Temporal Record of Atmospheric Sulphur dioxide Column Densities over Pakistan by using Satellite Observations

By

Palwasha Khattak

(2011-NUST-MSPhD-EnvS-08)

A thesis submitted in partial fulfillment of requirements for the degree of

Master of Science

in

Environmental Science

Institute of Environmental Sciences and Engineering (IESE)
School of Civil and Environmental Engineering (SCEE)
National University of Sciences and Technology (NUST)
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It is certified that the contents and forms of the thesis entitled

Temporal Record of Atmospheric Sulphur dioxide Column Densities over Pakistan by using Satellite Observations

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This thesis is dedicated to my Father and Mother

Their believe in me, support and unconditional love had made this all possible.

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Palwasha Khattak

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List of Acronyms

ACF	Auto Correlation
AMF	Air Mass Factor
ARL	Air Resources Laboratory
CCD	Charge Coupled Device
DMS	Dimethylsulfide
DOAS	Differential Optical Absorption Spectroscopy
DU	Dobson Unit
ENVISAT	Environmental Satellite
EOS	Earth Observing System
EPA	Environmental Protection Agency
ESA	European Space Agency
GOME	Global Ozone Monitoring Experiment
GOME-2	Global Ozone Monitoring Experiment-2
HYSPLIT4	Hybrid Single Particle Lagrangian Integrated Trajectory Model-4

MetOp-A	Meteorological Operational Satellite - A
NOAA	National Oceanic and Atmospheric Administration
OMI	Ozone Monitoring Instrument
PCSIR	Pakistan Council of Scientific and Industrial Research
SCD	Slant Column Density
SCIAMACHY	SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY
TEMIS	Tropospheric Emission Monitoring Internet Service
VCD	Vertical Column Density
WHO	World Health Organization

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Abstract

Sulfur dioxide (SO_2) is a chemically active trace gas and one of the major criteria pollutants. Pakistan lacks the monitoring facility on a larger scale to measure atmospheric gases on regular bases. This study presents the results of atmospheric SO_2 column densities obtained from satellite observation over Pakistan during the time period of 2004 – 2012. level-2 data product of satellite instruments SCIAMACHY onboard ENVISAT, OMI onboard Aura and GOME-2 onboard Metop retrieved by using Differential optical absorption spectroscopy (DOAS) technique are used. Spatio-temporal distribution of SO_2 column densities along with the seasonal variation over main cities and regions of Pakistan has been discussed. The Nabro volcano eruption in 2011 had caused high SO_2 columns over East Africa, Middle East and South Asian regions. Satellite images tracked the transported SO_2 pollution over Pakistan during this event. Other significant volcanic eruptions and their trans-boundary effect over Pakistan's atmosphere have also been discussed in this study. Back trajectory analysis is performed to track the origin of air masses with high SO_2 column densities detected over Pakistan. Temporal evolution of SO_2 column densities exhibited an overall increase of 70% (125% with fraction of trans-boundary SO_2 pollution from regional volcanoes) during the time period of 2004-2012. Spatial and temporal analyses of SO_2 pollution over Pakistan by using satellite observation has been discussed for the first time in Pakistan.

Chapter 1

Introduction

1.1. Background

Environmental concerns related to air quality is now a global issue, more particularly in the developing countries and urban centers. Air is a mixture of various gases, liquid particles and small solid particles. Source of these substance are both natural and anthropogenic activities such as industries, motor vehicles, domestic activities and many others. Problem arises when the quantity of these substances exceed the safe level and cause harm or discomfort to humans or plants, animals and materials. Such substances are known as air pollutants. Air pollutants are in the form of liquids, gases or particles (Alias *et al*, 2007).

The problem of air pollution and the efforts to control it is not a recent phenomenon. An early example of pollution control ordinance can be traced to thirteenth-century England, when King Edward I banned the burning of highly polluting coals in London (Schwela, 1997). Air pollution and its adverse effects were recognized early; despite this the fossil fuel consumption in the transport sector and industrialization in the pre and post industrial revolution caused the rise in air pollution in various urban areas (Bell *et al*., 2004). In December 1952, the London's great black smog had severe health impacts, causing about 4000 deaths and when considered the long term effects, approximately 12000 deaths were reported (Bell and Davis, 2001). Furthermore statistical studies on epidemiology held in 1950's, associated the deteriorating human health with air pollution, even on the lower levels of air pollution (Bell *et al*., 2004).

No doubt the development and advances in technology in different sectors has improved the quality of life and brought comfort to the people, nevertheless it has also increased the emission foot prints of each individual (Thornton, 2007). These emissions are associated with many health hazards and it also endangers the environmental sustainability. Rapid growth of population, usage of fuels in vehicles, continuous urbanization and rapid industrialization has a major role towards increasing air pollution (Thornton, 2007). Therefore air pollution is an important environmental concern and requires considerable attention.

In response to such a significant issue, with the passage of time extensive literature related to the air pollution effects on health and environment has been amassed by various countries around the globe. They have also developed standards and guidelines for the protection of human health and conserving the environment (Thornton, 2007). In recent years extensive research has been carried out on the causes and sources of air pollution, its effects on human health and its environmental impacts (Ferdous, 2008). Consequently research has also focused on understanding the impacts of air pollution by spatial analysis, which has emerged as a significant tool in today's research (Ferdous, 2008). Although air has various significant air pollutants that adversely affect atmosphere, present research project focuses mainly on an industrial pollutant Sulphur dioxide (SO_2).

1.2. Sulphur dioxide in Atmosphere

Sulphur dioxide (SO_2) is present in the atmosphere as a result of both natural and anthropogenic sources (Lee *et al*., 2008; Seinfeld and Pandis, 1998). Naturally it is produced due to the oxidation process occurring in the soil, oxidation of hydrogen sulfide (H_2S) and dimethyl sulfide (DMS) over oceans and also from volcanic

eruptions. Among other natural sources of SO_2, volcanic eruptions are the major contributor and are sporadic, emitting 7.5–13 Tg SO_2 per year (Halmer *et al*., 2002; Andres and Kasgnoc, 1998).Whereas combustion of fossil fuels and biomass burning contributes to the anthropogenic sources of SO_2 production (Lelieveld *et al*., 2007; Finlayson-Pitts, 2000; Eisinger and Burrows, 1998). Sulphur (S) is found mostly in oil and coal and when burnt, it combines with oxygen (O_2) and SO_2 is produced (Mirza *et al*., 2013).

SO_2 is a very reactive compound. It reacts easily to form other compounds such as sulphuric acid (H_2SO_4), sulphurous acid (H_2SO_3) and sulphate (SO_4^{-2}) particles. These compounds are very harmful to the environment as well as to the human health. SO_2 is a criteria pollutant (USEPA, 2013) and also one of the key precursors of acid rain. Acid rain is a hazard for forests and many fresh water ecosystems around the world (Ferrari and Salisbury, 1999).

SO_2 life time varies from few days to several weeks (Platt and Stutz, 2004). In troposphere due to its reaction with hydroxyl (OH) and other oxidizing agents, it has a limited lifetime of just a few days (Platt and Stutz, 2004; Atkinsen *et al*., 1997). However in lower stratosphere its lifetime exceeds from several weeks to 2 years (Platt and Stutz, 2004; Eisinger and Burrows, 1998).

1.3. Monitoring of Trace Gases

Traditionally, monitoring of atmospheric gases including SO_2 has been carried out via air quality monitoring stations located in the cities and also through the total ozone (O_3) monitoring station. These stations along O_3 estimates could also provide SO_2 measurements (e.g. Fioletov *et al*., 1998; Zerefos *et al*., 1986). Such monitoring stations are located sparsely and SO_2 monitoring on a global scale through these

stations is not possible. Since last few decades, with satellite observations and advancement of technology, now the atmospheric SO_2 monitoring on large scales has become possible (Carn *et al*., 2008; Khokhar *et al*., 2005) with good temporal and spatial coverage. Space borne instruments, for example Global Ozone Monitoring Experiment (GOME – since 1996) (Thomas *et al*., 2005; Khokhar *et al*., 2005) , Ozone Monitoring Instrument (OMI) (Krotkov *et al*., 2008, 2006; Lelieveld *et al*., 2006) and Global Ozone Monitoring Experiment-2 (GOME – 2 since 2008) in addition to SCanning Imaging Absorption spectroMeter for Atmospheric CHartographY (SCIAMACHY) (Lee *et al*., 2008; Bovensmann *et al*., 1999) have opened new corridors providing a continuous spatial and temporal analysis of such air pollutants around the globe.

Pakistan has no continuous monitoring facility for the monitoring of ambient air quality. Punjab Environmental Protection Agency (EPA) and Pakistan Council of Scientific and Industrial Research (PCSIR) have the facility of mobile laboratories. But these laboratories record intermittently in few cities. This study has first time focused to prepare database of atmospheric SO_2 and emphasized on the amount of SO_2 present in the atmosphere of Pakistan as a consequence of trans-boundary movement of air masses, by using satellite data. It has emphasized on spatial and temporal variation in SO_2 column densities during the time period of 2004 - 2012. For this purpose SO_2 column densities data of SCIAMACHY instrument is used. SO_2 absorption lines are between the wavelengths of 315 – 326 nm of Ultraviolet (UV) region (Rix *et al.*, 2012; Khokhar *et al*., 2006). The Differential Optical Absorption Spectroscopy (DOAS) (Khokhar *et al*., 2005; Van Roozendael, 1999; Richter, 1998; Perner, and Platt, 1979) technique is used for the retrieval of SO_2 column densities in the atmosphere from nadir measurements of SCIAMACHY. Daily data and images of

GOME-2 and OMI instrument have been used to monitor special events of high SO_2 columns as consequence of volcanic activity in the neighboring regions.

1.4. Research Objectives

Objectives of the present study are:

a. To prepare database of SO_2 column densities over Pakistan during the last decade (2004-2012).
b. To monitor and analyze the spatial distribution of SO_2 over Pakistan from satellite observation.

Literature Review

2.1.Earth's Atmosphere and Composition

Earth's atmosphere is made of various gases. Among these gases mainly O_2, 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 the atmosphere, out of the atmosphere and also within the earth's atmosphere. The principal source of this energy is sunlight at UV, visible, and near-infrared (NIR) wavelengths. This incoming energy is balanced at the top of the atmosphere by the outgoing emission of infrared (IR) radiation from the Earth's surface and from the atmosphere (Isaksen *et al*., 2009).

2.2.Layers of Atmosphere

The air from below is in contact with earth's surface. It is warmed from below. When it is warms up, it expands and with the expansion the air cools down. Temperature of air and density of air determines the humidity of the air. More the air can hold the amount of water vapors in it; more is the humidity of the air. These three properties together i.e. Temperature, density and humidity, enforces the atmosphere layered structure. Figure 2.1 shows this structure, the atmospheric layers are related to temperature, pressure and height.

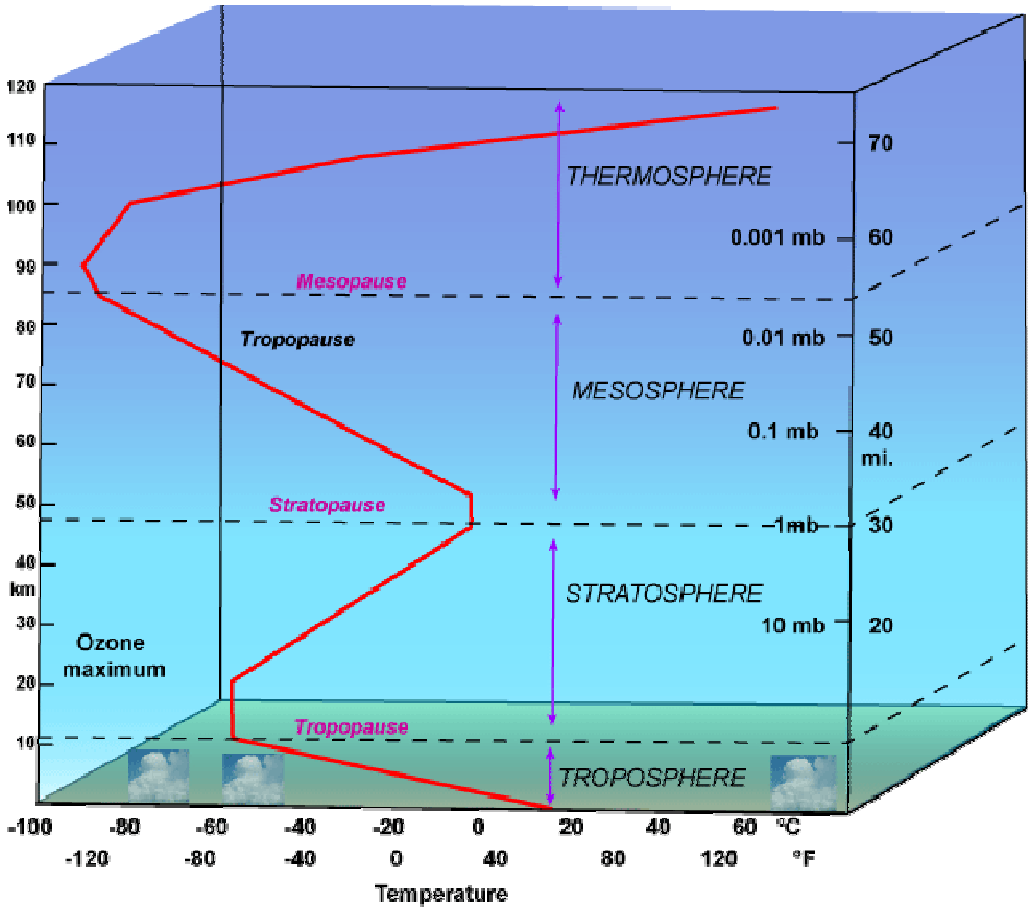


Figure 2.1: The different layers of atmosphere, temperature, and pressure profiles with respect to altitude (adapted from Lyndon state college meteorology department, 2006).

The first layer is the troposphere. It starts from surface and extends to the upper boundary; at about 11 km. The upper boundary is named as tropopause. The height of troposphere varies, around equator it is about 16 km and around poles it is 8 km. Atmospheric gases are most concentrated in this layer. In troposphere, there is an indirect relation between temperature and height, as height increases the temperature decreases, with the average rate of 6.5 °C km^{-1}.This rate is known as 'lapse rate' (Allaby, 1996). Above the tropopause, the next atmospheric layer is stratosphere. It extends up to 40 km and is mainly composed of stable dry air. In troposphere the pollutants disperse, whereas in stratosphere the pollutants do not disperse and remains

for long period of time. The significance of stratosphere lies in the presence of dense O_3 layer in it. The O_3 layer helps in preventing the UV light (which is harmful to living organisms) reaching the earth's surface (Van Der Leun, 2004).

2.3.Sulphur dioxide

2.3.1. Physical and Chemical Properties

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 μg m^{-3}. In the atmosphere, SO_2 undergoes series of conversion process. These processes result in the formation of various new compounds (MfE, 2004b), for further details refer to the section 2.3.3.1.1. Table 2.1 presents the physical and chemical properties of SO_2.

Table 2.1: The Physical and Chemical Properties of SO_2

Property	Value	Reference
Molecular weight	64.065	Lide, 2002.
Physical state	Colorless gas	
Melting point	-75.5 ºC	
Boiling point	-10.05 ºC	Lide, 2002.
Specific gravity (liquid)	1.50	RSC, 1999.
Specific gravity (gas)	2.26 (at 0ºC)	Genium, 1999; RSC, 1999.
	338 kPa (at 21ºC)	RSC, 1999.
(air =1) Vapor pressure	230 kPa (at 10ºC); 330 kPa (at 20ºC); 462 kPa (at 30ºC); 630 kPa (at 40ºC)	Weil and Sandler, 1997.
Solubility in water	17.7% (at 0ºC)	Genium, 1999.
	85 g/L (at 25ºC)	RSC, 1999.

	22.971 g/100 g H_2O (at 0ºC); 16.413 g/100 g H_2O (at 10ºC); 11.577 g/100 g H_2O (at 20ºC); 8.247 g/100 g H_2O (at 30ºC); 5.881 g/100 g H_2O (at 40ºC)	Weil and Sandler, 1997.
Solubility	Soluble in ethanol, ether and chloroform.	Lide, 2002.
	Moderately soluble in benzene, acetone and carbon tetrachloride.	Genium, 1999.
	Soluble in chloroform, ether, alcohol, methanol.	Budavari, 1996.
Acid/Base properties	Dissolves in water to form a slightly acidic aqueous solution of H_2SO_3.	Genium, 1999; Weil and Sandler, 1997.
Odor threshold in air	0.1 to 3ppm	Genium, 1999.
	0.45 ppm (low); 4.8 ppm (high); 1.9 ppm (irritating).	ATSDR, 1998; Ruth, 1986.
Conversion factors for vapor (at 25 °C and 101.3 kPa)	1 ppm = 2.62 mg/m^3	IARC, 1992.

2.3.2. Sources of SO_2

Sulphur is emitted into the atmosphere from both natural and anthropogenic sources. The natural sources include volcanoes (emitting 7.5–13 Tg SO_2 per year) (Halmer *et al*., 2002; Andres and Kasgnoc, 1998), DMS from the oceans (16–54 Tg S per year) (Kettle and Andreae, 2000) and wildfires. Wildfires are also categorized as anthropogenic sources of SO_2. Overall emissions of SO_2 from wildfires have increased since 1750 till 2000, from 1.46 Tg SO_2 per year to 4.1 Tg SO_2 per year (Dentener *et al*., 2006). The increase in anthropogenic emissions of SO_2 from the year 1850 to 1980 is 2 to 131 Tg SO_2 per year (Smith *et al*., 2011). Throughout these years, coal combustion has contributed majorly to the SO_2 emissions. Whereas SO_2 emissions from the petroleum combustion have increased mainly after the 1940's (Smith *et al*., 2011).

In following section, few major natural and anthropogenic sources of SO_2 have been discussed.

2.3.2.1.Volcanoes

Emissions from volcanoes are major natural source of SO_2 and also of other trace gases. Other than SO_2 volcanic eruptions can inject carbon dioxide (CO_2), water vapors (H_2O), hydrofluoric acid (HF), hydrochloric acid (HCl) and ash into the atmosphere. These gases can disturb the composition of atmosphere and perturb the atmospheric chemistry. This can potentially affect the environment and climate of the earth (Yang *et al*., 2009). The gases and particles from volcanic emissions are converted into tropospheric and stratospheric aerosols (Robock, 2000). These aerosols can persists in the stratosphere for many years and cause the lowering of global surface temperature by 0.5 °C, whereas the ash is sometimes removed from the atmosphere within days (McCormick *et al*., 1995). Highly explosive volcanic events affect climate on time scales of months to years (Robock, 2000; McCormic *et al*., 1995). Figure 2.2 shows volcanic activity and gases emitting from volcano and how they can affect the atmospheric composition.

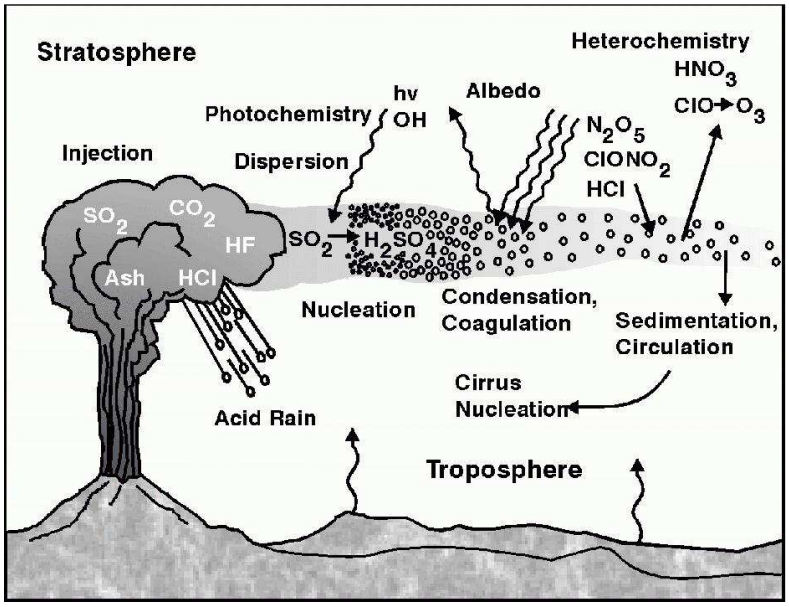


Figure 2.2: Volcanic gas emissions (Figure modified from McGee and Gerlach, 1995)

Generally the major volcanic eruptions are discussed; however most of the volcanic emissions are released from the continuous and non-eruptive degassing of the volcanoes. Out of total SO_2 released into the atmosphere from volcanic emissions, 99% of it is released from continuous volcanic degassing and around 1% is released due to the sporadic eruptions (Andres and Kasgnoc, 1998).

The large volcanic eruption events can be monitored and studied through satellite observations (Carn and Bluth, 2003). However with the development of ground-based remote-sensing techniques the local and regional influences of degassing volcanoes could also be observed (McGonigle and Oppenheimer, 2003; Galle *et al*., 2002).

2.3.2.2.Oceans and Wetlands

The biological reactions and geochemical process occurring on the terrestrial lands and in the oceans produce trace gases. The gases released from oceanic processes include DMS, carbonyl sulphide (COS), H_2S and carbon disulfide (CS_2).

The biogenic continental sources also release a variety of sulphur containing compounds, including H_2S, DMS, dimethyldisulfide (DMDS), CS_2, COS, methylmercaptan (MeSH) etc. These all trace gases are converted to SO_2 by oxidation process and finally to H_2SO_4 through a series of chemical reactions. However, these SO_2 emissions could not be identified via satellite observations (Khokhar, 2006) due to the less sensitivity of satellite instruments over ocean surfaces.

