Retrieval of SO_2 column densities during extreme weather conditions by using CAR MAX-DOAS in the cities of Faisalabad and Lahore.

Hassan Mohy Ud Din

(00000206232)

Institute of Environmental Sciences and Engineering,

School of Civil and Environmental Engineering,

National University of Sciences and Technology

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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 **“Retrieval of SO2 column densities during extreme weather conditions by using CAR MAX-DOAS in the cities of Faisalabad and Lahore”** submitted by **Mr. Hassan Mohy Ud Din**, Registration No. **00000206232** has been found satisfactory for the requirements of the degree of Master of Science in Environmental Science.

Principal: ________________
Dr. Tariq Mahmood
SCEE, NUST

Head of Department: ________
Dr. Muhammad Arshad
Associate Professor
IESE, SCEE, NUST

CERTIFICATE

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Supervisor: ___________________
Dr. Fahim Khokhar
Professor
IESE, SCEE, NUST

Member:

____
Dr. M. Zeeshan Ali Khan
Assistant Professor
IESE-SCEE, NUST

Member:

____
Dr. Sher Jamal
Professor
IESE-SCEE, NUST

I dedicate this thesis to my beloved parents and siblings who have been always a source of inspiration for me and stood beside me at every moment in my life.


بسم الله الرحمن الرحيم

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I would like to start with the name of **Almighty Allah**. All praise for Almighty “Allah˝ who blessed me with complete code of life. All respect for **Holy Prophet Muhammad (Peace Be Upon Him)** whose life is pattern and ideal for us. And we have to follow him in all the paths of life.

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Hassan Mohy Ud Din

Abstract

Deteriorating air quality is one of the global environmental issues, which is increasing with increase in the urban population and industrial development. Air is a blend of numerous gas particles, tiny liquid and solid particles, originating from both natural and anthropogenic actions such as industrial activities, vehicular emissions, domestic activities and several others. These become notorious when they breach their threshold limits and inflict harm or distress to ecosystem disturbing the chain linking biotic and abiotic elements. Beside other trace gases Sulfur Dioxide SO_2 is one of the main criteria pollutants. Increasing concentrations of SO2 is a major threat and is now widely included in health risk assessment studies. Faisalabad and particularly Lahore is densely populated and one of the important economic zones in Pakistan. In this study widely used remote sensing technique DOAS is used. Car based MAX-DOAS measurements were retrieved using mini MAX-DOAS in both the cities, and stationary monitoring in Lahore, at Lahore University of Management Sciences (LUMS) as well. These two cities were selected to observe SO2 concentrations during extreme weather conditions like winter fog. This paper presents the technical information and characteristics of the instrument, way of retrieval of SO2 concentrations and results of vertical column densities (VCD) of SO2, and most importantly the comparison of different settings and fitting intervals as well. Average diurnal variation of tropospheric SO2 in winter season over the research area yielded minimum values in late morning i.e. 8am-9am and noon i.e. 12pm-1pm with the concentration of 2.8E16 molecules/cm^2 and 2.9E16 molecules/cm^2 respectively. Whereas tropospheric SO2 reached the maximum value in the early evening i.e. 5pm-6pm with the concentration of 6.6E16 molecules/cm^2. Slight and gradual reduction in the SO2 concentration occurred on the weekends because of reduction in the pollutants and emissions particularly from vehicles over the weekends. Tropospheric VCDs were compared for both field campaigns and stationary monitoring to with those from Ozone Monitoring Instrument (OMI) satellite observations, resulting in R^2 of 0.499 with the Pearson value

of .70 for Filed campaigns and for the stationary monitoring at Lahore University of Management Sciences (LUMS) R^2 of 0.68 and Pearson value of 0.82.

Chapter 1

1. Introduction

1.1. Background

Among various environmental issues associated with air quality is currently a global concern, especially in developing regions and urban localities. Air is a blend of numerous gaseous particles, tiny liquid and solid particles. These particles originate from natural and man-made actions such as industrial activities, vehicular emission, domestic activities and several others. Issue arises when the amount of these elements surpasses the safe threshold limit and inflict harm or distress to ecosystems disturbing the chain linking biotic and abiotic elements. Such matter is widely known as air pollutants known to cause air pollution. Air pollutants are generally suspended in atmosphere in the form of liquid droplets, gases or tiny solid particles (Alias *et al*, 2007). The issue of air pollution and the struggles to mitigate it is not a fresh initiative. Primary example of air pollution regulation ordinance can be traced back to thirteenth- century England, during the time of King Edward who placed a ban on burning of impure coals in London (Schwela, 1997). Air pollution and its detrimental consequences surfaced soon; regardless of this the coal, oil and gas used in the transport and industrial sectors during the pre and post-industrial revolution triggered a record increase in air pollution in numerous urban regions (Bell *et al.*, 2001). In the history of worst air quality incidents one was on December 1952, the London's massive dense black smog that engulfed the whole region caused severe health effects, instigating about 4000 mortalities and when pondered on long term consequences, roughly 12000 deaths were testified (Bell & Davis, 2001). Additionally statistical figures on epidemiology reported in 1950's, related the declining human well-being with air pollution, even on the minor levels of pollution (Bell & Davis, 2001).

Without any doubt the expansion and growth in technology in various sectors has upgraded the standard of life and fetched comfort in people lives, however it has also amplified the emission footprints per individual (Thornton *et al.*, 2007). These releases are connected with many health threats and it also raise a question mark on environmental sustainability. Swift and escalating growth in population, use of fossil fuels in vehicles, nonstop urbanization and prompt industrialization plays a major role towards growing air pollution (Thornton et al., 2007). Therefore this is a grave concern which needs to address on urgent basis.

In reaction to such a noteworthy problem, with every passing day a time extensive literature associated with air pollution special effects on health and environment has been collected by numerous states worldwide. Certain standards and guidelines have also been devised by developed countries for the sole purpose of environmental protection and human well-being (Thornton et al., 2007). In current years vast level research has been conducted on the reasons and foundations of air pollution, its consequences on human health and its environmental effects (Ferdous, 2008). Subsequently research prospects have also concentrated on understanding the after effects of air pollution in spatial realm, which has appeared as an important tool in modern worlds research (Ferdous, 2008). Even though air has several significant criteria pollutants that poorly affect atmosphere, present-day research plans focuses primarily on manufacturing pollutant i.e. Sulfur dioxide (SO_2).

1.2. Atmospheric Sulfur Dioxide (SO_2)

Presence of Sulfur Dioxide (SO2) in atmosphere as a result of both natural and man-made sources (Lee et al., 2011; Seinfeld et al., 1998). Certainly it is the product of oxidation process happening in the soil medium which includes oxidation of hydrogen sulfide (H_2S) and dimethyl sulfide (DMS) over oceans and additionally from volcanic eruptions. Volcanic eruptions are catered as a major contributor, almost around 7.5-13 Tg/year (Andres et al., 1998; Halmer et al., 2002). Although burning of fossil fuels and biomass combustion contributes to the man-made foundations of SO_2 emissions (Eisinger et al., 1998). Sulfur (S) atoms are mostly found in oil and coal and when combusted, it chains with oxygen (O) and SO2 is formed. SO2 is a readily reacted compound (Mirza et al., 2013). It counters easily to form further compounds such as sulfuric acid (H_2SO_4), sulfurous acid (H_2SO_3) and sulfate (SO_4^{-2}) compounds and are extremely detrimental to the atmosphere as well as to the human wellbeing. It is one of the six criteria pollutants (USEPA, 2013) and also one of the vital precursors of acid rain. Acid rain is a threat for woodlands, marine and many fresh water environments around the globe (Ferrari et al., 1999). SO_2 life span in the atmosphere differs from several days to few weeks (Platt et al., 1980; Stutz et al., 2004). In troposphere its lifetime is reduced due to its reaction with certain oxidizing agents like hydroxyl (OH) (Atkinson *et al.*, 1997; Platt & Perner, 1980; Stutz et al., 2004). However in lower layers of stratosphere its life span surpasses from numerous weeks to 2 years (Eisinger & Burrows, 1998; Platt & Perner, 1980; Stutz et al., 2004).

1.3. The Instrument: MAX-DOAS

For the monitoring of trace gases in the atmosphere need great care and proper planning either directly from primary sources or from secondary sources. Samples can be taken directly from the vehicle tails, industrial stacks and emission pipelines of factories and can be interpreted on the spot. But there is a great need of properly designed instrument for the fractional distribution of gases in the atmosphere. For the monitoring of pollutants (NO_2, HCHO, SO_2, and O_3) etc. slant column densities can be retrieved from observations of MAX-DOAS. MAX-DOAS works on the principle of "Lambert Beer Law" at different elevation angles the scattering sunlight at different elevation angled and can monitor about the vertical distribution of different trace species. The mini MAX-DOAS instrument was mounted at Lahore University of Management Sciences (LUMS) for the purpose of point base observations of different trace gases.

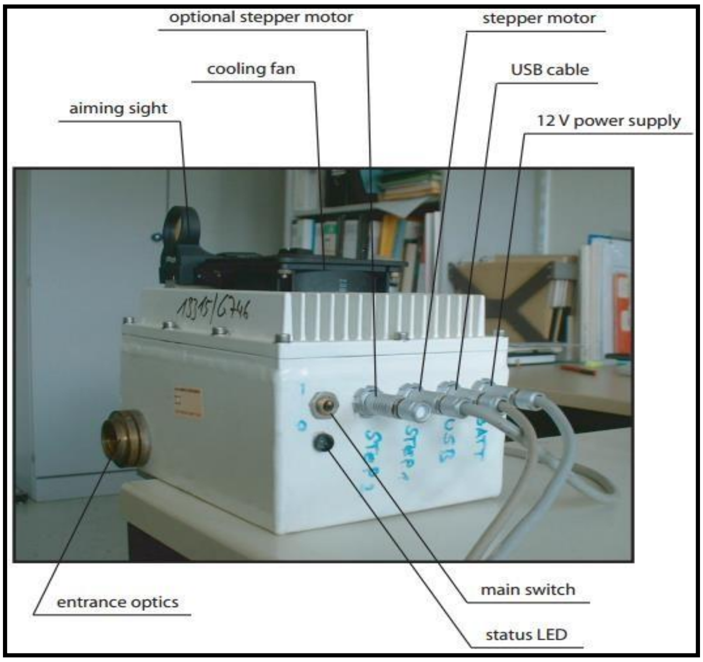


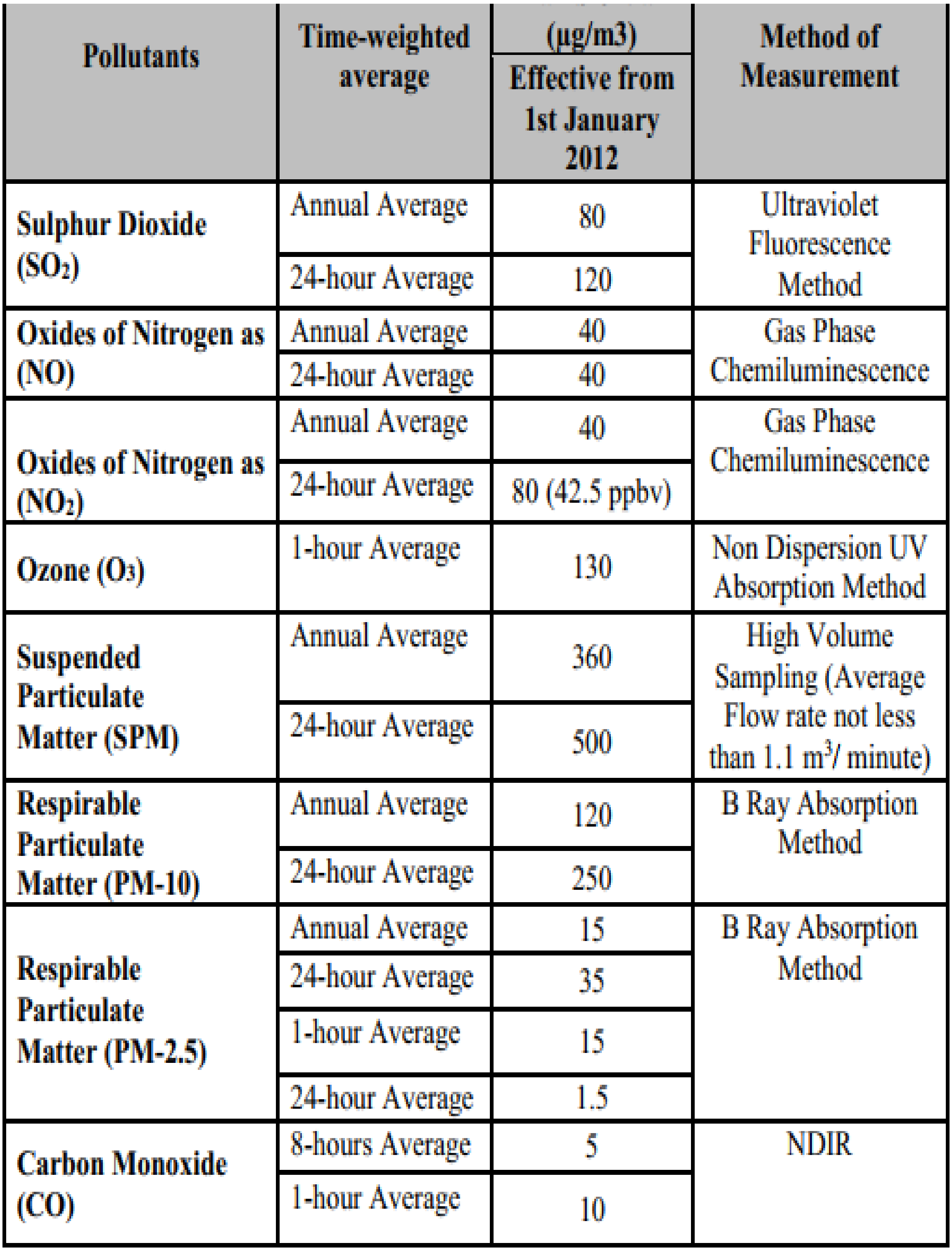
Figure 1 . MAX-DOAS mounded at LUMS

Absorbance in shallow atmosphere the MAX-DOAS instrument is very sensitive for the retrieval of vertical profile of traces gases by merging the measurement with Radiative Transfer Model calculations (Rivera *et al.*, 2010).

1.4. Pak-NEQs

Pakistan National Environmental Air Quality has formulated the standards (as listed below in table 1) for certain pollutant in the ambient air for controlling the quality of ambient air. Emission coming from industries and other sources are regulated by these quality standards in the ambient air, so air quality of ambient air are maintained in this way.

Table 1 Pak- NEQS for ambient air



Pollutants	Time-weighted average	(µg/m3) Effective from 1st January 2012	Method of Measurement
Sulphur Dioxide (SO_2)	Annual Average	80	Ultraviolet Fluorescence Method
	24-hour Average	120	
Oxides of Nitrogen as (NO)	Annual Average	40	Gas Phase Chemiluminescence
	24-hour Average	40	
Oxides of Nitrogen as (NO_2)	Annual Average	40	Gas Phase Chemiluminescence
	24-hour Average	80 (42.5 ppbv)	
Ozone (O_3)	1-hour Average	130	Non Dispersion UV Absorption Method
Suspended Particulate Matter (SPM)	Annual Average	360	High Volume Sampling (Average Flow rate not less than 1.1 m^3/ minute)
	24-hour Average	500	
Respirable Particulate Matter (PM-10)	Annual Average	120	B Ray Absorption Method
	24-hour Average	250	
Respirable Particulate Matter (PM-2.5)	Annual Average	15	B Ray Absorption Method
	24-hour Average	35	
	1-hour Average	15	
	24-hour Average	1.5	
Carbon Monoxide (CO)	8-hours Average	5	NDIR
	1-hour Average	10	

ulfur Dioxide (SO_2) WHO conversion factor 1 ppbv = 1.88 µg/m^3.

1.5. Objectives

Based on the problem statement, the study was designed based on the following objectives:

i. Ground based periodic monitoring of SO_2 concentrations in special weather conditions by using Car Max-DOAS in Lahore, Pakistan.

ii. To compare the results of satellite observation for SO_2 concentrations with ground-based and car Max-DOAS observations.

