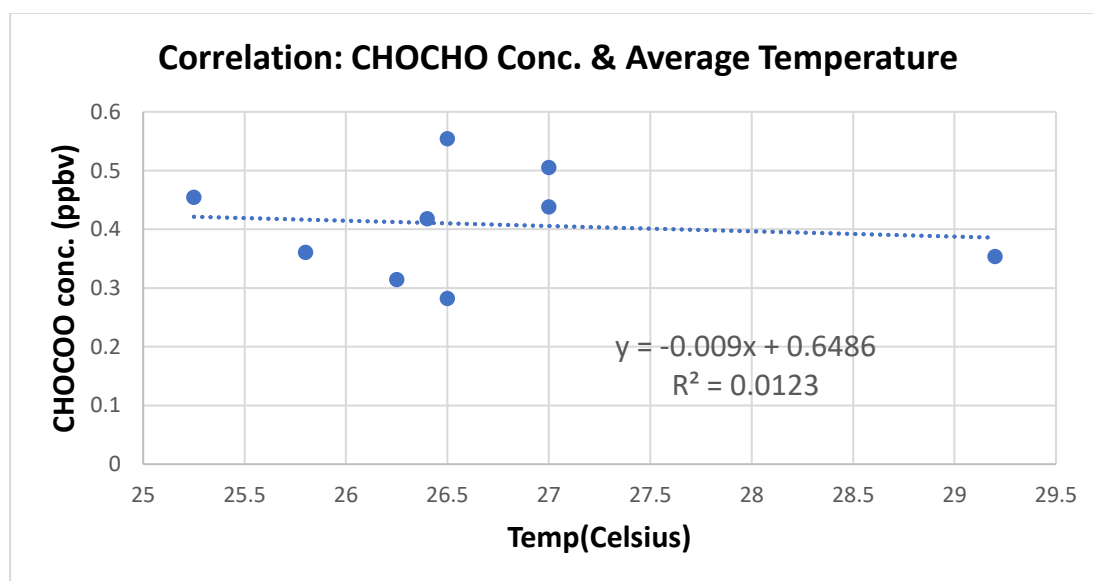


Figure 12: Correlation between CHOCHO concentration with the average temperature in different forest types of Pakistan

Also, the CHOCHO concentrations were compared with the relative humidity over the respective campaign sites. An anticorrelation of 0.70 was found between relative humidity and CHOCHO concentrations.

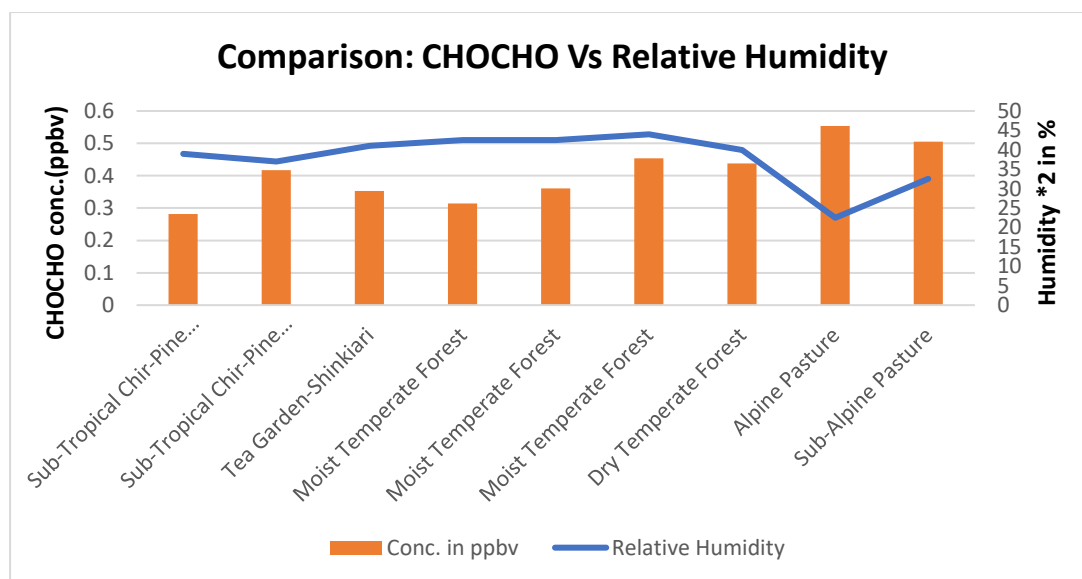


Figure 13: Comparison of CHOCHO concentration in different forest types of Pakistan with the Relative Humidity in these areas

