MONITORING AND COMPARING THE FORMALDEHYDE CONCENTRATION OVER ISLAMABAD AND PIR SOHAWA VALLEY BY EXPLOITING MAX-DOAS SATELLITE OBSERVATIONS

By

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This thesis is dedicated to my Parents

For their endless support and encouragement

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List of Abbreviations

HCHO	Formaldehyde
VOC's	Volatile Organic Compounds
GOME-2	Global Ozone Mointoring Experiment-2
SCIAMACHY	Scanning Imaging Absorption SpectroMeter for Atmospheric Chartography
DOAS	Differential Optical Absorption Spectroscopy
ATSR	Along Track Scanning Radiometer
CH_4	Methane
NMVOC's	Non-Methane Volatile Organic Compounds
O_3	Ozone
CFC's	Chloroflurocarbons
HO_2	Hydro Peroxy Radical
CEPA	Canadian Environmental Protection Act
NTP	National Toxicology Program
US EPA	United States Environmental Protection Agency
IARC	International Agency for Research on Cancer
GOME	Global Ozone Monitoring Experiment
ESA	European Space Agency
SCD	Slant Column density

VCD	Vertical Column Density
AMF	Air Mass Factor
TEMIS	Tropospheric Emissions Monitoring Inventory Service
CNG	Compressed Natural Gas
ACF	Auto Correlation Function
IPCC	Intergovernmental Panel on Climate Change
WHO	World Health Organization
ATSDR	Agency for Toxic Substances and Disease Registry
$\mu g/m^3$	Microgram per Cubic meter
AMF	Air Mass Factor
ArcGIS	Arc Geographic Information System
C-CARGO	Climate Change and Atmospheric Research GrOup
DOAS	Differential Optical Absorption Spectroscopy
DOASIS	Differential Optical Absorption Spectroscopy Intelligent System
DSCD	Differential Slant Column Densities
FTIR	Fourier Transform Infrared Spectrometry
FWHM	Full Width half Maximum
GOME-2	Global Ozone Monitoring Equipment - 2

HNO_3	Nitric Acid
IDW	Inverse Distance Weighting
Max-DOAS	Multi-axis Differential Optical Absorption Spectroscopy
NGO's	Non-Government Organizations
NH_3	Ammonia
NIOSH	National Institute for Occupational Safety and Health
NIPS	National Institute of Population Studies
NO	Nitric Oxide
NO_2	Nitrogen Dioxide
NOx	Oxides of Nitrogen
O_3	Ozone
OMI	Ozone Monitoring Instrument
OSHA	Occupational Safety & Health Administration
Pak-EPA	Pakistan Environmental Protection Agency
Pak-NEQS	Pakistan National Environmental Quality Standards
PCTs	Pollution Control Techniques
PM	Particulate Matter
ppb	Parts per Billion
QGIS	Quantum Geographic Information System
RMS	Root Mean Square

USEPA	United States Environmental Protection Agency
UTC	Universal Time Centre
UV	Ultra Violet
VOCs	Volatile Organic Compounds
WHO	World Health Organization
WinDOAS	Windows Differential Optical Absorption Spectroscopy

ABSTRACT

Formaldehyde is an intermediate product in the oxidation paths of non-methane hydrocarbons produced through biogenic activities and anthropogenic sources. Formaldehyde is a flammable, colorless, strong-smelling chemical that is used in building materials and to produce numerous domestic products and medical preservatives. Formaldehyde is also present naturally in the environment and produced in lesser amounts by most organisms as part of normal metabolic processes. Pakistan lacks the monitoring facilities on a larger scale to measure the atmospheric gasses on regular basis. The study presents the result of atmospheric Formaldehyde vertical column densities (VCDs) obtained from ground-based and satellite observation over Pakistan during the time period of 2014-2015. In order to explore the spatial distribution of Formaldehyde, various field campaigns were conducted by using Car MAX-DOAS instrument and involved international scientists as well. Level 2 data product of satellite instrument; Ozone Monitoring Instrument (OMI) retrieved by differential optical absorption spectroscopy (DOAS) technique was also compared with ground-based observations. Spatio-temporal distribution of Formaldehyde (HCHO) column densities over main cities and region of Pakistan are discussed. The results show that high Formaldehyde (HCHO) column densities exceeding permissible limit of 83 ppm were found over twin cities Rawalpindi-Islamabad of Pakistan. The highest VCDs were around 1.0×10^{16} to 8.5×10^{16} molecules/cm^2 higher than WHO guide lines, while in Pir Sohawa valley where there is less population and vehicular emission, HCHO VCDs were found within WHO permissible limits. Similarly, areas with major industrial activity and high population densities showed high amount of HCHO concentrations.

Keywords: Air quality, Formaldehyde, MAX-DOAS, Vertical column densities (VCDs)

Background

Rapid urbanization, industrialization and increase in automobile growth, are responsible for the release of large amounts of various gaseous pollutants in the atmosphere. In addition, development is not quite homogeneous as large number of regional disparities exist in industrialization, population density, energy consumption, vehicular density and level of resource utilization. The main industrial areas and big cities of Pakistan are heavily polluted. Concentrations of common air pollutants, such as sulfur dioxide (SO_2), nitrogen dioxide (NO_2) (Mehndi *et al.,* 2014), particulate matter (PM_{10} and $PM_{2.5}$), carbon monoxide (CO), ozone (O_3) and other toxic air pollutants increase in metropolitan areas and significantly exceed the WHO guidelines.

1.0 Introduction

Air pollution has emerged as a major concern of the mankind and poses severe threats to the environment. All major cities of Pakistan are experiencing serious air pollution problems that need to be addressed so that its negative impacts on human health and the environment are reduced. NO_2 is a strong oxidant and has been listed as a criteria pollutant (US EPA, 1990). There had been a 5-fold increase in NO_x emissions since the pre-industrial era, and the fastest growth observed in Asia is at the rate of 4-6% per year (Garg *et al.,* 2001; Van Aardenne *et al*., 1999).

Emission of greenhouse gases from human activities is a major culprit for observed increase in global temperature. On an average there is 70% increase in the emission of greenhouse gasses from 1970-2004 (IPCC, 2007). The results documented by Intergovernmental Panel on Climate Change (2007), concluded that sudden and abundant increase in the anthropogenic greenhouse gas is responsible for raised global temperature.

1.1 FORMALDEHYDE

Formaldehyde is a common hydrocarbon found in the atmosphere despite of the fact that it has very short half-life. It is the major representative of the photochemical activity along with the non-methane volatile organic carbon compounds (NMVOCs). Fossil fuel combustion and biomass burning result in formaldehyde (HCHO) as a major product being emitted (Vlemmix *et al.*,2015).

Methane oxidation is also responsible for formaldehyde (HCHO) release. It is responsible for half of the world's formaldehyde followed by NMVOCs (Stavrakou *et al*., 2008). HCHO is the most common carbonyl present in the ambient air, produced from photochemical reactions and through direct emissions. It is a reactive and volatile compound having lifetime of several hours. Its fate in the troposphere is mainly determined by the photolysis (photons with a wavelength less than 360 nm) and different oxidation radicals such as (OH, NO_3 etc.).

Formaldehyde (HCHO) is an important and highly reactive compound present in the atmosphere, resulting from the oxidation of nutrients and anthropogenic hydrocarbons. Formaldehyde (HCHO) is a key compound in the chemistry of the troposphere.

Differential optical absorption spectroscopy (Platt and Stutz, 2008) has been successfully applied to retrieved column densities of various atmospheric trace gases such as NO_2, HCHO, SO_2, BrO, and CHOCHO (Wittrock, 2004; J. P *et al*., 2004; Wagner, T. *et al.,* 2010).

1.1.2 Tropospheric Chemistry of Formaldehyde

Formaldehyde plays a vital part in tropospheric chemistry, regardless of the fact that formaldehyde has very small lifetime (T ≈ three hours) (Andrson *et al.*, 1996). It can still react with sunlight and many free radicals that are available at that time (Larsen and Larsen, 1998). Due to very short lifetime, the photolysis and its reaction with OH, it is readily removed from the atmosphere (Brune *et al.,* 1999). Formaldehyde having a very brief half-life of about 1.5 hrs is produced as a result of oxidative reactions of volatile compounds present in the atmosphere (Sander *et al.,* 2006). In urban areas the concentration range from 1 to 20 parts per billion and even more higher in the polluted areas (Finlayson-Pitts and Pitts, Jr. 2000).

Mucous membranes stimulation and decreased lung function results from chronic exposure to formaldehyde. Formaldehyde is now categorized as a carcinogen for human beings. (WHO, 1996).

1.2 MAX-DOAS

The device used in the study is MAX-DOAS instrument which is used for measuring the column density of formaldehyde and various other gaseous pollutants including NO_2, SO_2, CHOCHO, BrO and HONO etc. This research primarily focuses on the measurement of formaldehyde slant column density (SCD) and vertical column densities within the cities of Rawalpindi and Islamabad. These measurements are taken by MAX-DOAS (Multi-Axis Differential Optical Absorption Spectroscopy) which is mounted at IESE Atmospheric research lab, Sector H-12, Islamabad and field campaigns were conducted in different region of twin cities including Attock oil refinery, Benazir Bhutto international airport, Faizabad and Pir sohawa valley. Atmospheric parameters and its constituent's determination can be done either narrowly by sampling or widely by means of remote sensing techniques.

Since the discovery of the ozone layer, remote sensing measurements are used for its measurement (e.g., Dobson and Harrison, 1926). Satellites provides us a global view of trace gas distribution and weather conditions. In addition, ground base instruments are used for spectroscopic observations at several places.

MAX-DOAS instrument has been used to analyze concentration of different gasses, inclusive of formaldehyde, sulphur dioxide and CHOCHO (Bobrwski *et al.*, 2003; Wittrock *et al.*, 2004).; Hekel *et al.*, 2005; Sinrech *et al*., 2007; Pikelaya *et al.*, 2007; Theys *et al.*, 2007; and others Cl'mer 2009; Vlemmx *et al.*, 2010, Ir *et al*., 2011; Wagner *et al*., 2011) in various parts of the world.

1.3 Study

Rapid rate of urbanization and continuous increase in emission of vehicular pollution in Pakistan cause severe environmental, health and socio economic loses. This

study focuses primarily on determination of slant column densities of formaldehyde within the Islamabad and Rawalpindi. These measurements were made by using mini-MAX-DOAS and compared with satellite observations.

1.3.1 Study Area:

Islamabad and Rawalpindi are considered as one city. These both towns are located at 15 km from each other and can be regarded as one massive city. These both cities are located around 33° 40N, 73° 10E. The population of twin cities is around 4.5 million (Sheikh *et al.,* 2007). The atmospheric conditions of Islamabad have a characteristic of a subtropical humid climate. Prompt increase in population and urban development has placed a great amount of load on environment causing significant impact (Sheikh *et al.*, 2007).

Fig. 1.1: Google Map of Rawalpindi & Islamabad.

1.4 Significance of the Research:

Pakistan shift from agricultural eras to industrial ones has a dire need to investigate air quality in various regions. Study also captures attention because air quality baseline data is very limited in Pakistan. Further this research may provide guideline to regulatory authorities and air quality monitoring departments. Measuring the air pollution profile in industrial zones minimizes the threats to a certain limit. Data obtained thus can be used for establishing standards for air quality. While working on the Formaldehyde, its concentration and measurements will explore potential sources and areas which will be focused for air pollution prevention.

LITERATURE REVIEW

2.1. Atmospheric Chemistry

The Earth's atmosphere consists of 78% nitrogen, 20% oxygen and a low percentage of argon and other gases. The trace gases comprise less than 1% of the atmosphere. Many existing as residual gases in the atmosphere and may be observed through spectroscopic methods, while these gases absorb and scatter the sunlight. The well-known method to estimate different trace gases in the atmosphere is DOAS.

Chemicals are released into the atmosphere through a variety of sources. Some of these sources includes fossil fuels combustion as the result of human activity and are called anthropogenic. Still others, such as volcanoes, come from non-biogenic natural processes (James, 1999).