2.3.2.3.Fossil fuel Consumptions

Fossil fuels include coal, petroleum, natural gas, bitumen and shale oil. Fossil fuels are the foremost source of obtaining energy, specifically heat and electrical energy. The main constituents of these fuels are carbon (C), O_2 and hydrogen (H_2). Other than these sulphur, nitrogen (N_2) compounds and metals are also part of fossil fuels (Chmielewski, 2011). SO_2 emissions from the fuel, depends directly on the content of sulphur in fuel and also on the amount of fuel consumption (Vijay *et al*., 2004). Generally natural gas has less quantity of sulphur, whereas in coal and oil sulphur levels are variable and it is mostly high (USEPA, 1995). SO_2 is emitted most when fossil fuels are combusted in industrial facilities such as power plants (EPA, 2011). During the combustion process of coal, sulphur containing compounds are transformed into SO_2. After conversion, SO_2 along other flue gases are emitted into the air (Đurić *et al*., 2013).

2.3.2.4.Metal Ore Smelting Industry

Metal ores contain prevalent quantity of sulphur. These metals include aluminium (Al), zinc (Zn), copper (Cu), iron (Fe), lead (Pb), nickel (Ni) and many other common metals (Khokhar *et al*., 2008). For example, in earth's crust Cu is primarily found as

chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), chalcocite (Cu_2S) and covellite (CuS) (Emission Estimation Technique (EET), 1999).

Smelting is referred to the process through which normally a metal ion is reduced to a free metal. As a result of this process, sulphur is eliminated from the metal ore as SO_2 (Khokhar *et al*., 2008). SO_2 emissions from smelters can affect vegetation, forest, water reservoirs and land surface present near the smelters (AMAP, 2006; Savard *et al*., 2006; Telmer *et al*., 2006; Aamlid, 2002; EET, 1999).

2.3.2.5.Oil Refineries

Oil refineries transform the valuable constituents of crude oil, into various markedly important petroleum products that are used in everyday life. This is achieved by the extraction and up-gradation of crude oil products like jet fuel, diesel and gasoline (Ba-Shammakh, 2011). Crude oil has a high level of sulphur in it (Neidell and Lavaine, 2012). In a refinery, first the crude oil is broken into raw stocks. Further from these raw stocks, the finished products are made (Gary, 1994). The streams flowing out of distillation units of crude oil also accompany sulphur and some other impurities with itself (Ba-Shammakh, 2011). In France, about 20% of SO_2 is released from oil refineries (Soleille, 2004).

2.3.2.6.Biomass Burning

Biomass burning is considered as both natural and anthropogenic phenomena (khokhar, 2006). However it is primarily an anthropogenic activity (Alexander *et al*., 2004; Delmas and Servant, 1988). There are three reasons behind biomass burning: land clearing for shifting the agriculture, deforestation or land clearing for cultivation purposes and the annual bushfires in dry savannas. Bushfires are of special

importance in Africa, where around 40% to 60% savannas are burned annually (Deschler, 1974).

2.3.3. Atmospheric Chemistry and Fate

2.3.3.1.SO_2 Removal Mechanisms from the Atmosphere

SO_2 once emitted into the atmosphere, it can either convert to some other compounds or it can be removed completely from the atmosphere. The SO_2 removal from atmosphere involves various mechanisms for instance oxidation, dry deposition, wet deposition, dissolution, absorption by soil and vegetation, and few other processes (ATSDR, 1998; Katz, 1977). The removal process can also change SO_2 into sulphates and H_2SO_4 (ATSDR, 1998), this conversion accounts for 10% of atmospheric removal of SO_2 (Hegg and Hobbs, 1978). Out of all these processes related to removal, the dominant processes are wet deposition, wash out and absorption process (Hegg and Hobbs, 1978).

The following sections describe some of the significant removal mechanisms for SO_2 from the atmosphere.

2.3.3.1.1. Oxidation of SO_2

SO_2 oxidation can occur either homogenously or heterogeneously. It can also occur as combination of both homogenous and heterogeneous reactions (Bunce, 1994; Finlayson-Pitts and Pitts, 1986). Homogenously, SO_2 oxidation can occur in gas phase and in aqueous phase whereas heterogeneously, it can occur on the particles surface (Bunce, 1994; Finlayson-Pitts and Pitts, 1986).

Photochemistry and temperature are two important atmospheric parameters that influence the rate of SO_2 oxidation (Finlayson-Pitts and Pitts, 1986). Photochemistry

is significant in respect that some intermediate reactions in SO_2 oxidation process are photochemical and some of the reacting species are also produced by photochemical reactions (Finlayson-Pitts and Pitts, 1986). Temperature also plays a key role, as the rate of SO_2 oxidation in summer is higher than the oxidation process in winter. The rate is also higher in the midday compared to the rate at night (Finlayson-Pitts and Pitts, 1986).

Table 2.2: Mechanisms of Conversion of Sulphur Dioxide to Sulphates (adapted from Wilson, 1978)

Mechanism	Overall Reaction	Factors Affecting Reaction
Direct Photooxidation	$SO_2 \rightarrow H_2SO_4$ (in the presence of light, oxygen and water)	SO_2 concentration; sunlight intensity
Indirect Photooxidation	$SO_2 \rightarrow H_2SO_4$ (In the presence of smog, water, NOx, organic oxidants, hydroxyl radical,…)	SO_2 concentration; organic oxidants, OH, HO_2 and RO radical concentrations
Oxidation in liquid droplets	$SO_2 \rightarrow H_2SO_3$ (in the presence of liquid water) $NH_3 + H_2SO_3 \rightarrow NH_4^+ + SO_4^{2-}$ (in the presence of oxygen)	Ammonia (NH_3) concentration
Homogeneous aqueous phase oxidation*	SO_2 (aq) → sulphate (by dissolved H_2O_2, O_3, OH, SO_5^-, HSO_5^-, SO_4^-, PAN, CH_3COOH, $CH_3C(O)OOH$, HO_2, NO_3, NO_2, N(III), HCHO, Cl_2^-)	pH, ionic strength
Catalyzed oxidation in liquid Droplets	$SO_2 \rightarrow SO_4^{2-}$ (in the presence of oxygen, liquid water and metal ions)	Metal ion or salt concentrations (Vanadium (V), Manganese (Mn), Fe)
Catalyzed oxidation on dry Surfaces	$SO_2 \rightarrow H_2SO_4$ (in the presence of oxygen, liquid water and metal ions)	Carbon particle concentration (surface area)

***Seinfeld and Pandis, 1998; Bunce, 1994**

The oxidation process is also affected by some other atmospheric conditions, such as the humidity of the atmosphere and composition and concentration of the particulate matter in the environment (Bunce, 1994). Summary of the reactions involving SO_2 oxidation processes is given in the table.

SO_2 oxidation in the homogeneous gas phase involves three particular mechanisms. These oxidation mechanisms are (Eggleton and Cox, 1978):

a. Oxidation by the photo-chemically generated reactive intermediates.
b. Oxidation by thermally generated reactive intermediates.
c. Direct photo-oxidation of excited SO_2.

There are many reactive species which are generated by photochemical process, that participate in SO_2 oxidation reaction (Bunce, 1994; Calvert and Stockwell, 1984); for instance the oxidation reaction by atomic oxygen (O), O_3, HO_2, Criegee biradical (RCHOOH) and some organic radicals (Bunce, 1994; Finlayson-Pitts and Pitts, 1986; Eggleton and Cox, 1978). Among all the oxidation reactions, OH oxidation reaction with SO_2 is the most significant (Bunce, 1994; Calvert and Stockwell, 1984). Reason behind this is the slow reactions of other reactive species or their low concentration in most atmospheric conditions (Bunce, 1994; Finlayson-Pitts and Pitts, 1986). Following equation represents the reaction of OH with SO_2.

$$SO_2 + OH\ (+ M) \rightarrow HSO_3 \qquad \textbf{Eq. 2.1}$$

'M' represents another molecule, which can be H_2O, O_2 or N_2 in the air. M serves as the carrier of excess energy out of the reaction. This reaction leads to the SO_2 half-life of around 10 days (Calvert and Stockwell, 1984). The HSO_3 radical formed during the reaction, eventually results in the production of H_2SO_4 aerosols (Calvert

and Stockwell, 1984). The common reaction pathway of HSO_3 conversion into H_2SO_4 is presented by following reactions (Bunce, 1994; Finlayson-Pitts and Pitts, 1986).

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2 \qquad \textbf{Eq. 2.2}$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad \textbf{Eq. 2.3}$$

SO_2 oxidation process is also carried out by thermally generated reactive species. These species are olefins or alkenes, NO_3 and N_2O_5. For the oxidation reaction by alkenes, industrial areas or urban areas are best situated, as this reaction requires presence of high level of alkenes. Without the high amount of alkenes in atmosphere, this reaction would not occur. Whereas in the oxidation reaction by NO_3 and N_2O_5, SO_2 is not oxidized to a measurable extent (Eggleton and Cox, 1978).

Solar radiation causes the production of excited SO_2 (IARC, 1992). In direct photooxidation process, excited SO_2 reacts with O_2 and produce sulphur trioxide (SO_3). After SO_3 production, water vapors react with SO_3 and form H_2SO_4. This is a slow process (Eggleton and Cox, 1978; Kellogg *et al*., 1972) and therefore this reaction is not considered to be an important pathway for the removal of SO_2 from the atmosphere (Kellogg *et al*., 1972).

Homogeneous gas phase reactions lead to the production of H_2SO_4, which subsequently condenses either on to pre-existing particles or forms new particles with partial neutralization by NH_3 (Khoder, 2002). Through reaction with NH_3, H_2SO_4 is converted to $(NH_4)_2SO_4$ and/or NH_4HSO_4 (Khoder, 2002).

Catalytic oxidation of SO_2 occurs at the water body surfaces, on moist surface of soil and plants, in fog and in cloud droplets (Friend, 1973). This oxidation process is given in the following reaction (Friend, 1973):

$$SO_2 + ½\ O_2\ (\text{dissolved}) + H_2O \rightarrow 2H+ + SO_4^{2-} \qquad \textbf{Eq. 2.4}$$

In this reaction, SO_2 dissolves into aqueous solution to form H_2SO_3. After which molecular oxygen oxidize H_2SO_3 into H_2SO_4. The catalysts involved in this process include NH^{4+} and certain transition metal ions (in the form of salt) (Friend, 1973; Kellogg *et al*., 1972).

According to Bunce (1994), SO_2 oxidation in water droplets has been described since 1985. In this oxidation process H_2O_2, NO_2 and O_3 and other compounds are involved (Seinfeld and Pandis, 1998). The mechanisms involved in such reaction are not certain (Bunce, 1994). These processes are also influenced by some parameters, for instance ionic strength, temperature and pH (Seinfeld and Pandis, 1998).

2.3.3.1.2. Wet and Dry Deposition

In wet deposition, two processes are involved:

a. Washout

b. Rainout

Washout includes all the removal processes occurring within the cloud, whereas Rainout is defined as removal involving falling precipitation (Garland, 1978; Kellogg *et al*., 1972). The processes involved in washout for the SO_2 removal are coagulation, diffusional uptake and sulphate particles formation that serve as condensation nuclei (HSDB, 2002). Processes included in the rainout are diffusional uptake of SO_2 and interception of particles by falling raindrops (HSDB, 2002). There are number of factors on which SO_2 removal by wet deposition is dependent. These factors are precipitation intensity, type, frequency, duration, relative amounts of SO_2 to sulphate, and the size distribution of particulate sulphate (HSDB, 2002).

Dry deposition refers to the process in which gases and airborne particles are deposited on water surfaces or land as a consequence of various atmospheric processes (Porter, 2006). SO_2 direct transfer is the major dry removal mechanism for dry removal of atmospheric sulphur (HSDB, 2002). It can take place directly on surfaces, by gravitational pull and also by sulphate particles physical or chemical capture by moist surfaces (HSDB, 2002; Kellogg *et al*., 1978).

The factors on which SO_2 dry deposition depends are moisture content and pH of the soil (HSDB, 2002). Plants can also directly absorbed SO_2 from air (ATSDR, 1998). Wet and dry deposition both has its own significance. On the basis of relative importance, for larger area both are important, whereas when considering areas closer to the vicinity of source, dry deposition is more important (HSDB, 2002).

2.4.Residence Time of SO_2 in the Atmosphere

Atmospheric residence time of SO_2 is determined by the combined rate of all the removal processes (mentioned in the previous sections) and rate of SO_2 emissions. SO_2 life time varies from few days to several weeks. In troposphere due to its reaction with OH and other oxidizing agents, it has a limited lifetime of just a few days. However in lower stratosphere it has several weeks to months (Eisinger and Burrows, 1998). Katz (1977) gives SO_2 residence time in the atmosphere of 2 to 8 days. According to Hidy (1994), the SO_2 residence time in lower atmosphere is about 1 to 3 days and HSDB (2002) ranges it from 1 to 5 days.

2.5. Effects of SO_2

Air pollution is the cause of many short term and long term problems. Pollutants specifically SO_2 in the environment disturb the balance of many chemical reactions

which in turn destabilizes the environmental system and cause harm to human health, wildlife and environment. Therefore the monitoring of various pollutants concentration in air is now considered as an important measure (Ferdous and Kanaroglou, 2007) to assess the air quality. According to World Health Organization (WHO), air pollution causes 3 million deaths per year (Solaiman, 2007).

Exposure to SO_2 causes many health hazards including the throat, nose, eyes and skin irritation (Hansel and Oppenheimer, 2004). SO_2 is also associated with severe effects on respiratory system (Hansell and Oppenheimer, 2004) and SO_2 particulate matter causes visibility reduction and respiratory illness (Ferdous, 2008). A study was performed in New York by Shy *et al*., (1973) on school children of 5 -10 years old. The conclusion of the study showed that, exposure to SO_2 high concentrations may cause reduction in ventilatory function for prolonged time. According to a report by Clean Air Hamiton's (2007), exposure of SO_2 caused the death of 62 individuals out of 714.

SO_2 is a major contributor to the acid rain phenomena. SO_2 and other soluble gases emissions (such as HCL etc.) from volcanoes also cause the formation of acidic clouds and then acid rain. It may have negative impact on the surrounding ecosystems, infrastructure and eventually results in the economic losses (Delmelle *et al*., 2002).

2.6.Satellite Remote Sensing

Remote sensing is the collection and analysis of information or data regarding an area, event or object without any physical contact with that object. The two most common platforms used for remote sensing are satellite and aircrafts (Sandwell, 2009; Sanderson, 2000; Levin, 1999). Typically electromagnetic waves are used to carry the

collected information, although sometimes other means are also used. If man made emitter are used as a source of these electromagnetic waves, then the process is known as ‘active remote sensing’ and if natural waves are used as a source then it is called ‘passive remote sensing’ (Lenoble, 1993).

Satellite remote sensing offers obvious attractions as a means of monitoring, including a synoptic perspective unhindered by the sparse road network that constrains ground-based measurements. Satellite measurements are an important tool for monitoring the large scale distribution of chemical compounds in the atmosphere and their temporal evolution with global coverage.

2.6.1. Satellite observations

In the last few decades, satellite observations of chemical compounds such as SO_2, NO_2, CO, ozone and CH_4 has been very helpful in improving the capability to assess the effects of anthropogenic emissions on air quality (Schoeberl *et al*., 2007; Levelt *et al*., 2006; Richter*et al*., 2004). Such studies include the identification of key source regions, the quantification of sources strengths, and the assessment of changes and trends over past decades. Total Ozone Mapping Spectrometer (TOMS) instrument was used for the first time for extended satellite observation of tropospheric composition (Krueger, 1989), it was designed for the total ozone column observation but tropospheric ozone columns and volcanic SO_2 could also be retrieved. GOME (Burrows *et al*., 1999) was first satellite instrument with a spectral resolution that can observe some other compounds along with ozone. With the passage of time satellite instruments with better spectral resolution, capability to observe more compounds and improved coverage were designed such as SCIAMACHY instrument (Bovensmann *et al*., 1999), OMI instrument (Levelt *et al*., 2006) and GOME-2 (Callies *et al*., 2000).

Satellite observations provide information about the spatial distribution of atmospheric trace gases on both regional and continental scales. In addition, the availability of atmospheric pollutants or trace gases data archives for a whole decade or for a longer period of time provides important information related to the trend of some emission in the world (Fishman *et al*., 2008; Martin, 2008).

The table 2.3 provides the list of satellite instruments whose observations are used in the current study. All instruments in Table are in low-Earth, sun-synchronous polar orbits and in nadir (or limb/nadir) viewing geometry.

Table 2.3: Nadir Viewing Satellite Instruments used for the Remote Sensing of Atmospheric Chemistry (Martin, 2008; IGAC, 2007)

Instrument	SCIAMACHY	OMI	GOME-2
Platform	ENVISAT	AURA	METOP
Measurement period	2002-2012	2004-Present	2006-Present
Equator crossing time	10:00 am	01:45 pm	09:30 am
Nadir resolution(km^2)	60x30	24x13	80x40
Spectral region	UV-Vis-NIR-SWIR	UV-Vis	UV-Vis

2.6.1.1.Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY)

SCIAMACHY (Bovensmann *et al.,* 1999) is a multi-channel grating spectrometer onboard Environmental Satellite (ENVISAT). It was launched by European Space Agency's (ESA) on 1st March, 2002 and was active till August 2002, with a resolution of 60 x 30 km^2. It achieves the global coverage in 6 days (Lee *et al*., 2011). It does

measurements in several geometries during every orbit including nadir, limb and occultation geometries. Occultation geometry includes both solar and lunar geometries. SCIAMACHY instrument measures in the wavelength range from 220 nm to 2400 nm with a spectral resolution of 0.25 nm in UV region, 0.4 nm in visible region and less in Near Infrared (NIR) region. These regions of wavelength includes the detection of various trace gases (e.g., Wittrock *et al*., 2006; Buchwitz *et al*., 2005; Richter *et al*., 2005; Afe *et al*., 2004). For the retrieval of SO_2 column, channel 2 (ranges from 310-405 nm) spectra in nadir geometry is used (Lee *et al*., 2008; Khokhar, 2006).

2.6.1.2.Ozone Monitoring Instrument (OMI)

OMI instrument (Levelt *et al*., 2006) onboard Aura (Earth Observing System (EOS) CH-1) satellite on 15th July, 2004 into a sun-synchronous orbit (Lee *et al*., 2011). It has a spatial resolution of 13 x 24 km^2 at nadir and it provides daily coverage on global basis (Levelt *et al*., 2006). OMI is an imaging spectrometer and it uses two dimensional charge-coupled device (CCD) detectors (Levelt *et al*., 2006). Atmospheric SO_2 is retrieved by the backscattered solar radiation from the atmosphere and surface of Earth (Lee *et al*., 2011). OMI uses UV (270–365 nm) and VIS (366-500 nm) channels for measuring both back-scattered radiance and incoming solar irradiance (Yang *et al*., 2009). OMI instrument provides measurements of ozone profile, total ozone column, cloud characteristics, aerosols, and gases (SO_2, HCHO, NO_2, OCIO and BrO) column amounts etc. (Morales-Rivera, 2011; Levelt *et al*., 2006).

2.6.1.3.Global Ozone Monitoring Experiment – 2 (GOME-2)

The successor of GOME-1 instrument is the GOME-2 (Rix *et al*., 2012; Callies *et al*., 2000) launched on October 2006. GOME-2 instrument has been onboard the Meteorological Operational satellite-A (MetOp-A) with a resolution of 80 x 40 km^2 (Smedt *et al*., 2012). It is a UV-VIS spectrometer which measures in nadir geometry, has the wavelength range from 240 nm to 790 nm with a spectral resolution of 0.26 nm and 0.51 nm. It also directly records a sun spectrum once a day. GOME-2 achieves global coverage in almost 1.5 days (Rix *et al*., 2012). Owing to an optimized movement of the scan mirror, the ground pixel size remains nearly constant over the full scan (Rix *et al*., 2012).

2.6.2. Differential Optical Absorption Spectroscopy (DOAS) Technique

Beer-Lambert law (Khokhar, 2006) describes the absorption of radiation by matter. The absorption of light of the intensity I(λ) at the wavelength λ as it passes through an infinitesimally thin layer of an absorbing matter ds is:

$$dI(\lambda) = I(\lambda).\, c(s).\, \sigma(\lambda,T)ds \qquad \textbf{Eq. 2.5}$$

Here $\sigma(\lambda,T)$ is the absorption cross section of the absorbing species and c(s) is its concentration. Integration of equation (2.5) for a finite light path of length s through the absorbing species leads to the relationship between the incident light intensity $I_0(\lambda)$ and the transmitted light intensity $I(\lambda)$. This is known as the Beer-Lambert law:

$$I(\lambda, \sigma) = I_0(\lambda).\, e^{-\sigma(\lambda,T)\int_0^s c(s')ds'} \qquad \textbf{Eq. 2.6}$$

The law describes intensity reduction of a specific wavelength of light by the characteristic absorption σ of an atom or molecule. In reality instead of just an atom

or molecule several trace gases are present in the atmosphere. Therefore several absorbers having different cross sections simultaneously absorb light. In addition light is scattered through molecules and aerosols, and also the reflection characteristics of ground plays an important role in the measurement of trace gases. Thus the atmospheric absorption of several absorbers can be given by:

$$I(\lambda) = I_0(\lambda).e^{-\sum \sigma_i (\lambda,T)\, S_i (\lambda)}\, g(\lambda) \qquad \textbf{Eq. 2.7}$$

In above equation, g(λ) describes the additional attenuation of intensity by Rayleigh and Mie scattering in the atmosphere and reflection on the ground (Khokhar, 2006). Taking the logarithm gives:

$$\ln(I(\lambda)/ I_0(\lambda)) = -\sum \sigma_i (\lambda, T)\, S_i(\lambda) + \ln(g(\lambda)) \qquad \textbf{Eq. 2.8}$$

The measurement of I and I_0 for a set of wavelengths results in an over determined linear equation system for S_i. However, Eq. (2.8) cannot be solved as the actual shape of g(λ) is not known. This restriction is resolved by applying the DOAS method.