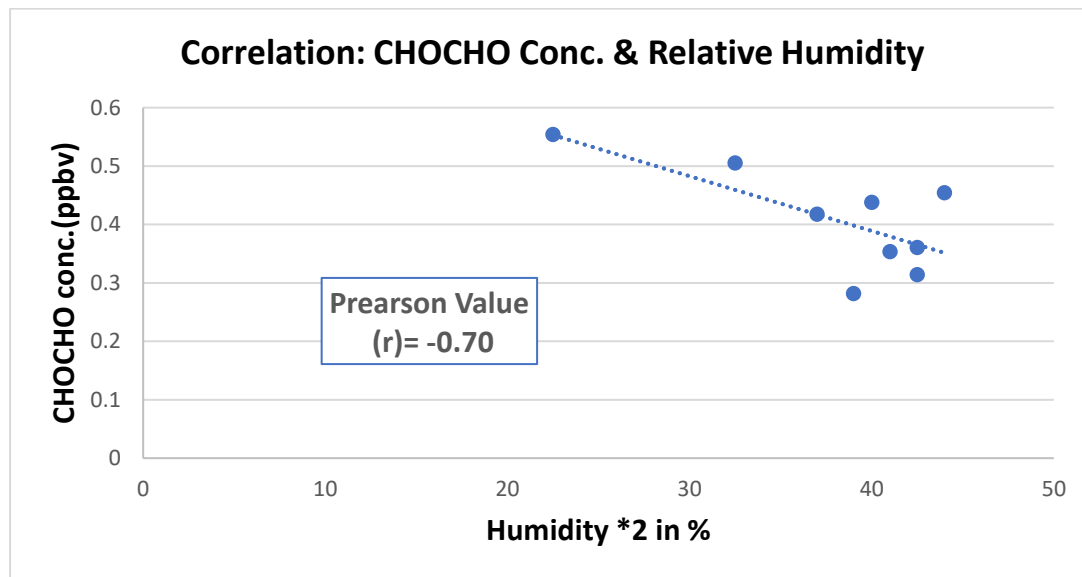


Figure 14: Correlation between CHOCHO concentration with Relative Humidity in different forest types of Pakistan

4.2. Glyoxal timeseries over IESE, NUST

Apart from measuring the glyoxal column densities in various forest types of Pakistan, continuous monitoring of glyoxal was carried out in Islamabad at the NUST-IESE rooftop for 2.5-year time period i.e. from February, 2016 to August, 2018. Figure 15 shows the glyoxal vertical column densities for a period of 2.5 years over IESE, NUST. This location in Islamabad has plentiful vegetation in its surroundings therefore, an effect of this vegetation on the overall glyoxal concentration measured at this site was studied. Figure 16 shows the mixing ratios of glyoxal in parts per billion by volume calculated from the VCDs measured by MAXDOAS at the concerned location (IESE).