The ability of nitrogen to form triple covalent bonds between its atoms requires the total energy of 942 KJ/Mol. Therefore, most of the chemical reactions that occur in the air between the substances involves oxygen and do not occur spontaneously as activation energy is required for these reactions. Therefore, chemical reactions in the atmosphere under normal conditions generally include five radicals (e.g.

, NO, NO_2, OH), having free electron pair, consequently, greater tendency to respond with other molecules. They are extremely variable and their variability depends upon many factors such as sunlight, distance from the source and availability of reactant molecules. Noble gases such as Helium, Argon and Neon are chemically inert and as a result their mixing ratio is steady. In comparison, water vapors have

mixing ratio depending upon local climatic conditions such as humidity which shows a larger variability. Carbon dioxide abundance shows a periodic inconsistency through uptake and sometime released from vegetation but the trend increases due to anthropogenic emissions. Water vapor and CO_2 are considered one of major greenhouse gases and their atmospheric composition is shown in Tab 2.1.

Constituent	Vol. Mixing Ratio
Nitrogen	78.08 %
Oxygen	20.95 %
Argon	0.93%
Carbon Dioxide	0.035 %
Water vapors	0-4 %
Helium	5.5 ppm
Neon	18 ppm
Methane	1.7 ppm

Tab 2.1: Composition of Atmosphere (Waynee, 2000)

Aerosols are solid and liquid particles suspended in the air and have a great influence on characteristics of radiation and transfer capability of atmosphere. For example, condensation of water vapors causes the formation of clouds. Heterogeneous reactions may occur at the particle surface

Transfer of radiation can also be observed through the naked eye, for example, in the case of dust, air mass received relatively less radiations. Aerosols come from natural and artificial sources such as combustion processes (combustion of biomass production), volcanoes, fast remains, windblown dust, splashing and sea.

2.2 Layers of Atmosphere

2.2.1 Troposphere:

It is the lowermost layer of the atmosphere and around seven miles (11 km) dense. Maximum of the clouds and climate originate in the troposphere of atmosphere. Around the poles the troposphere is about 8 km thick and denser in Ecuador (average of about 16 thick). The temperature decreases with height.

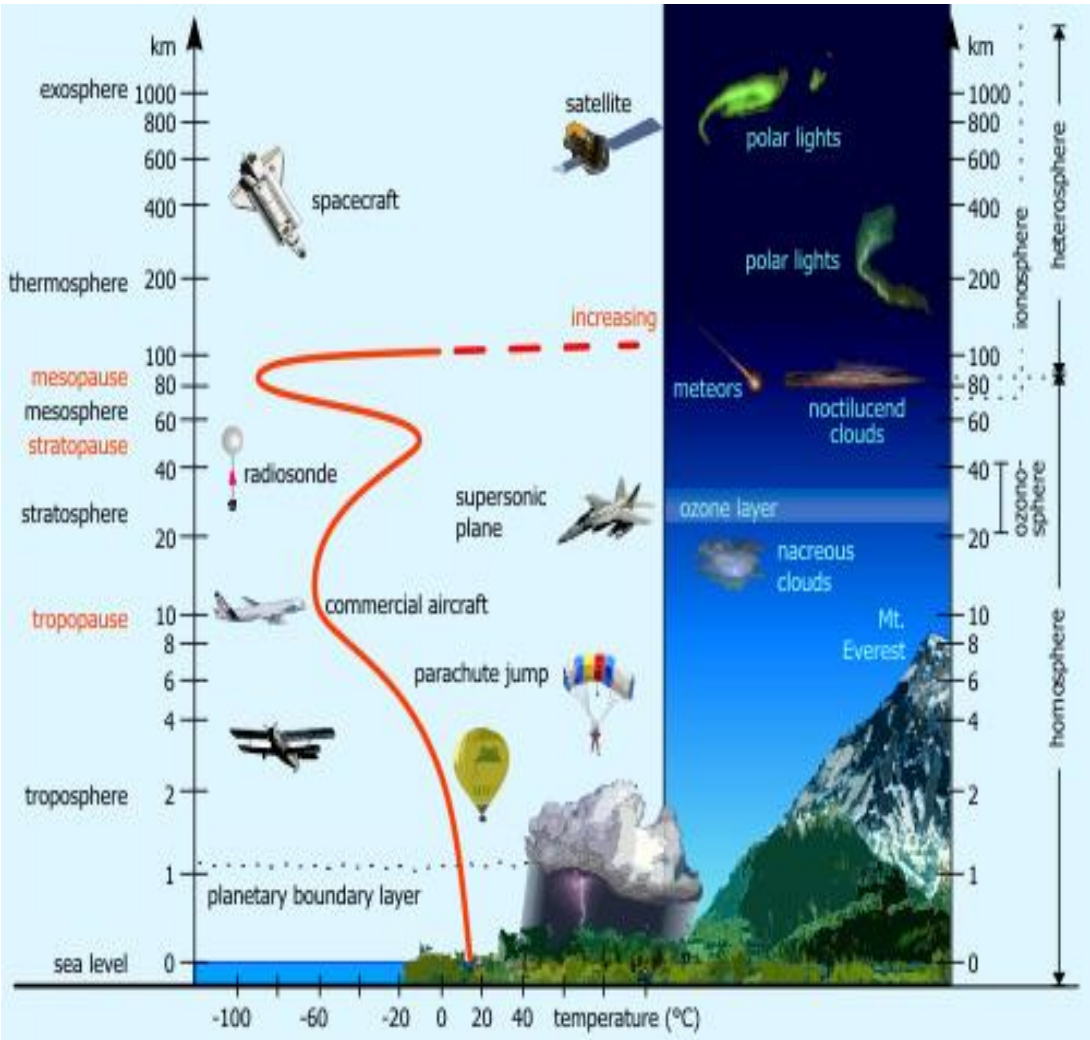

Fig.. 2.1: Atmospheric composition of Earth

2.2.2 Stratosphere: The stratosphere is 7-30 miles (11-48 km) above earth. At this layer the ozone layer is present, which absorbs maximum of the damaging UV radiation coming from sun. The maximum temperature especially for this region is around 33

degrees Celsius. In the stratosphere, there is more heat in upper portion than the lowermost. The lower portion have nearly persistent temperature that increase with altitude, but in the upper part of stratosphere the temperature surges with height due to the absorption of UV-sunlight by ozone molecules. This upsurge in temperature in this layer with altitude is unique if we compare it with tropospheric region

2.2.3 Mesosphere: Layer directly above the stratosphere and below the thermosphere is called mesosphere. It can extend up to ninety kilometer above the earth's surface. Very less is known about this layer of earth surface because balloons and jets cannot fly into this which makes it hard to study and explore.

2.2.4 The Thermosphere: Directly above the mesosphere, layer of earth surface is called thermosphere. It ranges from 90 km to 500 km or 1,000 km, above our planet. High energy UV rays and light photons are broken up in this layer. In upper portion of thermosphere, atomic oxygen and helium are commonly found.

2.2.5 Ionosphere: Ionosphere is the last layer and it is above other layers of the atmosphere, on top of the Earth. These ionized layers affect the transmission and reflection of radio waves.

2.3 Differential Optical Absorption Spectroscopy

Differential Optical Absorption Spectroscopy (DOAS), very sensitive and widely used method aimed at the determination of trace gases in the atmosphere (Perner and Platt, 1979; Platt, 1994). DOAS was used to measure column densities of many trace gas, for example, OH, HONO, NO_3, CHOCHO (Perner *et al.,* 1976, Platt *et al.,* 1980, Volkamer *et al.,* 2005) and in the troposphere by Haussmann and Platt 1994. Numerous other residual gases, absorbing in the visible and UV wavelength ranges can be detected, for example, NO_2, ClO, O_3, SO_2, HCHO, OClO, H_2O, and NH_3 (Perner *et al.,* 1976, Platt *et al.,* 1980). More recently, CH_4 can be measured in the near infrared region of wavelengths from the satellite (Frankenberg *et al.,* 2005) and ground observations (Woyde, 2007).

DOAS based on the absorption of light passing the gas volume and attenuated characteristically for each trace gas in this volume. From the spectral location of the absorbing lines and their strengths, trace gases can be identified and quantified. MAX-

DOAS can also detect very active forms, such as free radicals OH, NO_3, NO_2 and halogen oxides (Vlemmx *et al.,* 2010). Furthermore, MAX-DOAS capable of measuring simultaneously several gas mixtures, reducing the measurement time and allows analysis of various chemical components in the observed air mass.

Typically, DOAS may be performed actively using artificial light sources, as well as passive natural light sources, which is most frequently the sun because of its high intensity as compared with the moon. Passive DOAS can be divided into scattered light measurement, pointing off into the sky, and direct light measurements which point directly at the sun or the moon.

2.3.1 DOAS Technique:

DOAS is widely used method of spectroscopic studies of atmospheric comparisons. This method is dependent on different wavelengths. Using DOAS method, trace gasses are determined by absorption capacities in the UV/visible cross section of suitable molecules which include formaldehyde, ozone, Sulphur dioxide and nitrogen dioxide.

The main principle Lambert-Beer law states that attenuation of electromagnetic radiation is directly related to the no. of absorbing molecules in that optical path.

$$I(\lambda) = I_o(\lambda)\, e - \alpha LC \qquad \text{(Equation 2.1)}$$

"Io" refers as incident flux and "I" as measured flow. The occurrence of numerous gases and processes such as scattering processes (Raman, Rayleigh and Mie) and aerosols limits the application of Lambert-Beer law. DOAS technique used to overcome such limitations partially or entirely. The demonstration of DOAS principle is shown in Fig.. 1 (Platt, 1994).

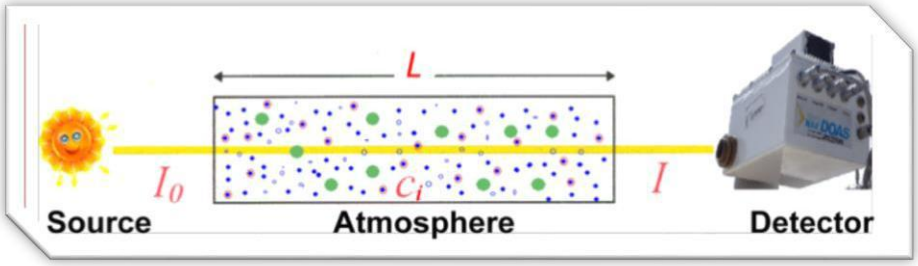

Fig. 2.2: Demonstration of DOAS principle

By accounting the scattering procedures, the DOAS equation develops (V.V Rozanov, 2010):

$$I(\lambda) = I_0(\lambda)\cdot\exp\left(-\int_0^L\left(\varepsilon_R(\lambda,l)+\varepsilon_M(\lambda,l)+\sum_i\sigma_i(\lambda,p,T)\cdot c_i(l)\right)dl\right) \quad \text{(Equation 2.2)}$$

$I(\lambda)$:	light intensity after passing through the atmosphere
$I_0(\lambda)$:	intensity of the light source
λ:	wavelength
$\varepsilon_R(\lambda, l)$:	Rayleigh scattering coefficient
$\varepsilon_M(\lambda, l)$:	Mie scattering coefficient

Broadband absorption due to this scattering and spreading process cannot be readily measured; however DOAS technique splits absorbable trace gas section in two main portions (A.V Rozanov, 2010).

$$\sigma(\lambda) = \sigma_b(\lambda) + \sigma'(\lambda) \quad \text{(Equation 2.3)}$$

$\sigma_i(\lambda, p, T)$:	absorption cross-section of the absorber
$c_i(l)$:	i concentration of the absorber i
p:	pressure
T:	temperature
L:	total light path length

σb symbolizes broadband spreading, absorption and scattering, although σ ', Beer-Lambert law can be presented as follows:

$$I(\lambda) = I_0(\lambda)\cdot\exp\left(-\int_0^L\left(\varepsilon_R(\lambda,l)+\varepsilon_M(\lambda,l)+\sum_i\sigma_{b,i}(\lambda)\cdot c_i(l)\right)dl\right)$$

$$\cdot\exp\left(-\int_0^L\left(\sum_i\sigma_i'(\lambda)\cdot c_i(l)\right)dl\right)$$

(Equation 2.4)

Eq.2.2 is formerly combined with preliminary intensity of light *I0* processing with the main differential intensity of baseline *I0* (V.V Rozanov, 2010):

$$I_0' = I_0(\lambda)\cdot\exp\left(-\int_0^L\left(\varepsilon_R(\lambda,l)+\varepsilon_M(\lambda,l)+\sum_i\sigma_{b,i}(\lambda)\cdot c_i(l)\right)dl\right)$$

(Equation 2.5)

Currently, Beer-Lambert Law can be articulated in the form of this formula.

$$\tau'(\lambda) = \ln\left(\frac{I_0'(\lambda)}{I(\lambda)}\right) = \int_0^L\left(\sum_i\sigma_i'(\lambda)\cdot c_i(l)\right)dl$$

$\tau'(\lambda)$ is referred to as the differential optical density, and can be considered the result of a DOAS measurement.