Chapter 2

2. LITERATURE REVIEW

2.1. Composition of Atmosphere

Earth’s atmosphere is made of various gases. Among these gases mainly Nitrogen (N_2) and Argon (Ar) makeup the 99.9% of the entire atmosphere. The composition of earth’s atmosphere is dependent upon the emissions that go into the air, whether they are by natural sources or by human activities. The composition is also determined by the energy which flows into and out of the immediate ambience and also within the earth’s layers. The major source of this drive is sunlight at usually in UV, visible, and near-infrared (NIR) windows. This inward bound energy is balanced out in the top layers of the atmosphere by the outgoing emanation of infrared (IR) radiation raising from within the Earth’s surface and tropospheric layer (Isaksen *et al.*, 2009).

2.2. Atmospheric Layers

The atmosphere is composed of several layers with its own definite composition. When the air from below is in contact with the surface, incoming radiations heat up the Earth’s crust resulting in the expansion. As a result the hot air moves upwards and cold air sinks in. this whole process is known as conventional currents. Volume, temperature and density of air determines the level of humidity. Layers are vitally dependent on pressure, height and temperature.

The chief layer is named as troposphere. It initiates from surface and spread out to the upper threshold; roughly about 10-11 km. The upper border is known as tropopause. The altitude of troposphere fluctuates, around equatorial line it is roughly about 16 km whereas around poles it is measured 8 km.

Atmospheric shift of gases are record concentrated at this level. In troposphere, there is a secondary relation between temperature and altitude, as height escalates, temperature drops, with the average rate of 6.5 °C km. This relation is known as ‘lapse rate’ (Allaby, 2014).

Post tropopause, the following atmospheric layer is named as stratosphere. Its upper threshold is estimated up to 40 km and is largely poised of steady dry air. In troposphere the contaminants scatter due to conventional currents, but in stratosphere the contaminants remain stagnant and sticks for an extended period of time. The importance of stratosphere deceits in the existence of dense O_3 film in it. The O_3 layer aids in averting the UV light (which is injurious to living entities) touching the earth’s surface (Van der Leun, 2004).

2.3. Sulfur Dioxide (SO_2) Cycle

The prime factor affecting sulfur chemistry is the availability of oxidizing medium. The pre-existing reduced species in the atmosphere (DMS, H_2S and OCS) are readily oxidized upon the availability of OH radicals in SO_2. This SO_2 is later converted into H_2SO_4 or SO_2^{-4} sulfate particles. However this is not the case with DMS. It follows a different cycle, converting itself into methyl sulfonic acid (MSA) (Glasow *et al.*, 2004) SO_2 in any oxidation process is always the secondary product of nearly all sulfur based species. Rapid reaction allows it to be released into the atmosphere directly from numerous sources (as listed in below sections). Once emitted into the atmosphere it meet its fate in form of both gaseous (SO_4^{-2}) and liquid state (H_2SO_4). The ultimate sulfate particles as a result of nucleation process result in cloud condensation nuclei (CCN) leading to negative radiative forcing (RF). Hydroxyl radicals are major contributors in oxidation process. Almost every reaction of sulfate specie is initiated by it, except for H_2S whose triggering specie is NO_3. Figure 2 shows all the major pathways in which SO_2 is an intermediate product, except for DMS. SO_2 further is oxidized into gaseous state by OH and into aqueous phase by H_2O_2.

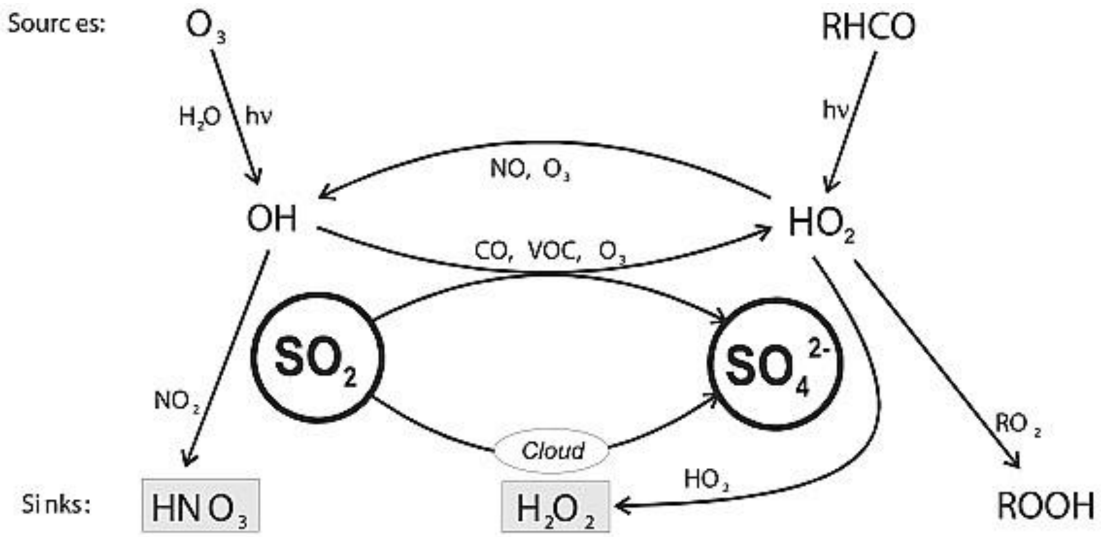


Figure 2 Dynamic transformation of SO2 & SO4-2 with the help of OH and HO2

(Adapted from [(Stein et al., 2002)])

2.4. Lifetime of Sulfur species

Nearly all sulfur species are framed in between moderately time zone ranging from few hours to few years. This lifetime greatly depends on specie altitude and numerous other factors like availability of OH radicals etc. It is well recorded that SO_2 is produced both from natural (SO_2 and reduced sulfur compounds) and anthropogenic (mainly H_2S and SO_2) sources in different forms. As stated by (Stevenson *et al.*, 2003), it has been estimated that nearly 70% of SO_2 gas is as it is deposited onto the surface before it can be transformed into sulfuric acid. Also that the average lifespan of SO_2 increases as its main oxidants (OH & H_2O_2) are zonally depleted by up to 40%. Lifespan is also greatly dependent on immediate ambience, for instance in pre-industrial era it was 1.6 days which later on escalated to 7-12 days in industrial times following the volcanic outbursts. Quantitatively for a given concentration of 1*106 radicals/cm^3 of OH, lifespan of SO_2 is 13 days (Atkinson & Tatnall, 1997).

However in other terms, SO_2 residence time as calculated (per global burden/global emission flux) based on deposition parameters ranges from 0.6 to 2.6 days. As a result of SO_2 deposition, it was recorded that nearly 46 to 82% of SO_2 in actual undergoes oxidation and forms respective compounds (IPCC, 2001).

2.5. Sources of SO_2

Sulfur is released into the air from both natural and manmade fonts. The routine emitting sources include volcanoes outburst (emitting roughly 7.5–13 Tg SO_2 (Andres & Kasgnoc, 1998; Halmer et al., 2002), Di-methyl sulfide (DMS) from the oceanic release (16–54 Tg S per year) (Kettle *et al.*, 2000) and random wildfires. Wildfires are also considered as manmade sources of SO_2. Total discharge of SO_2 escalated since 1750 till 2000. A huge jump have been observed from pre-industrial to post-industrial era, from 1.46 Tg SO_2 / year) from wildfires have per year to 4.1 Tg SO_2 (Dentener *et al.*, 2006). The upsurge in anthropogenic releases of SO_2 1850 to 1980 is 2 to 131 Tg SO_2 / year from the year to year (Klimont *et al.*, 2013). During these times, coal burning has contributed chiefly to the SO_2 releases. Whereas SO_2 releases from the burning of petroleum products have augmented mainly after mid 1940's (Klimont et al., 2013)

Table 2 Cumulative global sulfur fluxes from numerous sources

	Compounds	**Flux Tg S yr^{-1}**
Sources		
Volcanoes	SO_2, H_2S, OCS	7-10
Vegetation and soils	CH_3SCH_3,CS_2, CH_3SSCH_3, OCS, H_2S	0.4-1.2
Biomass burning	SO_2, OCS, H_2S	2-4
Ocean	CH_3SCH, CS_2, OCS,H_2S, SO_2	10-40
Anthropogenic	sulfates	88-92
Sinks		
Dry Settlement	SO_2, sulfates	50-75
Wet Settlement	SO_2, sulfates	50-75

(Table: Retrieved from [(Brasseur et al., 1999)])

Below are mentioned some of the prime natural and manmade sources of SO_2.

Natural Sources

2.5.1. Volcanoes

Emissions from volcanoes are major natural point source of SO_2. Apart from SO_2 there are numerous other trace gases that after reaction produce carbon dioxide (CO_2), hydrofluoric acid (HF), hydrochloric acid (HCl) and ash directly into the atmosphere. These pollutants can disrupt a casual conformation of atmosphere and disturb the natural atmospheric chemistry. This can possibly affect the atmosphere worst of all can trigger a massive climate shift on earth (Yang *et al.*, 2009). Depending upon the nature of the emissions they are converted into volcanic aerosols upon reaction (Robock *et al.*, 2008). In comparison to primary emissions these aerosols remains in the atmosphere for longer period. Based on their chemical properties sulfate aerosols are responsible for reflecting back the incoming radiations therefore on a larger scale they cause a drop in global surface temperature up to 0.5 °C, while the ash is at times looted from the atmosphere within a record of days (Khokhar *et al.*, 2005). As recorded in the history massive volcanic eruptions effect the global climate ranging from weeks to years depending upon the eruption intensity.

2.5.2. Oceanic Emission's

Di Methyl Sulfate (DMS) is the major product that is formed in deep seas. It is normally attributed to the "missing: global flux of gaseous state sulfur from oceans into the atmosphere. As stated by'(Scarratt *et al.*, 2000), DMS and its respective precursors, di methyl sulfonic propionate (DMSP) & di methyl sulfoxide (DMSO) are responsible for a huge pool of organic sulfur in marine ecosystem. Among all these, Di-Methyl Sulfide that is released into the ocean as a result of biological transformation is the most dominant sulfur containing compound. As soon as it produced, DMS tends to disintegrates within a day or two with the help of certain biological processes (Kieber *et al.*, 1996). Another important role that is played by DMS is its oxidation that results in the formation of sulfate aerosols, responsible for scattering and reflecting back the radiations and later on tends to form cloud condensation nuclei (CCN). Both these phenomena's are subjected to a direct concern as they are responsible for negative radiative forcing, conversely cooling down the climate. Recent flux estimates showed that it is concentrated enough to contribute in major global budget and plays a vital role in altering the atmospheric chemistry(Boucher *et al.*, 2003).

2.5.3. Burning of Fossil Fuels (Anthropogenic)

It is one of the biggest sources that contribute in the production of SO_2. In past few decades the blooming population, lavish life standards, increase of vehicles on the roads have led to escalated levels of SO_2 in the atmosphere. Major fossil fuels comprise of coal, petroleum, natural gas and crude oil. On the scale of development, fossil fuels are the leading source to fulfil energy demands, explicitly heat and electrical energy needs. The main components of these raw fuels are carbon (C), Hydrogen (H) and other than these sulfur (S), nitrogen (N) on conditional and trace amounts (Chmielewski *et al.*, 2011). SO_2 and hydrogen (H) based complexes and metals do also have their share in fossil emissions from the fuel, depending essentially on the quantity of fuel consumed and amount of sulfur present in it (Vijay *et al.*, 2004). Generally as extracted natural gas have minute traces of sulfur, while in coal and oil sulfur quantity are flexible based on the quality of refinement but it is mostly high (USEPA, 2013). The commercial scale combustion of these fuels is recorded in industrial sector, vehicle fuel burning, and power plants etc. as soon as the combustion process is initiated the locked sulfur in the fuel reacts with atmospheric oxygen under suitable temperature and transforms in SO_2. (EPA, 2011). In the absence of any mitigation device these end emissions are released directly into the atmosphere (Djuric *et al.*, 2013).

2.5.4. Smelting Process (Anthropogenic)

In regions like Peru, Norilsk where metal ore smelting is very common, quantity of SO_2 produced here is much more as compare to other regions. Metal ores hold variable quantities of sulfur. These metals mainly include the most abundant of all, aluminum (Al), followed by zinc (Zn), copper (Cu), iron (Fe^{+2}, Fe^{+3}), nickel (Ni) and several other metals (Khokhar *et al.*, 2008). For instance, in earth's upper layer Cu is principally found as chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcocite (Cu_2S) (Emission Estimation Technique (EET), 1999.

Smelting is stated as a procedure through which generally a metal ion is purified to a free metal. Which results in release of sulfur from the metal ore in the form of SO_2 (Khokhar et al., 2008). This resultant SO_2 detrimental to nearly all the spheres. It affects the vegetation, forest, water reservoirs and land surface present near the smelters (Monitoring, 2006; Savard *et al.*, 2006; Telmer *et al.*, 2006).

2.5.5 Refinement of Crude Oil in Refineries (Anthropogenic)

Refining of potentially low priced crude oil into its relevant fractions tend to earn a lot of profit. Commercially vital petroleum fractions that are combusted in our daily lives are the result of heavily operating oil refineries. This is achieved by the process of fractional distillation (extraction and up-gradation of crude oil products) like gasoline, jet fuel, diesel oil etc. (Ba-Shammakh, 2011). Crude oil tend to contain intensified levels of sulfur in it (Neidell *et al.*, 2012). Sulfur excluded from raw material is quantified to about 20% (Ba-Shammakh, 2011). Same amount has also been recorded in oil refineries of France (Neidell & Lavaine, 2012).

2.5.5. Burning of Biomass (Anthropogenic)

Biomass combustion is taken as both natural and man intruded occurrence (Khokhar, 2006). Though it is chiefly a self-intruded action (Alexander *et al.*, 2004). There are three basic reasons behind biomass combustion: slash and burn process (land clearance for crop shifting for agriculture process), forest clearance or land defrayal for cultivation intentions and the yearly bushfires in dry grasslands. Bushfires are of distinct reputation in Africa, where near about 40% to 60% grass lands are charred yearly (Deschler, 1974).

2.6. SO_2 Removal from Atmosphere

SO_2 once released into the immediate atmosphere, it can opt various fates, either it is converted to some other complexes or it can be disinterested totally from the atmosphere. The removal of SO_2 from the air includes various methods for example oxidation, dry & wet deposition, suspension, immersion by soil and vegetative cover, and several other procedures (Katz, 1977). The exclusion process can also transform SO_2 into H_2SO_4 (ATSDR, 1998), this transfiguration accounts for 10% of atmospheric deletion of SO_2 (Hegg *et al.*, 1978). Out of all these procedures related to mitigation, the dominant courses are wet deposition, wipe out and adsorption process (Hegg & Hobbs, 1978).

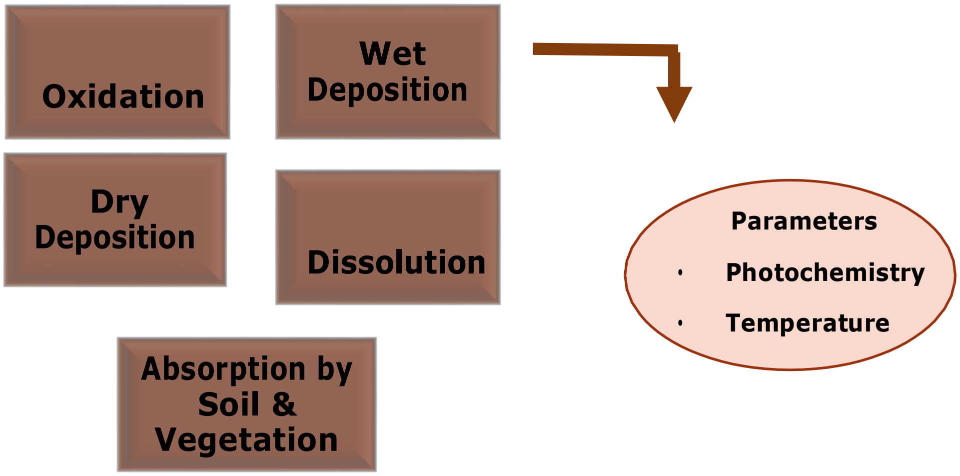


Figure 3: Removal methods of SO2 from the atmosphere

2.7. Physical and chemical properties of SO_2

SO_2 is a colorless and reactive gas. It is soluble in water and has a very pungent odor. Human nose can detect it due to its pungent odor, at the concentration of about 0.5 – 0.8 parts per million or 1329 - 2126 $\mu g\ m^{-3}$. In the atmosphere, SO_2 undergoes series of conversion process. These processes result in the formation of various new compounds, for further details Table 3 presents the physical and chemical properties of SO_2.