Perner and Platt in 1979 introduced the DOAS method. The DOAS technique principle is based on the fact that all trace gases absorb electromagnetic radiation in some part of the spectrum (Saiz-Lopez *et al*., 2009). If the radiation of the appropriate frequency is transmitted through the atmosphere, the absorption features of each molecule in that spectral region allow the identification and quantification of the gas concentration (Saiz-Lopez *et al*., 2009). The use of light paths which range from hundreds of meters to several kilometers can avoid the problems of local influences or small scale perturbations (Platt 1994; Plane and Saiz-Lopez *et al*., 2006).

2.7.Sulphur dioxide in Pakistan

The data of SO_2 measurements is very unbalanced in terms of time and location. There are few countries in the world which has pollutants concentration data for entire period of time, whereas most of the countries report data for less than a decade. In few countries large numbers of reporting stations are present, while many other nations feature only one (Begun and Eicher, 2007). In most cases, years of pollution concentration data are missing between observations not only on the station level, but also on the city and country level. Even in countries with extensive locational coverage, such as the United States (US), the time series for each monitoring station is highly unbalanced (Begun and Eicher, 2007).

Table 2.4: SO_2 Standards in Pakistan and other Neighboring Countries (µg/m3)

Country	SO_2 (1-hr)	SO_2 (24-hr)	SO_2 (Annual)
Pakistan	-	120	80
India[1]	-	80	50
India[2]	-	80	20
Bangladesh	-	366	78
China: Grade I	150	50	20
China: Grade II	500	150	60
China: Grade III	700	250	100

Source: CAI-Asia Center, 2010 (Collected from various sources).

***1** = NAAQS for Industrial, Residential, Rural and Other Areas.*

***2** = NAAQS for Ecologically Sensitive Areas (notified by Central Government).*

***China: Grade I** = applies to specially protected areas, such as natural conservation areas, scenic spots, and historical sites.*

***China: Grade II** = applies to residential areas, mixed commercial/residential areas, cultural, industrial, and rural areas.*

***China: Grade III** = special industrial areas.*

SO_2 standards for Pakistan are presented in the table 2.4. Pakistan has no continuous monitoring facility for the monitoring of ambient air quality. Punjab EPA and PCSIR have the facility of mobile laboratories. Such laboratories record intermittently in few cities and very occasionally. There are few studies conducted on SO_2 in Pakistan major cities (Colbeck *et al*., 2010; Qadir, 2002) e.g. Lahore (Ashraf *et al*., 2013; Mirza *et al*., 2013; Khwaja and Khan, 2005) Islamabad, Rawalpindi (Khwaja and Khan, 2005), Quetta (Ilyas *et al*., 2008).

However, none of these studies provide data on country level and of a whole decade. This study provides for the first time a database of SO_2 columns across Pakistan for time period 2004-2012, using satellite observations.

Materials and Methods

3.1.Data Retrieval

In order to get a quantitative analysis of SO_2 for Pakistan, SCIAMACHY level-2 data from 2004-2012 was used. Daily data of GOME-2 and OMI instrument has been used to evaluate high SO_2 columns as consequence of volcanic activity. The data was downloaded from Tropospheric Emission Monitoring Internet Service (TEMIS) European Research Project (http://temis.nl/). Database has been generated for the already mentioned time period.

As already mentioned in the previous sections, SCIAMACHY (Bovensmann *et al.*, 1999) is a multi-channel grating spectrometer. SCIAMACHY was launched on ENVISAT by ESA on 1st March, 2002. It is functioning since August 2002, with a resolution of 60 x 30 km^2. OMI instrument was launched on EOS on 15th July, 2004. It has a spatial resolution of 13 x 24 km^2 at nadir and it provides daily coverage on global basis (Levelt *et al*., 2006). GOME-2 instrument was launched on October 2006. It has been onboard the MetOp-A, with a resolution of 80 x 40 km^2 (Smedt *et al*., 2012). DOAS technique is used for simultaneous retrieval of various atmospheric constituents (Bovensmann *et al.*, 1999; Platt and Perner, 1979). The column densities measured from such systems can be used for the global mapping of various atmospheric trace gases including SO_2 (Khokhar *et al*., 2005), NO_2 (e.g. Richter *et al*., 2006; Beirle *et al*., 2004), O_3 and HCHO (e.g. De Smedt *et al*, 2012; Marbach *et al*., 2009; De Smedt *et al*., 2008) etc.

3.1.1. Slant Column Densities into Vertical Column Densities

Satellite instruments (in this case SCIAMACHY), measures earth shine spectra. Comparison of such spectrum with the sunlight spectrum provides the information about the concentration and distribution of SO_2 and other trace gases. Measurements by DOAS method yields slant column density (SCD) (Ma *et al*., 2013; Khokhar, 2006). As SCDs are the trace gas concentration integrated along the light path, it depends on the light path length and also on the geometry of observation. Therefore, SCD are needed to be converted into vertical column density (VCD), which is defined as the trace gas concentration integrated vertically from ground to top of the atmosphere (Khokhar, 2006). VCD depends on neither of these factors on which SCD depends and hence can be used for the comparison of different measurements (Ma *et al*., 2013). In the Figure 3.1 SCD (along the red line) and VCD (along the blue line) paths can be differentiated.

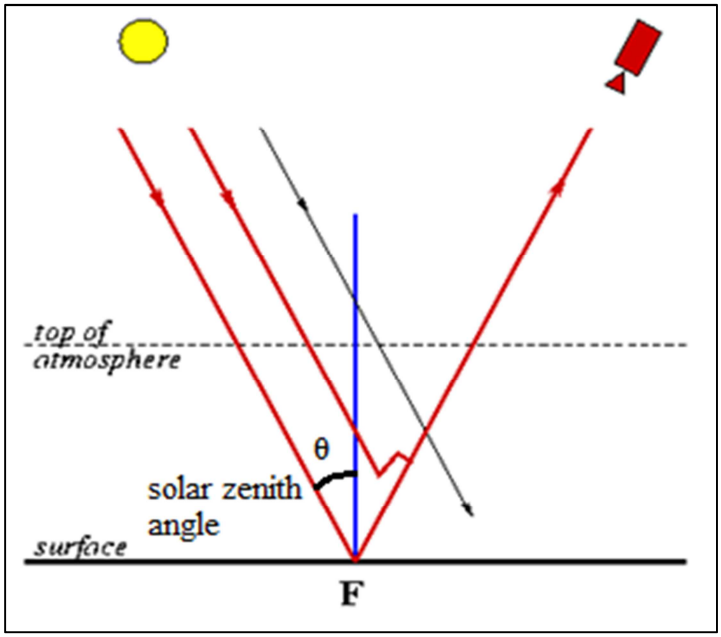


Figure 3.1: Schematic representation of the SCD and VCD (Adopted from http://sacs.aeronomie.be/info/scdvcd.php)

SCDs are converted into VCDs by using the air mass factor (AMF) (Ma *et al*., 2013). AMF is the ratio of SCD to the VCD, and is calculated as:

$$AMF = \frac{SCD}{VCD} \quad \textbf{Eq. 3.1}$$

Thus for the calculation of VCD from SCD, AMF is required.

$$VCD = \frac{SCD}{AMF} \quad \textbf{Eq. 3.2}$$

AMF value depends on various factors such as albedo effect, length of the light path etc. Different approaches are used to calculate the AMF. In this research study the AMF value of '1' has been used for all the scenarios, as on average the SO_2 VCD actually equals the retrieved SCD (Khokhar *et al*., 2008). However this simplification is useful for the purpose of trend analysis, for the individual cases (depending on cloud cover and surface albedo) large deviations from an AMF of about unity can occur (Khokhar *et al*., 2008).

SCIAMACHY observations with back ground correction, cloud fraction less than 10%, Solar Zenith Angle (SZA) less than 88 degree and fit error (Chi sq < 5e-5) are used only. Monthly mean SO_2 data gridded to a latitude-longitude grid of 0.25 by 0.25 degrees is used. For each grid cell the average of all measurement crossing that grid cell (using forward and backward scans) is computed, using all orbit files for the given month.

3.2.Spatial Mapping

ArcGIS 10.1 has been used for the visualization of monthly data in order to investigate spatial distribution of SO_2 column densities over Pakistan. Data was in

'hdf' format. SO_2 columns over Pakistan were extracted from SO_2 monthly data, using ArcGIS tools. For the analysis of temporal trends, time series analysis was carried out. OxMetrics5 software was used for the Regression analysis. Figure 3.2 depicts the flow chart of various steps, software and methods involved to get the results presented in this study.

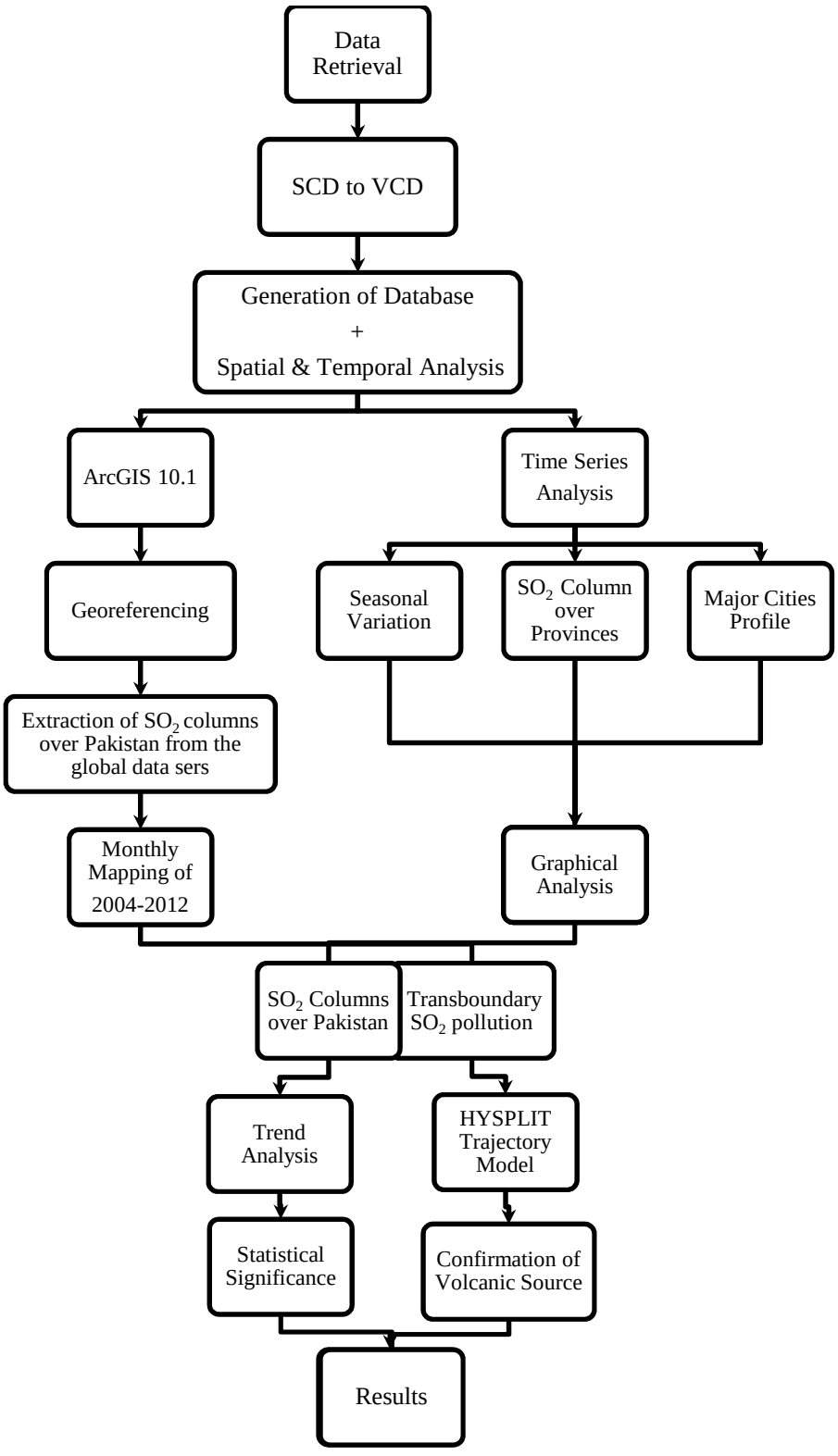


Figure 3.2: Schematic diagram for steps of the research methodology.

Results and Discussion

4.1.Database Generation and Spatial Distribution

Pakistan's climate is mainly arid to semi-arid with exception of slopes of Hindukush and Karakorum mountain ranges, where average rain fall ranges from 700 to 2000 millimeter (mm) per year. Pakistan receives monsoon rainfall in summer while in winter due to westerlies wind system.

According to recent reports from German watch Global Climate Risk Index 2013 (Harmeling and Eckstein, 2012), Pakistan is among the top ten countries most affected by extreme weather events from 1991 to 2010. As Pakistan is a resource constrain country with extra stress on its economy due to geopolitical activities in the region (e.g. war against terror, extremism and Afghan refugee etc.). Hence, it is strongly needed to implement efficient but cost effective strategies in order to cope with impacts of climate change. This study is part of such activities conducted at the School of Civil and Environmental Engineering - Institute of Environmental Sciences and Engineering (SCEE-IESE), National university of Sciences and Technology (NUST) to understand the evolution of atmospheric composition over Pakistan during last decade by utilizing satellite observations.

Generation of database for the years 2004-2012 was one of the main objectives of this research work. Database generation was attained by three ways:

- Record of ascii data
- Creation of monthly maps
- Spatial and temporal analysis

The atmospheric SO_2 column densities were plotted in the form of monthly maps exhibiting the spatial distribution of SO_2 column densities in Dobson units (DU: 1 DU=2.69 e+16 molecules per sq. cm) over Pakistan. An example of monthly SO_2 column densities for the year 2009 is presented in the proceeding figures. Black diamonds are representing the main cities of Pakistan.

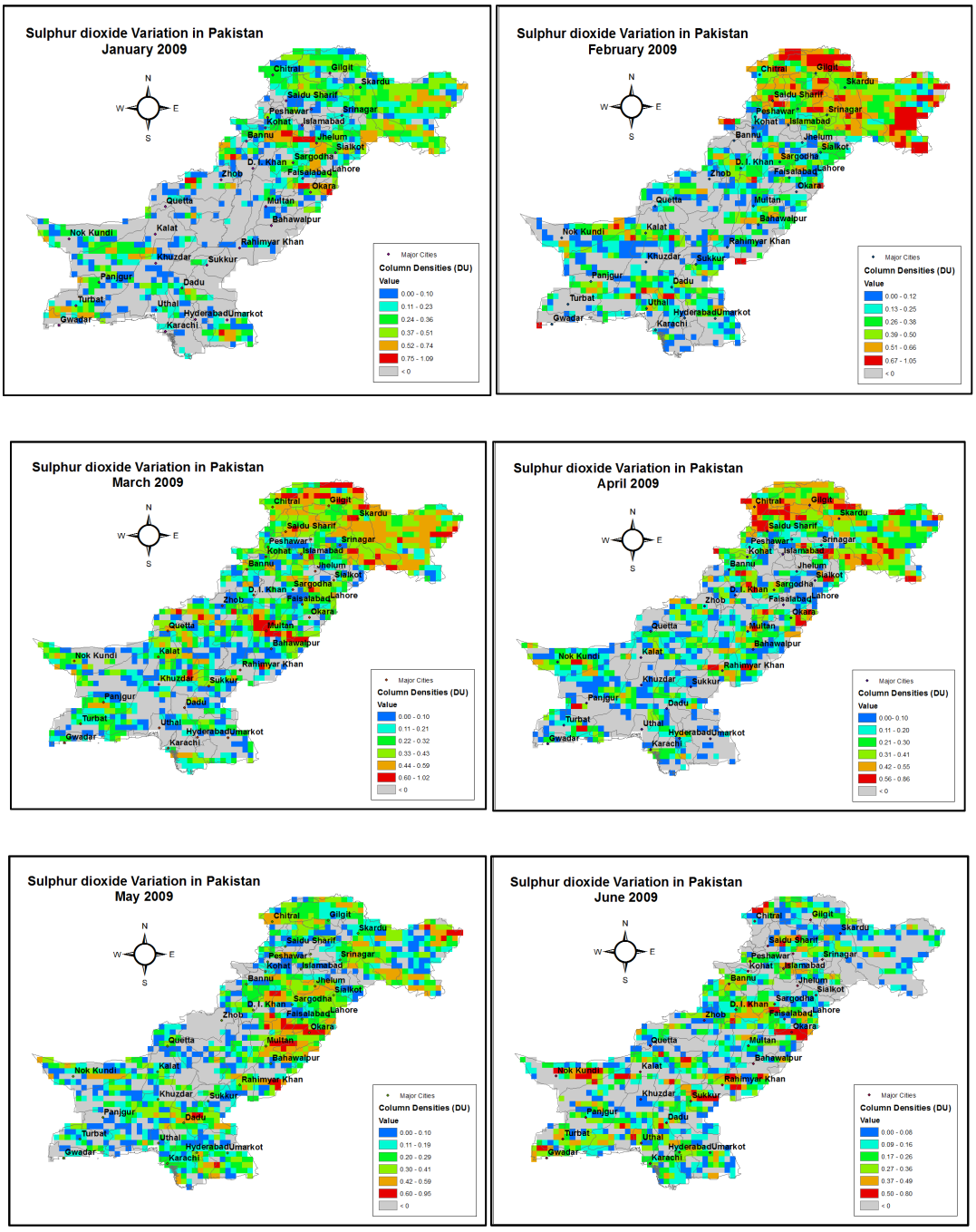


Figure 4.1: Series of maps from January 2009 to June 2009

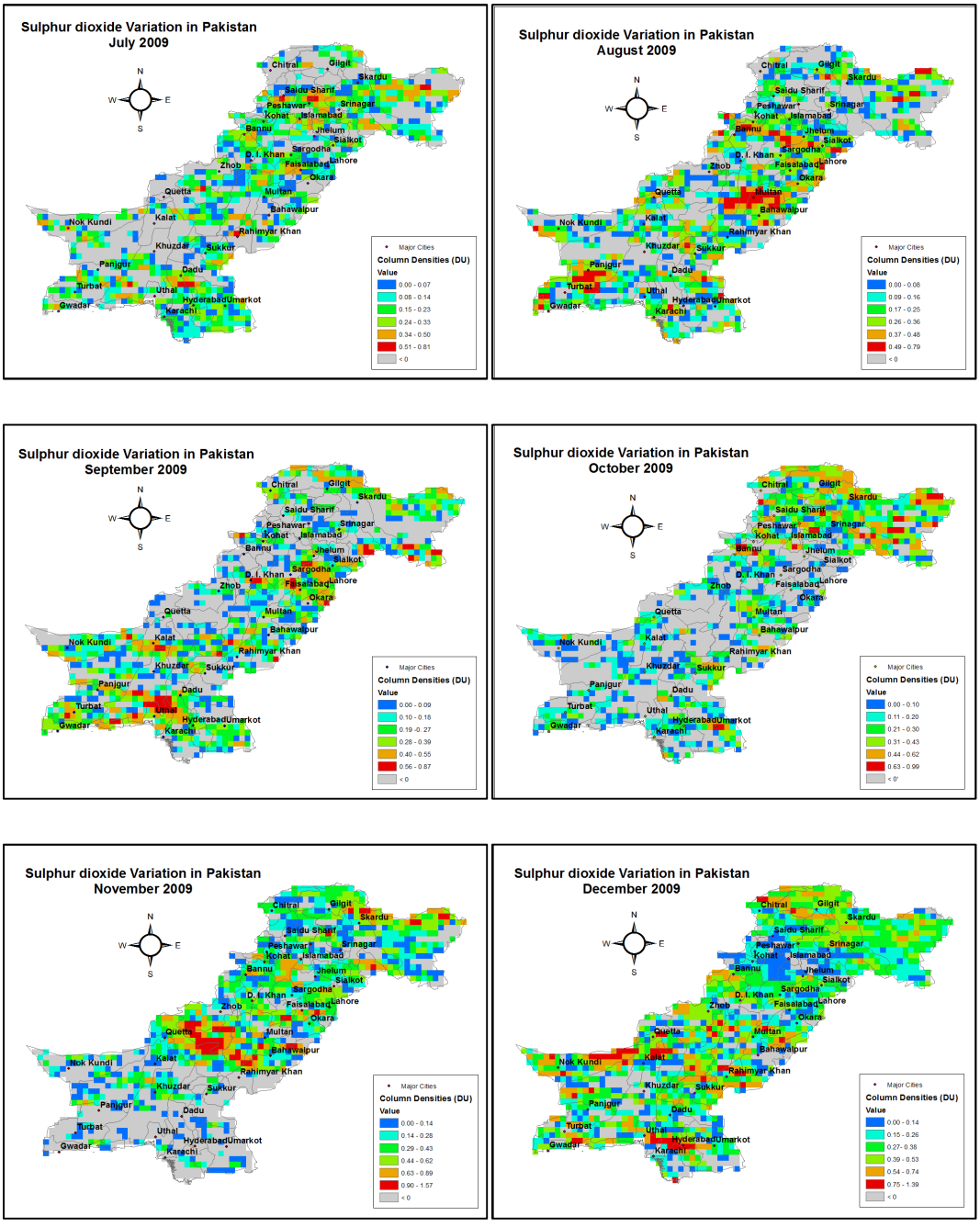


Figure 4.2: Series of maps from July 2009 to December 2009

SO_2 is mostly higher in Northern areas, in few major cities of Punjab and Khyber Pakhtunkhwa and in the western part of Baluchistan provinces. It is comparatively low in Sindh and Southern Baluchistan. Spatial distribution of SO_2 is discussed in further details in the following sections.

4.1.1. Northern Areas of Pakistan

Throughout these years, northern areas of Pakistan showed an interesting behavior. In this study the major cities including Skardu, Gligit, Chitral, and Srinagar are considered under the category of Northern areas of Pakistan. This region of country is comparatively the most cleanest of all the regions. Therefore it should have the least SO_2 pollution. However, spatial maps of Pakistan exhibited higher SO_2 during winter months over this region during some years.