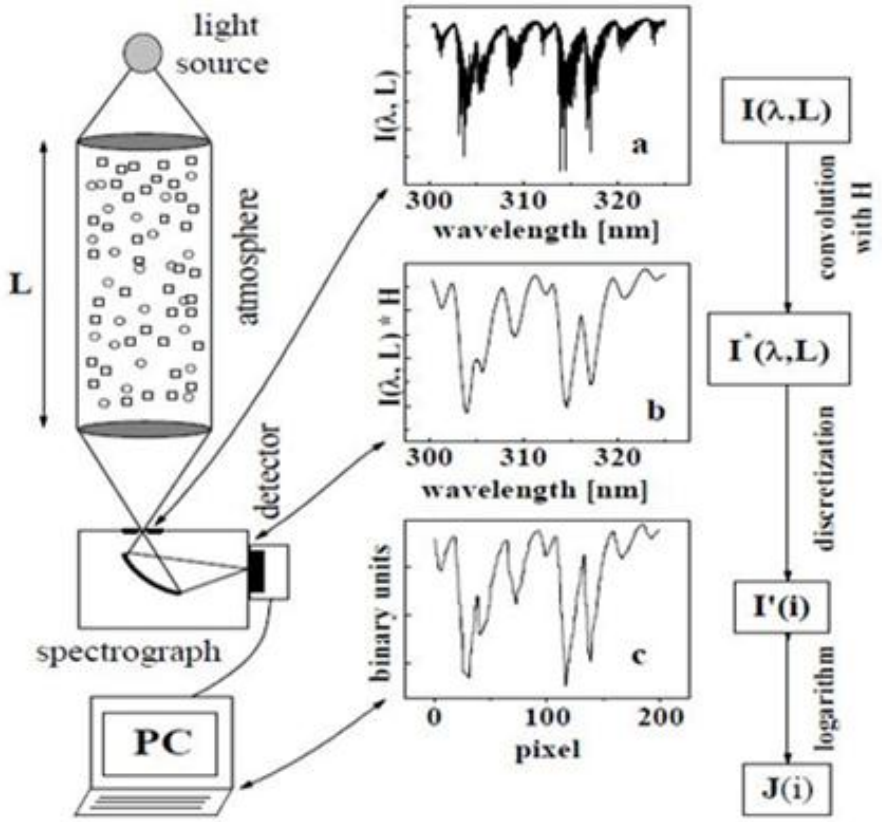

Fig 2.3 The components of a simplified DOAS setup. (a) shows the respective spectrum with the absorption structure of formaldehyde. In (b) the light was convolved by the spectrograph and (c) shows the mapping by the detector. Afterwards the spectrum consisting of discrete pixels is stored in a connected PC (Stutz and Platt, 1996)

2.4 Formaldehyde Sources:

Formaldehyde (HCHO) is also released from many sources into atmosphere due to combustion of fossil fuels (Olvier *et al.*, 2003), forest fire and vegetation (Andrea, 2001). HCHO can be considered precursor of many other substitutes like NMVOC by their photochemical activity and releases. Therefore, chemically decompositions of VOCs and many methane compounds are also considered as the main and important sources of formaldehyde in air. Oxidations of many different VOCs volatile organic compounds also generate HCHO. These are the main reason that the urban areas with high population shows formaldehyde 1 to 20 parts per billion and even in some places with more contaminations and have high concentrations (Finlayson-Pitts and Pitts, Jr. 2000).

2.4.1 Naturals Sources

Hydrocarbon oxidation and breakdown in the troposphere of the atmosphere cause formaldehyde and methane is the main culprit hydrocarbon which gives HCHO when breaks and other sources from which formaldehyde is produced in the air is production and released of isoprene from vegetation and plants. Many other sources (directly and indirectly) include many industrial manufacturing activities, combustion and burning of fossil fuels. Natural sources from which formaldehyde is produced is isoperne and emitted from vegetation. Due to this emission of isoprene rural areas have history of HCHO in the air and formaldehyde released in air.

The other sources in addition are the oxidation and combustion of Methane ($CH_{4)}$, which is a precursor to HCHO. The lifespan in the air is around 9 to 10 years so it is present abundantly in the air. Methane is present at around 15 to 20 km in troposphere (Finlayson-Pitts and Pitts, Jr. 2000).

2.4.2 Anthropogenic sources

Many other indirect sources from which formaldehyde is produced or come into the troposphere are the products of formaldehyde, which produce formaldehyde as wood, chipboard, insulation materials, adhesives, resins. Some other minor sources include cooking, and cigarette smoking. Concentration of HCHO varies from rural to urban areas in troposphere. In rural areas it may vary from 1 ppbc to 20 ppbv (Galloway *et al*., 2011a; Choi *et al.*, 2010; Muller *et al.*, 2006) and in municipal areas with high population and contamination its value is 45 ppbv (Dasgupta *et al*., 2005).

2.5 Significance and its challenges

Measurement of HCHO is a serious problem. Infect the value and concentration of HCHO is present in the air in very less amount or even in trace amount so it is very difficult and hard to measure HCHO accurately. To measure and detect HCHO in its proper form we must have very sophisticated and latest equipment. As oxidation of different VOCs cause many other trace gasses so to measure HCHO in its direct form is also very difficult and challenging.

2.6 Formaldehyde in air

Formaldehyde in air is present in a very common and most abundant form which is known as aldehydes. Natural formaldehyde mean concentration Is approximately <1 ppm (Weber *et al.,* 1977).

In rural or remote areas photo oxidation of hydrocarbon are the cause of formaldehyde (EC, 2001). Formaldehyde, which is existing in the room, is varied from 0.02 to 0.06 mg/m^3, while in house, formaldehyde is produced mainly from construction materials and some other materials like chipboards and insulators (IARC, 1995). Pervious students reported that this level is decreasing specially in household areas or in indoor environments because of changes in the types of construction materials that are used nowadays (IARC, 1995).

Certain natural and industrial sources are responsible for the production of formaldehyde in the atmosphere. Naturally formaldehyde obtained under reactive oxidation of many hydrocarbons, which counters with hydroxyl radicals and ozone with the formation of aldehydes including formaldehyde. Formaldehyde concentration in an urban atmosphere differs from 1-20 mg / m^3 (IARC, 1995; WHO, 1989).

HCHO is emitted mostly from vehicular exhaust in cities. Partial combustion of hydrocarbon fuels from automobiles can result in HCHO in urban areas. Formaldehyde concentration in urban areas during extreme traffic can reach up to a level of 100 mg / m^3 (WHO, 1989).

In 1997, Gaffney and his coworkers concluded that the use of oxygen-containing fuel in winter time in urban areas increases the formaldehyde emissions. During 1994, 13% increase within 2 months of the formaldehyde emission of the vehicle was found, because the oxygen content of fuel sold in the San Francisco area has increased by a few percent weights (Kirchstett *et al*., 1996). Photochemical formaldehyde production played a crucial role in contributing to a HCHO concentration and dominated the automobiles emissions emitted directly in Los Angeles (Grosjean & Wright, 1983).

2.7 Exposure of formaldehyde (HCHO) and its effects on health

The irritation of the nasal mucosa, upper respiratory tract and oral cavity are due to severe inhalation exposure of HCHO. This may cause annoyance, nausea, weakness, shortness of breath, pneumonia, coughing, pulmonic edema and coma. Its corrosive nature can cause skin blisters and eyes and nose irritation.

Mucous membranes irritation and retardation in respiratory system is related to prolonged HCHO exposure. Further, it is also categorized as a human carcinogen compound.

Significant adverse effects are observed in inhalation, irritation of ENT, respiratory system, chest pain and damage to nasal cavities.

Mucous membrane burning is caused by acute inhalation and the upper respirational tract (IPCS 1989). Main effects related to health are central nervous system deterioration, coma, convulsions, trachea and bronchi (IPCS 2004). Respiratory failure occurring due to great amounts HCHO can be fatal as well (NCB, 2002). It is also categorized as a carcinogen by the B1 group (causes tumor) and by power of US Environmental Protection 1998 and as 2A group carcinogen (WHO, 1996).

2.7.1 Carcinogenic Nature of Formaldehyde

HCHO is stated as human carcinogenic compound according to some conclusions. At the professional level of exposure it can cause nose cancer. Numerous researches have provided ample evidence of inhalation of formaldehyde causing cancer in animals (ATSDR, 1999).

It is classified as genotoxic compound as it can cause the formation of DNA adducts. Further, it can divide cells, leading to tumors in human body.

2.7.2 WHO guidelines and standards for formaldehyde

The main objective to establish guidelines are linked with human health protection. So a standard limit is given in order to protect those individuals who have already less immunity and show more vulnerability to toxic chemicals. These toxic chemicals are inhaled due to increased pollutant exposure in atmosphere (OECD, 2002; EC, 2001).

According to World Health Organization the amount of ambient HCHO of air should be at a level of 100 ug/m^3, 30 minutes exposure on average for overall protection. According to another recommendation its concentration should not exceed than 10 g/m^3 retaining at a minimum time (WHO, 2009).

2.8 HCHO studies by MAX DOAS

Pinardi *et al.,* (2013) presented the results of a comparative measurement of formaldehyde columns (HCHO) retrieved form that UV spectra of scattered sunlight were recorded by using MAX-DOAS at different angles of elevation in 2009.

Jeranu *et al.,* (2012) stated that CNG is an expensive and native energy resource and being used for most vehicles. Extensive CNG use in Dhaka largely dependent atmospheric composition for the continuous observation of the residual gases, such as ozone, sulfur dioxide, carbon monoxide, oxides of nitrogen and volatile organic compounds.

Lee *et al.,* (2008) measured the MAX-DOAS values and measurements of instrument showed high proportions between HCHO and CHOCHO which agrees to the high reactivity of the VOCs.

Hackel *et al.,* (2002) studied on Formaldehyde measurement of using the MAX-DOAS Poland over a valley in Italy. Slant column densities of HCHO and O_4 were received. The results ensured that these measurements can provide column information of troposphere including some personal information about HCHO in polluted areas with simple and automatic tool.

Constantin *et al.,* (2011) studied in July and August 2011 the measurement of nitrogen dioxide in the southeastern part of Romania. The experiment focused on areas with strong potential emissions of nitrogen dioxide, as these industrial zones or roads with heavy traffic. During the experiment, it was found out that the amount of nitrogen dioxide is very high, mainly because of steel and iron industry from urban areas, the excessive traffic in cities and areas around the cities.

Wagner *et al.,* (2010) studied MAX-DOAS monitoring via drive from areas (Brussels to Heidelberg) in September 2006 and tropospheric NO_2 distribution VCDs were obtained by driving route with a spatial resolution of about 1 km. Three elevation

angles (22°, 40°, and 90°) were used for the spectral measurement. All three elevations showed the sequence to extract NO_2 VCD, indicating that the method is an appropriate geometric approximation and the satellite inspection is subgrade.

The observations were made which showed that comparing with the MLA satellite observation gives a very justified agreement that satellite observations ranging from 25% to 100% more than the observations of MAX-DOAS instrument.