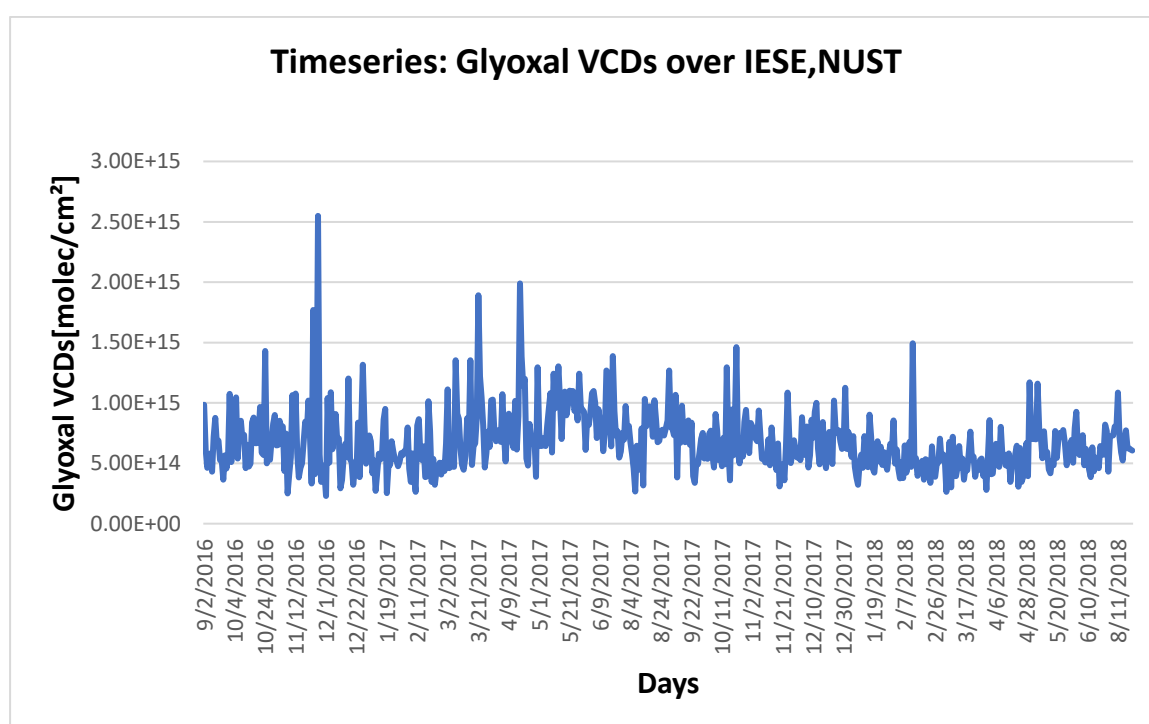


Figure 15: CHOCHO Vertical Column Densities over IESE, NUST

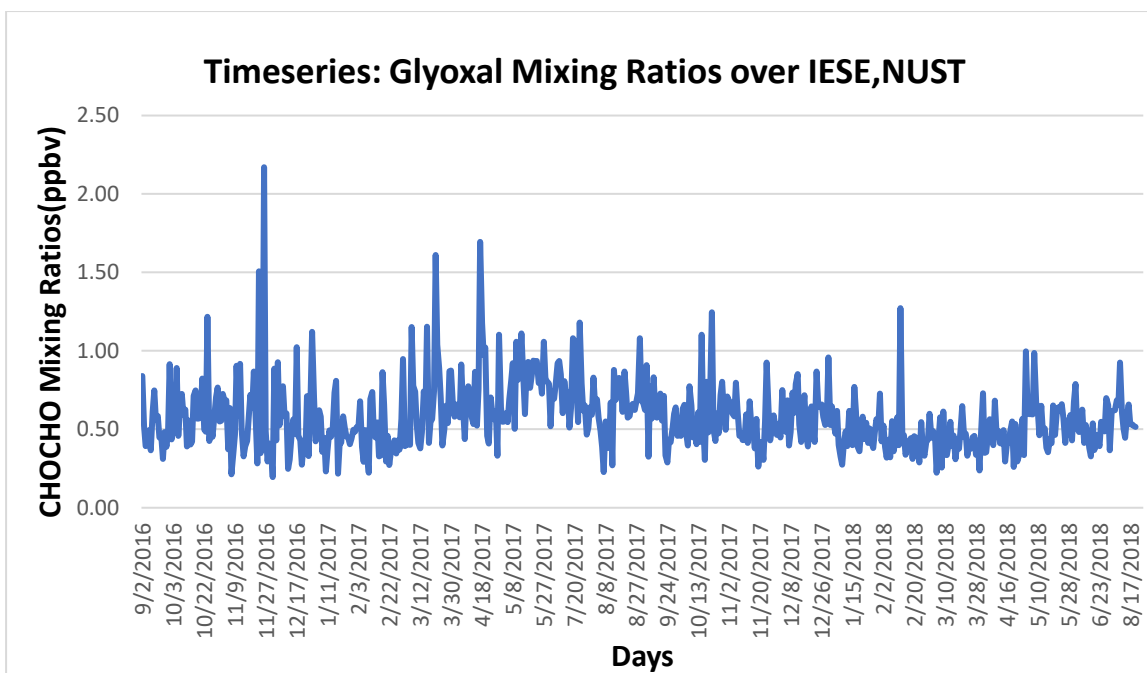


Figure 16: CHOCHO Mixing Ratios over IESE, NUST

4.3. CHOCHO Diurnal Cycle

The diurnal cycle of CHOCHO for 2.5 years from February, 2016 to August, 2018 time span is shown in figure. It can be observed in the figure 17 that initially the CHOCHO concentrations are high around 6-7 am this is because of the oxidation of accumulated VOCs from previous night due to lack of solar intensity at night. As the sun rises, oxidation of VOCs starts and glyoxal is produced as a by-product. But soon after the sunrise the concentration of CHOCHO tends to decrease due to its photolysis. As the day proceeds, the actinic flux increases and thus the temperature also tends to increase which causes an increase in the biogenic emissions of VOCs (such as isoprene) from vegetation. During this period the oxidation of VOCs to glyoxal tends to dominate its photolysis. In the evening the concentration of CHOCHO is also high mainly because of the traffic rush hours in the evening and also due to decrease of photolysis in the evening. The diurnal cycle when compared to GHI, shows that increase in GHI increases CHOCHO in the atmosphere (figure 18) mainly due to increase in oxidation of its precursors.