Table 3 Chemical and physical properties of SO2

Property	**Value**	**Reference**
Molecular weight	64.065	(Lide, 2004)
Physical state	Colorless gas	
Melting point	-75.5 ºC	
Boiling point	-10.05 ºC	(Lide, 2004)
Specific gravity (liquid)	1.50	(Gangolli, 2007)
Specific gravity (gas) (air =1)	2.26 (at 0ºC)	(Gangolli, 2007; Parent, 2000)
Vapor pressure	338 kPa (at 21ºC)	(Gangolli, 2007)
	230 kPa (at 10ºC); 330 kPa (at 20ºC); 462 kPa (at 30ºC); 630 kPa (at 40ºC)	(Weil *et al.*, 1997)
Solubility in water	17.7% (at 0ºC)	(Parent, 2000)
	85 g/L (at 25ºC)	(Gangolli, 2007)
	22.971 g/100 g H2O (at 0ºC); 16.413 g/100 g H2O (at 10ºC); 11.577 g/100 g H2O (at 20ºC); 8.247 g/100 g H2O (at 30ºC); 5.881 g/100 g H2O (at 40ºC)	(Weil & Sandler, 1997)
Solubility	Soluble in ethanol, ether and chloroform.	(Lide, 2004)
	Moderately soluble in benzene, acetone and carbon tetrachloride.	(Parent, 2000)
	Soluble in chloroform, ether, alcohol, methanol.	(Budavari *et al.*, 1996)
Acid/Base properties	Dissolves in water to form a slightly acidic aqueous solution of H2SO3.	(Parent, 2000; Weil & Sandler, 1997)

Odor threshold in air	0.1 to 3ppm	(Parent, 2000)
	0.45 ppm (low); 4.8 ppm (high); 1.9 ppm (irritating).	(Ruth, 1986)
Conversion factors for vapor (at 25 °C and 101.3 kPa)	1 ppm = 2.62 mg/m^3	(IARC, 1992)

2.8. SO_2 Deposition (Wet & Dry)

In wet settling, two procedures are involved:

- **a.** Washout
- **b.** Rain out

Washout comprises of all the removal procedures occurring within the region of clouds, whereas Rainout is illustrated as removal including falling rainfall (Garland, 1978). The methods linked to washout for the SO_2 exclusion are setting, diffusional acceptance and sulfate particles creation that assist as condensation nuclei (HSDB, 2002). Procedures included in the raining are diffusional uptake of SO_2 capture of particles by tumbling raindrops (HSDB, 2002). There are numeral other parameters which SO_2 elimination on which wet deposition is relying on. These features are precipitation amount, kind, frequency, period, relative quantities of SO_2 and the particle distribution of sulfate (HSDB, 2002).

Dry settling refers to the procedure in which gases and suspended particles are set down on water face or land as a result of various atmospheric phenomena's (Elias *et al.*, 2007)). SO_2 direct transmission is the main dry removal tool for dry elimination of atmospheric sulfur (HSDB, 2002). It has various mediums, for instance, it can occur directly on surfaces of numerous bodies, by gravitational attraction & also by sulfate atoms physical or chemical seizure by wet surfaces(HSDB, 2002; Kellogg *et al.*, 1972). The parameters on which SO_2 dry settling depends are water content and pH content of the soil (HSDB, 2002). Vegetation can also straight forward absorb SO_2 from immediate atmosphere (Ng *et al.*, 2003).

With respect to importance both wet and dry deposition both have their own distinct significance. With respect to relative significance, on broader prospect both are equally vital, whereas keeping in view regions near to the vicinity of foundation, dry deposition is more imperative (HSDB, 2002).

2.9. Detrimental Effects of SO_2

Alterations in climate takes place simultaneously as a consequence of both internal changes within the climatic frame and due to certain external factors (which consider both natural and man-made activities). A continuous increase in greenhouse gas concentrations result in positive radiative forcing hence increasing the Earth's average temperature. In contrary to this negative radiative forcing is a direct consequence of certain type of aerosols (i.e. sulfate aerosols) which cools the Earth's surface. In general, atmospheric aerosols are responsible to maintain the atmospheric heat balance, with the help of both reflecting and absorbing incoming UV radiations (directly) and on a longer course effecting the characteristics and phenomena's occurring high up in the clouds and most likely changing the chemistry of atmosphere (indirect).

2.10. Direct Effects of SO_2

The Jungle Layer in the stratosphere commonly known as sulfate-aerosol layer play a vital role in stabilizing the atmosphere chemistry in upper atmosphere. In particular their part in heterogeneous ozone chemistry. And there likely impacts on radiative forcing. Massive volcanic eruptions such as those of Dallaffilla (2008) and Nabro (2011) have significantly enhanced the aerosol loading in the atmosphere for post years resulting the cooling of that immediate region. Due to limited time span of sulfate aerosols they majorly exhibit their intensified effect in industrialized regions. Whereas the aerosol inclusion during the period of industrial times on global level is estimated to be -0.7 W/m2 (IPCC, 2015).

Since SO_2 is neither a part of natural atmospheric chemistry nor has any positive impacts on any of the layers. With regard to pollution levels many short span and long span problems are born. Toxic pollutants explicitly SO_2 in the atmosphere, disturb the natural balance, numerous chemical reactions which in return undermines the environmental arrangement and inflict harm to all spheres of life including wildlife and environment. Keeping in view their toxic effects now it has been catered important to monitor these gases and assess their possible impacts on every sphere of the life (Ferdous, 2008). This practice will also help in regulating the air quality. As reported by to World Health Organization (WHO), contamination in air is nearly responsible for 3 million deaths annually (King *et al.*, 2007) . SO_2 exposure when exceeds from a particular threshold, causes many health risks for example ENT (throat, nose, eyes) and variety of skin allergies (HANSELT *et al.*). Sulfur dioxide (SO_2) is also linked with austere effects on respiratory track i.e. asthma, throat cancer etc. (HANSELT & OPPENHEIMER) also SO_2 particles causes vision reduction, hazy images and acute and chronic respiratory illness (Ferdous, 2008). A study was steered by New York by (Shy *et al.*, 1973) on school going children of 5 -10 years old. The inference of the research concluded that, exposure to SO_2 particulate high concentrations may cause reduction in esophagus ability for extended period of time. According to a report by Clean Air Hamiton's (2007), exposure of SO_2 of 714.caused the death of 62 individuals out SO_2 is a major contributor to the acid rain phenomena. SO_2 along with other soluble gases releases (such as HCL etc.) from volcanic eruptions also root the creation of acidic clouds followed by acid rain. It may have undesirable impact on the nearby ecosystems, substructure and ultimately results in the economic damages (Delmelle *et al.*, 2002).

2.11. DOAS SPECTROSCOPIC METHOD

DOAS is one of the most extensively used spectroscopic technique in atmospheric research. It is used to classify the concentration of different trace gases in the atmosphere (Platt & Stutz, 2008). In 1979 platt and his companion introduce this technique. This technique works on the change in absorption at different wavelengths. It measures these trace gases in the Ultra-Violet and Visible region. DOAS can be used to measure the concentration of different trace gases includes SO_2, NO_2, BrO, O_3, HCHO,

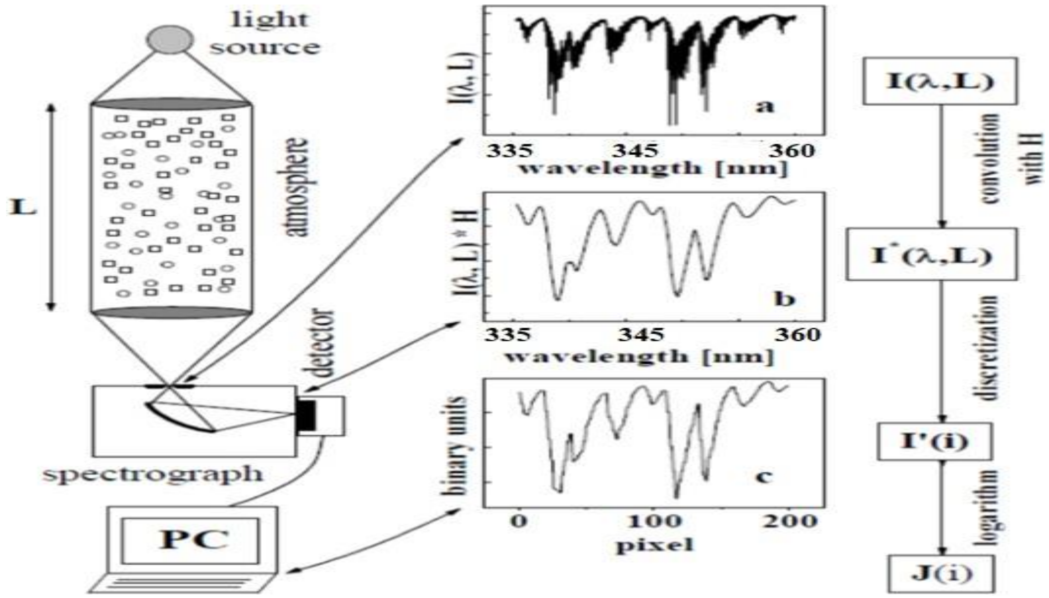


Figure 4 *The components of a simplified DOAS setup (a) shows the respective spectrum with absorption structure of SO2 (b) convolution of the light was achieved by means of the spectrograph and (c) shows the mapping by the detector (Platt et al., 2008).*

CHOCHO. Figure 4 explains the components of simplified DOAS setup.

By using this technique amounts of trace gases can be retrieved at the same time. It saves monitoring time and allows the analysis of different gases in the observed air mass. Normally, there are two types of DOAS. Those who use artificial light source are called active, while those who use natural light as their light source (e.g. Solar Radiations) are known as passive. The basic working principal of DOAS technique is based on “Lambert beer Law”, which states the linear relationship between light and matter. According to this law, the absorption of light is directly proportional to the path length and concentration of the analyte. In other word compare the incoming radiation ($I0_{\lambda}$) with outgoing (I_{λ}) by a function of path length (L) of the light and the concentration (c) and absorption cross-section (σ_{λ}) of the species in the equation given below:

$$I_{ʎ} = I_{0\,ʎ} .\, e^{-L\sigma(ʎ)\,c}$$

This relationship can be used to calculate the concentration of a trace gas by setting up a light source of known spectral intensity and a sensor at some distance (L). The pectoral demonstration of working principle is given in figure 5 given below.

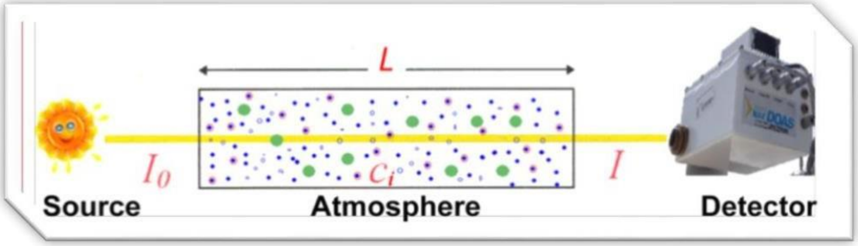


Figure 5 Illustration of DOAS Principle

2.12. Satellite Observation

Ozone Monitoring Instrument (OMI) has a high spectral resolution and has the ability to measure several trace gases in the UV/Vis wavelength range for the same air mass. It is an instrument of the European Global Ozone Monitoring Experiment (GOME).

2.13. OMI's Spectral Channels

The spectral range in which reflected light is observed by Ozone Monitoring Instrument (OMI) is usually laid between Ultra-violet to Visible (i.e. 270nm – 500nm). With a spectral resolution of 0.5nm OMI in two channels. Ultra-Violet Channel is further divided into two sub channels UV-1 (270-310nm) and UV-2 (310-365N).

Chapter 3

3. Material and Method

3.1. Instrument Mini-Max DOAS:

The Multi Axis-Differential Optical Absorption Spectroscopy (MAX-DOAS) is a highly sophisticated lightweight device that can be used both for stationary and mobile monitoring of trace gases. It is specially designed in order to monitor the backscattered sunlight. Optical Fiber cable spectrograph and some other controlling electronic parts are tightly closed in an aluminum box. A stepper motor is used to move the instrument at different elevation angle (Precision = 0.1 degree/step, Frequency= 784Hz). At the optics entrance, there exists a quartz lens with a focal length of 40mm. The spectral range is detected by a "Czerny Turner Spectrometer (Ocean Optics Inc., USB-2000+). For continuous ground-based monitoring and periodic field measurements, the detectable range of spectrometer was 305-440 nm having a spectral resolution equals to 0.7nm.

Having 2048 pixels, the portable instrument (coupled charged device 1 dimensional-CCD) was employed as a detector, which uses Peltier cooling (Thermoelectric cooling) as a means to regulate the internal temperature. Furthermore, to store and acquire the data, a computer system was continuously running with windows XP and DOASIS (Differential Optical Absorption Spectroscopy Intelligence System) operational algorithm.

Figure 6 Mini Max- DOAS Instrument

3.2. Monitoring Sites and Schedule

During this research a single instruments was used for the measurement of Sulfur dioxide SO_2. Instrument was deployed at Lahore University Management Sciences (LUMS), Lahore for the continuous monitoring from 24 December, 2015 – 31 January, 2016. Between these days the instrument was taken for periodic field campaigns as well. Furthermore detail of field Campaign is briefly given in table 4 below.

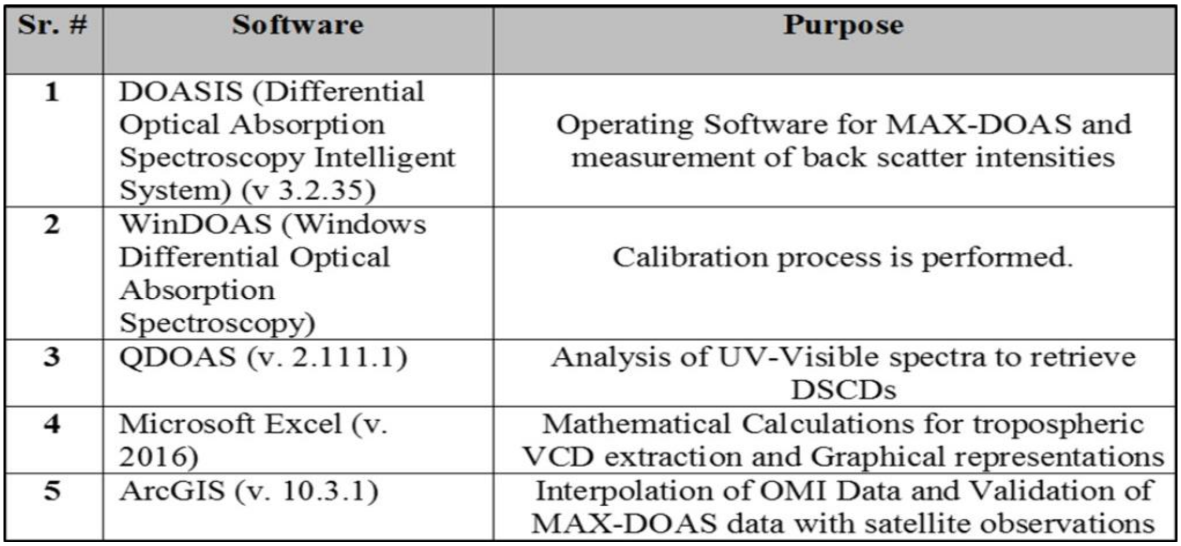
Table 4 Ground-based and Field Campaign schedule and other detail

Activity Detail	Location	Dates
MAX DOAS Field Campaign	Faisalabad	17 December,2015 3 & 16 Jan, 2016 1 & 23 Feb, 2016

MAX DOAS Field Campaign	Lahore	18 December,2015 2 & 15 Jan, 2016 2, 20, & 21 Feb, 2016
MAX DOAS Field Campaign	Faisalabad to Lahore	23 Feb,2016

For field campaign, two megacities of Punjab (Lahore and Faisalabad) were selected. In Lahore ring road for field monitoring and LUMS for stationary monitoring was selected, while in Faisalabad, Faisalabad bypass was selected for the campaign. Initially two rounds in a day were proposed to be completed but them depending upon the traffic loads and some instrumental errors the campaign was held accordingly. The round was started at early morning and second round was started in afternoon. During field campaign, the elevation viewing angle was used one 90^{o} and followed by four 30^{o} (i.e. 90^{o}, 3^{o}, 30^{o}, 30^{o}). The monitoring time at one angle was 60,000-mile sec/scan. The main reason for setting high elevation angles 90^{o} is to avoid the blockage from building and vehicles, while 30^{o} angles were used, just because air mass factor (AMF) can be easily calculated at this angle (Wagner et al., 2010). The elevation angle setting for fixed monitoring at LUMS, site was (2^{o}, 4^{o}, 5^{o}, 10^{o}, 15^{o}, 30^{o}, 45^{o}, 60^{o}).