Chapter 3

Materials & Methods

3.1 Mini MAX-DOAS Instrument:

This instrument is a completely automated, light weighted spectrometer having size of (13 cm × 19 cm × 14 cm) and used for the spectral analysis of dispersed sunlight (Bobrwski *et al.,* 2003). It comprises of an aluminum box with entrance optics, fiber spectrograph in combination and control electronic system. It is driven by stepper motor by increasing the viewing angle. The Max-DOAS stepper motor installed on outer side of the box that rotates the entire instrument. Input optics consisting of quartz lens with a focal length of 40 mm in conjunction with quartz bundle, send the gathered sunlight to a spectrograph. Scattered light is crossed by Czeny-Turnr spectrometer (USB2000+, Ocean Optics In.) with 0.7 nm spectral resolution lying in the range of 320-465 nm. One-dimensional CCD (2048 individual pixels, Sony ILX511) is used to detect and measurements were monitored with a laptop using DOAS intelligent system and (DOASIS) software (Krauss, 2006).

Fig. 3.1: Mini MAX-DOAS

3.2 Research Route Map:

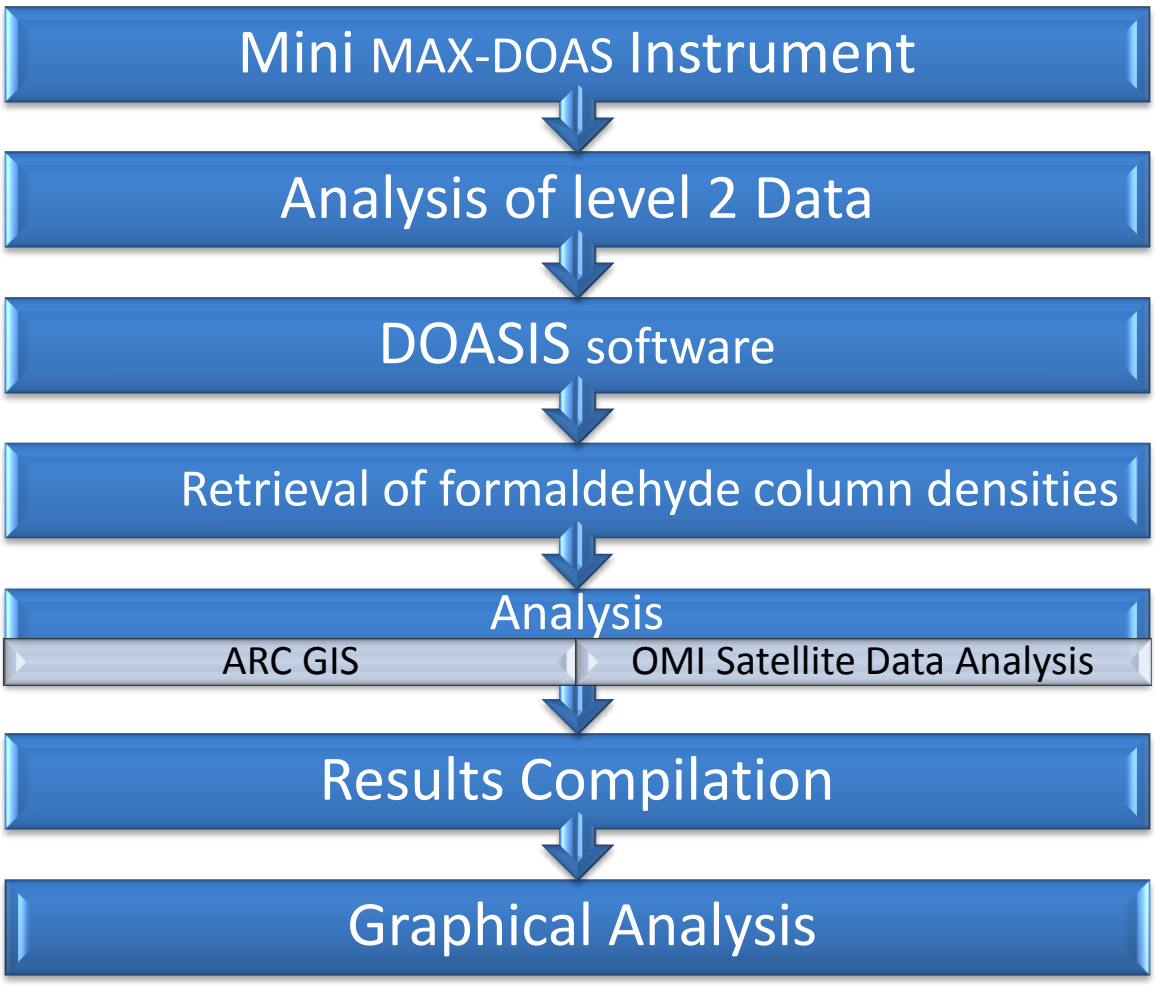

Fig. 3.2: Flowsheet diagram of MAXDOAS process

Mini MAXDOAS instrument is completely automated, light weighted spectrometer and used for spectral analysis of the dispersed sunlight. This MAX-DOAS instrument helps to collect raw data and then analyze through DOASIS software. DOASIS is Differential Optical Absorption Spectroscopy Intelligence System. The System is used to

run the instrument Max-DOAS by recording the measured spectra. DOASIS help to retrieval of formaldehyde slant column densities which are converted into Vertical column densities. The window chosen for analysis of HCHO wave was of wavelength 323.5-355 nm. Then through MS Excel calculations and formulas were put that helped to analyze our final results then these results were presented in maps through help of ARC-GIS software. Results were sent to Germany for verifications and finally compiled and then shown in the form of graphs, tables and maps.

3.3 Differential Optical Absorption Spectroscopy Intelligence System (DOASIS)

DOASIS is the System that used to operate instrument mini MAX-DOAS by getting the measured spectra, as presented in the fig. 3.3. Having the numerous functions, it controls the motor, helps to integrate the time resolution spectrum and spectrometer temperature. It is also used to calculate the spectrum ring, which is used in the analysis data.

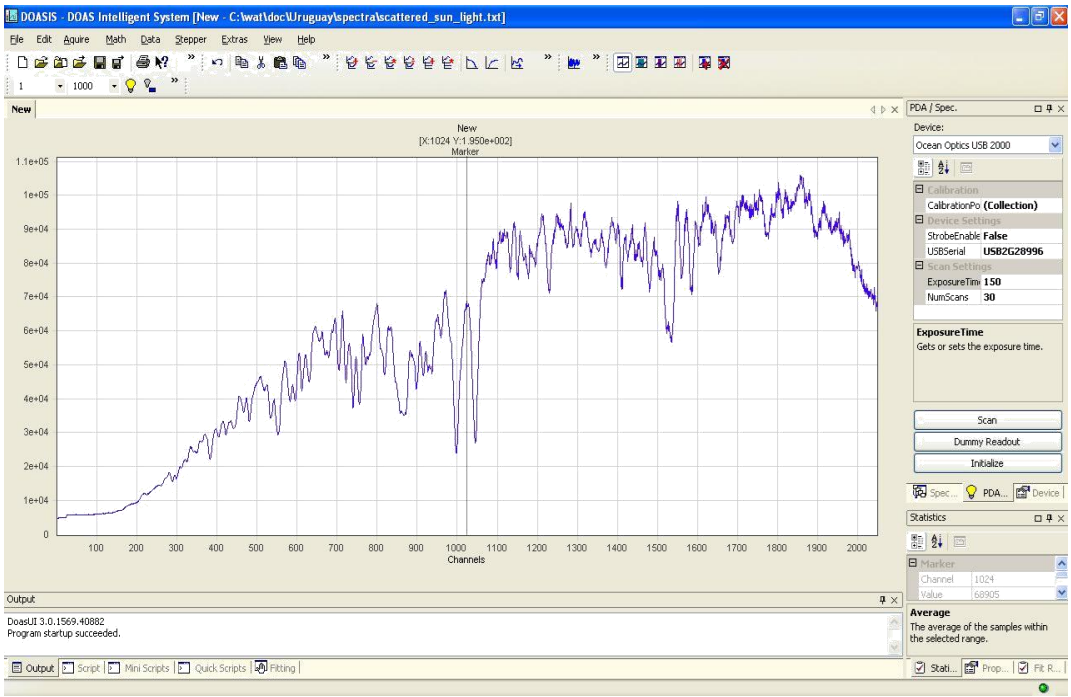

Fig.. 3.3: Measured Spectra by DOASIS

DOASIS is also designed to quantify the dark current and offset. Offset is the extensive range of the spectrometer in the dark. Offset spectra is analyzed by using small integration time per scan, for example, three milliseconds, and wide scanning such as 1000. While the dark current is comparatively small electric current flowing through the light sensitive devices such as a spectrometer. For its spectrum, modest integration time per scan, for example, 10,000 milliseconds and a small amount of the scan, for example 1, is used.

The window chosen for analysis of HCHO was 323.5-355 nm. For absorption cross-section trace gas were used; HCHO 298° K (Muller, 2000) Nitrogen dioxide at 294° K (VANDAELE *et al.*, 1996), ozone 223° K, 243 ° K (Bohumil *et al.*, 2003) oxozone in (Burkhdar), with a reference spectrum of the Fraunhofer (highly resolved solar spectrum) (Kurucz et al, 2010) and spectrum of the ring.

DOASIS Spectrum and fifth-order polynomial was involved in the spectral fitting procedure by using the software WinDOAS (Veit and van Roozendael, 2001).

For analysis of HCHO Win DOAS following steps were taken:

- Calibration Wavelength
- Convolution Wavelength
- Formaldehyde Analysis window

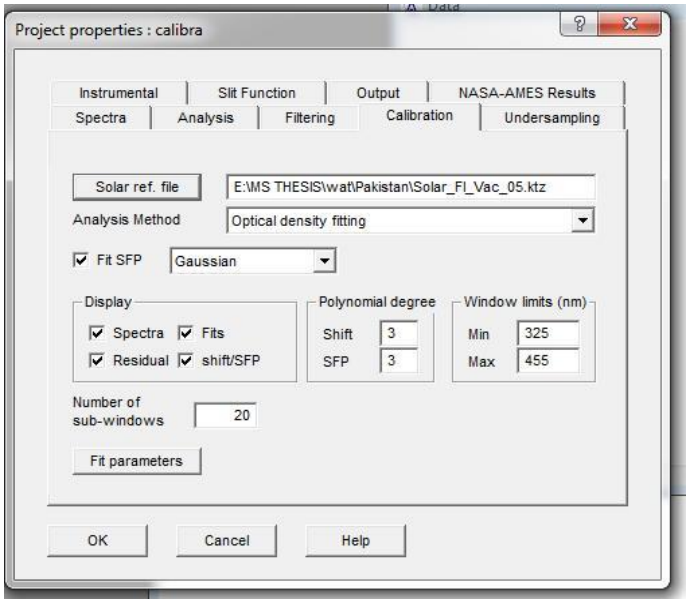

Fig. 3.4: Formaldehyde Calibration Window (WinDOAS)

This process of calibration was repeated again and again to reduce the residual fit error for the calibration. All calibrated spectra were measure within a selected wavelength.

3.3.2 Wavelength convolutions:

Wavelength convolution is a simple mathematical tool and it is important for wavelength calibration process. Different trace gas cross sections used for convolution were e.g. HCHO at 298° K (Mellr 2000) NO_2 at 294 ° K (Vandele *et al.*, 1996), O_3 at 223 ° K, 243 ° K (Boguml *et al.*, 2003), O_4 at (Bukhdr). Gaussan shape slit function was used in the window and analyzed at 355nm. FWHM of 0.5 nm was chosen, for this purpose as (SFP).