This region of the country has cold winters, and snow covered areas. Therefore one of the reasons for such high SO_2 column could be mainly due to the albedo effect of underlying snow during winter months (Khokhar *et al*., 2006), which enhances the instrument sensitivity. In these areas about 70-80% of household uses biomass fuel for the purpose of cooking and heating (Health & Environment, 2003) that also increases SO_2 amount in atmosphere. This usage increases in winter for heating purpose which may have slightly elevated the SO_2 column densities. Moreover, the non-availability of compressed natural gas (CNG) and usage of diesel and other petroleum fuel for motor vehicles also increases the SO_2 emissions. Another reason could be the trans-boundary SO_2 pollution from the neighboring regions.

4.1.2. Atmospheric SO_2 over Major Polluted Cities in Pakistan

Frequent high SO_2 columns are observed over many cities of Pakistan such as Quetta, D.I Khan, Peshawar, Bahawalpur, Faisalabad, Lahore, Sargodha, Skardu, Chitral, Karachi and Gilgit, as presented in Table 4.1. Fig. 4.3 shows the SO_2 average column densities over these cities during the time period of 2004-2011. The highlighted values in the Table 4.1 are the highest SO_2 columns observed from major cities during the years 2004 to 2011. A consistent behavior of steadily increasing SO_2

is observed for all cities till the year 2010 (with one exception of Skardu with maximum SO_2 column densities during year 2011) then the subsequent decrease in 2011 for all cities of Pakistan. Anomalous increased SO_2 emissions during 2010 are also observed, reason behind which is not clear yet. Moreover, this is the average annual behavior of SO_2 pollution and does not reflect the seasonal cycle over these cities. Analysis about seasonal variation in SO_2 column densities over major regions of Pakistan is presented in next section.

Table 4.1: SO_2 Averaged Columns in DU over the years 2004-2011

Cities	2004	2005	2006	2007	2008	2009	2010	2011
Bahawalpur	0.104	0.173	0.187	0.166	0.298	0.062	**0.367**	0.282
Chitral	0.129	0.146	0.177	0.186	0.185	0.238	**0.426**	0.151
D.I. Khan	0.149	0.147	0.16	0.203	0.298	0.193	**0.371**	0.261
Lahore	0.147	0.131	0.153	0.148	0.242	0.226	**0.355**	0.291
Faisalabad	0.161	0.171	0.18	0.228	0.241	0.233	**0.399**	0.151
Gilgit	0.186	0.191	0.285	0.203	0.212	0.244	**0.434**	0.405
Peshawar	0.111	0.149	0.116	0.195	0.171	0.215	**0.479**	0.145
Quetta	0.132	0.124	0.107	0.105	0.065	0.124	**0.318**	0.191
Sargodha	0.156	0.163	0.197	0.163	0.254	0.172	**0.436**	0.419
Skardu	0.16	0.239	0.295	0.205	0.168	0.23	0.393	**0.452**
Karachi	0.039	0.106	0.155	0.108	0.129	0.288	**0.541**	0.386

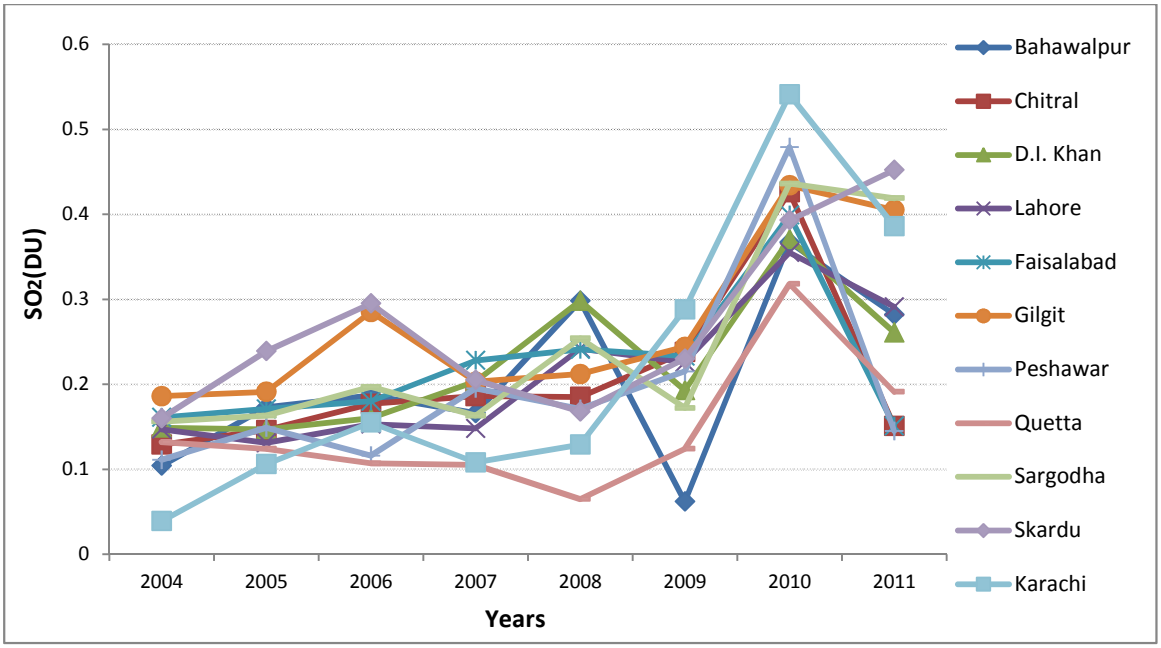


Figure 4.3: Annual Variation of atmospheric SO_2 in major polluted cities of Pakistan

4.1.3. Seasonal Variation

The OH radical is very important especially in the tropospheric chemistry of sulphur species (Finlayson-Pitts and Pitts, 2000). The oxidation process of almost all sulphur compounds (including reduced) are initiated by OH (Hassan *et al*., 2013; Finlayson-Pitts and Pitts, 2000 and Stockwell, 1994). In general low SO_2 amount is observed in summer (high OH productivity) compared to the high amount in winter (less OH productivity). SO_2 conversion into sulphate particles and H_2SO_4 involve its reaction with O_3, H_2O_2, OH and HO_2. Therefore, OH is the key parameter which determines the lifetime and seasonal cycle in the SO_2 emissions in addition to some other minor and local phenomena. Seasonal cycle may be slightly dependent on both anthropogenic (coal and biofuel burning) and natural (monsoon, snow) activities on regional basis. Such as northern part of Pakistan is covered with snow in winter and people burn biomass fuel for heating and cooking purposes which causes high SO_2

column in air (Health and Environment, 2003). As already mentioned the underlying snow causes the high surface albedo and enhances the instrument sensitivity (Khokhar, 2006)

SO_2 distribution varied for each year throughout the time period of 2004 - 2012. Despite this mostly the highest SO_2 column densities were observed in the months of January, February, March, November and December (winter months). Whereas from April to September SO_2 was generally lower than the rest of the months for that year. Fig. 4.4 exhibits the monthly average atmospheric SO_2 variation from 2004 – 2012 over the four provinces and northern areas of Pakistan. Northern part of the country was also affected from the Nabro volcano in June 2011. Satellite data showed high plumes of SO_2 over these regions. In June, 2011 the SO_2 values reached to a very high level of 1.5 DU. In order to avoid error in average seasonal variation, data of June 2011 for all regions has been excluded from this analysis.

Over Pakistan SO_2 seasonal cycle is highly affected by monsoon season (generally prevails from July to September). In these months SO_2 amount is low compared to the post monsoon months (September to late October). This is due to the washout effect of rain that causes lower SO_2 amount in rainy season. In general, Fig. 4.4 exhibits similar seasonal cycle of SO_2 column densities over all provinces of Pakistan. Although they differ in various aspects such as having different traffic density, population density and industrial activities. However, the monsoon season and high OH concentrations during summer months are dominant factors in determining the seasonality in SO_2 column densities over Pakistan.

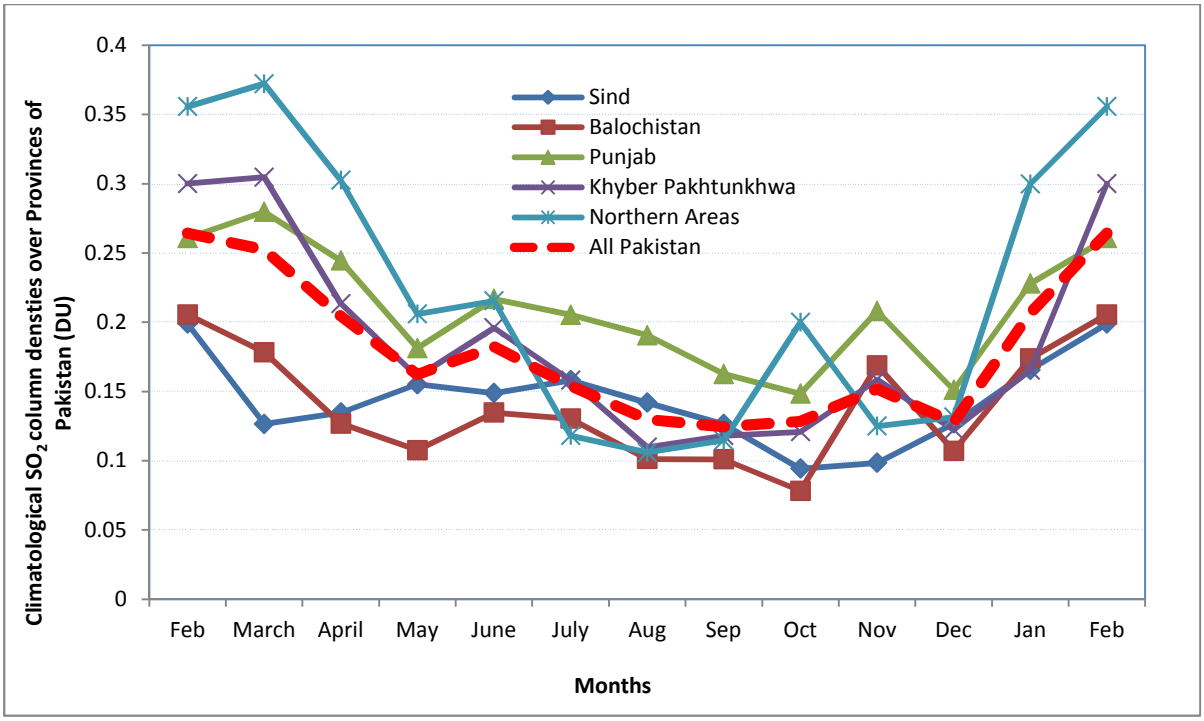


Figure 4.4: SO_2 seasonal observed over different regions of Pakistan devised from the SCIAMACHY observations over the period of 2004-2011.

4.1.4. Temporal Analysis

SCIAMACHY data from 2004 – 2012 was used for the spatial and temporal data analysis. Temporal record of SO_2 over Pakistan was analyzed by plotting average SO_2 variation from 2004 till 2012, presented in Fig. 4.5. This figure exhibits the monthly variation of SO_2 over Pakistan. The mean SO_2 columns were calculated by taking mean of overall cities of Pakistan. The bars show the spatial variation for each month for all years. In June, 2011 unexpected high SO_2 columns were observed. It was investigated and found that these exceptional high column densities were due to trans-boundary SO_2 pollution reached over Pakistan. These SO_2 enriched air massed was originated from Nabro volcano and reached to Pakistan within few days (further details are given in the next sections). Other peaks in the time series were also investigated and they were caused by various volcanic activities in neighboring

regions such as in October, 2007 (Jabal al-Tair, Yemen), November 2008 (Dalaffilla, Ethiopia) and January-March, 2010 (Tor Zawar, Pakistan). In spite of volcanic eruption, SO_2 column amount over Pakistan has increased since 2004. To determine this increase in SO_2 column over Pakistan, trend analysis was performed by fitting linear fits. The blue line represents the trend of SO_2 over the years including the SO_2 from volcanic eruptions, whereas the red line represents temporal trend in SO_2 column densities over Pakistan excluding the volcanic events. Analysis showed 1.25 (125%) increase in SO_2 with volcanic eruptions and 0.71 times (71%) increase in SO_2 without volcanic eruptions from 2004 to 2012. As Pakistan is a developing country, the cause of this increase in SO_2 can be associated with various factors including increase in motor vehicles, new industries, use of low quality and sulfur containing fuel, burning of low grade coal and biomass for domestic and industrial purposes, and burning of solid waste.

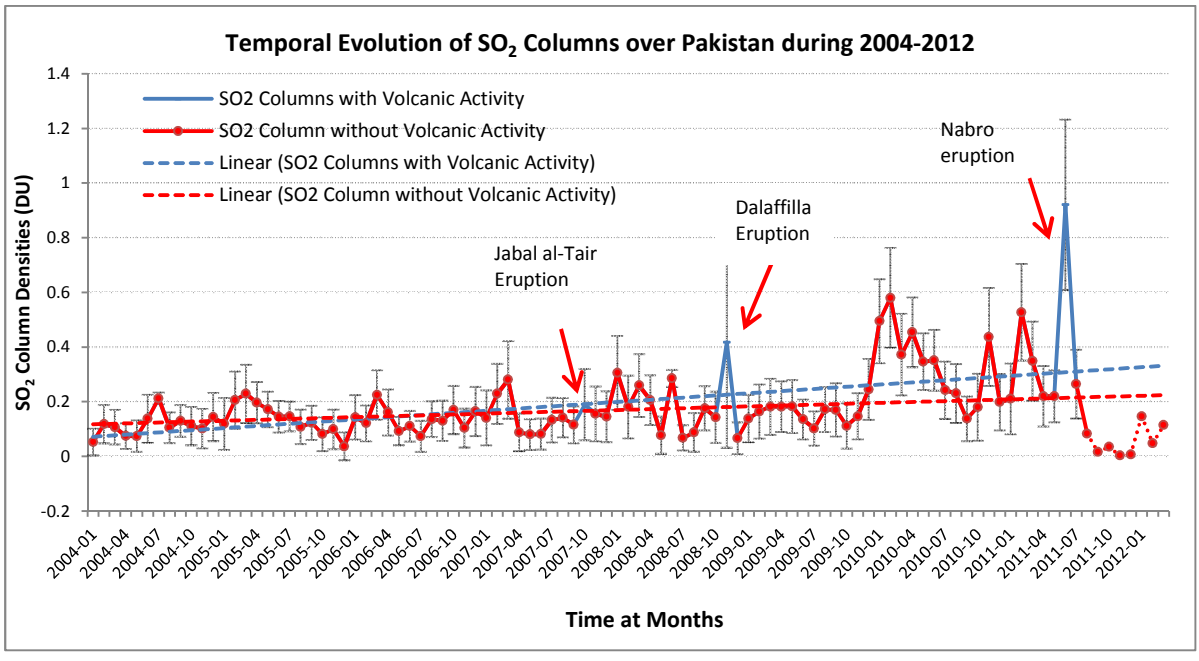


Figure 4.5: Temporal record of SO_2 column densities observed by SCIAMACHY over Pakistan during the time period of 2004-2012.

4.2.Regression Analysis

Autocorrelation Function (ACF) was applied on SO_2 column density data for the time period 2004-2012 in order to test the statistical significance of observed seasonal cycled temporal increase. The analysis showed lead-lag relation for the month of January (2004) identifying the dependence of January on previous months. However, the correlation dies out with progressive years as shown in the Fig. 4.6. This indicates the non-existence of dependence of other months on each other.

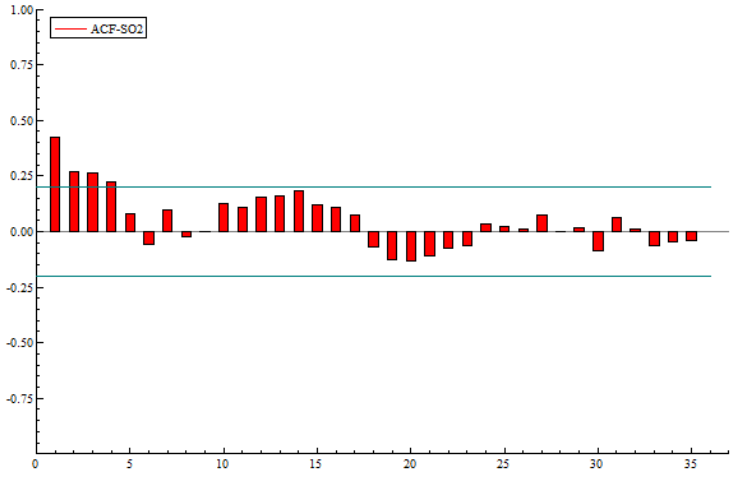


Figure 4.6: ACF plot for SO_2

For the identified lag, regression analysis was carried out. Null hypothesis for this was, 'SO_2 is not dependent on previous months'. The probability of null hypothesis was calculated less than 5% as shown in the Table 4.2.

Table 4.2: Regression Analysis

	Coefficient	**Standard Error**	**t-value**	**t-prob**
$SO_{2\text{-}1}$	0.427027	0.09189	4.65	0.0000
Constant	0.104023	0.02058	5.50	0.0000

Hence null hypothesis was rejected, showing the $SO_{2\text{-}1}$ (month of January for the year 2004) dependence on its previous months. Equation below displays the same relation. It also confirms that the calculated trend in SO_2 column densities is statistically significant.

$$SO_2 = 0.104 + 0.427\ SO_{2\text{-}1}$$

4.3.Source Apportionment

The four major air pollution sources that should be immediately addressed by Pakistan are: vehicular emissions, industrial emissions, emissions from solid waste burning and natural dust or trans-boundary pollution (Pakistan Clean Air Program, 2008). According to Pakistan Economic Survey 2011-2012 (MoF, 2012), number of motor vehicle on road has increased from 4.5 million in 2000 to 10.97 million in 2011. Euro II emissions standards on vehicular emissions has been implemented from July 1, 2012 in Pakistan. Pakistan is facing problems in achieving the standards and the level of sulphur in diesel is more than 500 ppm (CAI-Asia, 2008).

These statistics indicate the huge growth in transport sector of Pakistan, which is directly related to air quality degradation. Fig. 4.7 shows a slight correlation between number of vehicles and SO_2 column densities. The growth in motor vehicles on roads of Pakistan and annual SO_2 column densities averaged over main cities of Pakistan did not reflect the similar trend. As there is gradual increase in SO_2 emissions until year 2010 followed by a decrease in SO_2 column densities during the year 2011(contrary to trends in motor vehicles).

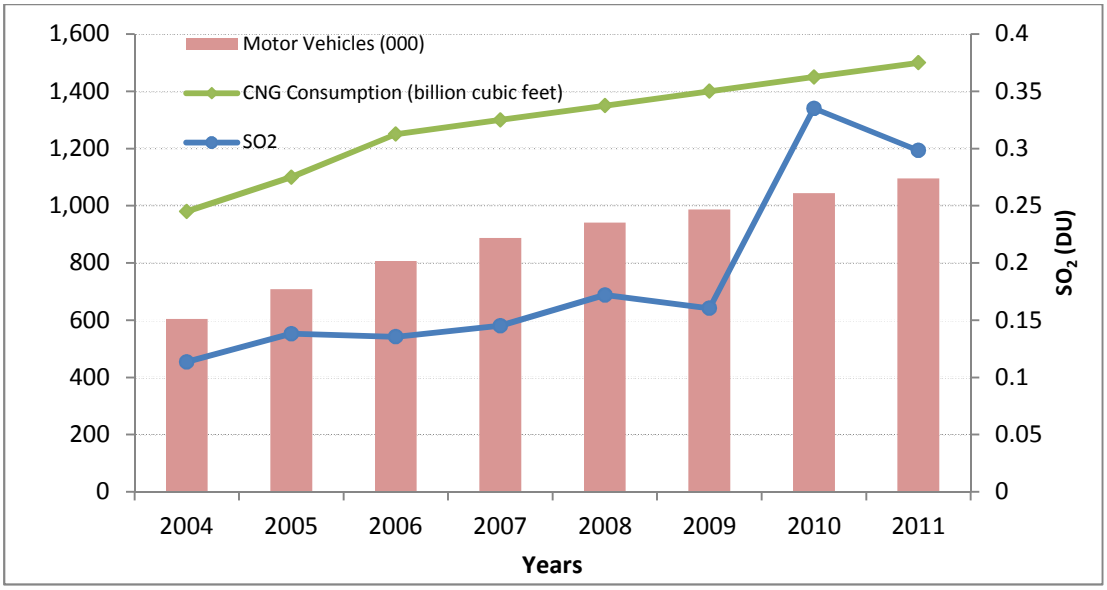


Figure 4.7: Compressed natural gas (CNG) consumption in billion cubic feet (y-axis, source: Ministry of Communication (NTRC), yearly mean SO_2 column densities in DU (on secondary y-axis) over Pakistan and total no of motor vehicles (y-axis source: Ministry of Transport and Communication (NTRC) in Pakistan during the time period of 2004-2011).

Similar discrepancy was indicated by calculating correlation between total no of motor vehicles and observed SO_2 columns with R^2=50 presented in Fig. 4.8 (green triangles). The correlation factor is not very high and R^2 indicates that the increase in the number of vehicles cannot fully explain the observed trend in the SO_2 columns. It was further investigated by taking into account the type of fuel consumed by the transport sector of Pakistan during the selected time period. Table 4.3 presents the statistics of share of fuel used by the transport sector of Pakistan, growth in compressed natural gas (CNG) as fuel and number of vehicles converted from conventional fuel to CNG fuel and SO_2 column densities during 2004-2011.

According to the International Association of Natural Gas Vehicles (IANGV) there are approximately 4 million Natural Gas Vehicles (NGVs) in use worldwide, of which 1.6 million are in Argentina and 1.5 million in Pakistan.