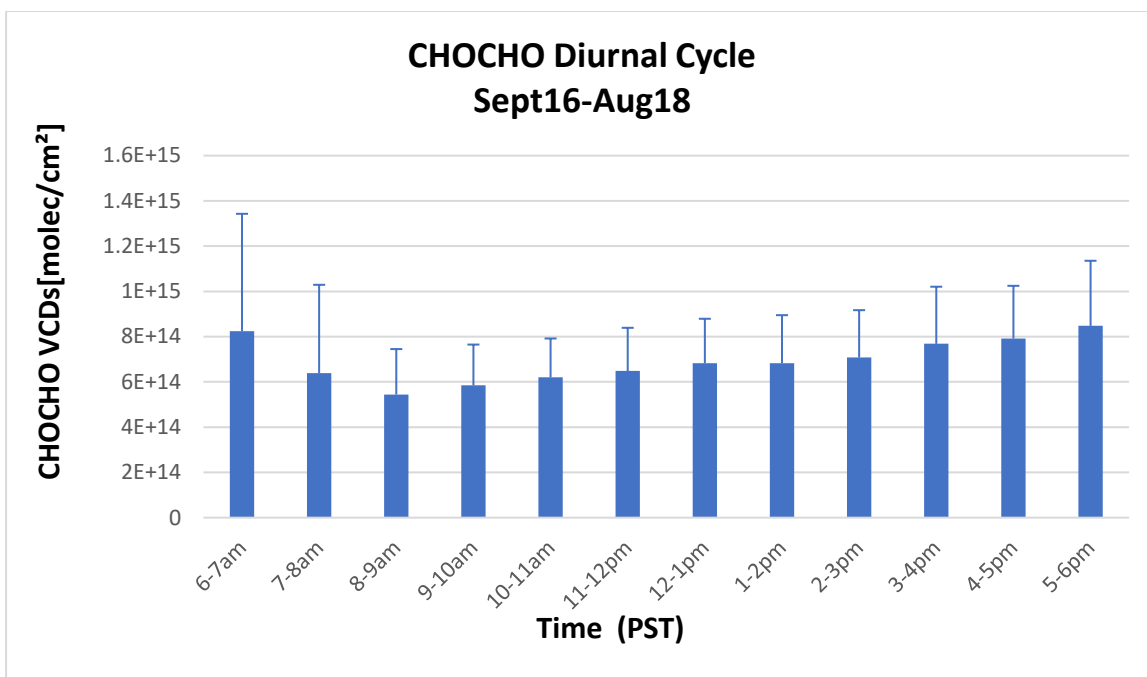


Figure 17: CHOCHO Diurnal cycle over IESE over a period of 2.5 years

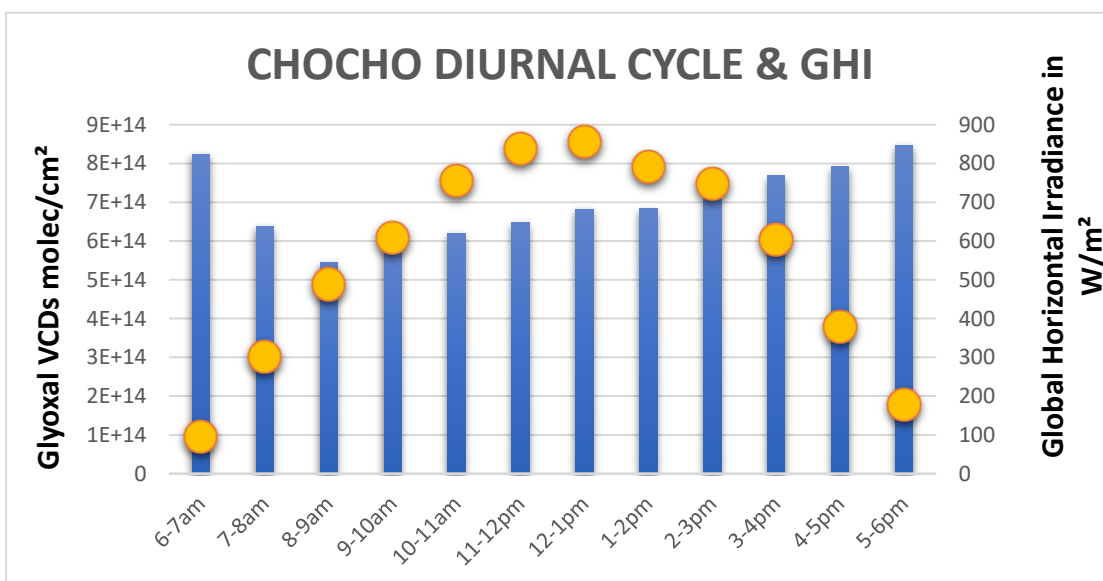


Figure 18: Comparison of GHI with CHOCHO Diurnal Cycle

4.4. CHOCHO Weekly Cycle

Figure 19 shows the weekly cycle for glyoxal VCDs measured at IESE. It can be observed that the measured CHOCHO VCDs are minimum compared to the other days of the week on Friday. This effect could be attributed to the fact that Friday is a business holiday so the contribution from the anthropogenic sources (e.g. transportation) of glyoxal and its precursors is limited on Friday.