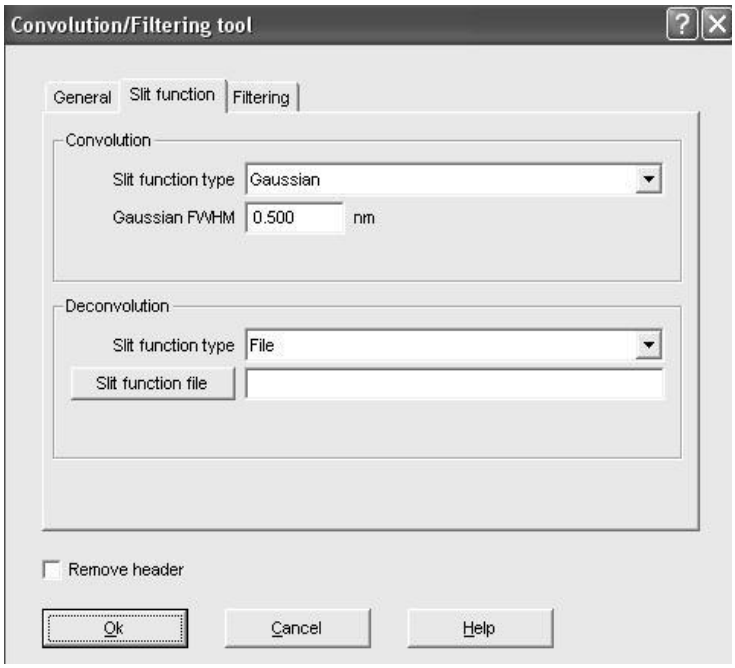

Fig. 3.5: Convolution Window (WinDoas)

3.3.3. HCHO analysis window:

Window HCHO analysis was selected at range from 323.5 nm to 355 nm (Wagner et al., 2010). This wavelength range is based on the smallest possible residual (error FIT). The calibrated spectrum was used as a reference spectrum for the analysis window. The polynomial order of 5 degrees was used for our window HCHO fitting analysis. In the

end, the path of the output file was given WinDOAS. Analysis is «RUN» for all measured spectra and HCHO DSCDs are obtained in the ASCII file.

A specimen of HCHO DOAS fit present underneath there in the picture:

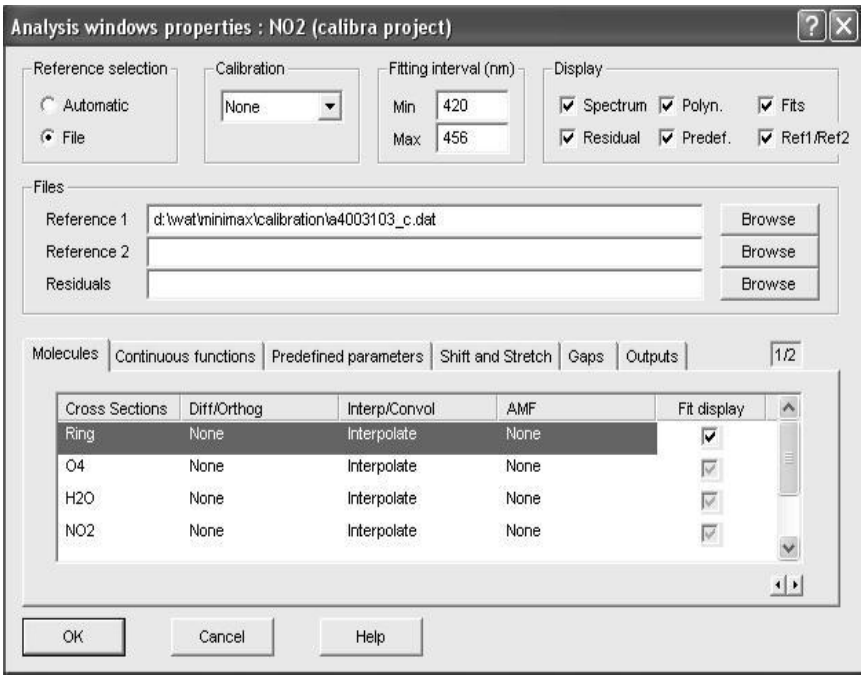

Fig.. 3.6: formaldehyde Analysis Windows of HCHO

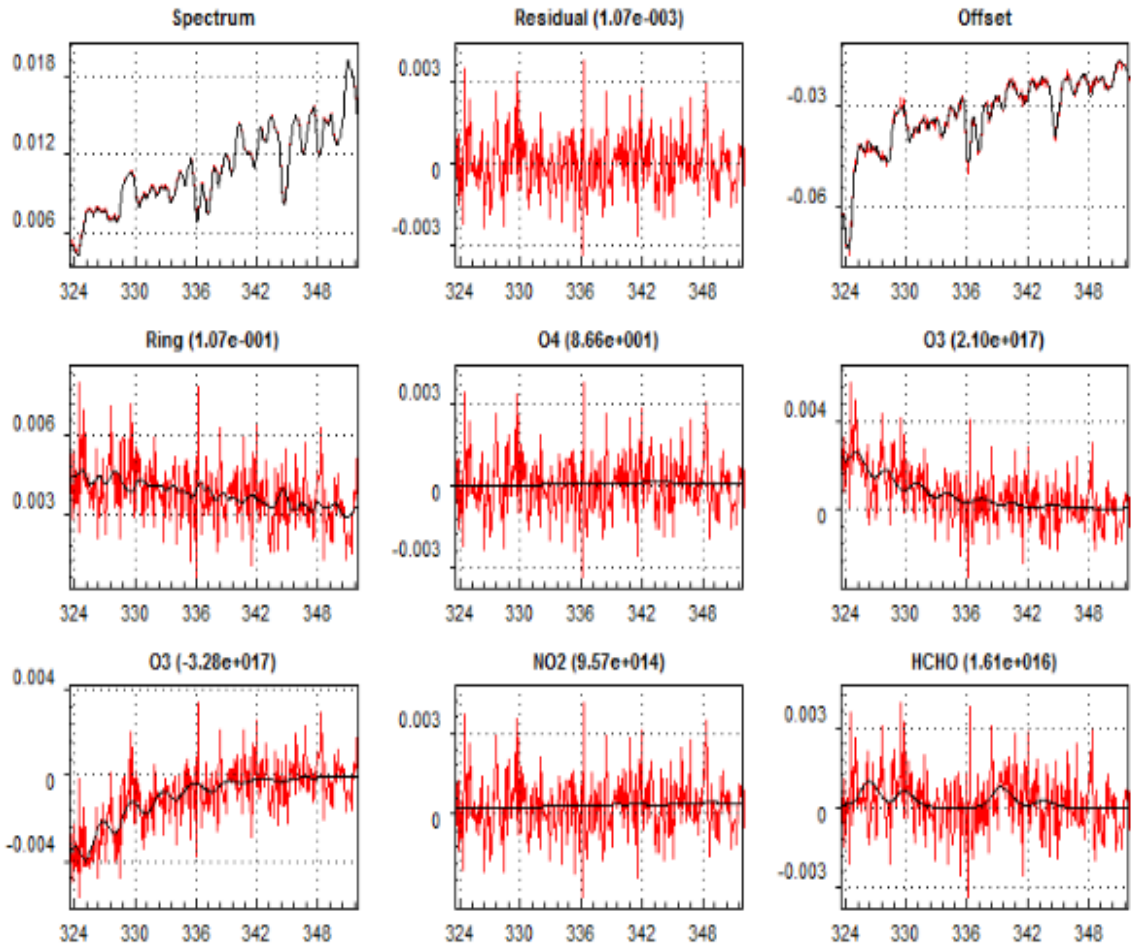

Fig. 3.7 Win-DOAS study presenting DOAS fit on a cloudless day

This Fig.. represents reference spectrum (red lines) and Formaldehyde values which is approximately 1.61×10^{16} (shown as black). The formaldehyde residual (fit error) which shows some uncertainty is lower than 0.3% (3 per mill). Formaldehyde residual SCDs can be kept in text type file as (.ascii) file with all additional parameters i.e date, time, SZA and elevation angles etc. as exhibited in fig. 3.7.

Analyzed formaldehyde measurements and results can be open in MS execl by using WinDOAS software as:

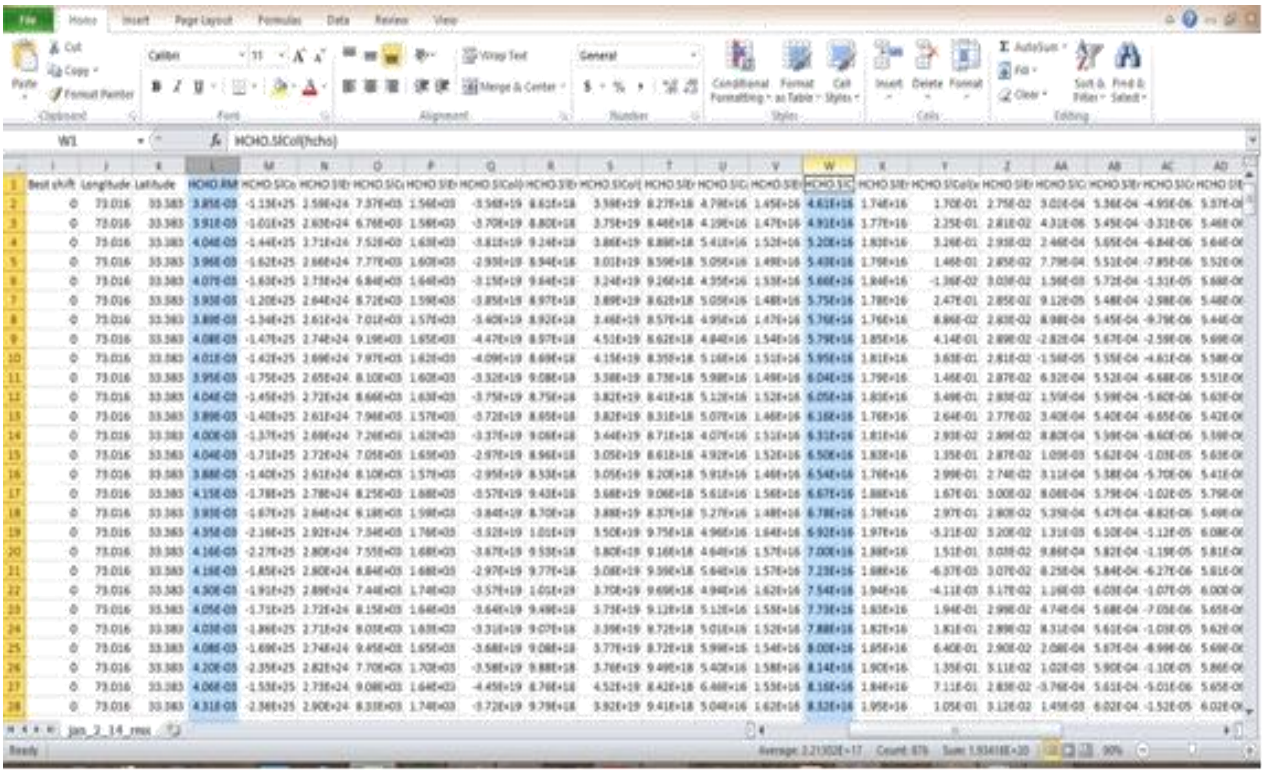

Fig. 3.8 MS Excel Windows presenting formaldehyde (DSCD) values and HCHO Root Mean Squares (RMS)

3.4 Excel Analysis

Excel analysis is used for processing and analyzing the raw data. SCDs are converted to VCDs through different formulas in excel and maps are made which are final graphical representation of results. Air mass is calculated through excel analysis which is the ratio between the actual/real path length for the solar radiation through atmosphere and vertical path length through atmosphere is air mass factor (AMF) which is a totally dimensionless quantity.

3.5. Estimation of the tropospheric VCD

Measured DSCDs are converted into Vertical column densities with the help of differential Air mas factor (DAMF). Differential Air mas factor (DAMF) may be defined as difference of air mas factor when angle of viewing is $\alpha \neq 90$ or $\alpha = 90^{o}$. The air mas factor for off-axis view and also for zenith can be anticipated as 1/sin α and 1 respectively (Li et al, 2013). Hence any trace gas tropospheric VCDs also be written as

$$VCD_{geo} = DCSD\ (\alpha) / DAMF\ (\alpha) \rightarrow (1)$$

$$VCD_{geo} = DCSD\ (\alpha) / (1/\sin\alpha)\text{-}1 \rightarrow (2)$$

Where "α" is the elevation angle of the telescope.