Table 5 Software and their purpose for use in Research Work

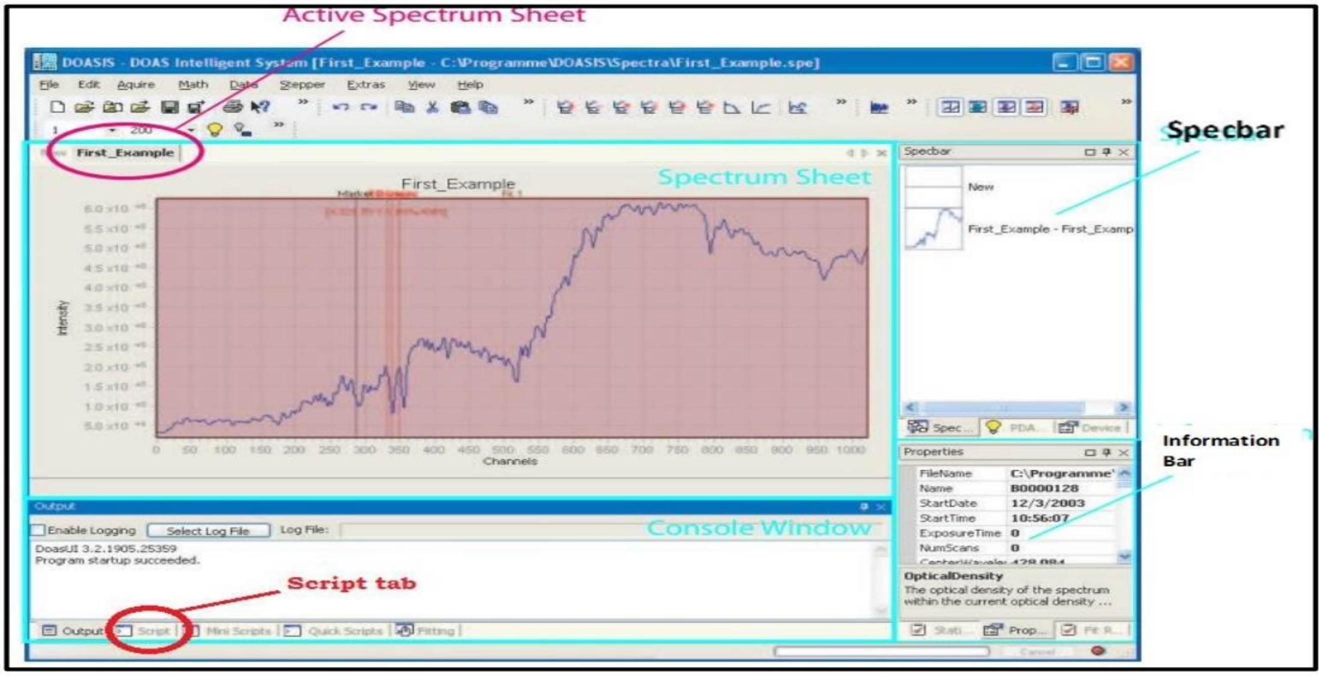


Sr. #	Software	Purpose
1	DOASIS (Differential Optical Absorption Spectroscopy Intelligent System) (v 3.2.35)	Operating Software for MAX-DOAS and measurement of back scatter intensities
2	WinDOAS (Windows Differential Optical Absorption Spectroscopy)	Calibration process is performed.
3	QDOAS (v. 2.111.1)	Analysis of UV-Visible spectra to retrieve DSCDs
4	Microsoft Excel (v. 2016)	Mathematical Calculations for tropospheric VCD extraction and Graphical representations
5	ArcGIS (v. 10.3.1)	Interpolation of OMI Data and Validation of MAX-DOAS data with satellite observations

3.3. Algorithm used in this study (DOASIS)

DOAS intelligent system is a software, mainly used to operate the Max-DOAS instrument. DOASIS plays many important roles, which includes data retrieval, controlling the stepper motor that is used for moving instrument at different elevation angles, regulate the temperature of the instrument by setting Peltier and spectrum integration time.

This software runs on java coded script that gives all necessary command to the software. To calibrate the instrument dark current and offset were taken manually and automatically as coded in the script. The DOASIS software is also used to calculate ring spectrum. Both ring spectrum and OSDC (Offset Dark current) are used during the analysis of data in QDOAS.



DoasUI 3.2.1905.25359
Program startup succeeded.

FileName C:\Programme'
Name B0000128
StartDate 12/3/2003
StartTime 10:56:07
ExposureTime 0
NumScans 0

OpticalDensity
The optical density of the spectrum within the current optical density ...

Figure 7 DOAS Intelligent System Software Interface

3.4. Dark Current

This small electric current is normally measured in the photosensitive instrument (e.g., Spectrometer). For dark current monitoring long exposure time and less number of scan is required.

3.5. Off set

The offset is taken in dark condition, in other words “in the absence of photon”. For offset measurement, small exposure and a greater number of scans are required.

Table 6 Values required to take OSDC

	Integration/ Exposure time (milliseconds)	Number of Scans
Dark Current	~1	10000
Offset	~100	1000

3.6. Retrieval of SO_2

Three main steps were used in the analysis of retrieved trace gases:

i. Wavelength Calibration
ii. Wavelength Convolutions
iii. SO_2 Analysis Window

3.6.1. Wavelength Calibration

Window differential optical absorption spectrometer (WinDOAS) software was used to calibrate the wavelength. At noontime (11:30 – 12:30) the high concentration spectrums at 90^o having least solar zenith angle (SZA) were taken, mostly used for calibration. The fit was applied between retrieved spectra and convoluted spectra to perform the calibration. Throughout the process, the wavelength of solar spectra was assigned to the single detector's pixels. The calibration fit is also known as "Kurucz-fit". To perform and analyze the fit, wavelength range was divided into sub-windows (6 Sub-windows).

In order to adjust and shift of the spectra between measured and convoluted spectrum "shift and squeeze" option was applied in the calibration process. The polynomial degree was used in Slit function parameter. The Slit function is used to interpolate the result of sub windows. Repetition of calibration process usually minimizes the residual process. Using the calibration file against a reference spectrum, all measured spectra are being evaluated.

3.6.2. Wavelength Convolution

Convolution is a mathematic method, which is important in wavelength processing operations. In QDOAS software “convolution tool” option was used to execute the convolution. There are two types of convolution.

3.6.2.1. Online Calibration

In this type of convolution, the cross sections without any pre-processing are simply inserted in SO_2 analysis windows. Because in this convolution, cross sections are automatically convoluted during analysis of spectra.

3.6.2.2. Offline Calibration

In offline type, the cross sections are convoluted before inserting them in analysis windows. In a current study, the online convolution of cross sections was used.

3.6.3. Cross Section and window interval

The cross sections of different trace gases used in the convolution process with their convolution specifications, and window interval for SO_2 are listed in table 7.

Table 7 Cross sections of different trace gases with their convolution specifications

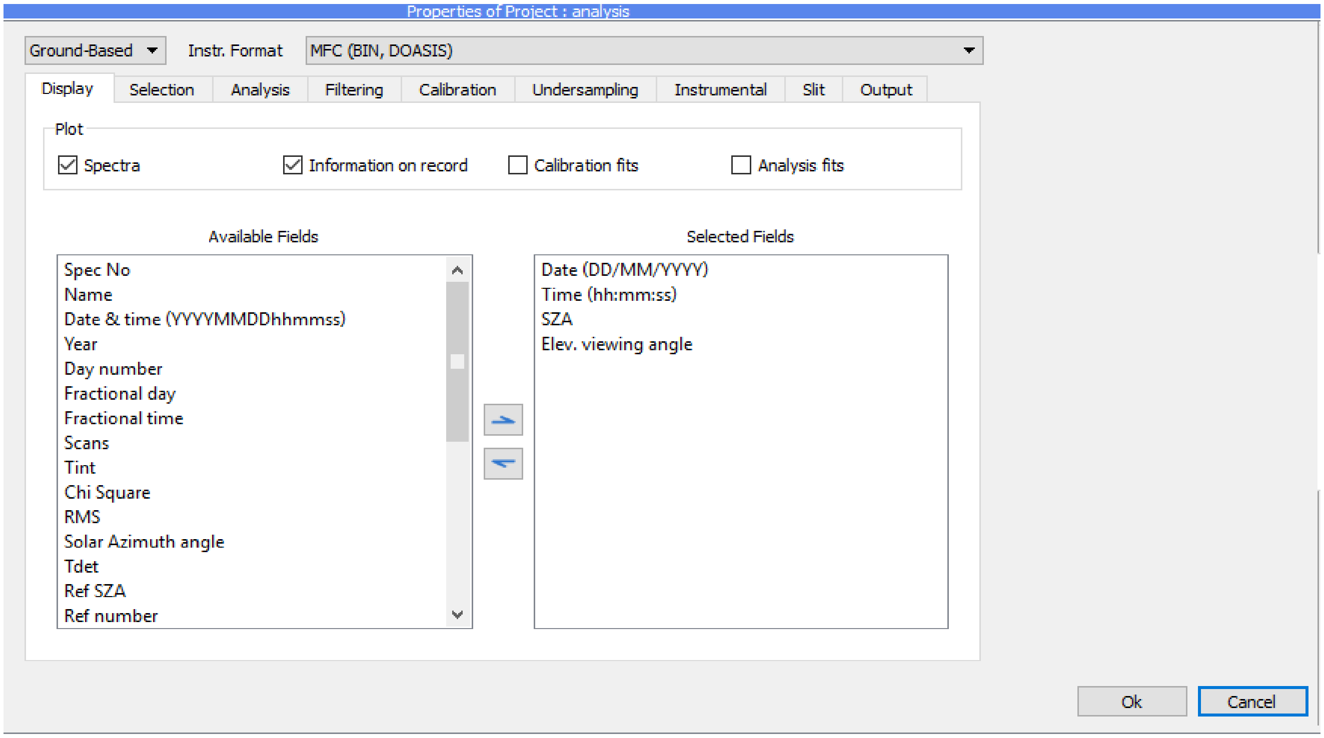
	SO2 settings for DOAS fit
Fitting window	307.5-328nm
SO2	SO_2_294K_ vanDaele
NO2	NO_2_298K_vanDaele
O3	O_3_223K_Bougmil
O3a	O_3a_293K_ Bougmil
Polynomial Degree	For this spectral fitting 5th polynomial order was used and also

	calculated by Fraunhofer spectrum
Ring	Ring (for this spectral fitting 5th polynomial order was used and also calculated by Fraunhofer spectrum)

The cross-section having a high resolution is convoluted by “Standard convolution” (Convolve Std) option. In addition to this option, slit function type Gaussian (FWHM = 0.5nm) and calibration file that is generated in wavelength calibration step were also used. While to evaluate the optical depth in convolution “I_0 correction” (Convolve I_0) option was used (Schreier *et al.*, 2015).

3.7. SO_2 DOAS Analysis

Analysis of SO_2 is performed in QODAS software. For analysis of SO_2, different parameters (date, time, SZA and EVA) were selected and check analysis fit block from display option as shown in figure 8.



Properties of Project : analysis

Ground-Based

Instr. Format: MFC (BIN, DOASIS)

Display | Selection | Analysis | Filtering | Calibration | Undersampling | Instrumental | Slit | Output

Plot

☑ Spectra ☑ Information on record ☐ Calibration fits ☐ Analysis fits

Available Fields

Spec No
Name
Date & time (YYYYMMDDhhmmss)
Year
Day number
Fractional day
Fractional time
Scans
Tint
Chi Square
RMS
Solar Azimuth angle
Tdet
Ref SZA
Ref number

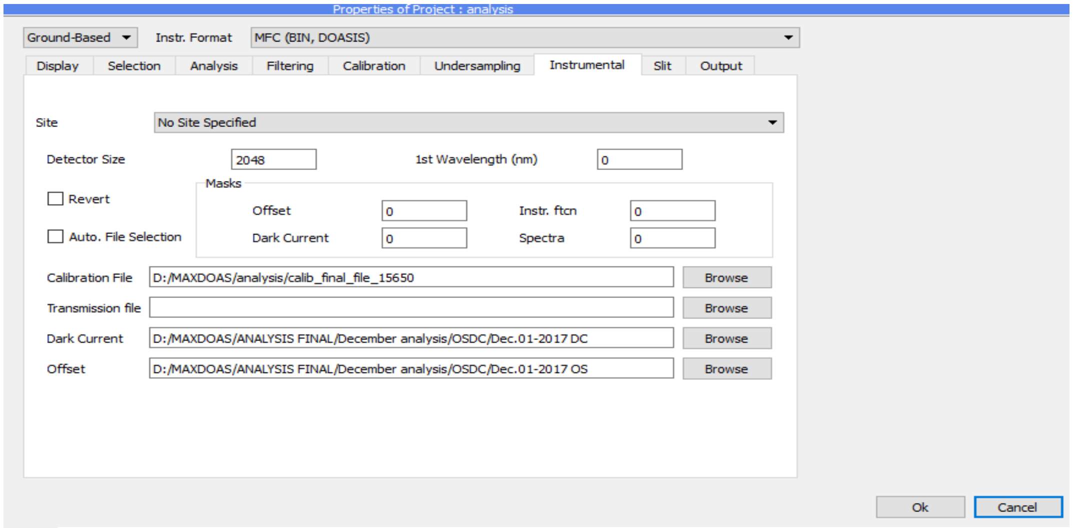
Selected Fields

Date (DD/MM/YYYY)
Time (hh:mm:ss)
SZA
Elev. viewing angle

Ok | Cancel

Figure 8 Display Tab Properties of DOASIS software

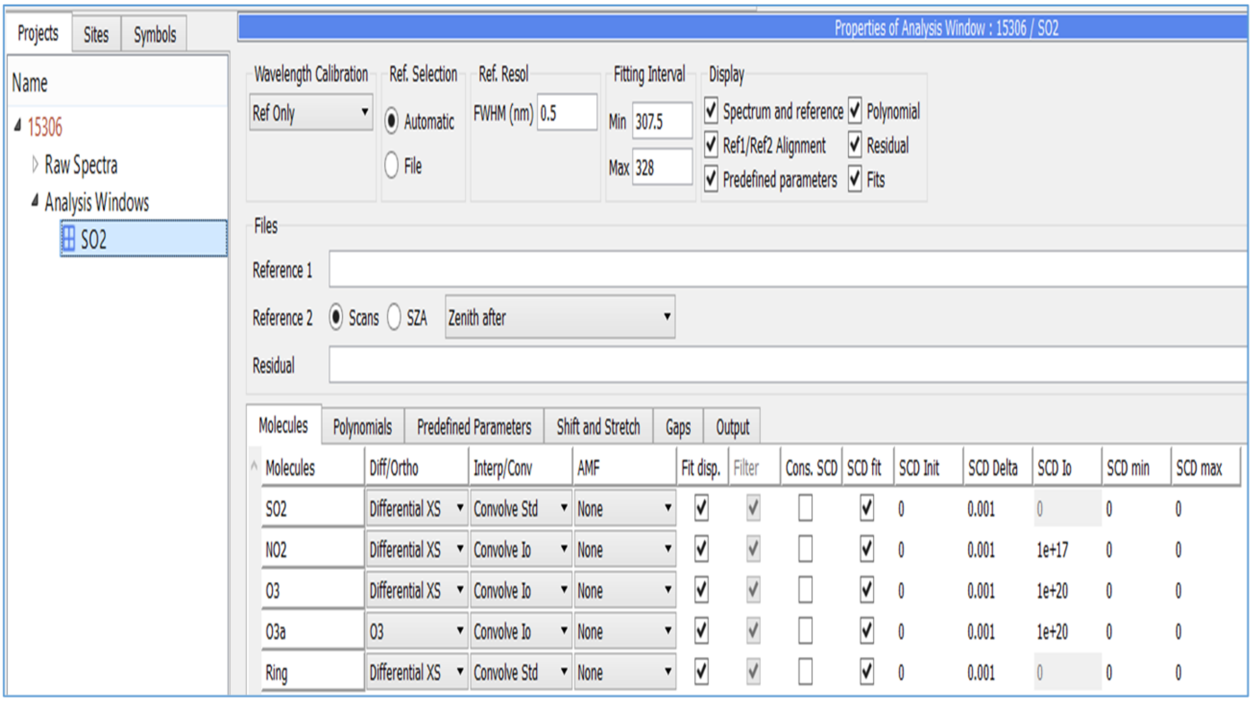
Than OSDC, detector size (2048) and calibration file is put in instrumental Tab as shown in figure 9. This 2048 is the instrument specific pixel value that we put manually in the software.