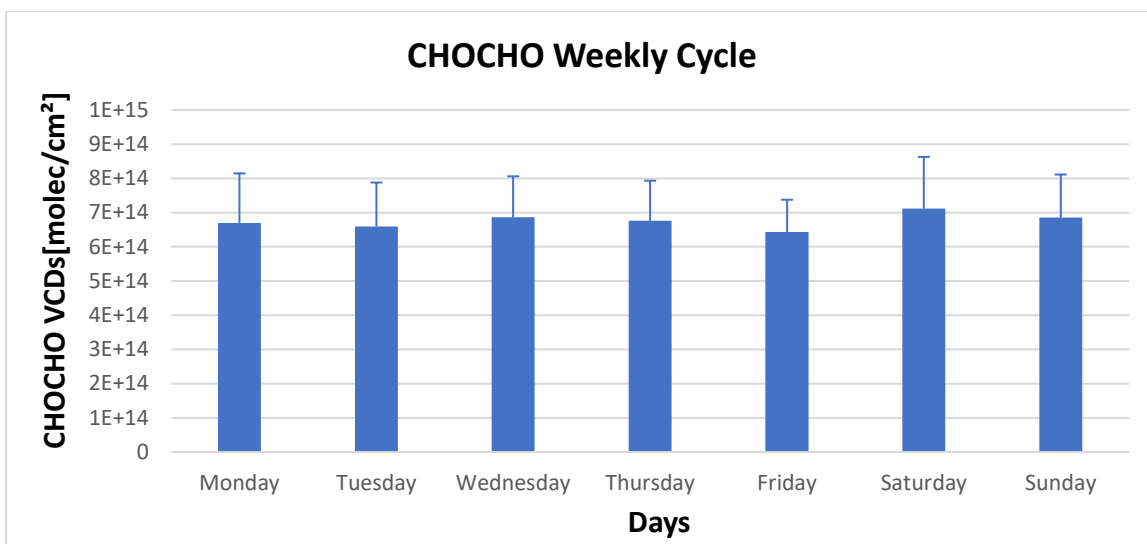


Figure 19: CHOCHO Weekly cycle over IESE for a period of 2.5 years i.e. from September 2016 to August 2018

4.5. CHOCHO seasonal cycle

Figure 20 shows the trend of variation in CHOCHO VCDs in different seasons of the year for 2.5-year timespan at IESE, Islamabad. It can be evidently seen in the figure that highest VCDs were recorded in summer season while lowest CHOCHO VCDs were recorded in winter season. This trend is mainly due to the temperature difference in both seasons. Higher temperature brings about greater emissions of glyoxal precursors e.g. isoprene from the vegetation. Hence the biogenic sources of glyoxal are at their peak in summer season and are found at minimum levels in winter.

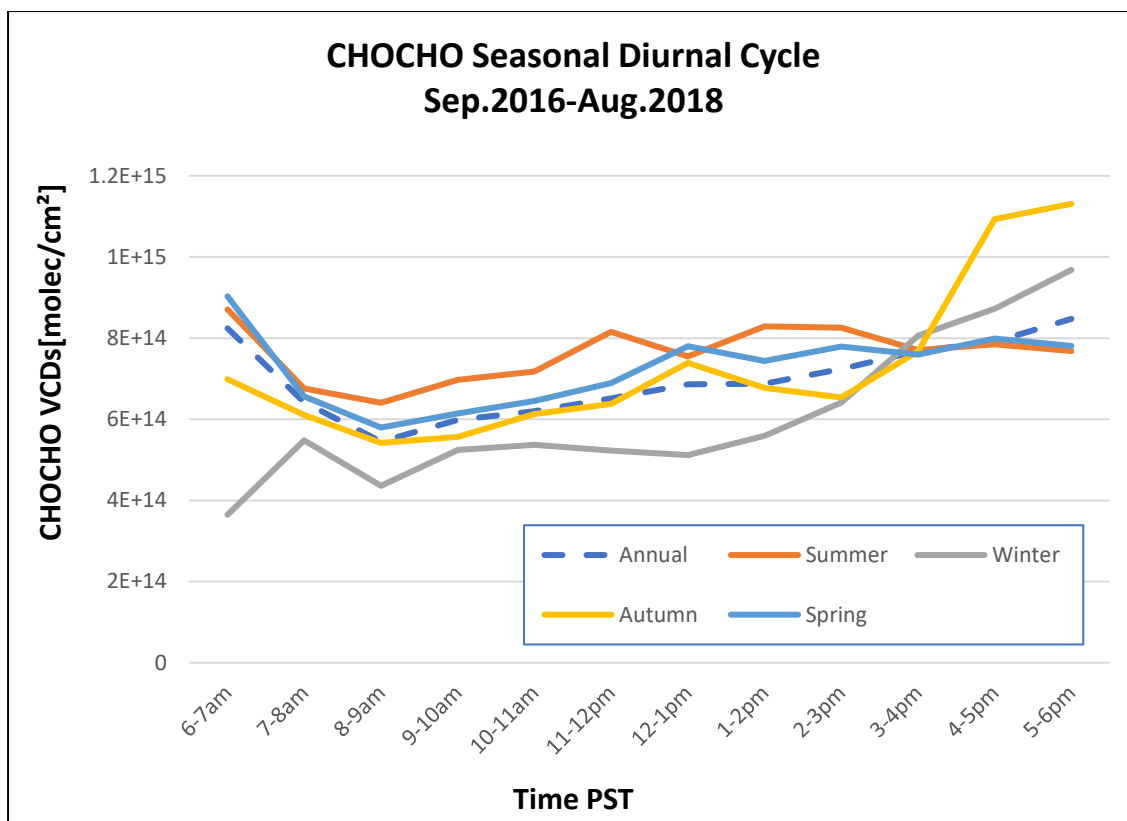


Figure 20: CHOCHO Diurnal cycle over IESE for different seasons of the year from September 2016 to August 2018

4.6. CHOCHO Monthly Cycle

A box and whisker plot were made to depict the monthly CHOCHO VCD variation over IESE, Islamabad (figure 21). It is clear from the figure that in summer months highest CHOCHO VCDs were recorded and on contrary, minimum CHOCHO VCDs were recorded in winter months. This particular trend is the effect of three major factors i.e. solar radiation, temperature and vegetation cover.