3.6 Software used for Research Work

Table 3.1: Software used their importance in research

Sr. No.	Software	Purpose
1.	Differential Optical Absorption Spectroscopy Intelligent System (DOASIS)	Operating Software for MAX-DOAS and measurement of back scatter intensities
2.	Windows Differential Optical	Analysis of UV-Visible
3.	Absorption Spectroscopy (WinDOAS)	Spectra by DOAS to retrieve DSCDs
4.	Microsoft Excel	Mathematical Calculations for tropospheric VCD extraction and Graphical representations
5.	ENVI 5.0	Geospatial analysis and spectral image processing
6.	Arc Geographic Information System (ArcGIS)	Interpolation of OMI Data and Validation of MAX-DOAS data with satellite observations

3.7 Formaldehyde Satellite Monitoring/Measurements

Tropospheric formaldehyde vertical column densities (VCDs) from Ozone monitoring instrument (OMI- Boerma *et al.,* 2007) was used to compare with ground based measuring instrument mini MAX-DOAS observations which was suited at IESE--NUST. Ozone monitoring instrument (OMI) from National Aeronautics and Space Administration (NASA) and Earth Observation Satellite (AURA) was in space since 2004.

Earth observation satellite Aura's local (Pakistan) equator passage time is between around 13:40 pm to 13:50 pm. The spatial resolution of this satellite is 24×13 km^2, and can increases to 68×14 km^2 on swath edges. In this research, Ozone monitoring instrument (OMI) was used to get Formaldehyde tropospheric vertical column densities (VCDs) level-2 product data from National Aeronautics and Space Administration (NASA) Goddard Earth Sciences Data and Information Service Center (GES DISC). Details of ozone monitoring instrument (OMI) was taken from Levelt *et al.,* 2006 and Boersma *et al.,* 2007.

Instruments	OMI
Platform	AURA
Measurement Period	2004-Present
Equator Crossing Time	1:45 pm
Spatial Resolution (km2)	24×13
Spectral Resolution (nm)	0.5
Spectral Region	UV-Vis
Global Coverage	1 day
Grid Size	0.25×0.25

Table 3.2: Instrument specification (OMI)

RESULTS & DISCUSSIONS

4.1 Temporal Analysis of Formaldehyde

Tropospheric Formaldehyde vertical column densities (VCDs) were retrieved and analyzed from March 2014 till July 2015. Increase in Formaldehyde concentration was observed in summer season when Volatile organic emissions are high due to high biogenic emissions. Methane plays a key role in increasing formaldehyde concentration when its reach with hydroxyl radical (OH) and used in automobiles. So in this fig. 4.1 we can clearly see an increasing trend of formaldehyde concentration during summer and decrease in formaldehyde during winter season.

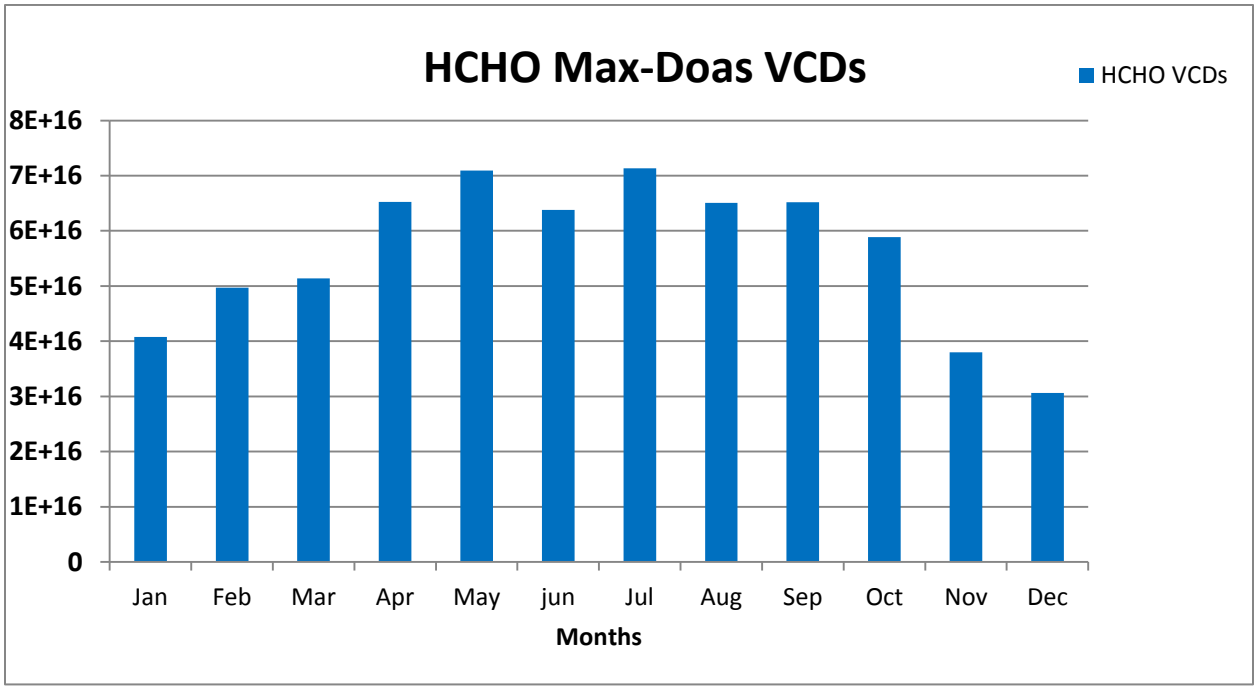

Fig. 4.1: Seasonal variation of tropospheric mean HCHO Columns molecules/cm^2 from 2014-2015 measured from MAX- DOAS

4.2 Mixing Ratios:

Formula can be applied to convert formaldehyde Vertical Colum densities to mixing ratios present in ambient air. Most of time formaldehyde is expected to found near to the emission sources and also ground surface. Supposing that formaldehyde is restrained in a box profile, of 500m. The measured formaldehyde VCDs was changed to number density with dividing it with above presumed vertical height:

Formaldehyde No. Density (molecules/cm^3) = formaldehyde VCD (molecules/cm^2)/3000 cm

From here observed Formaldehyde no. densities are then converted into the mixing ratios with the help of following:

Formaldehyde mixing ratio (ppbv) = Formaldehyde Number densities (molecules/cm^3) /2.503×10^{10} (molecules/cm^3)

4.3. Diurnal Profile of Formaldehyde

Fig.. 4.2 shows the average diurnal profile of HCHO over the study site for the time period March 2014 to May 2015.

Formaldehyde column densities exhibits higher column densities during noon, as the hydrocarbon level increases in the morning and then decreases as the compounds are oxidized to form PAN's and other species (Andrea, 2001). As an air mass moves toward an urban center, it picks up NO, and hydrocarbons. Within a time scale of an hour, OH· begins to degrade hydrocarbons (Peter *et al.,* 2013). The increase in concentration is also attributed to rush hours and traffic

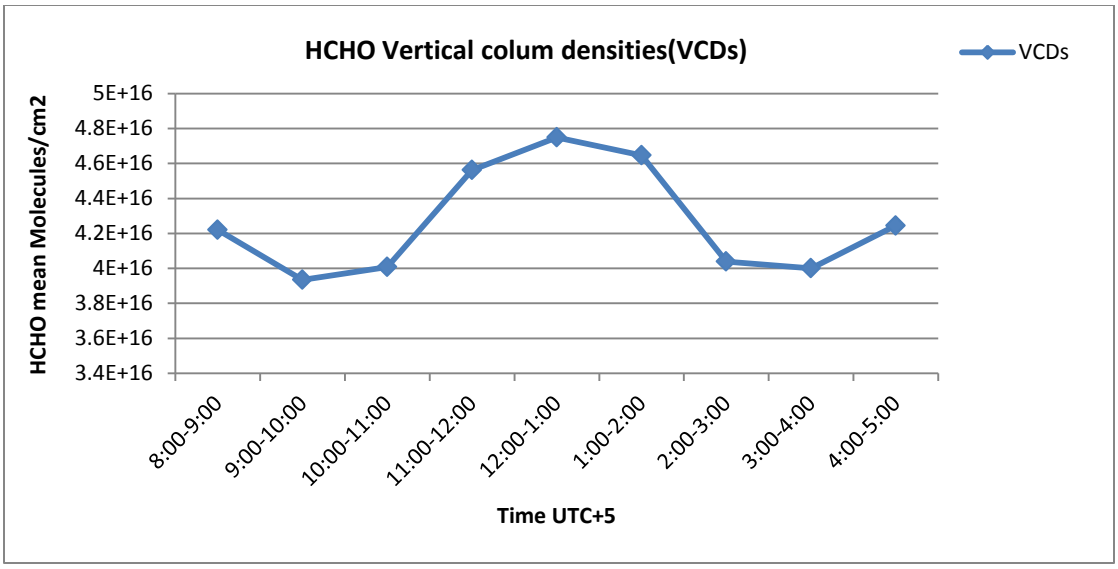

Fig. 4.2: Diurnal Cycle of HCHO molecules/cm^2 from March 2014-July 2015

4.4 CNG availability and Formaldehyde

Compressed natural Gass (CNG) is primarillary methane. Oxidation and burning of methane cause increase in formaldehyde concentration in the atmosphere mainly thoes provinces of Pakistan wherever CNG usage is in greater extent..

It is estimated that Pakistan is world's largest users of CNG in 2010. Now in 99 cities and towns, they are around 3000 CNG stations.

A heave in the amount of CNG-fuelled vehicles intensified the use of Compressed Natural Gas (CNG) that cause a shortage in Pakistan especially in winter season. During last 5 years or more around 80% of vehicles have CNG cylinders. CNG burning and consumption has amplified in Pakistan. The noteworthy increase is demonstrated in (Fig.. 4.3).

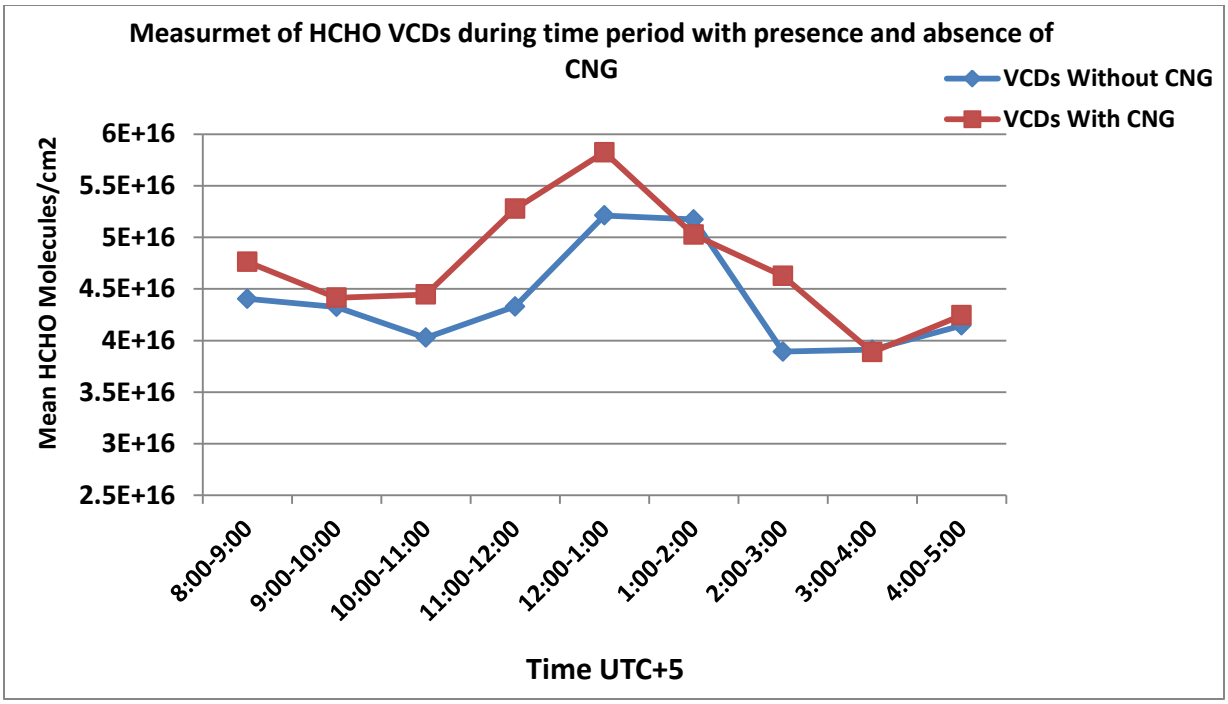

Fig. 4.3: HCHO VCDs With & without CNG availability during the Time period of March 2014-July2015

As stated earlier, oxidation of methane is one of the major sources of formaldehyde production in troposphere. In this research, we tried to find a co-relation between availability of CNG and concentration of Formaldehyde over the study area. CNG was accessible to cars & vehicles throughout first three days of the week, (Monday, Tuesday & Wednesday). Fig.. 4.4, shows the bar chart that CNG was available throughout first three days, Monday, Tuesday & Wednesday and we get the maximum concentration of formaldehyde on these three particular days. On very next day, Thursday the concentration of formaldehyde start decreasing which attributes to short life time. No doubt there are many other sources of formaldehyde in troposphere but here we just try to make a link with CNG as methane is major producer of formaldehyde production.