Ground-Based
Instr. Format: MFC (BIN, DOASIS)
Site: No Site Specified
Detector Size: 2048
1st Wavelength (nm): 0
☐ Revert
☐ Auto. File Selection
Masks
Offset: 0
Instr. ftcn: 0
Dark Current: 0
Spectra: 0
Calibration File: D:/MAXDOAS/analysis/calib_final_file_15650
Transmission file:
Dark Current: D:/MAXDOAS/ANALYSIS FINAL/December analysis/OSDC/Dec.01-2017 DC
Offset: D:/MAXDOAS/ANALYSIS FINAL/December analysis/OSDC/Dec.01-2017 OS

Figure 9 Instrumental tab Properties of DOASIS software

Then opened the analysis window and fitting length of SO_2 was set to 307.5- 328nm. All the cross sections their convolution setting was inserted in “Molecules Tab” as shown in figure 10. The polynomial degree 2 was used for SO_2 analysis.



Properties of Analysis Window : 15306 / SO2

Wavelength Calibration: Ref Only

Ref. Selection: ● Automatic ○ File

Ref. Resol: FWHM (nm) 0.5

Fitting Interval: Min 307.5 Max 328

Display: ☑ Spectrum and reference ☑ Polynomial ☑ Ref1/Ref2 Alignment ☑ Residual ☑ Predefined parameters ☑ Fits

Files

Reference 1

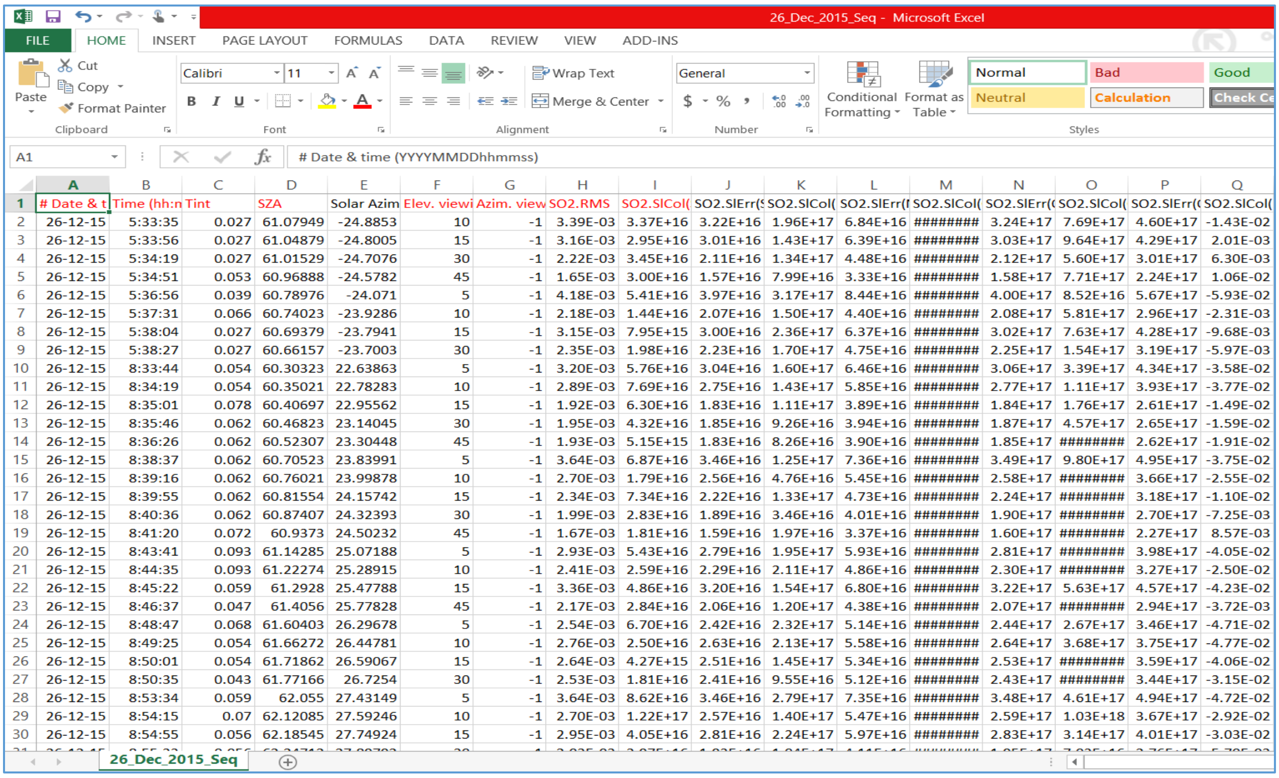
Reference 2 ● Scans ○ SZA Zenith after

Residual

Molecules	Diff/Ortho	Interp/Conv	AMF	Fit disp.	Filter	Cons. SCD	SCD fit	SCD Init	SCD Delta	SCD Io	SCD min	SCD max
SO2	Differential XS	Convolve Std	None	☑	☑	☐	☑	0	0.001	0	0	0
NO2	Differential XS	Convolve Io	None	☑	☑	☐	☑	0	0.001	1e+17	0	0
O3	Differential XS	Convolve Io	None	☑	☑	☐	☑	0	0.001	1e+20	0	0
O3a	O3	Convolve Io	None	☑	☑	☐	☑	0	0.001	1e+20	0	0
Ring	Differential XS	Convolve Std	None	☑	☑	☐	☑	0	0.001	0	0	0

Figure 10 Analysis window in QDOAS, showing the fitting interval used for SO_2

The required parameters (RMS, SZA, EVA and time etc.) for results were then selected and output path for the result file was given in “Output Tab”. The analysis was performed on all retrieved spectra and SO_2 DSCDs and results were generated in ASCII format file. These results file is then opened in Microsoft Excel, which contains all selected parameters and dSCDs and error of all trace gases as shown in fig 11.



	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q
1	# Date & t	Time (hh:n	Tint	SZA	Solar Azim	Elev. viewi	Azim. view	SO2.RMS	SO2.SlCol(	SO2.SlErr(S	SO2.SlCol(	SO2.SlErr(I	SO2.SlCol(	SO2.SlErr((	SO2.SlCol(	SO2.SlErr((	SO2.SlCol(
2	26-12-15	5:33:35	0.027	61.07949	-24.8853	10	-1	3.39E-03	3.37E+16	3.22E+16	1.96E+17	6.84E+16	########	3.24E+17	7.69E+17	4.60E+17	-1.43E-02
3	26-12-15	5:33:56	0.027	61.04879	-24.8005	15	-1	3.16E-03	2.95E+16	3.01E+16	1.43E+17	6.39E+16	########	3.03E+17	9.64E+17	4.29E+17	2.01E-03
4	26-12-15	5:34:19	0.027	61.01529	-24.7076	30	-1	2.22E-03	3.45E+16	2.11E+16	1.34E+17	4.48E+16	########	2.12E+17	5.60E+17	3.01E+17	6.30E-03
5	26-12-15	5:34:51	0.053	60.96888	-24.5782	45	-1	1.65E-03	3.00E+16	1.57E+16	7.99E+16	3.33E+16	########	1.58E+17	7.71E+17	2.24E+17	1.06E-02
6	26-12-15	5:36:56	0.039	60.78976	-24.071	5	-1	4.18E-03	5.41E+16	3.97E+16	3.17E+17	8.44E+16	########	4.00E+17	8.52E+16	5.67E+17	-5.93E-02
7	26-12-15	5:37:31	0.066	60.74023	-23.9286	10	-1	2.18E-03	1.44E+16	2.07E+16	1.50E+17	4.40E+16	########	2.08E+17	5.81E+17	2.96E+17	-2.31E-03
8	26-12-15	5:38:04	0.027	60.69379	-23.7941	15	-1	3.15E-03	7.95E+15	3.00E+16	2.36E+17	6.37E+16	########	3.02E+17	7.63E+17	4.28E+17	-9.68E-03
9	26-12-15	5:38:27	0.027	60.66157	-23.7003	30	-1	2.35E-03	1.98E+16	2.23E+16	1.70E+17	4.75E+16	########	2.25E+17	1.54E+17	3.19E+17	-5.97E-03
10	26-12-15	8:33:44	0.054	60.30323	22.63863	5	-1	3.20E-03	5.76E+16	3.04E+16	1.60E+17	6.46E+16	########	3.06E+17	3.39E+17	4.34E+17	-3.58E-02
11	26-12-15	8:34:19	0.054	60.35021	22.78283	10	-1	2.89E-03	7.69E+16	2.75E+16	1.43E+17	5.85E+16	########	2.77E+17	1.11E+17	3.93E+17	-3.77E-02
12	26-12-15	8:35:01	0.078	60.40697	22.95562	15	-1	1.92E-03	6.30E+16	1.83E+16	1.11E+17	3.89E+16	########	1.84E+17	1.76E+17	2.61E+17	-1.49E-02
13	26-12-15	8:35:46	0.062	60.46823	23.14045	30	-1	1.95E-03	4.32E+16	1.85E+16	9.26E+16	3.94E+16	########	1.87E+17	4.57E+17	2.65E+17	-1.59E-02
14	26-12-15	8:36:26	0.062	60.52307	23.30448	45	-1	1.93E-03	5.15E+15	1.83E+16	8.26E+16	3.90E+16	########	1.85E+17	########	2.62E+17	-1.91E-02
15	26-12-15	8:38:37	0.062	60.70523	23.83991	5	-1	3.64E-03	6.87E+16	3.46E+16	1.25E+17	7.36E+16	########	3.49E+17	9.80E+17	4.95E+17	-3.75E-02
16	26-12-15	8:39:16	0.062	60.76021	23.99878	10	-1	2.70E-03	1.79E+16	2.56E+16	4.76E+16	5.45E+16	########	2.58E+17	########	3.66E+17	-2.55E-02
17	26-12-15	8:39:55	0.062	60.81554	24.15742	15	-1	2.34E-03	7.34E+16	2.22E+16	1.33E+17	4.73E+16	########	2.24E+17	########	3.18E+17	-1.10E-02
18	26-12-15	8:40:36	0.062	60.87407	24.32393	30	-1	1.99E-03	2.83E+16	1.89E+16	3.46E+16	4.01E+16	########	1.90E+17	########	2.70E+17	-7.25E-03
19	26-12-15	8:41:20	0.072	60.9373	24.50232	45	-1	1.67E-03	1.81E+16	1.59E+16	1.97E+16	3.37E+16	########	1.60E+17	########	2.27E+17	8.57E-03
20	26-12-15	8:43:41	0.093	61.14285	25.07188	5	-1	2.93E-03	5.43E+16	2.79E+16	1.95E+17	5.93E+16	########	2.81E+17	########	3.98E+17	-4.05E-02
21	26-12-15	8:44:35	0.093	61.22274	25.28915	10	-1	2.41E-03	2.59E+16	2.29E+16	2.11E+17	4.86E+16	########	2.30E+17	########	3.27E+17	-2.50E-02
22	26-12-15	8:45:22	0.059	61.2928	25.47788	15	-1	3.36E-03	4.86E+16	3.20E+16	1.54E+17	6.80E+16	########	3.22E+17	5.63E+17	4.57E+17	-4.23E-02
23	26-12-15	8:46:37	0.047	61.4056	25.77828	45	-1	2.17E-03	2.84E+16	2.06E+16	1.20E+17	4.38E+16	########	2.07E+17	########	2.94E+17	-3.72E-03
24	26-12-15	8:48:47	0.068	61.60403	26.29678	5	-1	2.54E-03	6.70E+16	2.42E+16	2.32E+17	5.14E+16	########	2.44E+17	2.67E+17	3.46E+17	-4.71E-02
25	26-12-15	8:49:25	0.054	61.66272	26.44781	10	-1	2.76E-03	2.50E+16	2.63E+16	2.13E+17	5.58E+16	########	2.64E+17	3.68E+17	3.75E+17	-4.77E-02
26	26-12-15	8:50:01	0.054	61.71862	26.59067	15	-1	2.64E-03	4.27E+15	2.51E+16	1.45E+17	5.34E+16	########	2.53E+17	########	3.59E+17	-4.06E-02
27	26-12-15	8:50:35	0.043	61.77166	26.7254	30	-1	2.53E-03	1.81E+16	2.41E+16	9.55E+16	5.12E+16	########	2.43E+17	########	3.44E+17	-3.15E-02
28	26-12-15	8:53:34	0.059	62.055	27.43149	5	-1	3.64E-03	8.62E+16	3.46E+16	2.79E+17	7.35E+16	########	3.48E+17	4.61E+17	4.94E+17	-4.72E-02
29	26-12-15	8:54:15	0.07	62.12085	27.59246	10	-1	2.70E-03	1.22E+17	2.57E+16	1.40E+17	5.47E+16	########	2.59E+17	1.03E+18	3.67E+17	-2.92E-02
30	26-12-15	8:54:55	0.056	62.18545	27.74924	15	-1	2.95E-03	4.05E+16	2.81E+16	2.24E+17	5.97E+16	########	2.83E+17	3.14E+17	4.01E+17	-3.03E-02

Figure 11 ASCII files obtained by QDOAS opened in Microsoft Excel; majorly representing RMS, DSCDs and slant column errors.

3.8. Calculation of dAMF and Tropospheric VCD

The Air Mass Factor is a ratio of solar radiation path length coming directly from the atmosphere to coming vertically through the atmosphere, mathematically dAMF is defined as a difference of AMF between $\alpha \neq 90°$ and $\alpha = 90°$, where $\propto$ is elevation angle. Microsoft Excel software was used to calculate air mass factor because this software is convenient to drive the VCD. The calculation of VCDs from stationary mobile data is different from mobile data. If the last dissipating event of energy packets (photon) been recorded by the instrumental telescope occurs higher than the layer of gas, the AMF for zenith and off-axis view can be evaluated as 1 (sin 90°=1) and 1/sinα, respectively (Li *et al.*, 2012).

$$\mathbf{dAMF\alpha = (1/\sin\alpha) - 1}$$

As AMF is a ratio of slant column densities to vertical column densities, so VCD is derived from AMF by converting it into dSCD than into VCD. The AMF for zenith and off-axis view can be evaluated as 1 (sin 90°=1) and $1/\sin\alpha$, respectively (Li *et al.,* 2012).

$$\mathbf{VCD = dSCD\ (\alpha)\ /\ dMAF\ (\alpha)\ ------\ Eq.\ 1}$$

$$\mathbf{VCD = dSCD\ (\alpha)\ /\ (1/\ sin\alpha) - 1------\ Eq.\ 2}$$

Where, α = Elevation Angle and geo = Geometric Approach. In the current study, for SO^2 VCD for a corresponding dSCD at the off-zenith elevation angle, i.e. $\alpha = 30^{\circ}$ was used for both ground and field campaign.

3.9. Projection of Field Campaigns VCD

The map of Vertical Column Densities (VCD) SO^2 from Lahore and Multan were plotted as per their coordinate of measurement. We used a GPS device to measure the latitude and longitude of the whole campaign route. Then the VCD values were put against correspondent latitude and longitude by matching the time of both GPS logger and Max- DOAS device reading and save the file in CSV (comma delimited) format. In the next step. This CSV file was opened in ArcMap (version 10.3.1) and mapped the VCDs as shown in Figure 12.