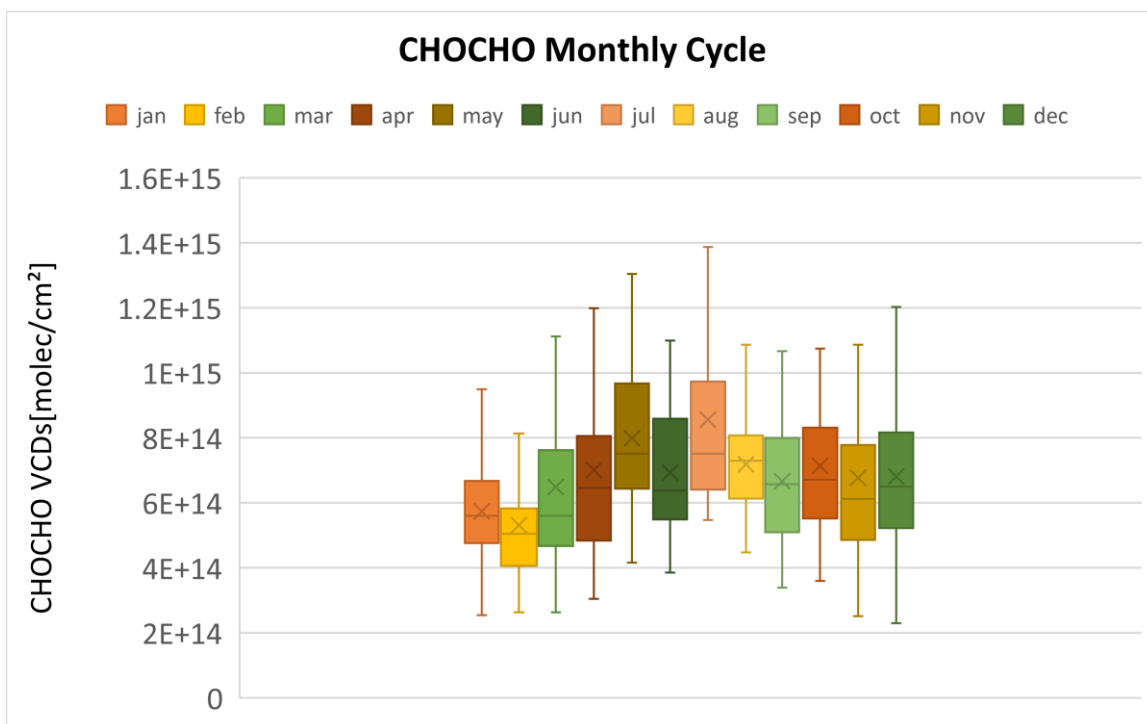


Figure 21: CHOCHO Monthly cycle over IESE for a period of 2.5 years

The CHOCHO monthly cycle was compared with monthly average temperature data and solar radiation data for the 2.5-year study period over Islamabad as shown in figure 22. It was observed that the CHOCHO VCDs increase with the increase in temperature and Global Horizontal Irradiance (GHI). A considerably good correlation of 0.72 and 0.59 was found between MAX-DOAS observations of CHOCHO with temperature and GHI (figure 25). Also, CHOCHO VCDs were compared with % relative humidity (figure 23) which also showed a positive but weak correlation.