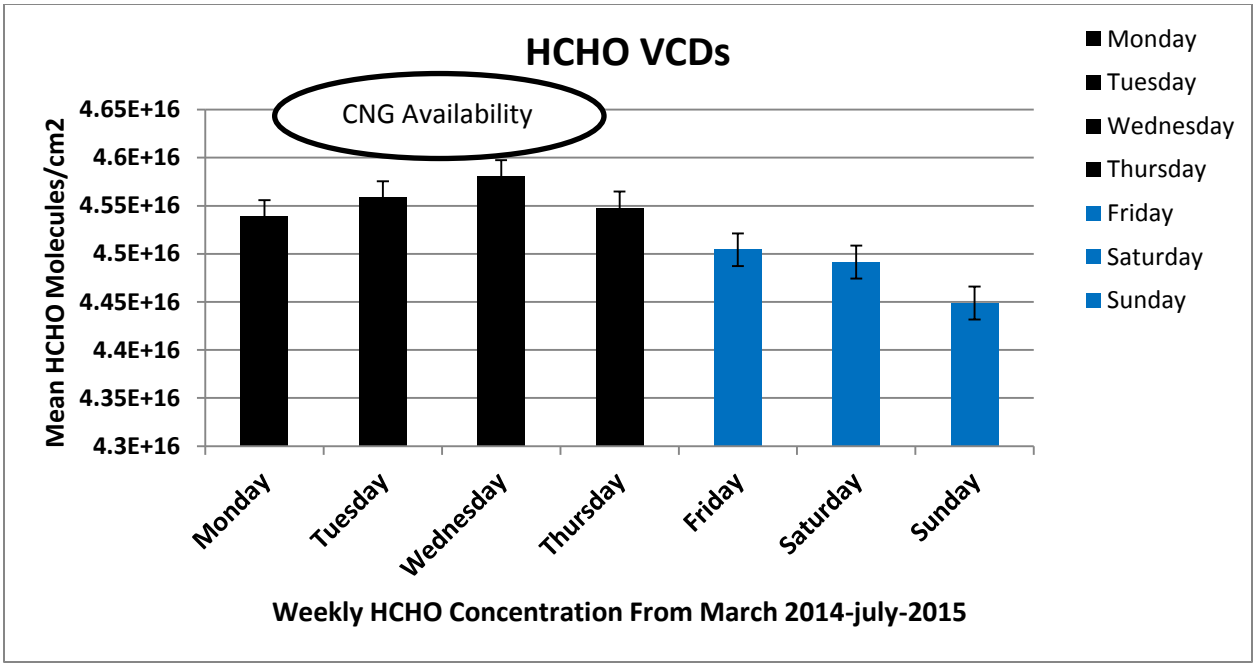

Fig. 4.4: Linkage between CNG availability and Weekly HCHO Concentration

4.5 Field Campaigns

Several field campaigns were conducted by using Car MAX-DOAS instrument. Population explosion and vehicular pollution cause increase in formaldehyde concentration (Alexander *et al.*, 2014). In Fig.. 4.6 we can see high formaldehyde concentration in highly intense urban areas of Rawalpindi and Islamabad like G-9, Faizabad. High HCHO concentration can also be seen in the area of the Attock Oil refinery and less HCHO concentration can be seen in Pir-Soahawa valley due to less population, vehicles and high vegetation. HCHO concentration varied from 5.02×10^{15} molecules/cm^2 to 8.9×10^{16} molecules/cm^2.

Several field campaigns were done and cloud free days was selected for field campaigns to get maximum of exact results. First field campaign was done in April, 2016, starting from NUST route was selected I-9, Faizabad, G-9. High concentration of formaldehyde was observed on Faizabad and G-9 due to dense urban area while Industrial I-9 area also has high formaldehyde concentration.

A 2nd field campaign was done in May, 2016. NUST, Atoock oil refinaray, Faizabad, Airport, and Pir-sohawa valley. High formaldehyde concentration was observed close to Faizabad, IJP road due to high vehicular pollution and Attock oil refinery due to production and process of refining of hydrocarbons and its emissions while less HCHO concentration was observed in Pir-Soahawa valley due to less population, vehicles and high vegetation.

Field campaigns of same route was done in Sept, 2016 and here comparatively more less formaldehyde concentration was observed on Pir-sohava valley due to relatively less VOCs were present due to less biogenic emissions. While same trends were observed on Faizabad, Attock oil refinaray and Airport area.

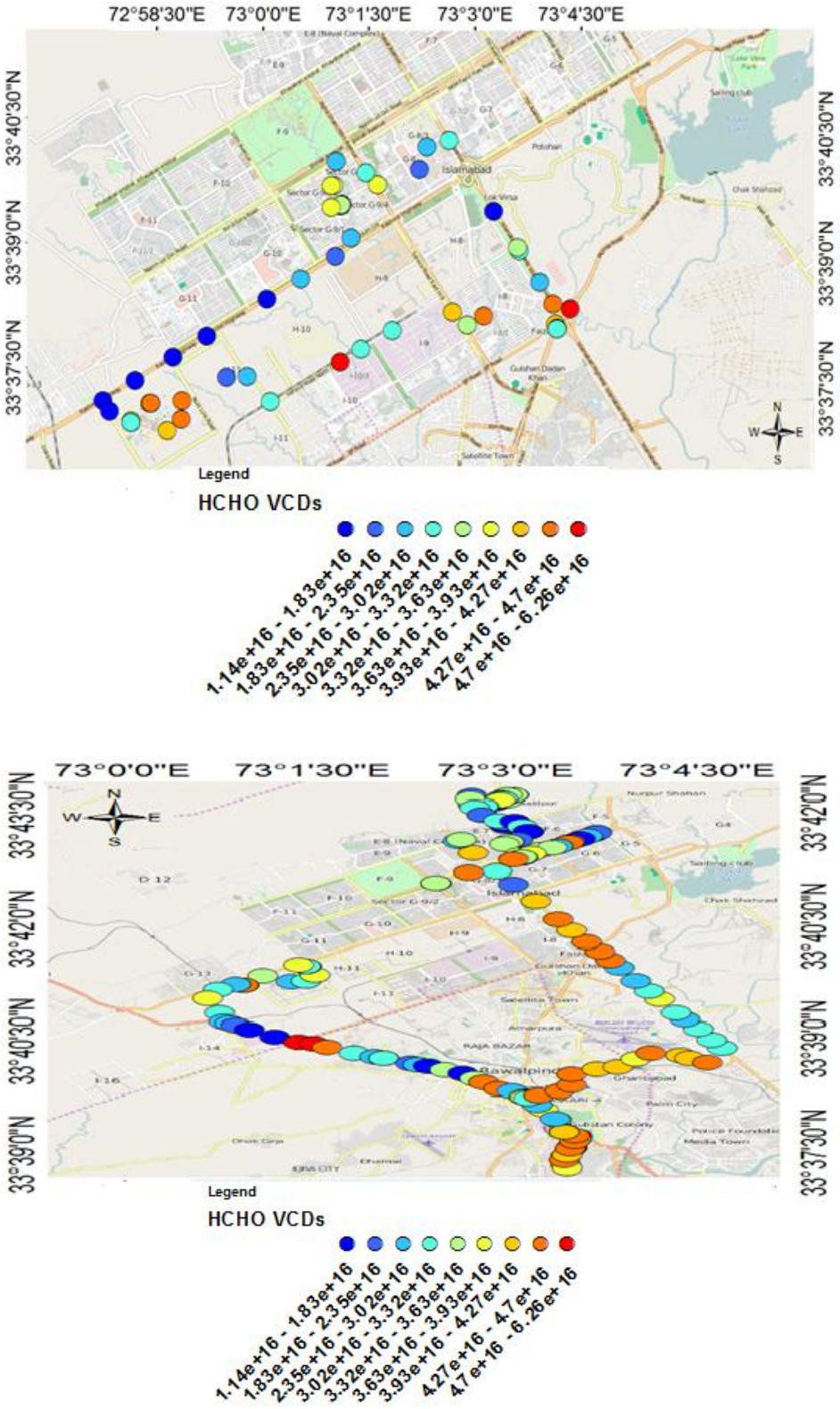

Fig.: 4.5 & 4.6: HCHO Vertical column densities over Rawalpindi-Islamabad through Car MAX-DOAS on May and April 2015

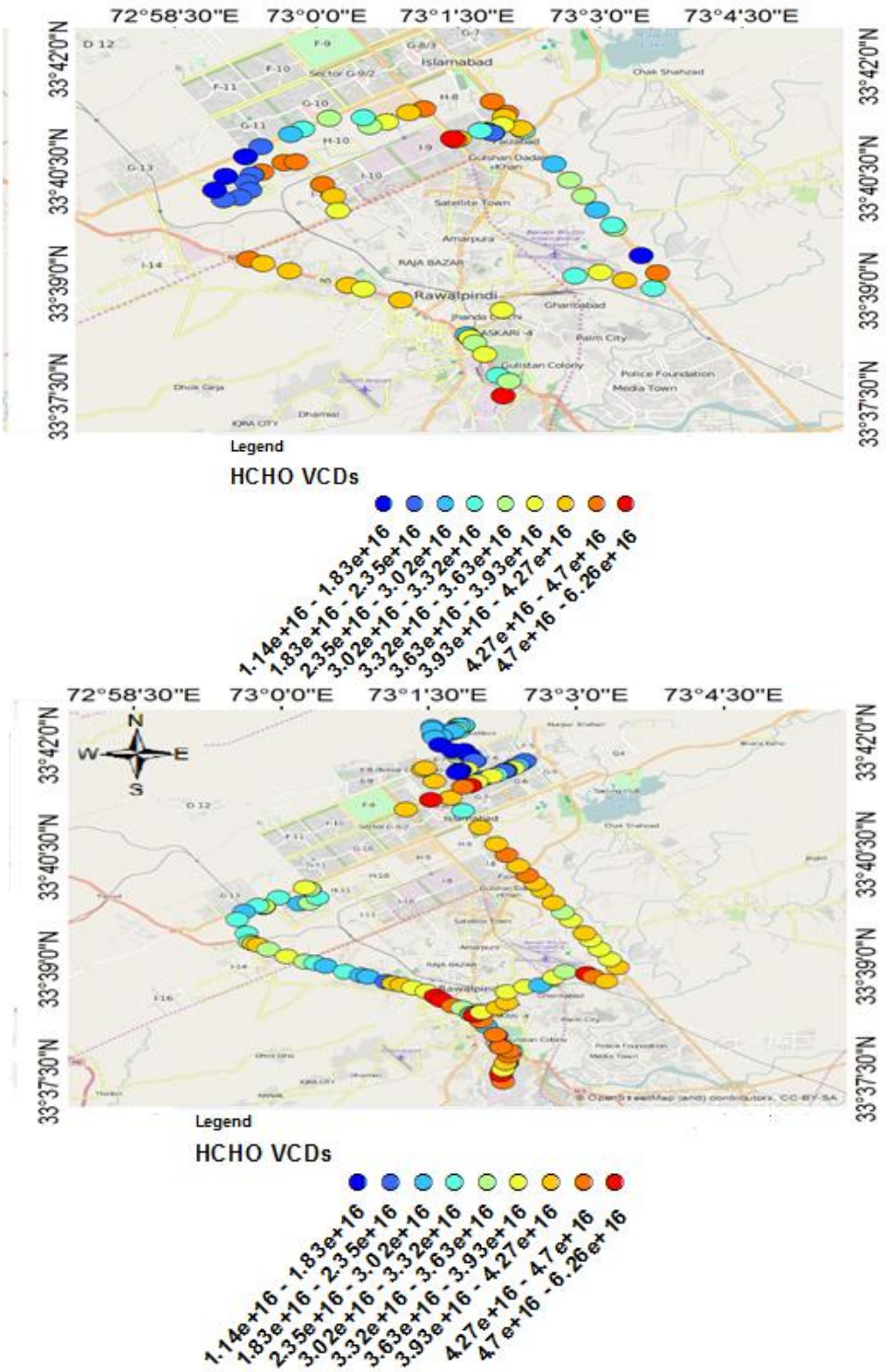

Fig.: 4.6 & 4.7: Comparison between HCHO Vertical column densities over Rawalpindi-Islamabad & Pir Sohawa through Car MAX-DOAS on May & Sept 2015

4.6 Satellite Validations

These MAX-DOAS observations were used to validate with the help of Ozone monitoring satellite (OMI) data. Data is taken from TEMIS (tropospheric emissions on Monitoring internet service. VCDs Vertical column densities are taken and compare with MAX-DOAS data.