Table 4.3: Share of Oil and CNG Consumption by Transport Sector of Pakistan

Year	Share of Oil/petroleum products Consumption by Transport sector (%)[1]	Share of CNG Consumption by Transport sector (million cubic feet)[1]	No of vehicle converted to CNG (million) [2]	Total No of vehicle (million) [3]	Yearly mean SO_2 Column Densities Over Pakistan (DU)
2004	63.07	1.5	0.45	2.9635	0.114
2005	61.50	2.1	0.66	3.1464	0.138
2006	55.77	3.2	1.05	3.8688	0.136
2007	47.38	4.6	1.30	4.5429	0.145
2008	51.90	5.6	1.40	5.1263	0.172
2009	49.34	7.0	1.70	5.4564	0.161
2010	46.32	7.8	2.00	5.5012	0.335
2011	47.08	9.3	2.74	5.5586	0.298

1*: Source: Hydrocarbon Development Institute of Pakistan (CNG and oil consumption by Transport sector)*

2*: Source: OGRA, Ministry of Petroleum & Natural Resources (CNG fitted vehicles)*

3*: Source: National Transport Research Centre (total number of vehicles)*

Additionally, due to its affordability (CNG is cheaper than gasoline and diesel in Pakistan) during the last few years, a large number of motor vehicles has been shifted from conventional fuel (petroleum and diesel) to CNG. Therefore, the use of CNG as fuel has resulted in less emissions of SO_2 and other pollutant from motor vehicles

(Chelani and Devotta, 2007; Goyal, 2003). The change in fuel type is probably the main cause behind the rather poor correlation between SO_2 columns and total number of motor vehicles in Pakistan. It is further supported by the correlations calculated among SO_2 columns and CNG consumption by transport sector in Pakistan (R^2=70, dark brown circles in Fig. 4.8) and number of motor vehicles converted to CNG fuel from conventional fuel (R^2=70, blue diamonds in Fig. 4.8). This explains the fact that SO_2 emissions decreased in year 2011. Although, the number of motor vehicles in Pakistan were still increasing in year 2011 but on the other side the number of vehicles converted to CNG from conventional fuel was maximum during year 2011. Similar trend can be seen in Table 4.3 that share of petroleum products consumed by transport sector was also decreased during year 2011.

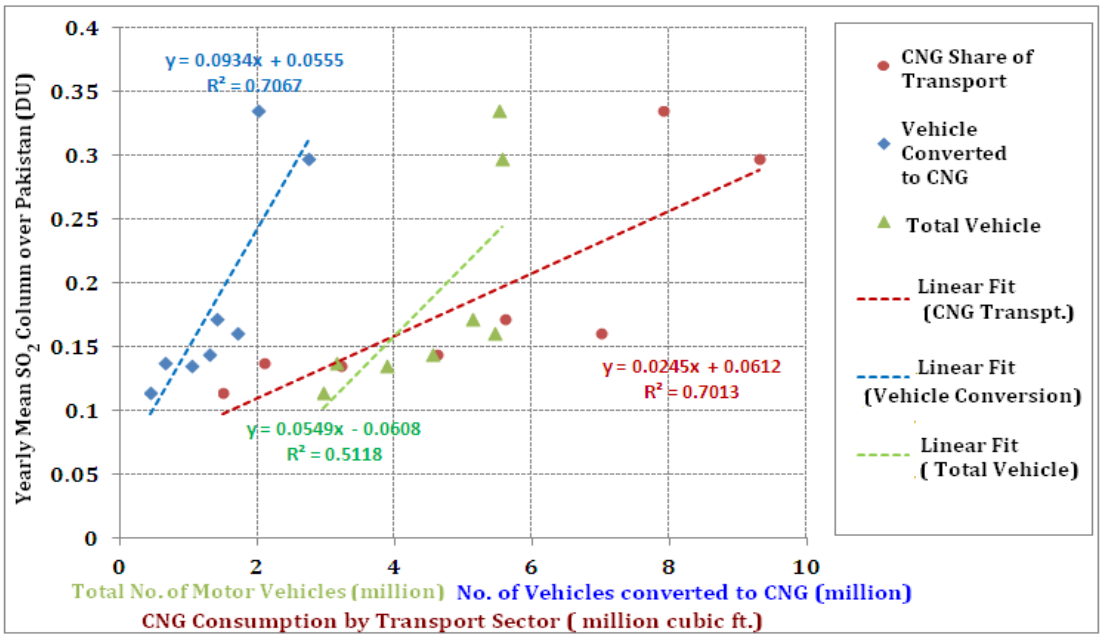


Figure 4.8: Correlation plot among SO_2 column densities, total number of motor vehicles in Pakistan during the year 2004-2011 (green triangles), no. of vehicles converted to CNG from conventional fuel (blue diamonds) and amount of CNG fuel consumed by transport sector in Pakistan. Dashed lines are showing the linear fits for respective datasets.

4.4.Trans-boundary SO_2 Pollution over Pakistan

Temporal record of SO_2 column densities over Pakistan was prepared by plotting average SO_2 variation from 2004 till 2012. As already mentioned the analysis showed various high SO_2 events during this time period. Further investigation related these high SO_2 events with the world volcanic activities. In Pakistan, only a historical fissure vent volcano named 'Tor Zawar' was active in the context of minor seismic activity but no emission has been reported (Global Volcanism Program (GVP), 2013).

Table 4.4: Volcanoes in Pakistan and its Neighboring Countries

Volcanoes in Pakistan and its neighboring countries				
Volcano Name	**Volcano Type**	**Last Known Eruption**	**Volcano Status**	**Location**
Tor Zawar	Fissure vents	2010	Historical	Pakistan
Barren Island	Stratovolcano	2011	Historical	India
Dacht-i-navar group	Lava domes	Unknown	Holocene	Afghanistan
Vakak group	Volcanic feild	Unknown	Holocene	Afghanistan
Sabalan	Stratovolcano	Unknown	Holocene	Iran
Damavand	Stratovolcano	5350 BC ± 200 years	Uranium-Series	Iran
Qal'eh hasan ali	Maars	Unknown	Holocene	Iran
Bazman	Stratovolcano	Unknown	Fumarolic	Iran
Taftan	Stratovolcano	Unknown	Holocene	Iran

Source: Global Volcanism Program, 2013.

Table 4.5: Volcanoes in the African Region

Volcanoes in the African region along their last known eruptions since 2003 AD				
Volcano Name	**Region**	**Year**	**Location**	
			Long.	**Lat.**
Nyiragongo	DR Congo, Central Africa	2012	29.25	-1.52
Nyamuragira	DR Congo, Central Africa	2012	29.20	-1.41
Erta Ale	Ethiopia, Northeastern Africa	2012	40.67	13.60
Nabro	Eritrea, Northeast Africa	2011	41.70	13.37
OI Doinyo Lengai	Tanzania, Eastern Africa	2010	35.91	-2.76
Manda Hararo	Ethiopia, Northeastern Africa	2009	40.82	12.17
Dalaffilla	Ethiopia, Northeastern Africa	2008	40.55	13.79
Jabal al Tair	Yemen, Red Sea	2008	41.83	15.55
Karthala	Comoros, Western Indian Ocean	2007	43.38	-11.75
Dabbahu	Ethiopia, Northeastern Africa	2005	40.48	12.60

Source: Global Volcanism Program, 2013.

It is located in Ziarat region, west-central Pakistan at Latitude 30.479 and longitude 67.492. The most recent eruption took place in January 2010. It was a minor volcanic outburst with no previous post-tertiary volcanic activity. There are few other volcanoes located in the countries adjacent to Pakistan boundaries as presented in Table 4.4. According to GVP, currently in Iran and Afghanistan there are 11 Holocene volcanoes. In India one historical Stratovolcano is present. But none of these volcanoes (other than discussed in the present study) is associated with a significant volcanic activity in the past decade which has caused SO_2 emission.

Pakistan is situated in region which is affected by volcanic eruption occurring in African region due to the movement of both inter-continental and regional air masses

mainly due to western trade winds. African region encompasses few volcanoes which are active since 1800 AD. The table 4.5 presents the details of volcanoes in the region along with their last known eruptions since 2003 AD.

In the following section the volcanic eruption which has significantly contributed in SO_2 column densities over Pakistan are discussed.

4.4.1. Nabro Volcano, Eritrea, Northeast Africa

In the month of June, 2011 unexpected and abnormally high SO_2 column was observed over Pakistan. It was most significant over the northern and central part of the country. In Fig. 4.9 and Fig. 4.10 high SO_2 could be clearly observed.

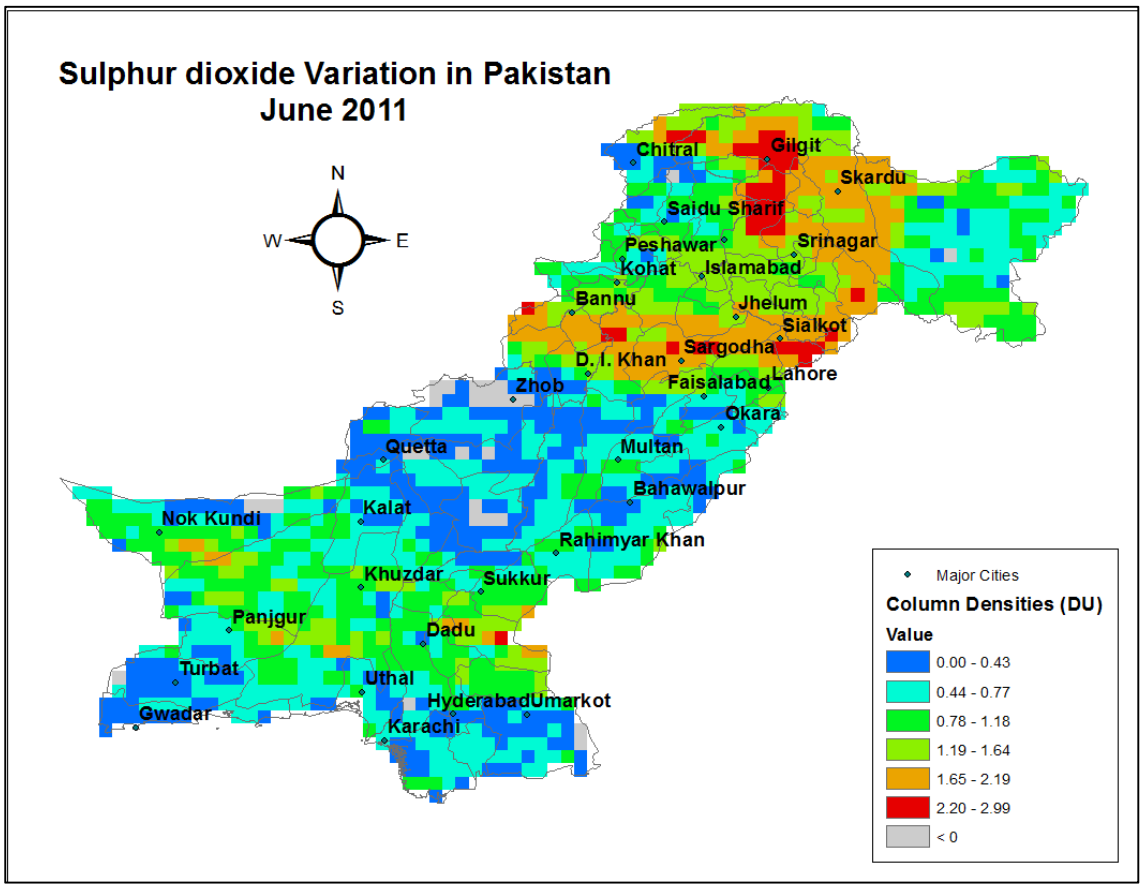


Figure 4.9: Atmospheric SO_2 Columns in DU averaged during June 2011 over Pakistan

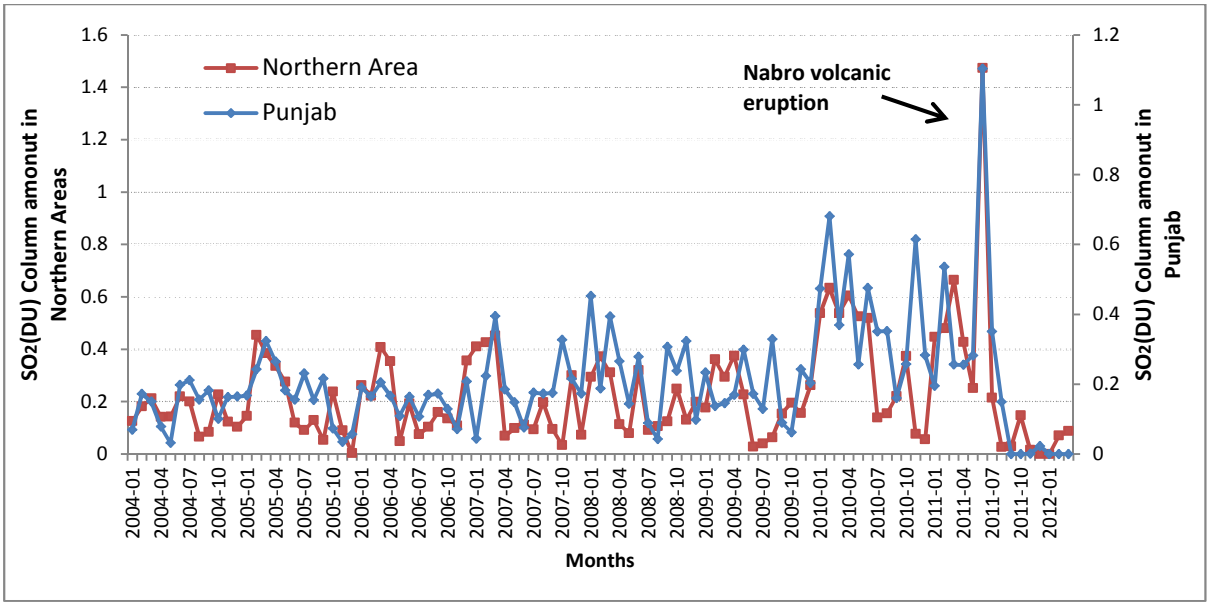
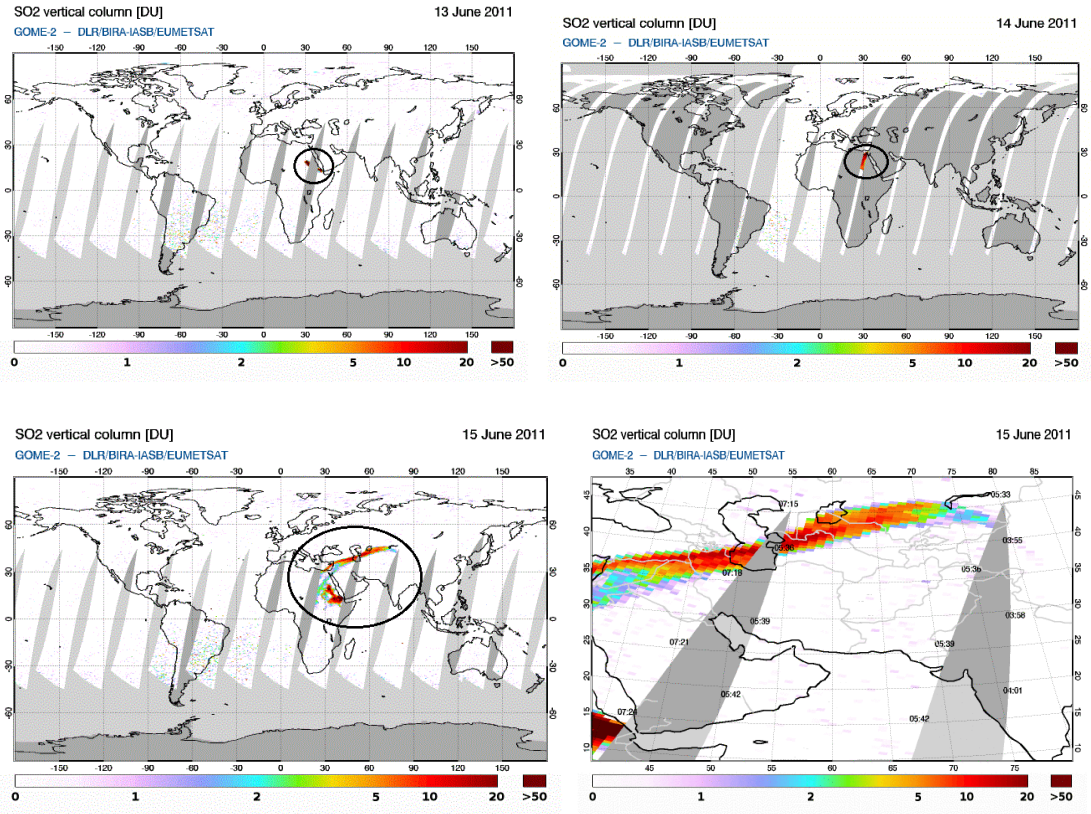


Figure 4.10: Atmospheric SO_2 Columns averaged in Northern area and Punjab during June 2011 over Pakistan

The reason behind such high SO_2 column was investigated and found to be the Nabro volcanic eruption. Nabro is a stratovolcano volcano, located in the isolated northeast African nation of Eritrea. The eruption started explosively after a series of earthquakes on the evening of 12 June, 2011 (GPV, 2013) and continued till the mid of July, 2011. The eruption produced the highest SO_2 column ever retrieved from space (Fee *et al.*, 2011) and also contributed largely to the SO_2 column densities over Pakistan as seen in the Fig. 4.10 (the labeled peak). It was very explosive and SO_2 rich volcanic eruption (Carn *et al.*, 2012; Fee *et al.*, 2011), caused stratospheric aerosol load (e.g. Bourassa *et al.*, 2012) and huge amount of SO_2 amounts were detected over surrounding regions, for instance Clarisse *et al.*, 2012 reported total SO_2 mass of 1.5 Tg retrieved from daily Infrared Atmospheric Sounding Interferometer (IASI) observations, Carn *et al.*, 2012 estimated 1-2 Tg SO_2 based on OMI and Atmospheric Infrared Sounder (AIRS) data.

Nabro volcano eruption had sent ash drifting over much of East Africa and the Middle East. The proceeding Fig. 4.11 shows GOME-2 images of SO_2 plumes over east Africa and its travelling towards Middle East and South Asia, specifically over Pakistan. In the maps, SO_2 plumes propagation from 13 to 17 June can be clearly observed. On 13 June (day after volcanic eruption) plume is just confined to the northeast region of Africa. On 14th June, SO_2 plumes have covered 1650 km (distance traveled was calculated as 1° of longitude is equals to about 110 km) distance towards Northeast and it is drifted towards the Middle East region. On 15th June, plume has traveled around 5390 km towards East and reached closer to Pakistan. On 16 and 17 June, SO_2 plume has split into two narrow plumes and spread towards the North and Central Pakistan. As mentioned earlier the eruption continued till the mid of July, but significant SO_2 amount as its consequence was observed for almost two weeks over



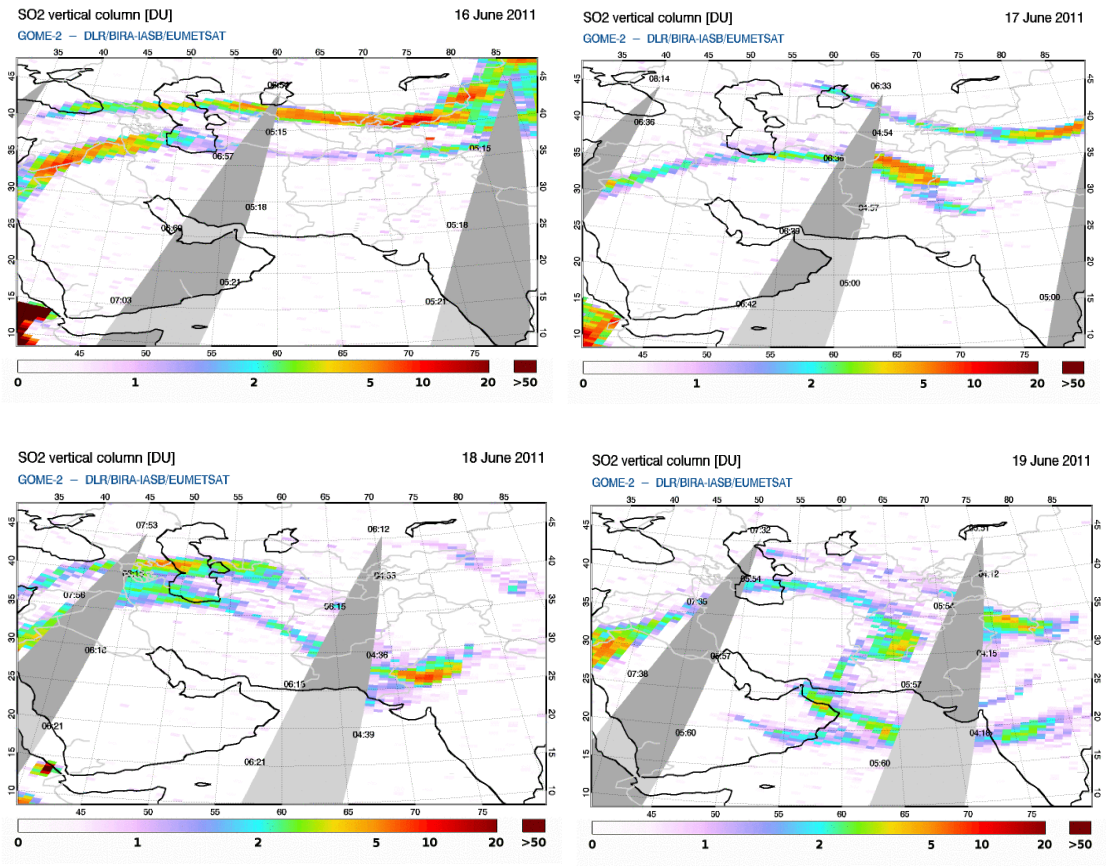


Figure 4.11: Series of maps from 13th June to 19th June, 2011 exhibiting SO_2 plumes propagating over Pakistan

Pakistan as can be clearly identified in the block of maps (global and zoomed over South Asian region) in Fig. 4.11.

4.4.2. Dalaffilla, Ethiopia, Northeastern Africa

Dalaffilla volcano is a stratovolcano, located in Ethiopia (Erta Ale range). It has a twin volcano, known as Alu volcano. Both Dalaffilla and Alu volcanoes are part of the same volcanic system. In November 2008, major effusive eruption started in the Dalaffilla volcano. According to GVP, the eruption started on November 3rd, 2008 and ended in December, 2008.