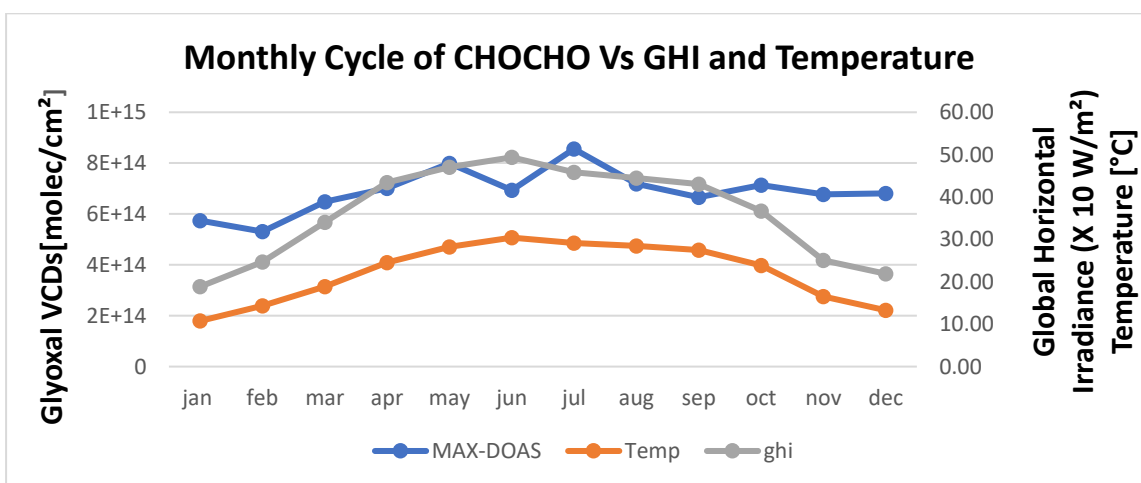


Figure 22: Comparison of CHOCHO Monthly VCDs with GHI and Average Temperature

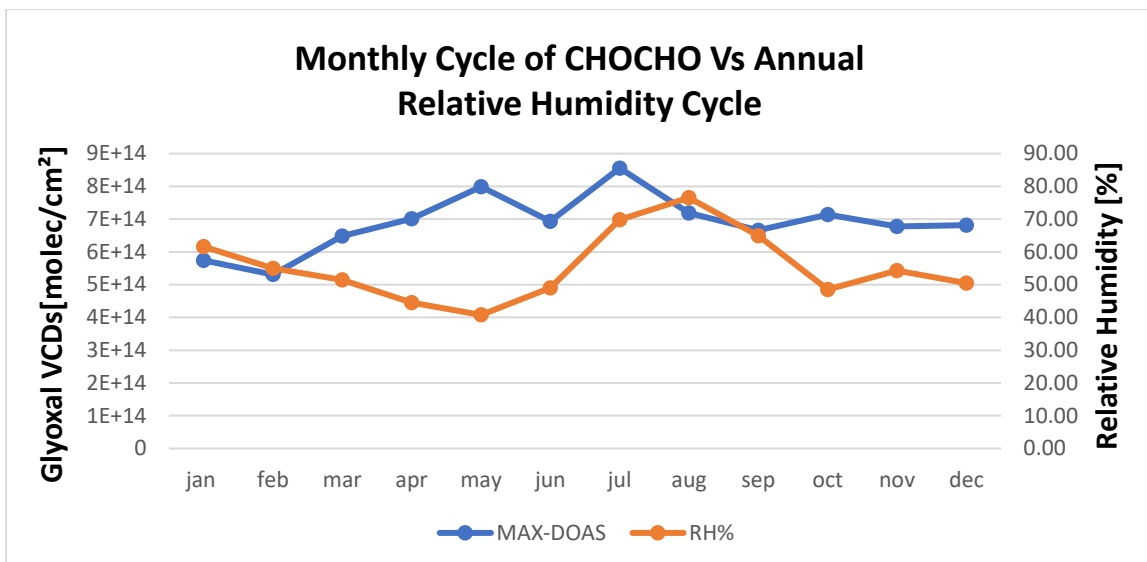


Figure 23: Comparison of CHOCHO VCDs with Relative Humidity

High temperature induces stress on many species of plants and different VOCs are released by them to cope up with the heat stress as a response (Holopainen & Gershenzon, 2010). One of the major CHOCHO precursor, isoprene is also released by plants in such response pathway. So, it is expected to have greater CHOCHO concentrations in the areas where there is greater vegetation cover. To study the impact of vegetation in surroundings of IESE, NDVI values for a point location in IESE surrounding, were compared with CHOCHO VCDs measured using MAX-DOAS (Figure). A positive correlation of 0.44 was observed between MAX-DOAS measurements and NDVI (Figure).