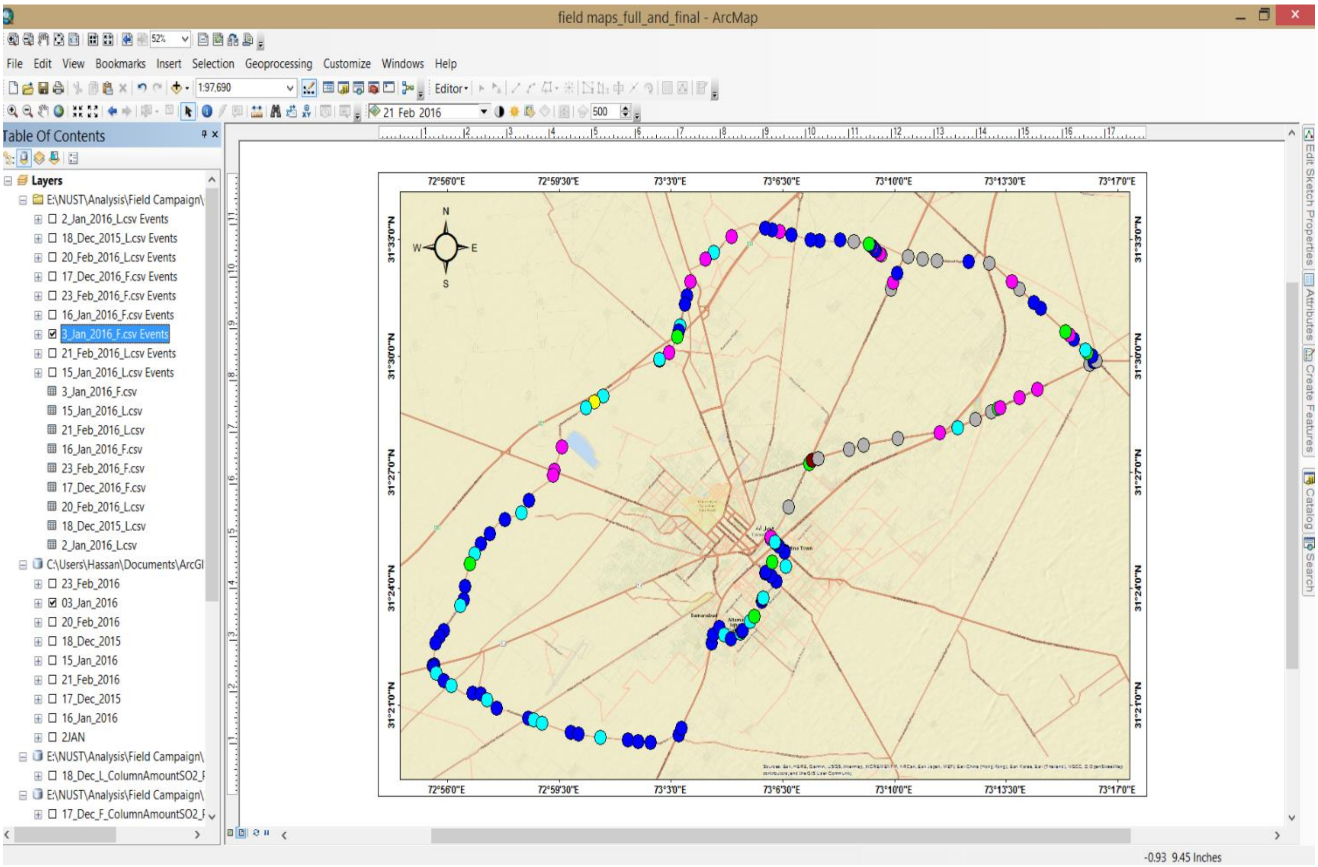
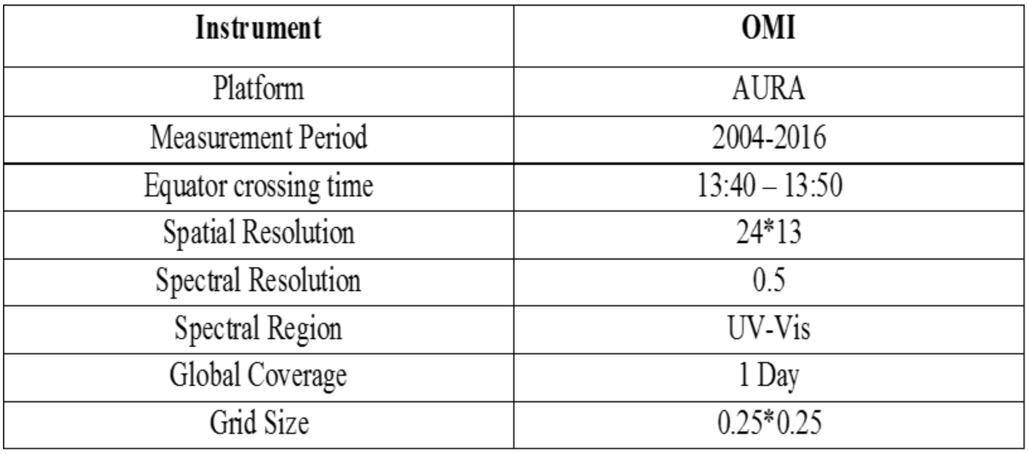


Figure 12 SO2 field campaign map generated by ArcGIS from CSV file in ARCMAP 10.3

3.10. Validation of Ground-Based and Satellite-Based Data

For the validation purpose, the comparison of ground-based (IESE-NUST) with satellite data was carried out. The SO^2 satellite was taken from ozone monitoring instrument (OMI) (Boersma et al., 2007). The specifications of the ozone monitoring instrument are given in Table 7.

Table 8 Specifications of ozone monitoring instrument



Instrument	**OMI**
Platform	AURA
Measurement Period	2004-2016
Equator crossing time	13:40 – 13:50
Spatial Resolution	24*13
Spectral Resolution	0.5
Spectral Region	UV-Vis
Global Coverage	1 Day
Grid Size	0.25*0.25

The software used to process the satellite data is ARCMAP 10.3. The raster data after conversion in the ARCMAP is opened in ArcMap to make it georeferenced. Lahore and Faisalabad’s shapefile were used to extract VCDs and produce spatial maps of these cities from global data.

Chapter 4

4. RESULTS AND DISCUSSION

4.1. SO_2 concentrations during Field campaigns

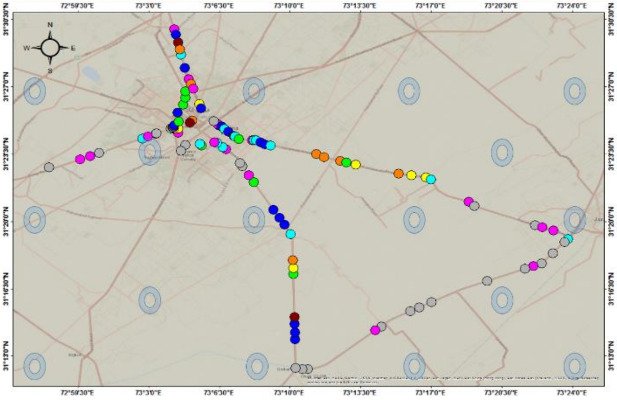
SO_2 VCD extracted from car MAX-DOAS measurements (DSCDs) performed periodically within and around the cities of Faisalabad and Lahore from 17th December 2015 to 23rd February 2016 as enlisted in table 4.1. Tropospheric SO_2 VCDs are plotted against date and presented in figure 9. The high SO2 concentrations shown in figure 9, on 2nd January 2016 was observed in the city of Lahore. Especially, the peaks are observed along the road segments (mainly at Sandha Road, Niazi Chowk and Ghazi Road) with dense traffic, near Baray Bhai Chemicals & Packages on Sandha Road and near the airport. The highest SO^2 VCD was found within Lahore estimated to be 9.64×10^{16} molecules/cm^2 (129.9ppbv) and the average value was 6.8×10^{16} molecules/cm^2 (91.61ppbv). Similarly, on 20th February 2016 at Lahore, the maximum values are observed near the foundries, roads with heavy traffic load, and near the airport.

On 17th December 2016, the maximum SO_2 VCDs for Faisalabad was found to be 3.63×10^{16} molecules/cm^2 (48.92ppbv). At Faisalabad, the peaks were observed on Satyana road near the garment industries and tanneries. It can clearly be observed on 17th December that as we are moving away from the populous/congested area, the values are gradually decreasing and as we are moving towards the main city area, the concentration started to increase. On 16th January 2016 at Faisalabad, the higher concentration of sulfur dioxide (3.385×10^{16} molecules/cm^2) was observed near the Steam Power Plant and near the railway station. After 16th January, on 23rd February, the highest concentration was observed with the concentration of 3.28×10^{16} molecules/cm^2. High concentration is observed on Faisalabad Bypass, near the Rafhan Maize Products’ Company.

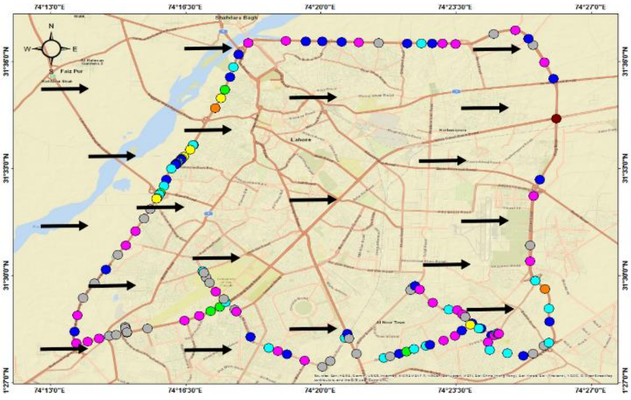
Table 9 Showing max and average SO_2 Concentrations observed in Field Campaigns

Sr #	**Dates**	**Site**	**Avg_SO_2 VCDs** ($molcm^{-2}$)	**Max_SO_2 Conc.** (ppbv)	**Threshold**	**Distance km (Round)**
1	17 Dec,2015	Faisalabad	3.63E+16	48.91	63.8	137.6
2	18 Dec,2015	Lahore	3.14E+16	42.37	63.8	81.3
3	2 Jan,2016	Lahore	4.80E+16	64.65	63.8	93.3
4	3 Jan,2016	Faisalabad	2.94E+16	39.61	63.8	96.2
5	15 Jan,2016	Lahore	2.42E+16	32.61	63.8	75.3
6	16 Jan,2016	Faisalabad	1.28E+16	17.28	63.8	184
7	1 Feb,2016	Faisalabad	2.47E+16	33.36	63.8	78.4
9	20 Feb,2016	Lahore	5.18E+16	69.83	63.8	88
10	21 Feb,2016	Lahore	3.82E+16	51.51	63.8	82.3
11	23 Feb,2016	Faisalabad	3.28E+16	44.15	63.8	160

FSD_17_Dec_2015

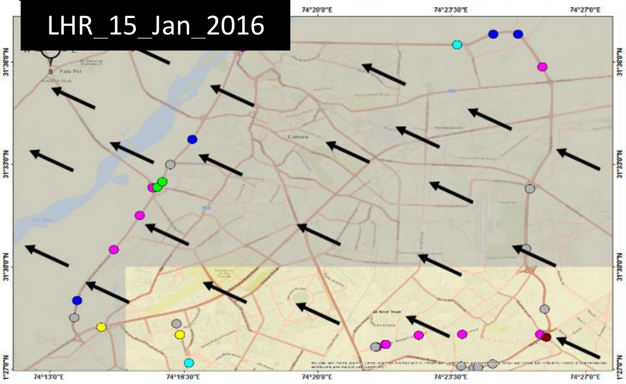


LHR_18_Dec_2015



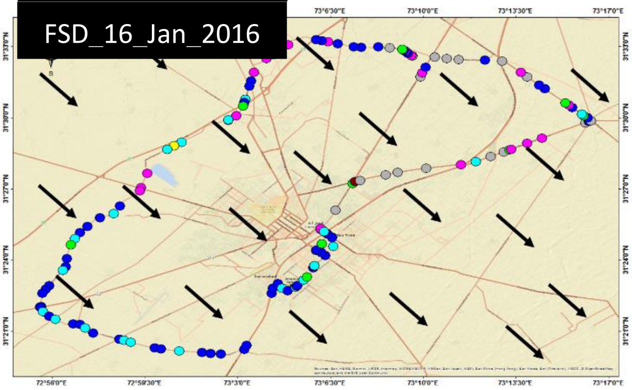
LHR_02_Jan_2016

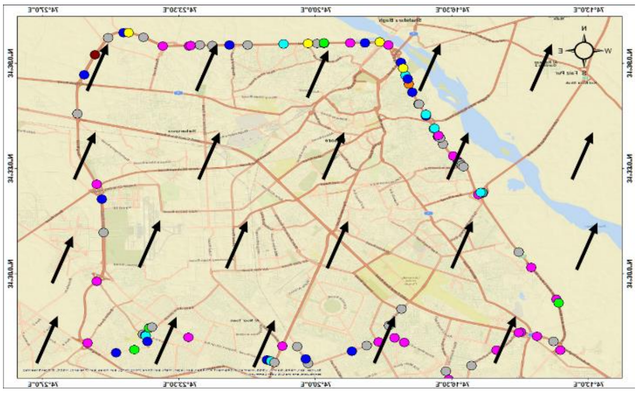
LHR_15_Jan_2016



LHR_03_Jan_2016

FSD_16_Jan_2016




74°27'0"E
74°23'30"E
74°20'0"E
74°16'30"E
74°13'0"E
Shahdara Bagh
N
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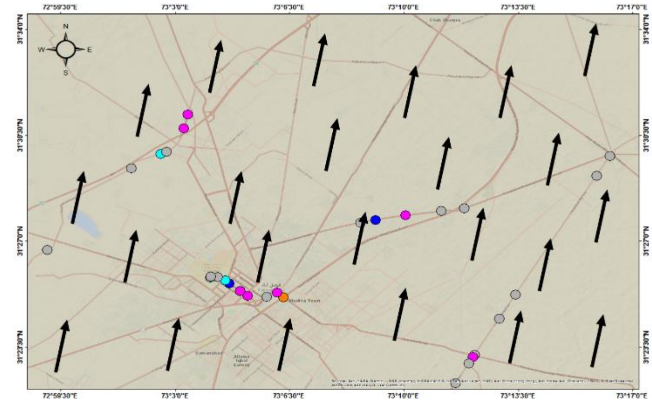
Faiz Pur


72°59'30"E
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73°6'30"E
73°10'0"E
73°13'30"E
73°17'0"E
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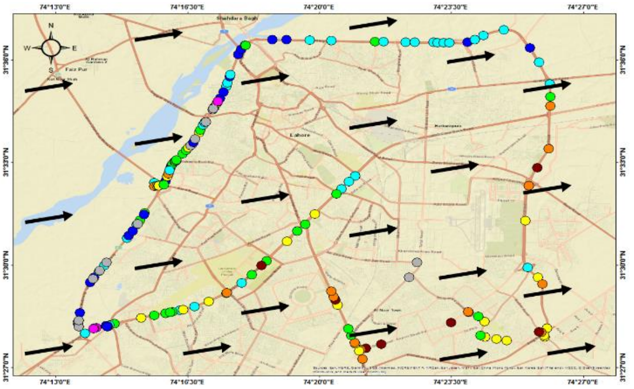
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74°20'0"E
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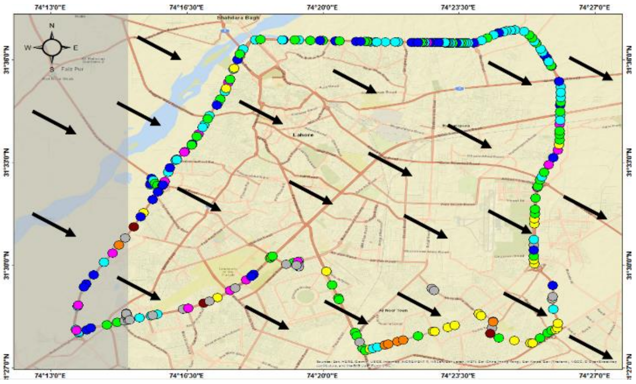
Shahdara Bagh
Lahore
Al Noor Town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Al Noor Town