In Fig. 4.12, GOME-2 satellite observation shows the day after eruption to the day SO_2 plume has reached Pakistan. On November 4, SO_2 plume is near the eruption site.

It has traveled approximately 1650 km towards North. With proceeding days the plume propagated more towards east. On 5th November, ashes have covered approximately a distance of 3300 km towards east and entered Pakistan. On 5th and 6th November, SO_2 plumes have spread over Pakistan, mainly affecting the areas of Baluchistan and Punjab provinces. Fig. 4.13 exhibits the monthly mean map of SO_2 for the month of November, 2008. It clearly shows the elevated amount of SO_2 for the region of Baluchistan and Punjab province.

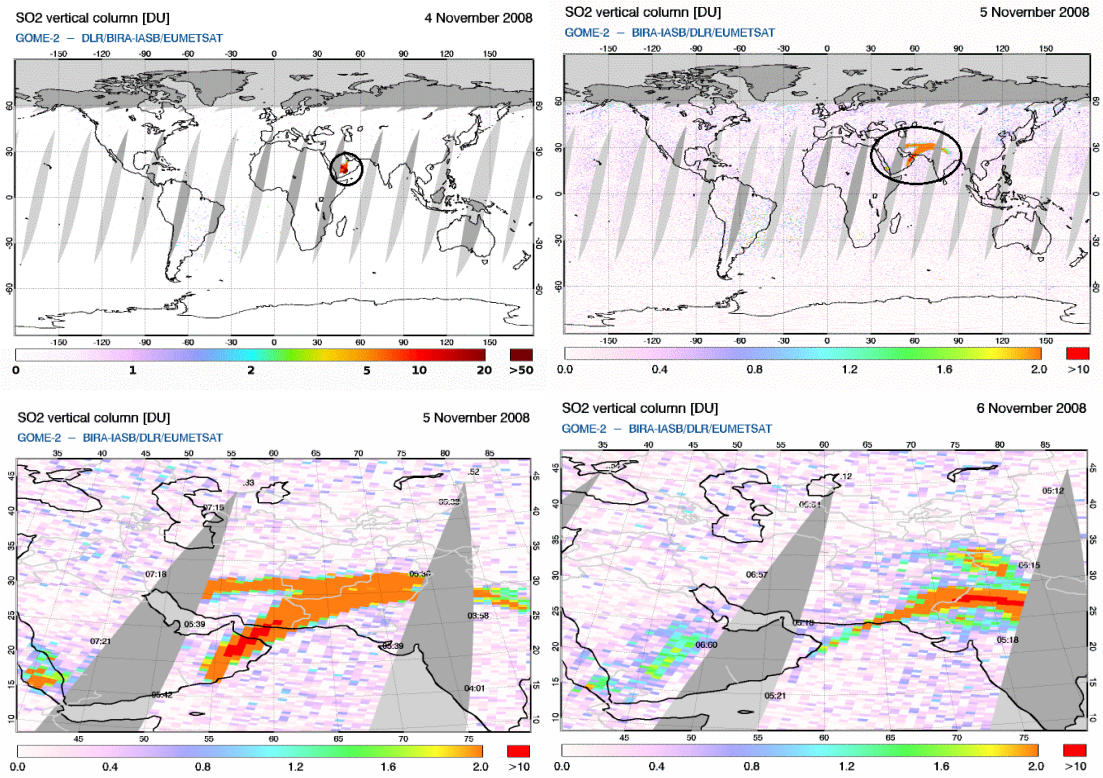


Figure 4.12: Series of maps from 4th November to 6 November, 2008 showing SO_2 plumes after volcanic eruption

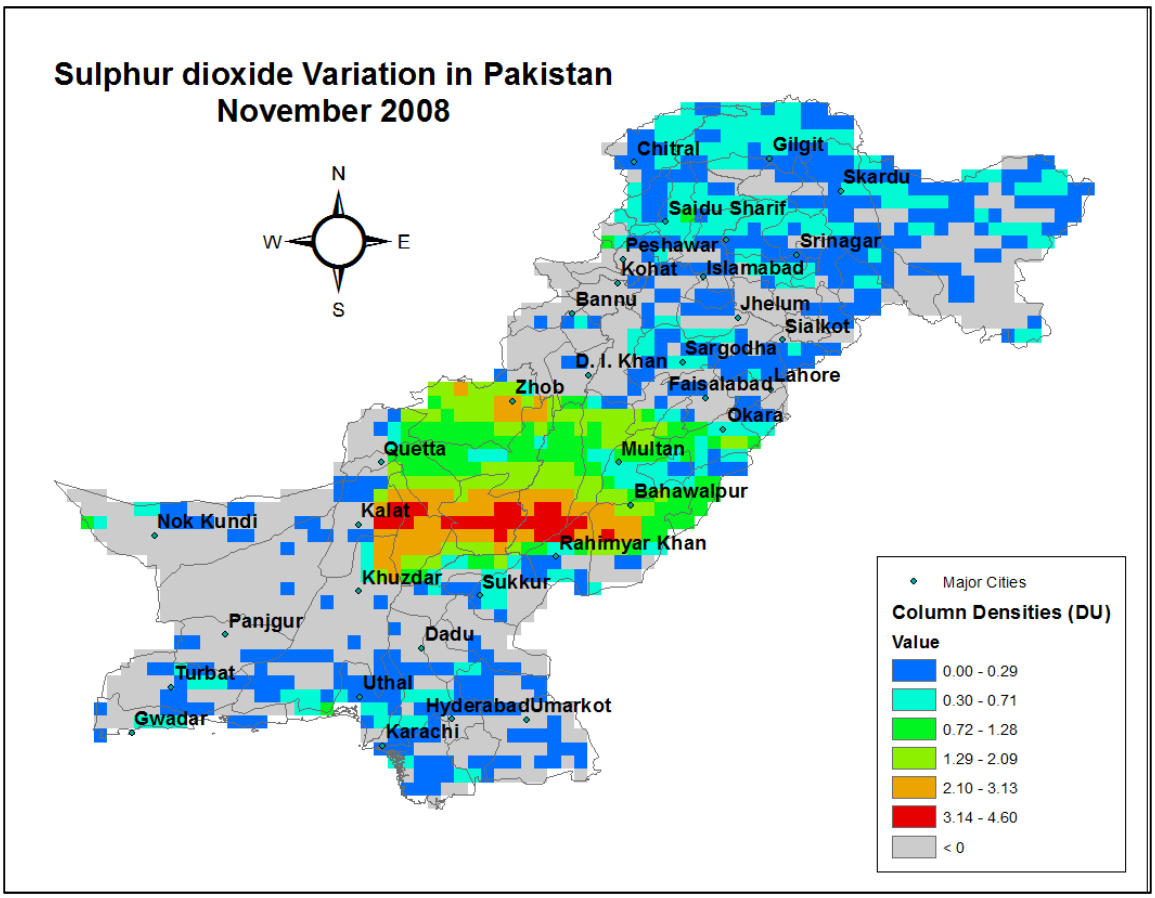


Figure 4.13: SO_2 plume over Pakistan

4.4.3. Jabal al Tair, Red Sea

Jabal al Tair is a stratovolcano, located in Red sea. According to GVP's monthly report, the eruption started on the afternoon of September 30th, 2007 and continued till early December, 2007. The eruption caused SO_2 large plumes, directed lava flows into the ocean and also caused the death of soldiers on the island.

Fig. 4.14 presents the OMI images for SO_2 plumes after the eruption. On 1st October, plume of SO_2 is visible near the vent of the volcano. During the following days SO_2 plume has traveled a distance of 1430 km and 1210 km towards east on 2nd and 3rd October respectively. Finally, SO_2 plume had reached over Pakistan on 4th October, 2007 affecting mainly the areas of Baluchistan and Punjab provinces. Fig.

4.15 shows the monthly mean SO_2 column density over Pakistan. The effect of volcanic eruption in the form of elevated SO_2 columns can be clearly seen in this map and also in time series presented in Figure 4.5. The effect is not as significant compared to the Nabro and Dalaffilla volcano, but it is still identifiable.

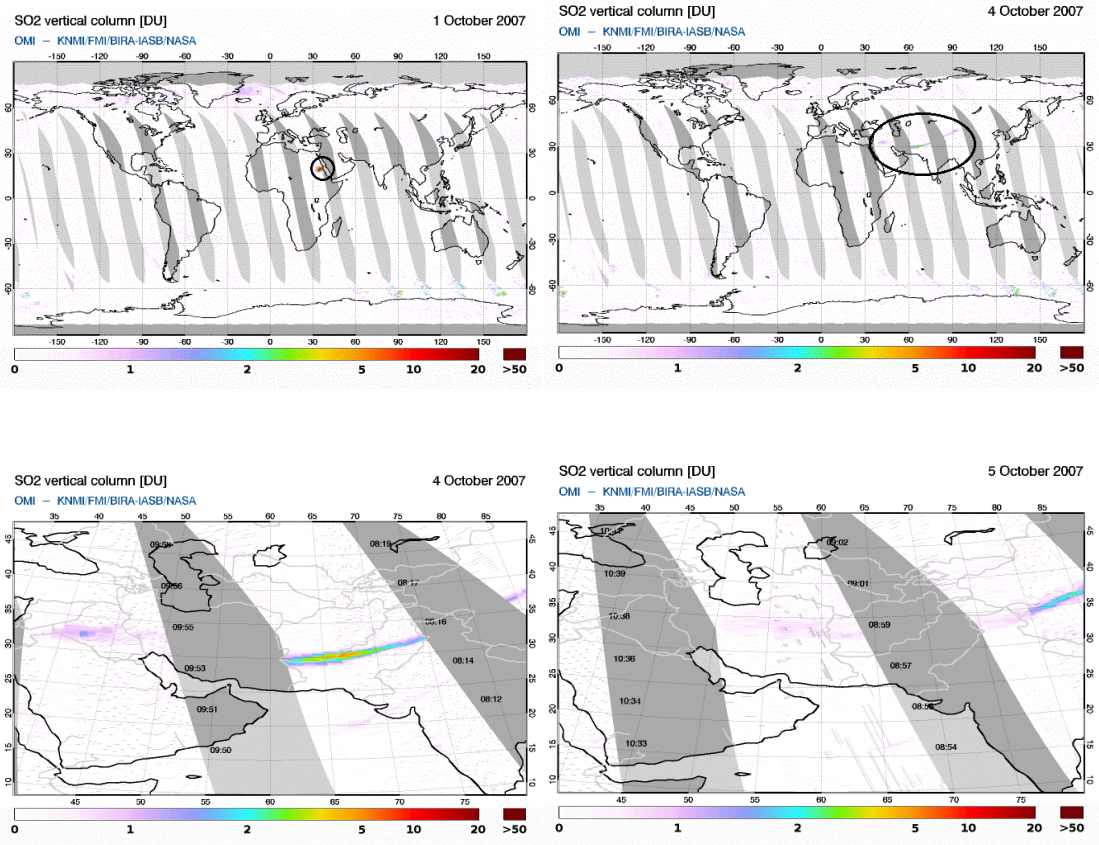


Figure 4.14: Series of maps from 1st October to 5th October, 2007 showing SO_2 plumes after volcanic eruption

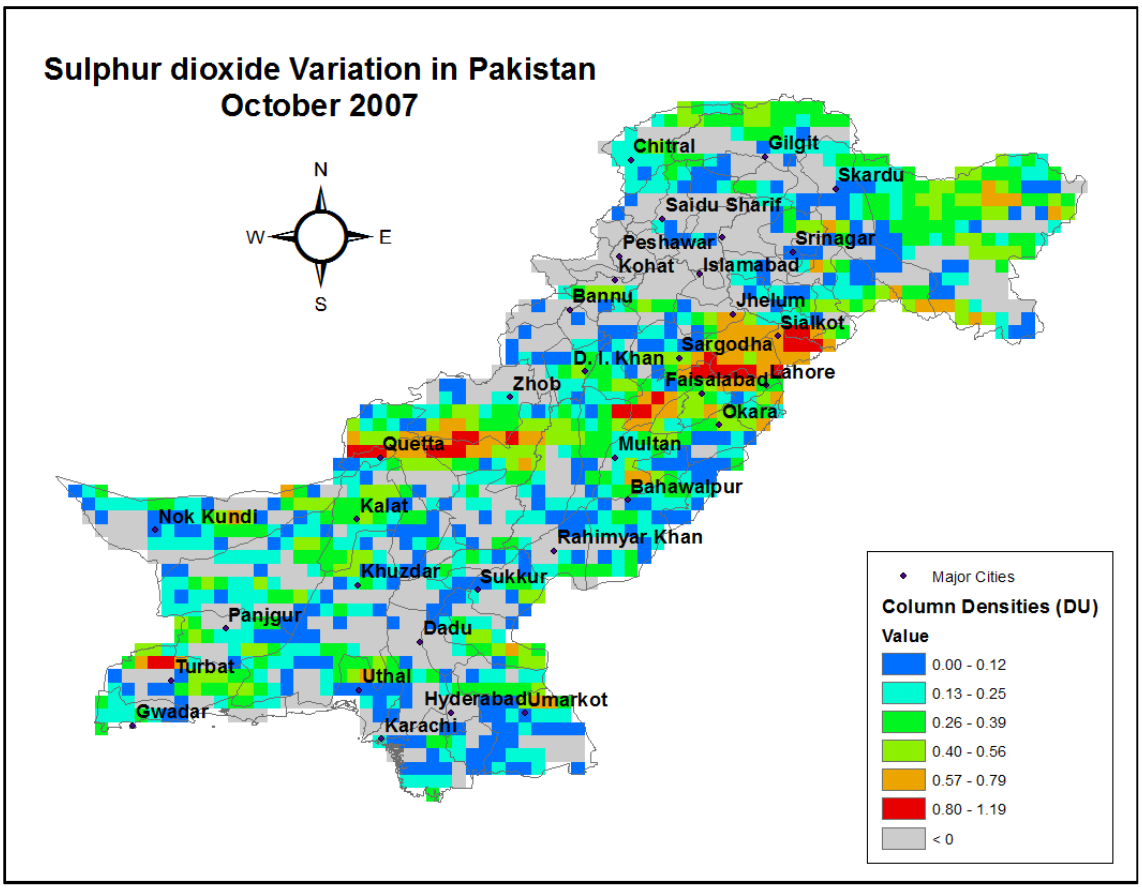


Figure 4.15: SO_2 plume over Pakistan

4.5.Back Trajectory Analysis

In order to verify the trans-boundary SO_2 plume over Pakistan resulted from different volcanic eruptions, analysis of backward trajectory of air masses (back trajectories - Robinson *et al*., 2011) was performed to locate the origin of air masses enriched with SO_2 concentration. Maps consisting of backward trajectory were created for each volcanic event, for the identification of SO_2 source and its pathway through which it entered Pakistan boundaries. Hybrid Single Particle Lagrangian Integrated Trajectory Model-4 (HYSPLIT4) (Draxler *et al*., 2013; Draxler and Rolph, 2013; Rolph, 2013) is an online available analysis. HYSPLIT model used for this purpose is developed by National Oceanic and Atmospheric Administration (NOAA) / Air Resources Laboratory (ARL). A qualitative spatial analysis was done with back

trajectory data. The meteorological data used for the analysis was taken from Global Data Assimilation System (GDAS1) of National Centers for Environmental Prediction (NCEP).

Meteorological variables such as potential temperature, rain fall, mixed layer depth, and relative humidity were computed by HYSPLIT. There is a chance of 15% to 30% of error (of the travel distance) associated with the trajectories generated by HYSPLIT model (Draxler and Hess, 2004; Stohl, 1998). The error increases with the increasing distance (Sogacheva *et al*., 2007). For the current paper, the back trajectory accuracy is sufficient enough to confirm the pathway of air masses with the pathway and altitude of SO_2 plume reaching Pakistan.

4.5.1. Nabro Volcano, Eritrea, Northeast Africa

During 16 and 17 June, 2011 the HYPSLIT indicates that SO_2 plumes were hitting Pakistan boundaries over Northern areas and Baluchistan. The back trajectory of air masses and altitude of SO_2 plume reaching Pakistan is shown in the Fig. 4.16 and 4.17. According to GVP, initially the plume from volcanic eruption rose to the height of 9100-13700 m (30,000-45,000 ft) above sea level (a.s.l.) later on; the plume was detected at the altitude of 6100-10700 m (20,000-35,000 ft) a.s.l. The trajectory was calculated 120 hours backwards in time and at height 400, 5000 and 11000 meters above ground level (mAGL) on 16 June. On 17 June trajectory was calculated 144 hours backwards on 400, 7000 and 9000 mAGL arrival height. The back trajectory shows that the air mass originated over Bay of Bengal, crossed the volcanic eruption site and carried the SO_2 plume to Pakistan. Air masses carrying SO_2 pollution hit Pakistan over two different locations. The average altitude of these air masses calculated with HYSPLIT is around 9000 mAGL. The reason of calculating air

masses on low and high height levels is to identify the SO_2 plume altitude and any possible contribution from the local sources.

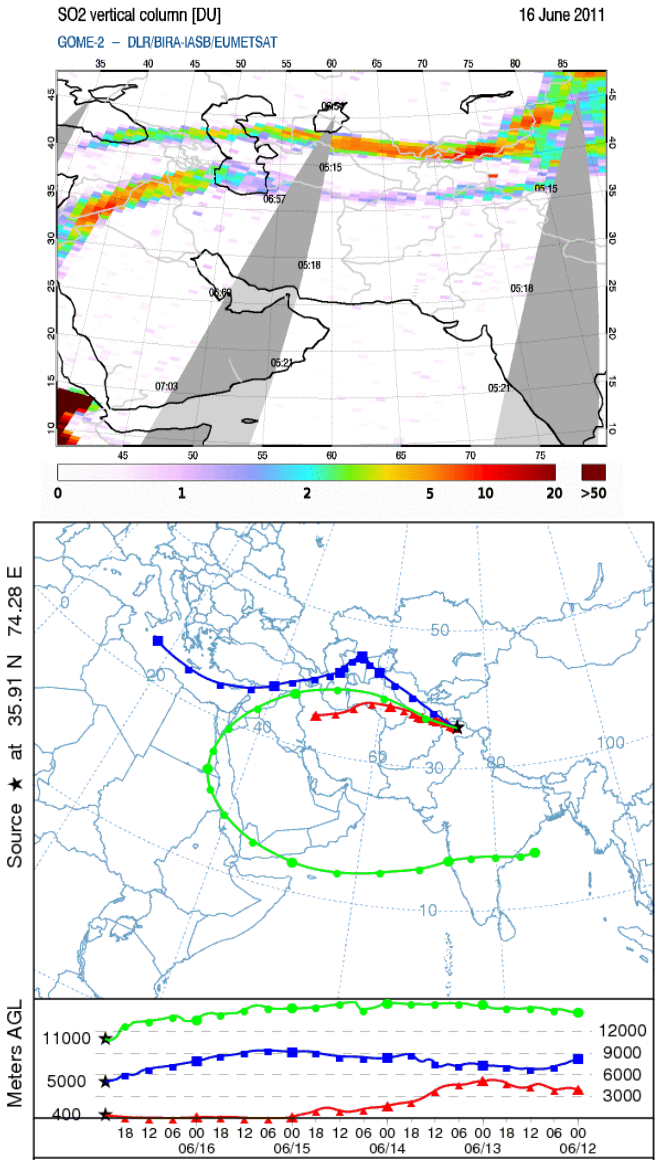


Figure 4.16: Backward trajectory for 16 June, 2011.

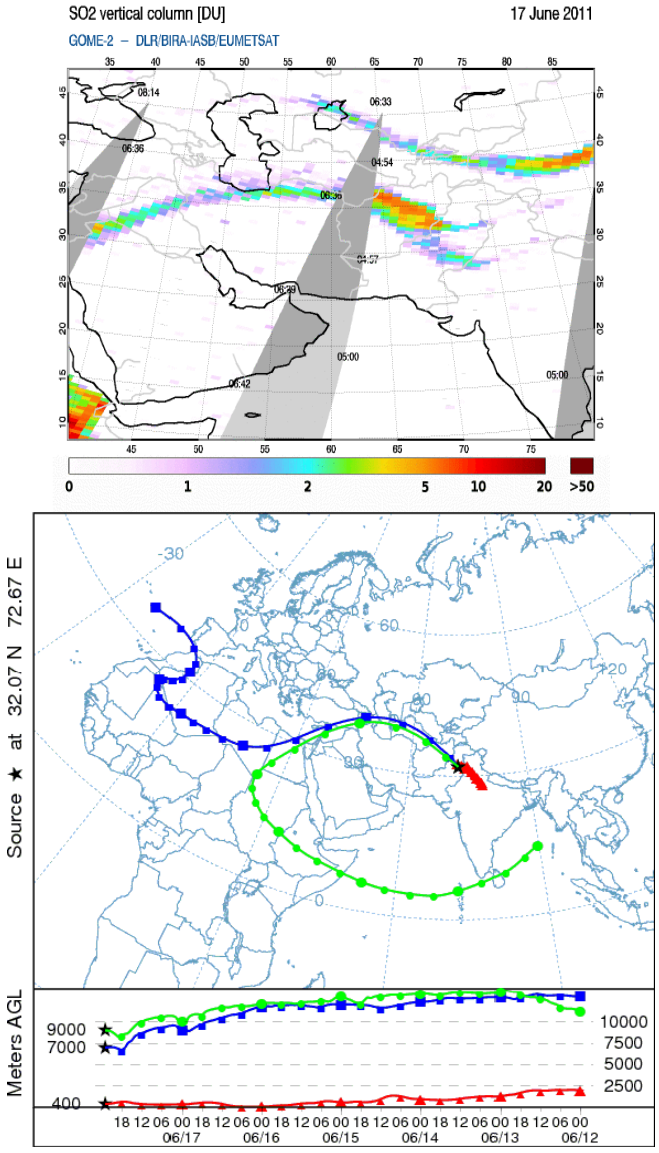


Figure 4.17: Backward trajectory for 17 June, 2011. In both Figures each gap represents a 6 hours interval

4.5.2. Dalaffilla, Ethiopia, Northeastern Africa

Trajectory analysis for 5th November, 2008 indicates that air masses polluted with SO_2 entered Pakistan from west side as shown in Fig. 4.18. The trajectory was calculated 72 hours backwards in time and at height 500, 4000 and 9000 mAGL. The analysis of backward trajectory of air masses showed that they have encountered with SO_2 plume in the vicinity of volcano and followed the SO_2 pathway accurately before

reaching Pakistan. These air masses came across and intersected with the air masses directed from the Arabian Sea, and reached to Pakistan on 5th November. The average altitude of the plume calculated with HYSPLIT is between 4000 and 9000 mAGL. It confirmed the direction and altitude of SO_2 plume reaching Pakistan and also confirming the source to be in Ethiopia region.