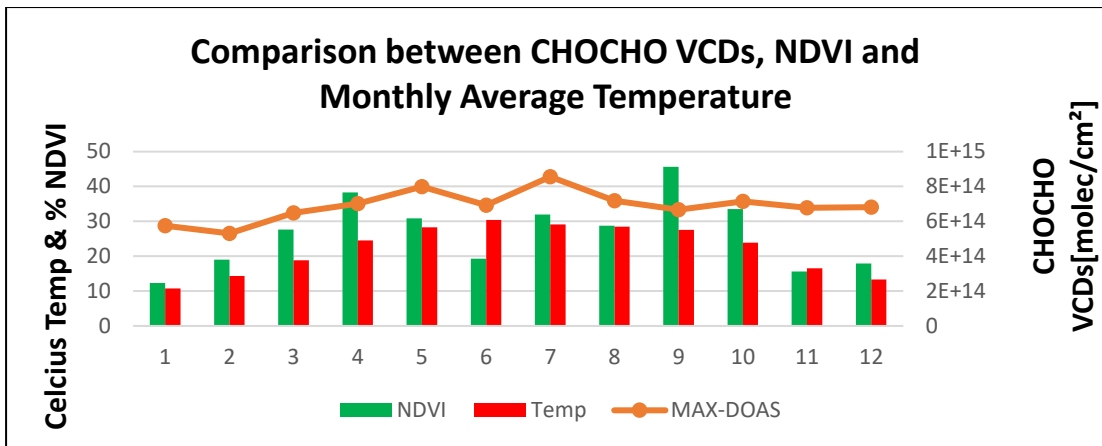


Figure 24: Comparison of CHOCHO with NDVI and Monthly Average Temperature

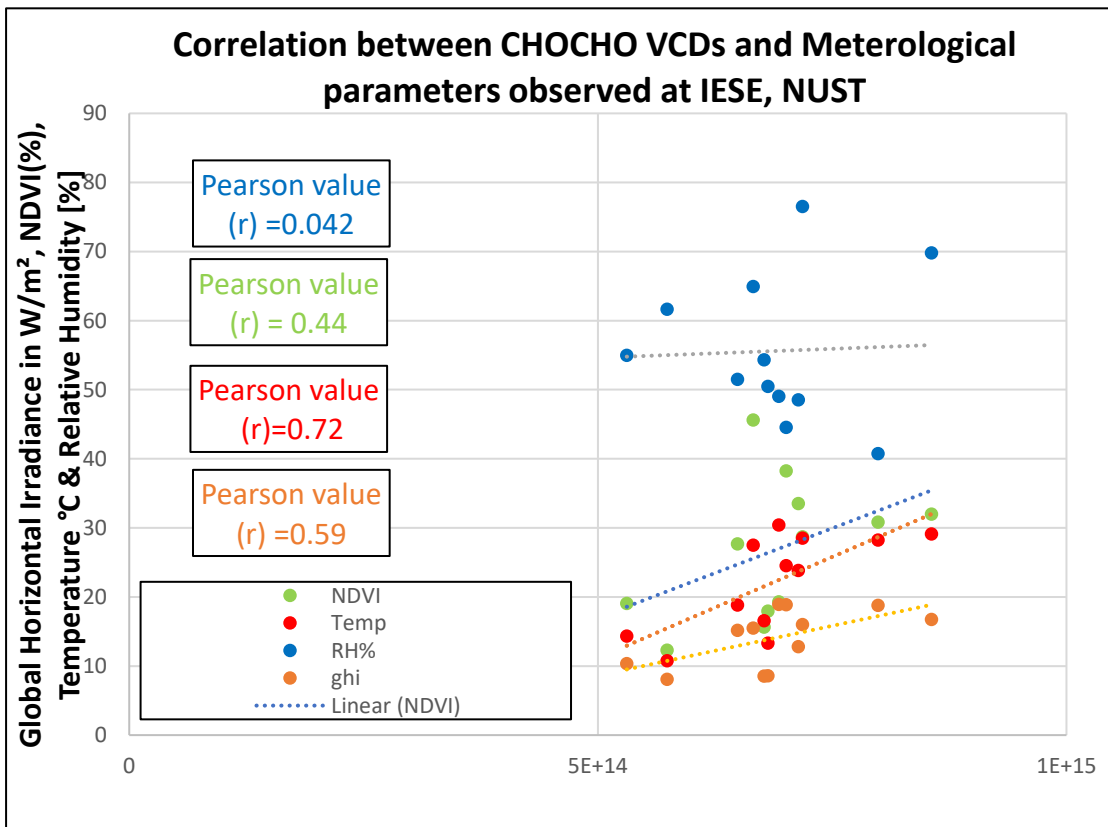


Figure 25: Correlation between CHOCHO with; 1) Temperature 2) GHI 3) Relative Humidity 4) GHI over IESE, NUST

5. Conclusions and Recommendations

5.1. Conclusions

The field campaigns carried out in different forest types to investigate the concentration of glyoxal in those areas and inter-comparison of the CHOCHO concentrations in these areas showed that considerable amounts of CHOCHO was found in different forest areas with the highest concentration of 0.554 ppbv found in the Alpine Forests in Deosai, Gilgit Baltistan followed by 0.505 ppbv in Sub-Alpine forest in Batakundi, Naran, Khyber Pukhtoonkhwa. While the lowest average concentration of 0.281 ppbv was found in Sub-Tropical Chir-Pine Forest in Shinkiari, Khyber Pukhtoonkhwa. Temperature and Relative Humidity in the respective forest areas of the campaign were compared with the CHOCHO mixing ratios and an anticorrelation of -0.11 and -0.70 was found with the CHOCHO mixing ratios.

Also, a continuous 2.5-year fixed monitoring of CHOCHO was carried out at IESE, NUST, Islamabad to study the contribution of surrounding vegetation on CHOCHO production in the atmosphere.

5.2 Recommendations:

1. Air quality monitoring should be done at national, provincial as well as at city level.
2. Better understanding of the glyoxal production from oxidation of isoprene, terpenes and monoterpenes is also required.
3. In addition, data can be used as a reference by policy makers, environmental agencies, researchers, and non-governmental organizations (NGOs) working on different aspects of air pollution i.e. health impacts, climate change and for better mitigation and adaptation studies.
4. Regular ambient air monitoring should be done for the generation of authentic National data base. And NEQS (national environmental quality standards) should be formulated.

5. In order to control traffic pollution, carpooling and mass transit system should be introduced in larger Urban areas of Pakistan.
6. In addition, public awareness should be done through effective media campaigns to improve the understanding and concern for air quality among public. And educating children at school level to develop a sense of responsibility to care our environment.
7. Monitoring of different forest types should be measured in order to check the air quality and one should know the gasses presences there which could be harmful.

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