In fig. 4.8 here we can see the correlation of MAX-DOAS and satellite observations.

- Correlation between OMI and MAX-DOAS VCDs for 1.5 year from March 2014 to July 2015 is 66%
- Correlation between OMI and MAX-DOAS VCDs of 12: 00pm to 2:00 for 1.5 year from March 2014 to July 2015 is 89.4 %

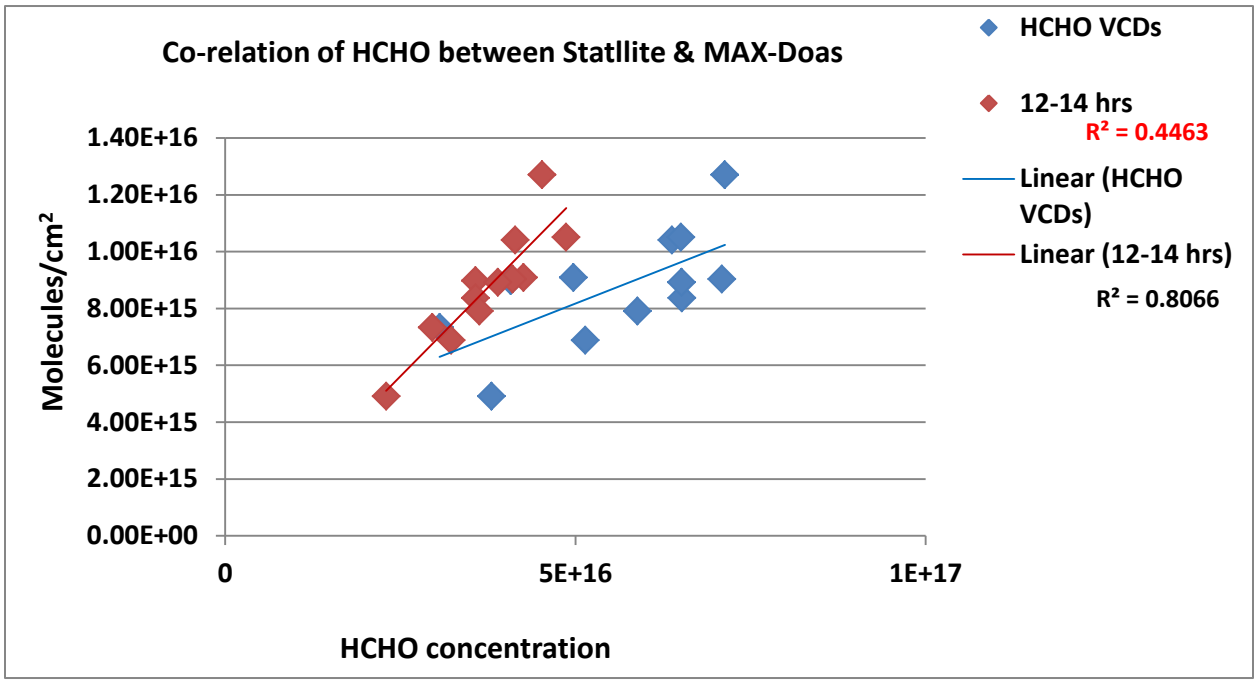

Fig. 4.8 MAX-DOAS Correlation with Satellite

The fig.. 4.8 indicates similar temporal trends of measured formaldehyde VCDs Concentration at IESE SCEE-NUST site. The basic difference between OMI and MAX-DOAS observation are that MAX-DOAS have point base observation while OMI have averaged over ground pixel size of 13 x 24 km^2

. In fig. 4.9 we can find a similar trends of Formaldehyde over a time period of 1.5 years we got high HCHO values in summer and low values in winter while in fig.

4.10 we can see HCHO VCDs of MAX-DOAS when the satellite pas over Pakistan between same time period but from 12:00 pm to 2:00 pm.

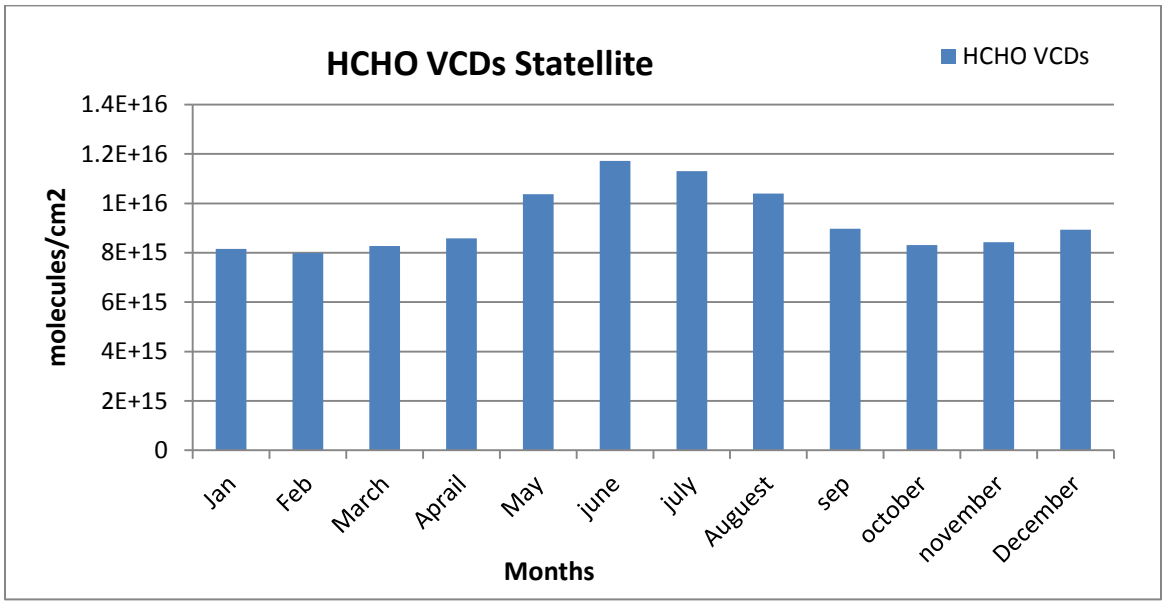

Fig. 4.9: Satellite observations of Formaldehyde from March 2014 to July 2015

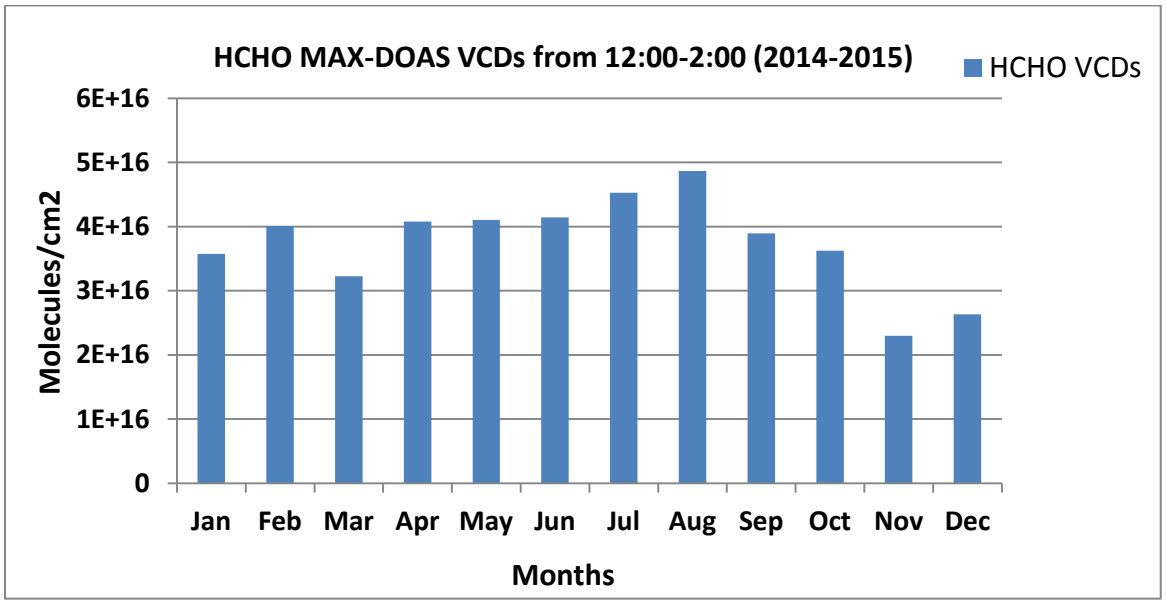

Fig. 4.10 MAX-DOAS Formaldehyde VCDs during Satellite Over Pass

Conclusion & Discussion

MAX-DOAS instrument was used to retrieve Formaldehyde column densities throughout the time period of March, 2014- July 2015. The formaldehyde column densities concentration were observed more then WHO guidelines in mainly urban areas of Rawalpindi and Islamabad. Formaldehyde concentration was similar or less then WHO guidelines in the Pir-Sohawa, and area with less population and low vehicular density. Use of CNG played a vital role in increasing the formaldehyde concentration over Rawalpindi and Islamabad. Spatial trends of ground base observations were found similar when compared with ozone monitoring instrument (OMI).

Wind directions and speed playing the crucial role in transportation of pollutants away from the emission sources.

Rapid rate of urbanization and increase in population, associated with transport and other provisions like unplanned and unexpected growth that cause increase in industrial sector have caused havoc of air pollution problems in major cities of Pakistan as observed in metropolitan cities in Asian region.

Limited data is collected and analyze in Pakistan from different mobile and stationary measuring units and showed that concentrations of numerous air pollutants are well above Pak-NEQS (Khokhar *et al.*, 2015). Therefore, monitoring of formaldehyde concentration is very importance and will help to provide an authentic baseline for future research in Pakistan.

A relationship was established between formaldehyde concentration and availability of compressed nature gas which shows positive significant increase in formaldehyde concentration in air due to incomplete combustion and release of methane. So this data of formaldehyde concentration may provide regulatory authorities, a basic guideline for continuous improvement of existing air quality for the VOC emissions.

Recommendations:

- Monitoring of Formaldehyde should be on continuous and regular basis.
- Pak-NEQS should be established for Formaldehyde.
- Mass transit system should be encouraged to use.
- Media and awareness campaigns to teach public and all stakeholders.
- Air quality environmental management plan should be implemented and evaluated on regular basis.
- More studies are needed to know where formaldehyde and from which sources produce how much amount of formaldehyde is produced from oxidation of terpenes and some other organic compounds.
- Reliable National data base of Formaldehyde concentration must be generated.
- Health impacts from formaldehyde must be studied.

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