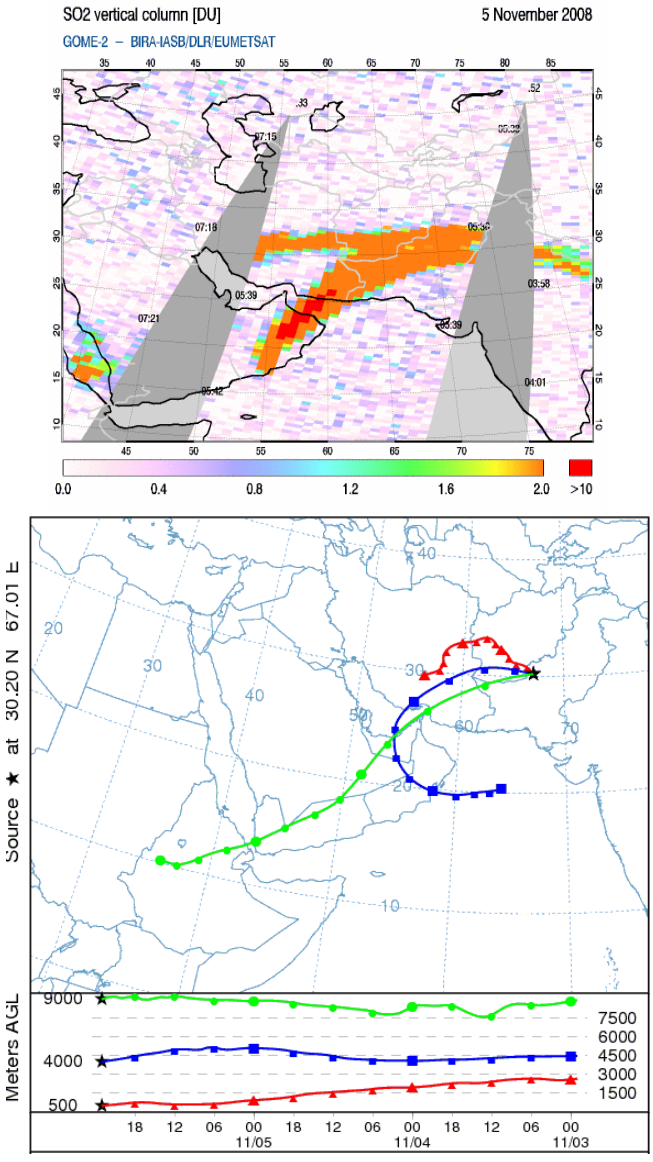


Figure 4.18: Backward trajectory for 5th November 2008. Each gap represents a 6 hours interval.

4.5.3. Jabal al Tair, Red Sea

HYSPLIT model was also run for the backward trajectory of air masses on 4th October, 2007. The trajectory was calculated 120 hours backwards in time and at height 500, 5000 and 15000 mAGL.

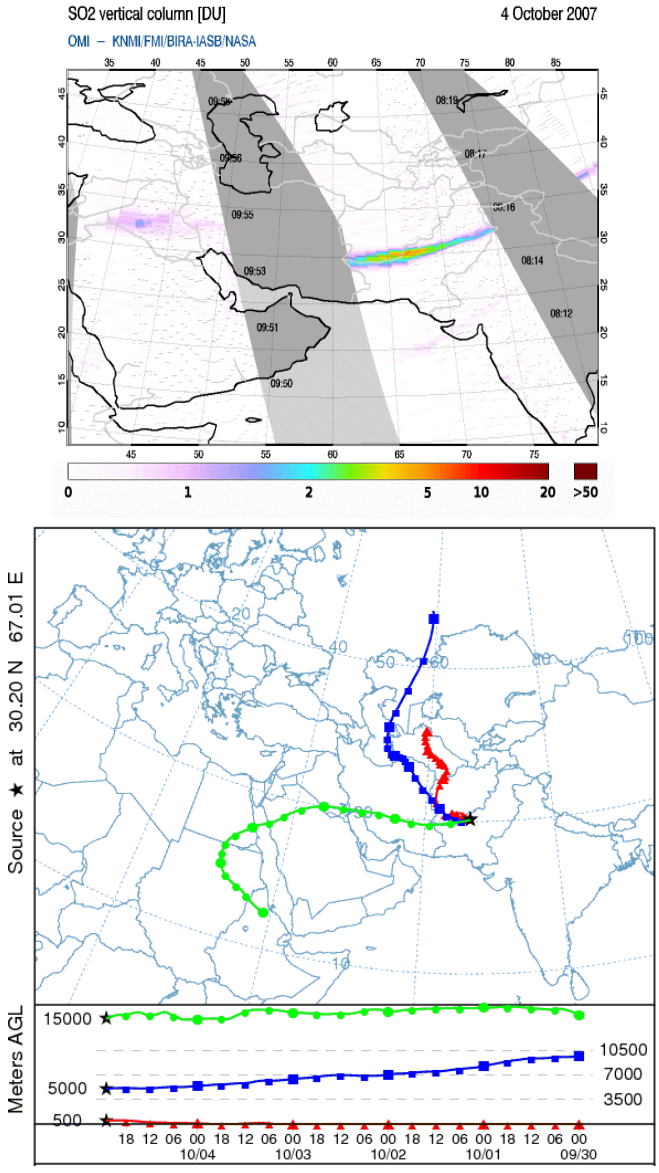


Figure 4.19: Backward trajectory for 4 October, 2007. Each gap represents a 6 hours interval

Back trajectory showed that air masses encountered the SO_2 near the volcanic eruption, and following the pathway traveled towards Pakistan. It reached Pakistan from the west side. Air mass average altitude calculated with HYSPLIT is around 15000 mAGL. The trajectory confirmed the pathway of air masses with the pathway and altitude of SO_2 plume reaching Pakistan. This is shown in the Fig. 4.19.

Conclusion and Recommendations

5.1.Conclusion

This study for the first time has prepared a database of SO_2 columns present in the atmosphere of Pakistan and emphasized on the trans-boundary SO_2 pollution present in the atmosphere of Pakistan as a consequence of volcanic eruption, by using SCIAMACHY data. For the discussion of volcanic case studies SCIAMACHY, OMI and GOME-2 data has been used. SO_2 columns for the years 2004 to 2012 have been used to investigate the spatio-temporal variation of SO_2 over Pakistan. Main findings of this study are:

- SO_2 column densities showed variation throughout the country. The annual average distribution of SO_2 showed that SO_2 is mostly higher in Northern part of the country during winter months, which cab attributed to albedo effect (Khokhar, 2006), biofuel burning and usage of low quality fuel in motor vehicles. It is also high in few major cities of Punjab and Khyber Pakhtunkhwa and in the North of Baluchistan. It is comparatively low in Sindh and Southern Baluchistan.
- Trend analysis showed that SO_2 has increased since 2004. SO_2 trend calculation showed 1.25 times (125%) increase with volcanic eruptions and 0.71 times (71%) increase without volcanic eruptions from 2004 to 2012.
- This increase in SO_2 columns over Pakistan is mainly due to use of poor quality petroleum products, use of bio fuel (char coal) for cooking and space heating, open solid waste burnings and no implementation of strict

emission standards for industry and motor vehicles (EURO II emission standards are not implemented yet in true spirit). Although, there is no strong correlation observed among the increase in number of motor vehicle in Pakistan and SO_2 column densities but still it may be partially attributed to extensive increase in vehicular emission and related activities in Pakistan during the time period of 2004-2011. The observed poor correlation is mainly due to extensive use of CNG as a fuel rather than a conventional fuel during last few years.

- Seasonal variation showed high SO_2 in winter and comparatively low values in summer months which are mainly driven by OH concentration and monsoon season, typical for the monsoon region.
- SO_2 column densities show a strong gradient in spatial distribution across the whole Pakistan with mainly high concentration in few of the regions with industrial activities.
- The study also revealed in past few years some major volcanic eruption in the world has affected Pakistan atmospheric air quality through trans-boundary transport of SO_2 pollution. Among those eruptions, the Nabro volcano event in during June 2011 has caused the major effects.
- The Nabro volcanic eruption has caused major increase in SO_2 column over northern and central part of the country.
- The Dalaffilla volcanic eruption in 2008 has caused elevated amount of SO_2 for the region of Baluchistan and Punjab province.
- Jabal al Tair in 2007 has affected few areas of Baluchistan and Punjab province. The effect was not significant compared to the Nabro and Dalaffilla volcano.

- The Tor Zawar volcano located in Pakistan, erupted in 2010. This volcano event was not reported and SO_2 emissions were not detected by satellite observations.
- Back trajectory analysis performed by HYSPLIT has confirmed the SO_2 pollution pathways and was also enabled to identify the SO_2 plume altitude and its origin.

5.2. Recommendations

For future few of the recommendations are:

- To continue the preparation of database and data analysis of SO_2 from the year 2012 onwards.
- To continue further research on SO_2 emission's sources apportionment.
- To share the results and exchange views and skills with other working groups in the same field.
- There is a need of efforts for establishing and strengthening the trace gases monitoring system in Pakistan.
- To collaborate with NGOs and government agencies to incorporate programs in their policies in order to cope with air quality issue in Pakistan.

References

Aamlid, D. (2002). Air pollution effects in the Norwegian-Russian border area. A status report. Statens forurensningstilsyn (SFT) Rapport TA. 36.

Afe, O. T., Richter, A., Sierk, B., Wittrock, F. and Burrows, J. P. (2004). BrO emission from volcanoes: a survey using GOME and SCIAMACHY measurements. Geophysical Research Letters., 31(24): L24113.

Agency for Toxic Substances and Disease Registry (ATSDR). (1998). Toxicological Profile for Sulfur Dioxide. ATSDR, Public Health Service, US Department of Health and Human Services. Atlanta, GA.

Alexander, B., Savarino, J., Kreutz, K. J., and Thiemens, M. H. (2004). Impact of preindustrial biomass-burning emissions on the oxidation pathways of tropospheric sulfur and nitrogen. Journal of Geophysical Research: Atmospheres., 109(D8): D08303.

Alias, M., Hamzah, Z. and Kenn, L. S. (2007). PM10 and Total suspended particulates (TSP) measurements in various power stations. Malaysian Journal of Analytical Sciences., 11(1): 255-261.

Allaby, M. (2000). Basics of Environmental Science 2nd Edition. Routledge. New York, NY.

AMAP (Arctic Monitoring and Assessment Program) Assessment Report. (2006). Arctic Pollution Issues, Oslo, Norway.

Andres, R. J. and Kasgnoc, A. D. (1998). A time-averaged inventory of subaerial volcanic sulfur emissions. Journal of Geophysical Research: Atmospheres., 103(D19): 25251–25261.

Ashraf, N., Mushtaq, M., Sultana, B., Iqbal, M., Ullah, I. and Shahid, S. A. (2013). Preliminary monitoring of tropospheric air quality of Lahore City in Pakistan. Sustainable Development. International Journal of Chemical and Biochemical Sciences., 3 (1): 19-28.

Atkinson, R., Baulch, D.L., Cox, R.A., Hampson, R.A., Kerr, J. A., Rossi, J.A. and Troe. J. (1997). Evaluated kinetic, photochemical, and heterogeneous data for atmospheric chemistry: Supplement VI, IUPAC subcommittee on gas kinetic data evaluation for atmospheric chemistry. Journal of Physical and Chemical Reference Data., 26 (6): 521–1011.

Ba-Shammakh, M. S. (2011). Optimal SO_2 Reduction Strategies in an Oil Refinery Based on Arabian Light Crude Oil. 21st Annual Saudi-Japan Symposium. Catalysts in Petroleum Refining & Petrochemicals. Dhahran, Saudi Arabia.

Begun, J., and Eicher, T. S. (2007). In search of a sulphur dioxide environmental Kuznets curve: a Bayesian model averaging approach. Working paper 79. Center for Statistics and the Social Sciences, University of Washington, Seattle.

Bell, M. L. and Davis, D. L. (2001). Reassessment of the lethal London fog of 1952: novel indicators of acute and chronic consequences of acute exposure to air pollution. Environmental health perspectives., 109(Suppl 3): 389 - 394.

Bell, M.L., Samet, J.M. and Dominici, F. (2004). Time-series studies of particulate matter. Annual Review of Public Health., 25: 247 - 280.

Bourassa, A. E., Robock, A., Randel, W.J., Deshler, T., Rieger, L.A., Lloyd, N.D., Llewellyn, E.J. and Degenstein, D.A. (2012). Large Volcanic Aerosol Load in the Stratosphere Linked to Asian Monsoon Transport. Science., 337 (6090): 78-81.

Bovensmann, H., Burrows, J.P., Buchwitz, M., Frerick, J., Noe¨ l, S., Rozanov, V.V., Chance, K.V. and Goede, A.P.H. (1999). SCIAMACHY: mission objectives and measurement modes. Journal of the Atmospheric Sciences., 56 (2): 127–150.

Buchwitz, M., de Beek, R., Burrows, J. P., Bovensmann, H., Warneke, T., Notholt, J., Meirink, J. F., Goede, A. P. H., Bergamaschi, P., Korner, S., Heimann, M. and Schulz, A. (2005). Atmospheric methane and carbon dioxide from

SCIAMACHY satellite data: initial comparison with chemistry and transport models. Atmospheric Chemistry and Physics., 5 (4): 941–962.

Budavari, S. (1996). The Merck Index 12th Edition. Merck & Co., Rahway, N.J.

Bunce, N.J. (1994). Environmental Chemistry, Second Edition. Wuerz Publishing.

Burrows, J.P., Weber, M., Buchwitz, M., Rozanov, V., Landsta¨tter-Weißenmayer, A., Richter, A., Debeek, R., Hoogen, R., Bramstedt, K., Eichmann, K.U., Eisinger, M. and Perner, D. (1999). The global ozone monitoring experiment (GOME): mission concept and first scientific results. Journal of the Atmospheric Sciences., 56 (2): 151–175.

Callies, J., Corpaccioli, E., Eisinger, M., Hahne, A. and Lefebvre, A. (2000). GOME-2-MetOP's second-generation sensor for operational ozone monitoring. ESA bulletin., 102: 28-36.

Calvert, J.G. and Stockwell, W.R. (1984). Mechanisms and rates of gas-phase oxidations of sulfur dioxide and nitrogen oxides in the atmosphere. In SO_2, NO and NO_x oxidation mechanisms: atmospheric considerations. Butterworths, Toronto.

Carn, S. A. and Bluth, G. J. S. (2003). Prodigious sulfur dioxide emissions from Nyamuragira volcano, DR Congo. Geophysical Research Letters., 30(23): 2211.

Carn, S. A., Krueger, A.J., Arellano, S., Krotkov, N.A. and Yang, K. (2008). Daily monitoring of Ecuadorian volcanic degassing from space. Journal of Volcanology and Geothermal Research., 176 (1): 141-150.

Carn, S. A., Yang, K., Wang, J. and Park, S. P. F. (2012). Satellite Measurements and Modeling of the 2011 Nabro (Eritrea) Volcanic Clouds. American Geophysical Union Chapman Conference Selfoss, Iceland. Abstract, RS-5.

Chelani A.B. and Devotta, S. (2007). Air Quality Assessment in Delhi: Before and After CNG as Fuel. Environment Monitoring and Assessment., 125 (1-3):257–263.

Chmielewski, A.G. (2011). Environmental effects of fossil fuel combustion. Encyclopedia of life support systems (EOLSS).

Clarisse, L., Hurtmans, D., Clerbaux, C., Hadji-Lazaro, J., Ngadi, Y. and Coheur, P.F. (2012). Retrieval of sulphur dioxide from the infrared atmospheric sounding interferometer (IASI). Atmospheric Measurement Techniques., 5 (3): 581–594.

Clean Air Hamilton. (2007). 2005-2006 Progress Report.

Clean Air Initiative Asia (CAI-Asia). (2010). CAI-Asia Factsheet No. 4.

Clean Air Initiative for Asian Cities Center (CAI - Asia). (2008). Current fuel quality and vehicle emission standards - challenges and opportunities in Asia. Regional Workshop on Partnership for Clean Fuels and Vehicles for East Asia.

Colbeck, I., Nasir, Z. A. and Ali, Z. (2010). The state of ambient air quality in Pakistan-a review. Environmental Science and Pollution Research., 17(1): 49-63.

De Smedt, I., Müller, J.F., Stavrakou, T., Van der A, R., Eskes, H. and Van Roozendael, M. (2008). Twelve years of global observations of formaldehyde in the troposphere using GOME and SCIAMACHY sensors. Atmospheric Chemistry and Physics., 8(16): 4947–4963.

De Smedt, I., Van Roozendael, M., Stavrakou, T., Müller, J.F., Lerot, C., Theys, N., Valks, P., Hao, N. and Van der A, R. (2012). Improved retrieval of global tropospheric formaldehyde columns from GOME-2/MetOp-A addressing noise reduction and instrumental degradation issues. Atmospheric Measurement Techniques., 5(11): 2933–2949.

Delmas, R. and Servant, J. (1988). The atmospheric sulfur cycle in the tropics.

Delmelle, P., Stix, J., Baxter, P., Garcia-Alvarez, J. and Barquero, J. (2002). Atmospheric dispersion, environmental effects and potential health hazard

associated with the low-altitude gas plume of Masaya volcano, Nicaragua. Bulletin of Volcanology., 64(6): 423-434.

Dentener, F., Kinne, S., Bond, T., Boucher, O., Cofala, J., Generoso, S., Ginoux, P., Gong, S., Hoelzemann, J. J., Ito, A., Marelli, L., Penner, J. E., Putaud, J.-P., Textor, C., Schulz, M., Van der Werf, G. R. and Wilson, J. (2006). Emissions of primary aerosol and precursor gases in the years 2000 and 1750 prescribed data-sets for aerocom. Atmospheric Chemistry and Physics., 6(12): 4321–4344.

Deschler, W.W. (1974). An examination of the extent of grass fires in the savannah of Africa along the southern side of Sahara. 9th International Symposium on Remote Sensing of the Environment. Environ. Res. Inst. Mich., Ann Arbor, Michigan.

Draxler R. R. and Hess, G. D. (2004). Description of the HYSPLIT4 Modeling System, NOAA Technical Memorandum ERL ARL-224.

Draxler, R., Stunder, B., Rolph, G., Stein, A., and Taylor, A. (2013). HYSPLIT4 user's guide overview.

Draxler, R.R. and Rolph, G.D. (2013). HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model access via NOAA ARL READY Website, http://ready.arl.noaa.gov/HYSPLIT.php. NOAA Air Resources Laboratory, Silver Spring, Maryland.

Đurić, S., Ćeranić, M., Kosanić, T., Brankov, S., Božičković, R. and Milotić, M. (2013). The 6th PSU-UNS International Conference on Engineering and Technology (ICET-2013), Novi Sad, Serbia.

EET (Emission Estimation Technique): Manual for Copper Concentrating, Smelting and Refining, National Pollutant Inventory, Environment Australia (1999).

Eggleton, A.E.J. and R.A. Cox. (1978). Homogeneous Oxidation of Sulphur Compounds in the Atmosphere. Atmospheric Environment., 12:227-230.

Eisinger, M. and Burrows, J.P. (1998). Tropospheric sulfur dioxide observed by the ERS-2 GOME Instrument. Journal of Geophysical Research., 25 (22): 4177-4180.

Environmental Protection Agency (EPA) (2011).

EUMETSAT, Global Ozone Monitoring Experiment–2 (GOME-2) products guide. (2005). http://www.eumetsat.int/en/area4/eps/product_guides/GOME-2/GOME2-PG.pdf.

Fee, D., Carn, S., A. and Prata, F. (2011). Infrasound and SO_2 Observations of the 2011 Explosive Eruption of Nabro Volcano, Eritrea. American Geophysical Union, Fall Meeting 2011. Abstract, V41E-07.

Ferdous, F. (2008). Characterization of Nitrogen Dioxide and Sulphur Dioxide Ambient Concentrations over an Urban Area through Land use Regression Modeling: An application to Hamilton, Ontario.

Ferdous, F. and Kanaroglou, P. (2007). Land use regression modeling for predicting ambient concentration of sulphur dioxide: an application to Hamilton, Ontario, Canada, presented in the 54th annual north American meetings of the regional science association international Savannah Georgia.

Ferrari, L. and Salisbury, J. (1999). Sulfur dioxide, National environmental health forum.

Finlayson-Pitts, B. J. and Pitts Jr, J. N. (1986). Atmospheric chemistry. Fundamentals and experimental techniques. Wiley, New York

Finlayson-Pitts, B. J. and Pitts Jr, J. N. (1999). Chemistry of the upper and lower atmosphere: theory, experiments, and applications.

Fioletov, V. E., Griffioen, E., Kerr, J. B., Wardle, D. I. and Uchino, O. (1998). Influence of volcanic sulfur dioxide on spectral UV irradiance as measured by Brewer Spectrophotometers. Journal of Geophysical Research., 25(10): 1665–1668.

Fishman, J., Bowman, K. W., Burrows, J. P., Richter, A., Chance, K. V., Edwards, D. P., Martin, R.V., Morris, G.R., Pierce, R.B., Ziemke, J.R., Al-Saadi, J.A., Creilson, J.K., Schaack, T.K. and Thompson, A. M. (2008). Remote Sensing of Tropospheric Pollution from Space. Bulletin of the American Meteorological Society., 89(6): 805-822.