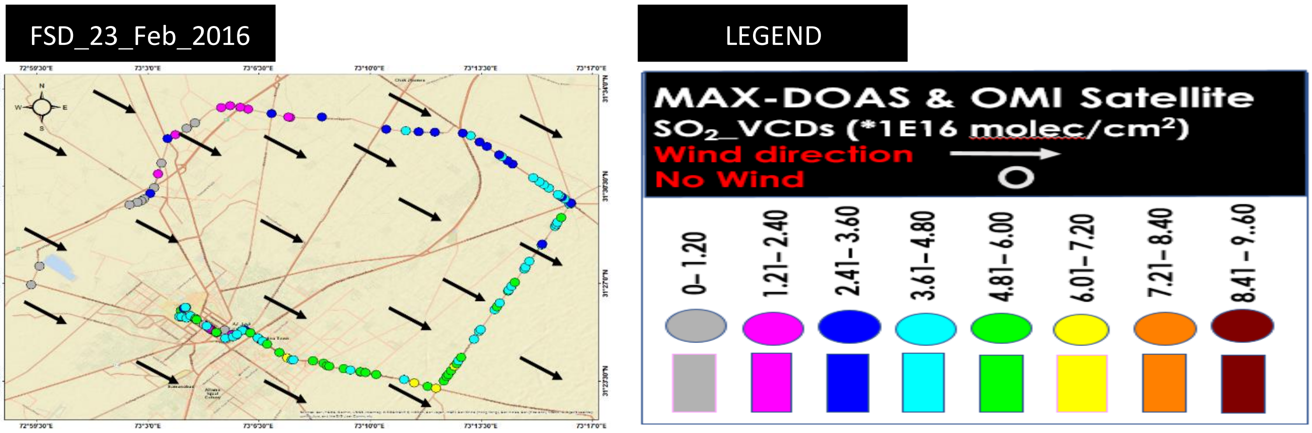
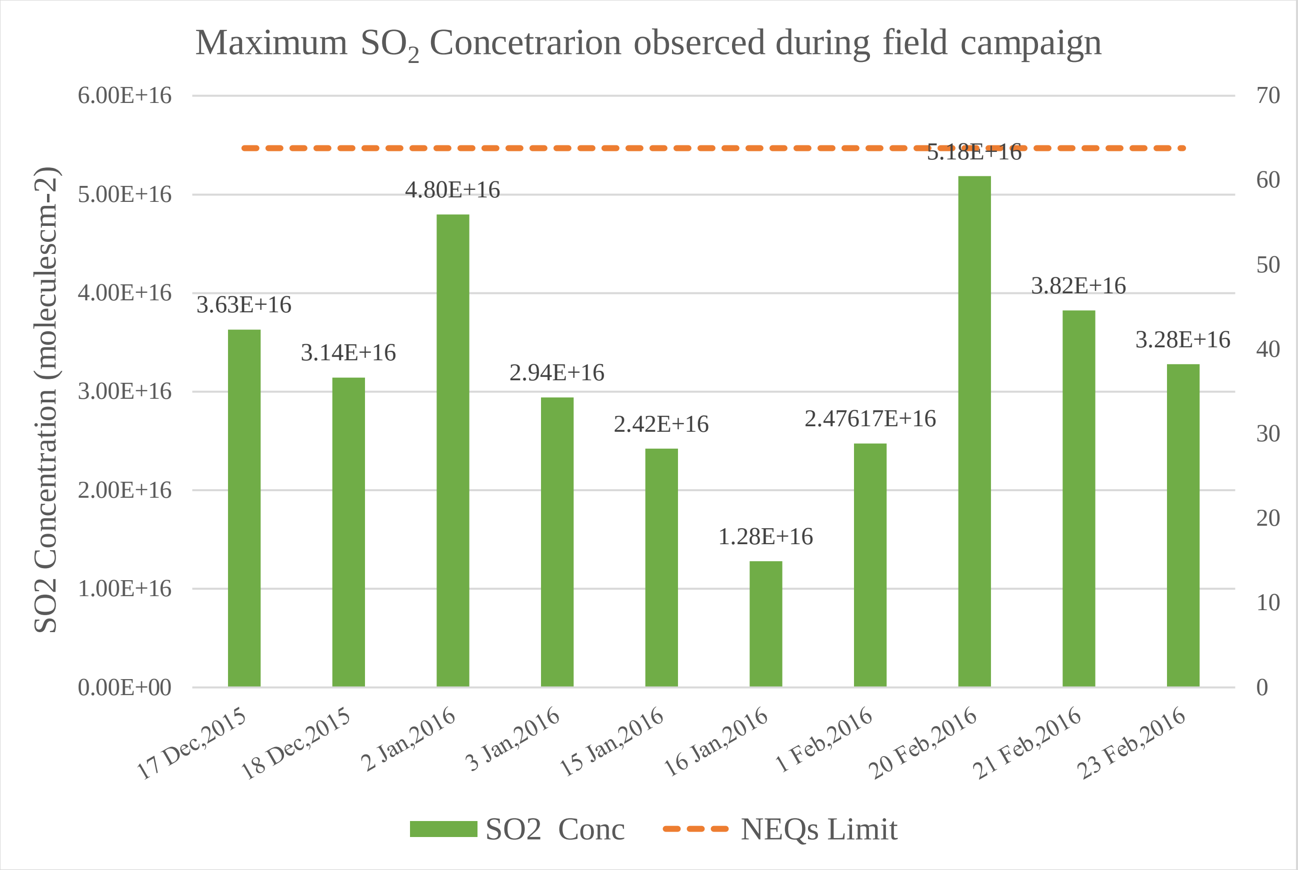


Figure 13 SO_2 Concentration with legend retrieved from CAR MAX-DOAS and OMI satellite observations conducted in the city of Lahore and Faisalabad. Wind vectors are also included to represent the average wind direction during each particular field campaign observations

4.2. Ground Monitoring of SO2 for Field Campaign

During field campaign conducted for this particular study the concentrations observed are shown in the figure 15 which are observed by MAX-DOAS. In this study we converted SO_2 VCDs into SO_2 concentrations in the ambient air by assuming the car MAX-DOAS sensitivity to boundary layer SO_2 up to 1200 m (vertically) only, which was calculated using panoply software. The resulting concentrations are presented in table 9 at various cities. Similar to the other studies, we also observed that the SO_2 mixing ratios are not exceeding the National Environmental Quality Standards (NEQS) but at a single day i.e. 20th of February, 2016 in Lahore (figure 16), following the reason of heavy industries at industrial road, dense traffic congestion for long period of time and then the airport nearby. The Pak-NEQS standard for SO_2 is 63.8 ppb.

Figure 15 Illustrates the SO_2 concentration (ppb) are not exceeding from NEQs Limit



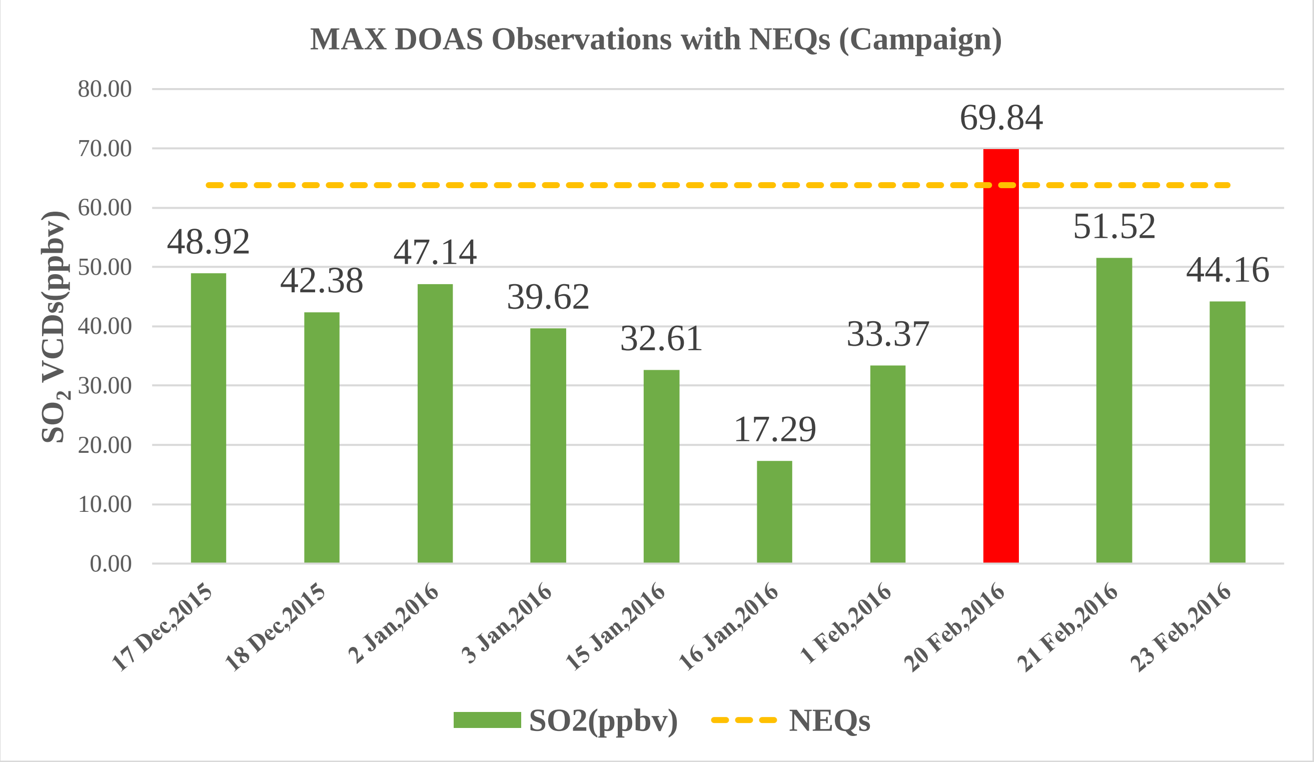


Figure 16 MAX-DOAS Observation with Pak NEQs

4.3. Comparison of Field Campaign Monitoring and satellite

For the validation of the results from filed campaign, field campaign results were validated with the satellite averaged values for each particular day. It can be seen in figure 17 that the pattern of the concentration for the all the days of field campaign are almost similar to the pattern of the satellite but concentrations are not showing the good correlation with the Pearson value of 0.70

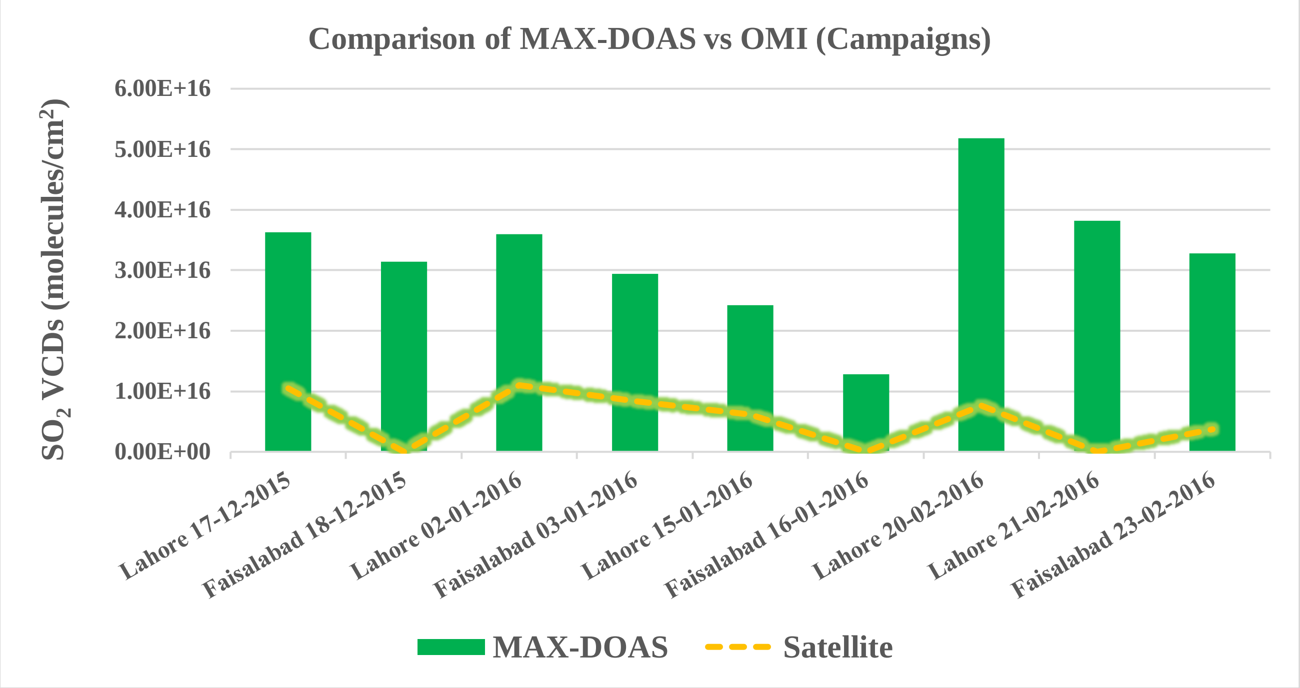


Figure 17 Comparison of MAX-DOA and satellite observations

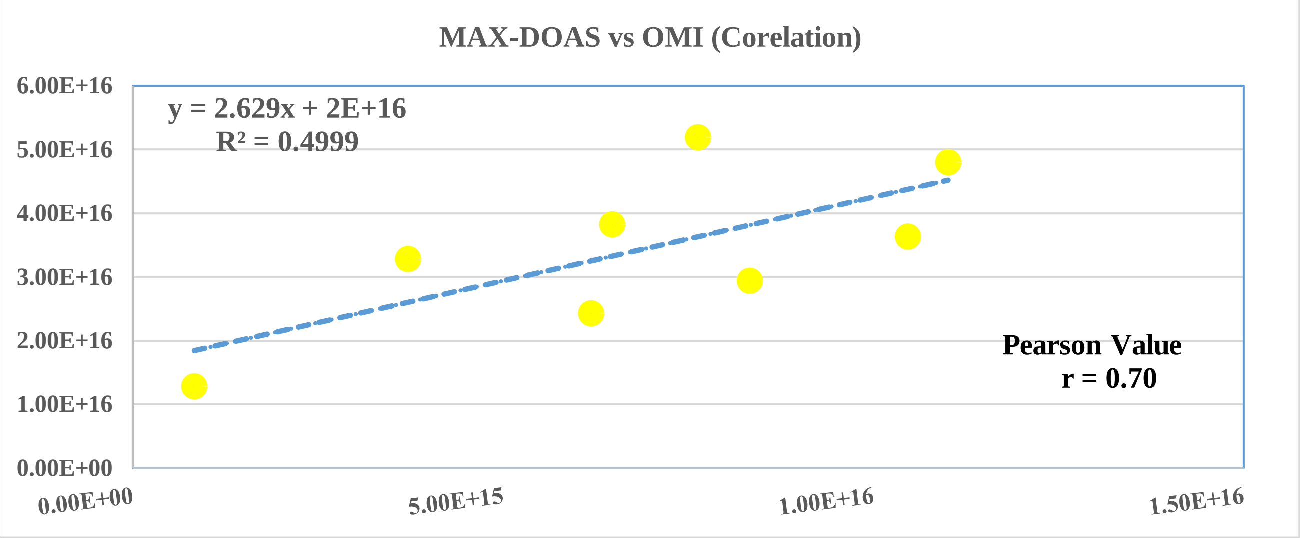


Figure 18 Correlation of MAX-DOAS vs Satellite

4.4. Diurnal cycle of Sulfur dioxide

Figures below show the diurnal and weekly variations averaged for the whole time the instrument was mounded at LUMS (23 December-2015 to 18 Feburary-2016). In Diurnal cycle (figure 19), the sulfur dioxide showed a decreasing trend during the daytime and higher concentrations in morning and evening time, it is particularly due to the traffic emission of the city. There is a slightly peak around 9:00 am due to high traffic around the roads in morning peak hours. The other reason for the peak at 9am and 6pm is because of the low temperature during winter because of which the SO_2 is not dissipated into the atmosphere so quickly resultantly residing for long time into the atmosphere, whereas the opposite to these causes, the decreasing trend is observed during from noon until day shown in (figure 19). Decreasing trend follows the pattern like, as the sunlight increases its intensity keeps on increasing as well so the SO_2 under these conditions go through two phenomenon which is because of the presence of both mass independent positive and negative anomaly. SO_2 Firstly dissipate through photolysis which occur in the range of 190nm-220nm, and the when the intensity of the sunlight increases further, the SO_2 undergoes photoexcitation. In both the cases the SO_2 is dissipated into the atmosphere.