Friend, J.P. (1973). The Global Sulfur Cycle. In Chemistry of the Lower Troposphere. Rasool, S.I. (ed.). Plenum Press, New York, NY. 177-201.

Galle, B., Oppenheimer, C., Geyer, A., McGonigle, A., Edmonds, M., and Horrocks, L. (2002). A miniaturised ultraviolet spectrometer for remote sensing of SO_2 fluxes: a new tool for volcano surveillance, Journal of Volcanology and Geothermal Research., 119: 241–254.

Garland, J.A. (1978). Dry and Wet Removal of Sulfur from the Atmosphere. Atmospheric Environment., 12: 349-362.

Gary, J. H. (1994). Handwerk, G. E. Petroleum Refining: Technology and Economics. 3rd ed. New York.

Genium Publishing Corporation (Genium). (1999). Genium's Handbook of Safety, Health and Environmental Data for Common Hazardous Substances. McGraw Hill, New York, New York.

Global Volcanism Program. (2013). Available at: http://www.volcano.si.edu/index.cfm (Accessed: April, 2013)

Goyal, P. (2003). Present scenario of air quality in Delhi: a case study of CNG implementation. Atmospheric Environment., 37 (38):5423-5431.

Halmer, M. M., Schmincke, H. U. and Graf, H. F. (2002). The annual volcanic gas input into the atmosphere, in particular into the stratosphere: A global data set for the past 100 years. Journal of Volcanology and Geothermal Research., 115(3-4): 511–528.

Hansell, A. and Oppenheimer, C. (2004). Health hazards from volcanic gases: a systematic literature review. Archives of Environmental Health., 59(12): 628-639.

Harmeling, S. and Eckstein, D. (2012). Global Climate Risk Index 2013: Who Suffers Most From Extreme Weather Events? Weather-related Loss Events in 2011 and 1992 to 2011. Germanwatch.

Hassan K., S., El–Abssawy, A.A. and Khoder, M.I. (2013). Characteristics of gas–phase nitric acid and ammonium–nitrate–sulfate aerosol, and their gas–phase precursors in a suburban area in Cairo, Egypt. Atmospheric Pollution Research., 4(1): 117-129.

Hazardous Substances Data Bank (HSDB). (2002). Hazardous Substances Data Bank Sulfur Dioxide (HSN 228). Toxicology and Environmental Health Information Program, National Library of Medicine, Bethesda, MD. http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB.

Hegg, D. A. and Hobbs, P. V. (1978). Oxidation of sulfur dioxide in aqueous systems with particular reference to the atmosphere. Atmospheric Environment., 12(1): 241-253.

Hidy, G.M. (1994). Atmospheric Sulfur and Nitrogen Oxides: Eastern North America Source receptor Relationships. Academic Press Inc., San Diego.http://www.cleanair.hamilton.ca/downloads/CAH-Report-2005-2006-FINAL.pdf

IARC. (1992). Abstract: Sulfur Dioxide and Some Sulfites, Bisulfites and Metabisulfites. IARC Working Group. TA: IARC Monographs on the Evaluation of Carcinogenic Risk to Human. 54:131-188.

IGAC. (2007). Satellite observations of tropospheric trace gases and aerosols, in: IGACtivities Newsletter.

Ilyas, S. Z., Nasir, S. M. and Raza, S. M. (2008). Air pollution problems and diseases caused by hazardous gases in Quetta, Pakistan. Journal of Applied Sciences and Environmental Management., 12(1): 123-126.

Isaksen, I.S.A., Granier, C., Myhre, G., Berntsen, T.K., Dalsøren, S.B., Gauss, M., Klimont, Z., Benestad, R., Bousqueti, P., Collins, W., Coxk, T., Eyring, V., Fowlerm, D., Fuzzi, S., Jockel, P., Laj, P., Lohmann, U., Maione, M., Monks, P., Prevot, A.S.H., Raes, F., Richter, A., Rognerud, B., Schulz, M., Shindell, D., Stevenson, D.S., Storelvmo, T., Wang, W. C., van Weele, M., Wild, M., Wuebbles, D. (2009). Atmospheric composition change: Climate–Chemistry interactions. Atmospheric Environment., 43(33): 5138–5192

Katz, M. (1977). The Canadian Sulphur Problem. In Sulphur and Its Inorganic Derivatives in the Canadian Environment. Ad hoc Panel of Experts Management Subcommittee, NRC Associate Committee on Scientific Criteria for Environmental Quality, National Research Council of Canada, Ottawa. 21-67.

Kellogg, W.W., Cadle, R.D., Allen, E.R., Lazrus, A.L. and Martell, E.A. (1972). The Sulfur Cycle. Science., 175(4022): 587-596.

Kettle, A. and Andreae, M. (2000). Flux of the dimethylsulfide from the oceans: A comparison of updated data sets and flux models. Journal of Geophysical Research., 105(D22): 26793– 26808.

Khoder, M.J. (2002). Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogen dioxide to particulate nitrate and gaseous nitric acid in an urban area. Chemosphere., 49 (6): 675-684.

Khokhar, M. F., Frankenberg, C., Van Roozendael, M., Beirle, S., Kuhl, S., Richter, A., Platt, U. and Wagner, T. (2005). Satellite observations of atmospheric SO_2 from volcanic eruptions during the time-period of 1996-2002. Advances in Space Research., 36(5): 879–887.

Khokhar, M. F., Platt, U., and Wagner, T. (2008). Temporal trends of anthropogenic SO_2 emitted by non-ferrous metal smelters in Peru and Russia estimated from Satellite observations. Atmospheric Chemistry and Physics Discussions., 8(5): 17393-17422.

Khokhar, M.F. (2006). Retrieval and Interpretation of Tropospheric SO_2 from UV/VIS Satellites Instruments. M.sc thesis, der Universität Leipzig.

Khwaja, M. A. and Khan, S. R. (2005). Air pollution: key environmental issues in Pakistan. Sustainable Development Policy Institute (SDPI).

Krotkov, N. A., Carn, S. A., Krueger, A. J., Bhartia, P. K. and Yang, K. (2006). Band residual difference algorithm for retrieval of SO_2 from the Aura Ozone Monitoring Instrument (OMI). IEEE Transactions on Geoscience and Remote Sensing., 44(5): 1259–1266.

Krotkov, N. A., Krueger, A. J. and Bhartia, P. K. (1997). Ultraviolet optical model of volcanic clouds for remote sensing of ash and sulfur dioxide. Journal of Geophysical Research., 102 (D18): 21891-21904.

Krotkov, N. A., McClure, B., Dickerson, R. R., Carn, S. A., Li, C., Bhartia, P. K., Yang, K., Krueger, A.J., Li, Z., Levelt, P.F., Chen, H., Wang, P. and Lu, D. (2008). Validation of SO_2 retrievals from the Ozone Monitoring Instrument over NE China. Journal of Geophysical Research., 113 (D16).

Krueger, A.J. (1989). The global distribution of total ozone – Toms satellite measurements. Planetary and Space Science., 37 (12): 1555–1565.

Krueger, A.J., Walter, L.S., Bhartia, P.K., Schnetzler, C.C., Krotkov, N.A., Sprod, I. and Bluth, G.J.S. (1995). Volcanic sulfur dioxide measurements from the Total Ozone Mapping Spectrometer (TOMS) Instruments. Journal of Geophysical Research., 100 (D7): 14057 - 14076.

Lee, C., Martin, R. V., van Donkelaar, A., Lee, H., Dickerson, R. R., Hains, J. C., Krotkov, N., Richter, A., Vinnikov, K. and Schwab, J. J. (2011). SO_2 emissions and lifetimes: Estimates from inverse modeling using in situ and global, space-based (SCIAMACHY and OMI) observations. Journal of Geophysical Research: Atmospheres., 116(D6).

Lee, C., Richter, A., Weber, M. and Burrows, J. P. (2008). SO_2 retrieval from SCIAMACHY using the Weighting Function DOAS (WFDOAS) technique:

Comparison with standard DOAS retrieval. Atmospheric Chemistry and Physics., 8(20): 6137-6145.

Lenoble, J. (1993). Atmospherics Radiative Transfer. A. Deepak Publishing. Hampton, Virginia.

Levelt, P. F., G. H. J. van den Oord, M. R. Dobber, A. Malkki, H. Visser, J. de Vries, P. Stammes, J. Lundell, and H. Saari (2006). The ozone monitoring instrument. Geoscience and Remote Sensing, IEEE Transactions., 44(5): 1093-1101.

Levelt, P.F., van den Oord, G.H.J., Dobber, M.R., Malkki, A., Visser, H., de Vries, J., Stammes, P., Lundell, J.O.V. and Saari, H. (2006). Science objectives of the Ozone monitoring instrument. IEEE Transactions on Geoscience and Remote Sensing., 44 (5): 1199–1208.

Levin, N. (1999). Fundamentals of Remote Sensing.1st Hydrographic Data Management course, IMO - International Maritime Academy, Trieste, Italy

Lide, D.R. (2002). CRC Handbook of Chemistry and Physics. 83rd Edition. CRC Press, Boca Raton, FL.

Lyndon state college meteorology department. 2006. Available on: http://apollo.lsc.vsc.edu/classes/met130/notes/chapter1/vert_temp_all.html.

Ma, J. Z., Beirle, S., Jin, J.L., Shaiganfar, R., Yan, P and Wagner, T. (2013). Tropospheric NO_2 vertical column densities over Beijing: results of the first three years of ground-based MAX-DOAS measurements (2008–2011) and satellite validation. Atmospheric Chemistry and Physics., 13 (3): 1547–1567.

Marbach, T., Beirle, S., Platt, U., Hoor, P., Wittrock, P., Richter, A., Vrekoussis, M., Grzegorski, M., Burrows, J.P. and Wagner, T. (2009). Satellite measurements of formaldehyde from shipping emissions. Atmospheric Chemistry and Physics., 9 (21): 8223-82234.

Martin, R. V. (2008). Satellite remote sensing of surface air quality. Atmospheric Environment., 42(34): 7823-7843.

McCormick, M. P., Thomason, L. W. and Trepte, C. R. (1995). Atmospheric effects of the Mt Pinatubo eruption. Nature., 373(6513): 399-404.

McGee, K.A. and Gerlach, T.M. (1995). Volcano hazards fact sheet: Volcanic Gas. Volcanic Gas: U.S. Geological Survey Open-File Report. 95-85. Available on: http://vulcan.wr.usgs.gov/Glossary/Emissions/Publications/OFR95-85/OFR95-85.html.

McGonigle, A. J. S., and Oppenheimer, C. (2003). Optical sensing of volcanic gas and aerosol emissions. Geological Society, London, Special Publications., 213(1): 149-168.

MfE (Ministry for the Environment). (2004). Health effects of CO, NO_2, SO_2, ozone, benzene and benzo(a)pyrene in New Zealand. Air Quality Technical Report No. 43. Ministry for the Environment, Wellington, New Zealand.

Mirza, A.I., Kazmi, J.H. and Shirazi, S.A. (2013). Spatio-periodic monitoring and analysis of atmospheric Sulphur dioxide (SO_2) in the metropolitan areas of Lahore-Pakistan. Pakistan Journal of Science., 65 (1): 83-89.

MoF: ministry of finance. (2012). Pakistan economic survey 2011-12, transport and communications, ministry of finance, government of Pakistan.

Morales-Rivera, A.M. (2011). Comparisons between OMI SO_2 data and ground-based SO_2 measurements at Turrialba Volcano. MS Thesis. Michigan Technological University.

Neidell, M. and Lavaine, E. (2012). Morbidity and sulfur dioxide: evidence from French strikes at oil refineries.

Northern areas strategy for sustainable development. (2003). background paper. Health and environment International Union for Conservation of Pakistan (IUCN). Pakistan program.

Pakistan Clean Air Program. (2008). Government of Pakistan. Pakistan environmental protection agency. Ministry of environment.

Pakistan Economic Survey 2011-12. (2012). Transport and communications. Ministry of finance, government of Pakistan.

Perner, D. and Platt, U. (1979). Detection of nitrous acid in the atmosphere by differential optical absorption. Geophysical Research Letters., 6(12): 917-920.

Platt, U. (1994). Differential optical absorption spectroscopy (DOAS). In M. W. Sigrist (Ed.). Air monitoring by spectroscopy techniques. London: Wiley.

Platt, U., and Stutz, J. (2004). Differential Optical Absorption Spectroscopy: Principles and Applications (Physics of Earth & Space Environments). Springer-Verlag Berlin and Heidelberg GmbH & Co. KG. Germany.

Porter, E. (2006). Dry Deposition Monitoring Protocol for the National Park Service. National Park Service. U.S. Department of the Interior. Washington, D.C. http://www2.nature.nps.gov/air/Monitoring/docs/200605FinalDryDepProtocol.pdf

Qadir, N. F. (2002). Air quality management in Pakistani cities: Trends and challenges. Better Air Quality in Asian and Pacific Rim Cities (BAQ).

Richter, A., Burrows, J. P., Nuss, H., Granier, C. and Niemeier, U. (2005). Increase in tropospheric nitrogen dioxide over China observed from space. Nature., 437(7055): 129-132.

Richter, A., Eyring, V., Burrows, J.P., Bovensmann, H., Lauer, A., Sierk, B. and Crutzen, P.J. (2004). Satellite measurements of NO_2 from international shipping emissions. Geophysical Research Letters., 31 (23).

Richter, A., Wittrock, F., Eisinger, M. and Burrows, J.P. (1998). GOME observations of tropospheric BrO in Northern Hemispheric spring and summer 1997. Journal of Geophysical Research., 25 (14): 2683-2686.

Rix, M., Valks, P., Hao, N., Loyola, D., Schlager, H., Huntrieser, H., Flemming, J., Koehler, U., Schumann, U. and Inness, A. (2012). Volcanic SO_2, BrO and plume height estimations using GOME-2 satellite measurements during the

eruption of Eyjafjallajökull in May 2010. Journal of Geophysical Research., 117 (D6).

Robinson, N. H., Newton, H. M., Allan, J. D., Irwin, M., Hamilton, J. F., Flynn, M., Bower, K. N., Williams, P. I., Mills, G., Reeves, C. E., McFiggans, G., and Coe, H. (2011). Source attribution of Bornean air masses by back trajectory analysis during the OP3 project. Atmospheric Chemistry and Physics., 11(18): 9605-9630.

Robock, A. (2000). Volcanic eruption and climate. Reviews of Geophysics., 38(2): 191-219.

Rolph, G.D. (2013). Real-time Environmental Applications and Display sYstem (READY) Website, http://ready.arl.noaa.gov. NOAA Air Resources Laboratory, Silver Spring, Maryland.

Royal Society of Chemistry (RSC). (1999). Dictionary of Substances and Their Effects Database. Royal Society of Chemistry, Cambridge, UK.

Ruth, J. H. (1986). Odor thresholds and irritation levels of several chemical substances: a review. American Industrial Hygiene Association Journal., 47(3): A-142.

S, John. Dalaffilla Volcano. Volcanolive.com. Available at: http://www.volcanolive.com/dalaffilla.html (Accessed: May 1, 2013).

Saiz-Lopez, A., Adame, J. A., Notario, A., Poblete, J., Bolívar, J. P. and Albaladejo, J. (2009). Year-Round Observations of NO, NO_2, O_3, SO_2, and Toluene Measured with a DOAS System in the Industrial Area of Puertollano, Spain. Water, Air, and Soil Pollution., 200(1-4): 277-288.

Saiz-Lopez, A., Notario, A. and Martinez, E. (2006). Seasonal evolution of levels of gaseous pollutants in an urban area (Ciudad Real) in central-southern Spain: a DOAS study. Water, Air, and Soil Pollution., 171(1-4): 153-167.

Sanderson, R. (2000). Introduction to remote Sensing. New Mexico Space Grant Consortium.

Sandwell, D. (2009). Overview of remote sensing for GIS. http://sopac.ucsd.edu/projects/sio110/2009/GISLecture10_2009_RemoteSensing.pdf

Savard, M. M., Bonham-Carter, G. F. and Banic, C. M. (2006). A geoscientific perspective on airborne smelter emissions of metals in the environment: an overview. Geochemistry: Exploration, environment, analysis., 6(2-3): 99-109.

Schoeberl, M.R., Ziemke, J.R., Bojkov, B., Livesey, N., Duncan, B., Strahan, S., Froidevaux, L., Kulawik, S., Bhartia, P.K., Chandra, S., Levelt, P.F., Witte, J.C., Thompson, A.M., Cuevas, E., Redondas, A., Tarasick, D.W., Davies, J., Bodeker, G., Hansen, G., Johnson, B.J., Oltmans, S.J., Vo¨mel, H., Allaart, M., Kelder, H., Newchurch, M., Godin-Beekmann, S., Ancellet, G., Claude, H., Andersen, S.B., Kyro¨ , E., Parrondos, M., Yela, M., Zablocki, G., Moore, D., Dier, H., von der Gathen, P., Viatte, P., Stu¨ bi, R., Calpini, B., Skrivankova, P., Dorokhov, V., de Backer, H., Schmidlin, F.J., Coetzee, G., Fujiwara, M., Thouret, V., Posny, F., Morris, G., Merrill, J., Leong, C.P., Koenig-Langlo, G., Joseph, E., 2007. A trajectory-based estimate of the tropospheric ozone column using the residual method. Journal of Geophysical Research-Atmospheres., 112 (D24).

Schwela, D. (1997). The Air Management Information Sytem (AMIS) and a Global Air Quality Partnership. World Health Organisation, Geneva.

Seinfeld, J.H. and Pandis, S.N. (1998). Atmospheric chemistry and physics: from pollution to climate change. John Wiley & Sons, Inc., New York.

Shy, C. M., Hasselbad, V., Burton, RM., Nelson, C. J. and Coles, A. A. (1973). Air pollution effects on ventilatory function of US school-children. Archives of Environmental Health., 27: 124-128.

Smedt, I.D., Van Roozendael, M., Stavrakou, T., Muller, J.F., Lerot, C., Theys, N., Valks, P., Hao, N. and van der A, R. (2012). Improved retrieval of global tropospheric formaldehyde columns from GOME-2/MetOp-A addressing noise reduction and instrumental degradation issues, Atmospheric Measurement Techniques., 5 (11): 2933-2949.

Smith, S. J., van Aardenne, J., Klimont, Z., Andres, R. J., Volke, A. and Delgado Arias, S. (2011). Anthropogenic sulfur dioxide emissions: 1850-2005. Atmospheric Chemistry and Physics., 11(3): 1101–1116.

Sogacheva, L., Hamed, A., Facchini, M. C., Kulmala, M., and Laaksonen, A. (2007). Relation of air mass history to nucleation events in Po Valley, Italy, using back trajectories analysis. Atmospheric Chemistry and Physics., 7 (3): 839–853.

Solaiman, T. (2007), Air pollution modeling and forecasting in Hamilton using data - driven methods. M. A. Sc. Thesis. Department of Civil Engineering, McMaster University, Hamilton, Canada.

Soleille, S. (2004). Lìndustrie du raffinage et le devenir des fiouls lourds. Report, French national institute for industrial environment and risks, INERIS.

Stohl, A.(1998). Computation, accuracy and applications of trajectories – a review and bibliography. Atmospheric Environment, 32 (6): 947–966.

Telmer, K. H., Daneshfar, B., Sanborn, M. S., Kliza-Petelle, D. and Rancourt, D. G. (2006). The role of smelter emissions and element remobilization in the sediment chemistry of 99 lakes around the Horne smelter, Quebec. Geochemistry: Exploration, environment, analysis., 6(2-3): 187-202.

Thomas, W., T. Erbertseder, T. Ruppert, M. Van Roozendael, J. Verdebout, D. Balis, C. Meleti, and C. Zerefos. (2005). On the retrieval of volcanic sulfur dioxide emissions from GOME backscatter measurements. Journal of Atmospheric Chemistry., 50(3): 295–320.

Thornton, D.P. (2007). The New Zealand national environmental standards for ambient air quality: analysis and modeling case study. MS Thesis. University of Canterbury.

United States Environmental Protection Agency (USEPA). (1995). Compilation of air pollutant emission factors (AP 42). Volume I: Stationary point and area sources. Research Triangle Park, NC: United States Environmental Protection Agency Office of Air Quality Planning and Standards.

United States Environmental Protection Agency (USEPA). (2013). http://www.epa.gov/oaqps001/sulfurdioxide/implement.html

Van Der Leun, J. C. (2004). The ozone layer. Photodermatology, Photoimmunology & Photomedicine., 20(4): 159-162.

Van Roozendael, M., Fayt, C., Lambert,J.C., Pundt, I., Wagner, T., Richter, A. and Chance, K. (1999). Development of a bromine oxide product from GOME. In Proc. ESAMS., 99: 543-547.

Vijay, S., Molina, L. T., and Molina, M. J. (2004). Estimating air pollution emissions from fossil fuel use in the electricity sector in Mexico. Integrated program on urban, regional and global air pollution, Prepared for North American commission for environmental cooperation.

Weil, E.D. and Sandler, S.R. (1997). Sulfur Compounds. In Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc.

Wilson, W.E. (1978). Sulfates in the Atmosphere: A Project Report on Project MISTI. Atmospheric Environment., 12: 537-547.

Wittrock, F., Richter, A., Oetjen, H., Burrows, J. P., Kanakidou, M., Myriokefalitakis, S., Volkamer, R., Beirle, S., Platt, U., and Wagner, T.: Simultaneous global observations of glyoxal and formaldehyde from space. Geophysical Research Letters., 33(16): L16804.

Yang, K., Liu, X., Krotkov, N. A., Krueger, A. J. and Carn, S. A. (2009). Estimating the altitude of volcanic sulfur dioxide plumes from space borne hyper-spectral UV measurements. Geophysical Research Letters., 36(10).

Zerefos, C. S., Mantis, H.T., Bais, A.F., Ziomas, I.C. and Zoumakis, N. (1986). Solar ultraviolet absorption by sulphur dioxide in Thessaloniki, Greece. Atmosphere Ocean., 24 (3): 292– 300.