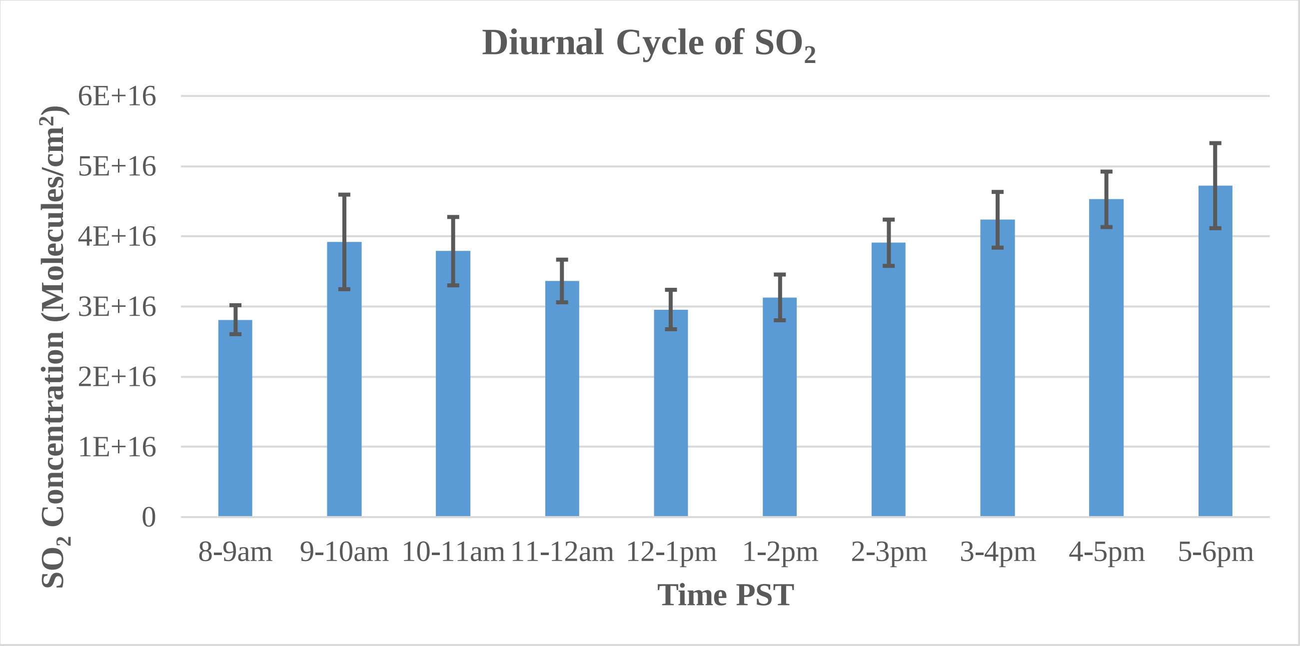


Figure 19 Averaged (6am to 6pm) Diurnal Cycle observed over LUMS by MAX- DOAS

4.5. Weekly cycle of Sulfur dioxide

In weekly trend (figure 20), it is observed that the SO_2 concentration is high during the week days, peak at Monday, and it decreases on weekends. On Sunday, the minimum values were observed. It mainly depends on human activities which are increased in week days and decreased on Saturdays and Sundays due to holiday. Another way to explain the weekly trend is the industrial activities work business as usual throughout the week and month but due to the decrease in road and human activities over the weekend resultantly show the decrease in the sulfur dioxide concentration on weekends. These same trend has already been observed by (Kanaya, 2014).

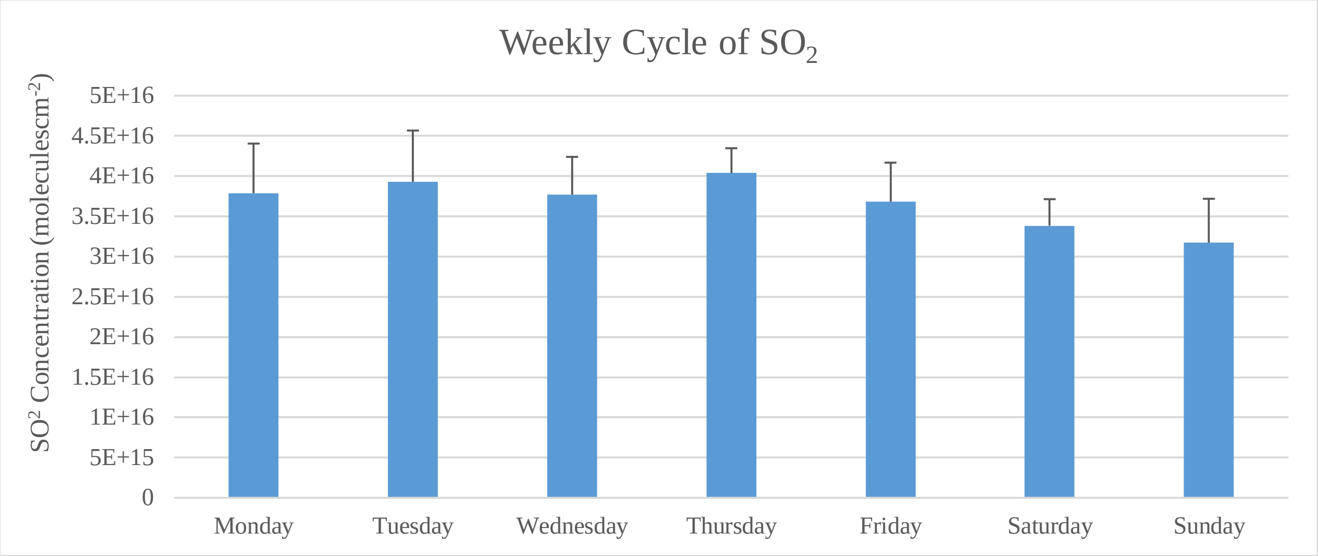


Figure 20 Weekly Averaged sulfur dioxide concentrations monitored by MAX-DOAS observation

4.6. Daily Average Concentration of SO_2

The instrument MAX-DOAS was mounted at LUMS for the stationary monitoring for total of 54 days. The average concentration of every day is achieved after obtaining data through analysis of the raw spectra. Daily average concentration throughout the stationary monitoring at LUMS is shown in the figure 21.

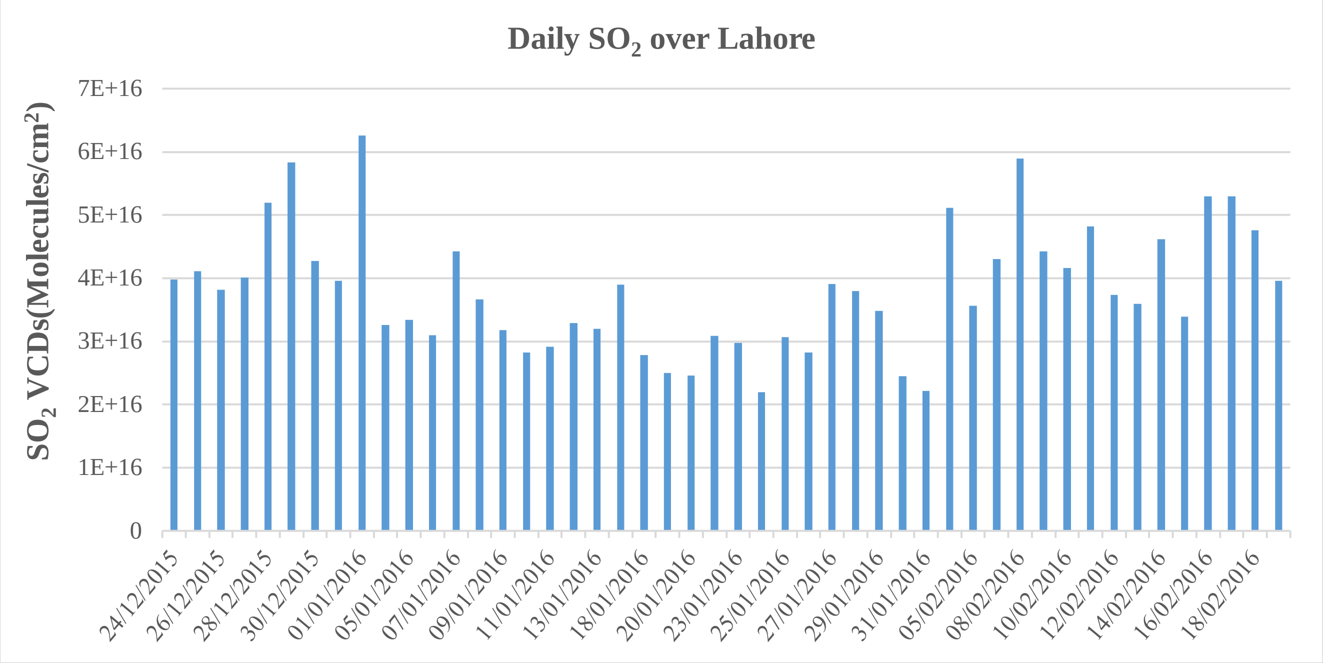


Figure 21 Daily Averaged sulfur dioxide concentrations monitored by MAX-DOAS observations

4.7. Comparison of Stationary Monitoring and Satellite

For the validation of the results obtained from stationary monitoring, comparison with satellite concentration was done. The satellite data was retrieved from OMI satellite through GIOVANNI. The satellite concentrations were downloaded for each particular day in NETcdf format which was further processed by ARCMAP 10.3. The averaged VCDs for each particular day was compared with the satellite averaged value of that day, after all this the satellite and ground based data showed almost the similar trend (figure 22) along with showing the good correlation i.e. Pearson value r = 0.74(figure 23).

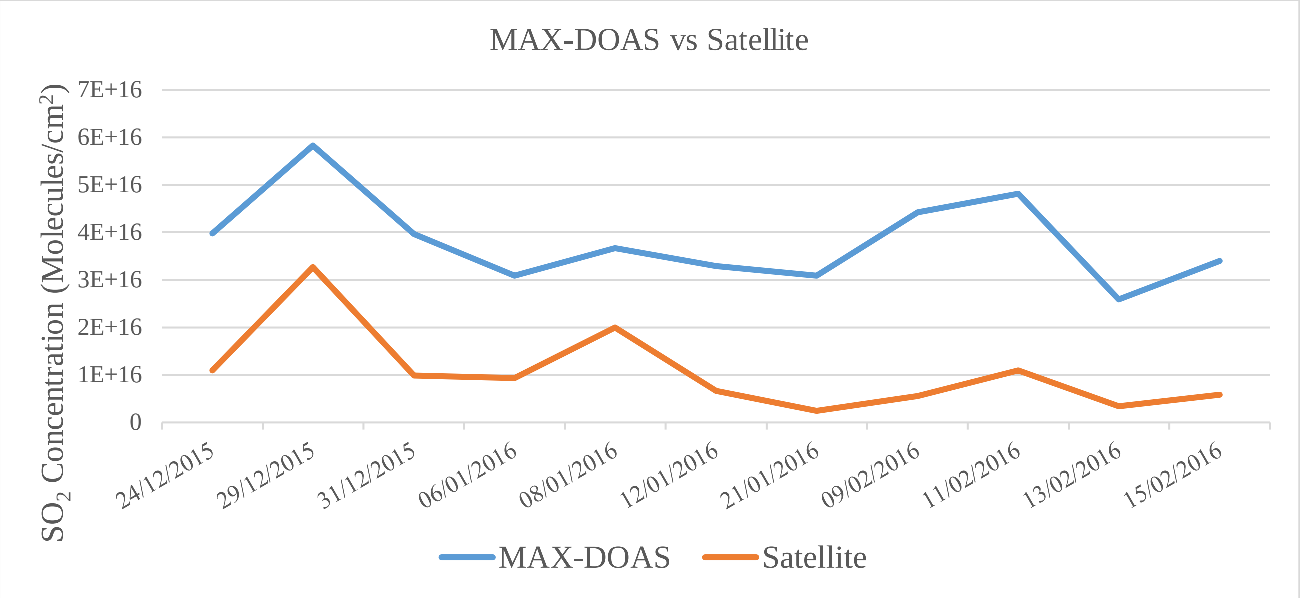


Figure 22 Comparison of Ground value with Satellite values

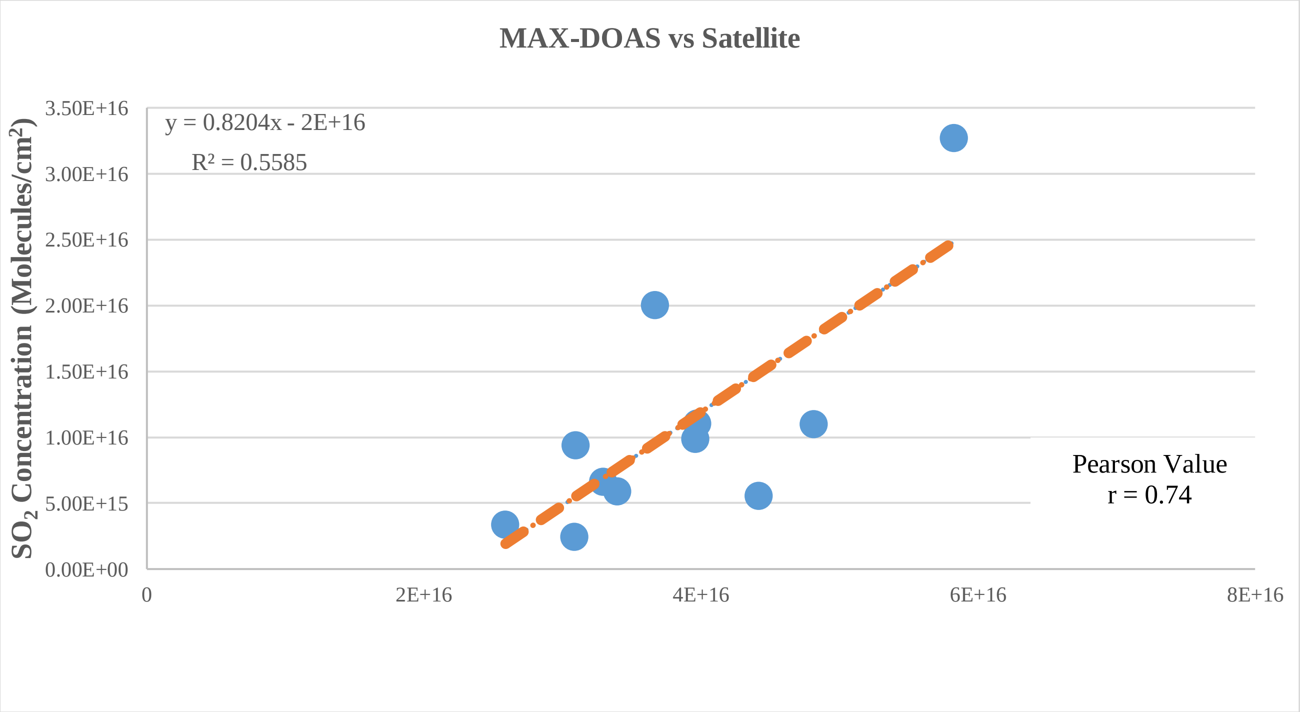


Figure 23 Correlation of Ground based and Satellite observations

Chapter 5

CONCLUSION AND RECOMMENDATIONS

“The Car MAX-DOAS observations at Lahore, Faisalabad, along with one fixed point/continuous air quality monitoring at LUMS, were conducted in order to identify the sulfur dioxide pollution levels in the study area. The pollution levels have been increased due to traffic and population increase in the major cities during the last decade. In this work, Sulfur Dioxide vertical column densities (SO_2 VCDs) attributed to potential sources have also been discussed.

- As per the observations of Field campaigns at the two main cities; Faisalabad and Lahore have an airport, a landfill site, and industrial zones within the city boundaries. These two cities had maximum SO_2 VCDs of 5.1 x 10^{16} (69.8 ppbv) and 3.82 x 10^{16} (51.51 ppbv) molecules/cm^2 respectively. NO_2 concentrations measured by car MAX- DOAS indicated that the NEQS limits (63.8 ppbv) for the major city of Lahore were violated at a single point on 20 Feb, 2016 due to traffic congestions, landfill sites airport and industrial areas. Honda power plant, Mian tyre and Rubber, Nestle and Float Glass Mill etc.

- As one fixed point (continuous) monitoring was also carried out at Lahore, which revealed that Lahore had maximum sulfur dioxide concentration near but still below the NEQs i.e. 63.8 ppbv. The similar trend was observed for the months (December, January, and February) over the city of Lahore.

- In order to improve and have better comparison of boundary level pollution with satellite observations, such field campaigns need to be done on regular basis, worldwide and under different atmospheric conditions.

Recommendations

Following recommendations based on our findings from this study are suggested in order to combat air quality related issues and to further improve the air quality monitoring practices in the country.

1. The outcomes of this study may be used to identify, a relationship between air pollutants and their sources, therefore, effective Pollution Control Techniques (PCTs) can be proposed for the abatement of pollution. As use of coal burning is some industries and fossil fuels in both industry and vehicles is the main reason of SO_2 emissions, therefore, SO_2 pollution levels can be reduced by energy saving strategy, alternative fuels, improved combustion technology, use of catalytic converter technology.

2. On state level, mass transit system should be introduced in larger urban areas in order to avoid unnecessary traffic jams and consequently to abate traffic emissions.

3. To run effective media campaigns to teach the public and other stakeholders, will improve the understanding and will raise the concern for air quality. Educating school children, citizen groups etc. by sharing the results of such field campaigns.

4. Furthermore, at state, provincial and city government level, air quality management planning should be done and models should be used for assessment of the air quality, besides incorporating legislations in Environmental Laws on emission reductions of SO_2 and other criteria pollutants.

5. To conduct such field campaigns on monthly or quarterly basis, the analysis of pollution trends over the whole year will help us to understand the impact of seasons on trace gas concentrations. The data acquired will be helpful to be used in academics to further improve the understanding of students regarding air pollution levels within Pakistan.

6. Establish the air pollution inventory, It can be used as a baseline by other research organizations, environmental agencies and Non-Government Organizations (NGO’s) working on other aspects of air pollution impacts i.e. health impacts, climate change, mitigation and adaptation studies etc.”

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