MONITORING OF POLLUTANT GASES AND PARTICULATE MATTER IN THE VICINITY OF HATTAR INDUSTRIAL STATE

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ABSTRACT

In this study concentration of pollutant gasses like Sulfur dioxide (SO_2), Nitrogen dioxide (NO_2), Ozone (O_3), Carbon dioxide (CO_2), Carbon monoxide (CO) and concentration of particulate matter i.e $PM_{2.5}$ and PM_{10} followed by detection of heavy metal and its quantification were carried out. Sampling was performed with help of portable ambient air devices. SO_2, NO_2 and O_3 were analysed from Vairo plus MRU, CO_2 was analysed from Telaire 7001, CO was analysed from Smart sensor AS8700a, PM_{10} and $PM_{2.5}$ were analysed from Low volume duel air sampler at six selected locations including four factories and two residential areas in Hattar industrial estate, located in the provence of Khyber Pakhtunkhua. At each location gas samplers were installed for consecutive 3 days to collect data of SO_2, NO_2, O_3, CO_2 and CO for 1 hour a day and consecutive 3 days to collect PM_{10} and $PM_{2.5}$ data for 24 hours from March 2019 to April 2019. Maximum concentrations of SO_2, NO_2, CO_2 and CO were found at Labour colony 600 quarters which was 82.9 $\mu g/m^3$, 102.1 $\mu g/m^3$, 477.6 ppm and 12 mg/m^3 respectively and minimum concentration of 41.1 $\mu g/m^3$, 53.03 $\mu g/m^3$, 424.6 mg/m^3 and 3.1 mg/m^3 respectively at Gold wing roof factory. O_3 highest concentration was observed in Labour colony 600 quarters (53$\mu g/m^3$) and lowest at Dewan cement factory (21$\mu g/m^3$). PM_{10} maximum concentration was observed at Dewan cement factory (301.889 $\mu g/m^3$) and minimum concentration was observed at 400 quarters colony (156.25$\mu g/m^3$) whereas concentration of $PM_{2.5}$ was higher at Dewan cement factory (192.78$\mu g/m^3$) and lowest at 400 quarters colony (115.741$\mu g/m^3$). The results showed that overall selected gaseous concentration was below the permissible limits but the concentration of PM_{10} and $PM_{2.5}$ was much higher than permissible limits of Pak-NEQS and WHO. Analysis of heavy metal was carried out at National Agricultural Research Centre Laboratory by using Atomic Absorption Spectroscopy (AAS). Results showed that heavy metals in PM_{10} at all sampling sites were found in order of Zn > Pb > Cr > Ni > Cu > Cd with the mean concentration of 5.976 $\mu g/m^3$, 0.8412 $\mu g/m^3$, 0.2488 $\mu g/m^3$, 0.1938 $\mu g/m^3$, 0.1508 $\mu g/m^3$ and 0.0225 $\mu g/m^3$ respectively and Zn > Pb > Cr > Cu > Ni > Cd with the mean concentration of 4.4425 $\mu g/m^3$, 0.7500 $\mu g/m^3$, 0.1816 $\mu g/m^3$, 0.1141 $\mu g/m^3$, 0.0793 $\mu g/m^3$ and 0.0195 $\mu g/m^3$ respectively was found in all samples of $PM_{2.5}$. Heavy metals maximum concentration was found at Dewan cement factory and Labour colony 600 quarters.

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ABBREVIATIONS

WHO	World health organisation
Pak-EPA	Pakistan environmental protection agency
MPI	Multi pollution index
TSP	Total suspended particulate
PCAP	Pakistan clean air program
GEMS	Global environmental monitoring system
SPM	Suspended particulate matter
JICA	Japan international collaboration agency
UV	Ultra violet
SPAMS	Smart personal air quality monitoring system
OMI	Ozone monitoring instrument
AQEI	Air quality exposure index
AAS	Atomic absorption spectroscopy
NEQS	National environmental quality standards
AQI	Air quality index
CPEC	China Pakistan economic corridor

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CHAPTER 1

INTRODUCTION

1.1 Introduction

Air pollution is becoming worldwide major environmental issue and considered one of the major contributing agent towards global warming, climate change, eco-physiological responses of plants, altering atmospheric composition and humans health problems (Li et al., 2016). In industrial areas air pollution is one of the important problem and it can cause hazardous effects on health of humans. Discharge of smoke, toxic fumes, dust and gases in to the environment causes air pollution (Kolle and Thyavanahalli, 2016). Increased number of vehicles and development of residential and industrial area are major reason of air pollution and causing bad effects on health of humans (Zhang et al., 2014). Expansion of industrial areas, transport penetration and brick kilns growth are the reason that not only air pollution is considered as the urban phenomenon but it is also becomes a rural problem. There are inadequate and tend to be the urban-centered air pollution control and monitoring efforts. Globally the serious and most emerging environmental problem faced by the humans is considered to be air quality issue. One of the most basic necessities of life is clean air and continuously degradation of the quality of air is significant human health threat (Desauziers, 2004). Air pollution can cause several problems such as adverse agricultural effects, livestock, archaeological monuments and culture, structures and building material, health problems especially for children and women. Chronic respiratory illness risk increases in long term air pollution exposure (Luo et al., 2015) and various types of cancers can be develop (Sperling et al., 2004). In urban area with high level of air pollution exposure by human beings is believed to cause several adverse health impacts. More than two million premature deaths are each year caused by adverse impact of indoor and outdoor air pollution. With the fact that vulnerability of developing countries to these impacts are more as half of this disease burden bear by population of developing countries is reported (Krzyzanowski, 2008).

Asia have been undergone a substantial growth over last decade in urbanization and development coupled with increase in energy usage of energy and motorization. A noticeable rise has been occurred in number and type of air pollutants emission sources in the region (Gurjar et al., 2008). Motor vehicles usage

unprecedented rise, large population, intense industrial activities are the reason of severe environmental impact in region (Hopke et al., 2008). As consequence a significant threat emerged as air pollution which can harms quality of life, environment and population health in Asia, south Asian countries especially because they do not adopt strategies and technologies regarding emission control. Poor air quality is affecting heath of locals (WHO, 2002). Different kinds of studies were conducted in developed countries regarding association between air pollution level and rates of human disease. In developed countries climatic conditions, air pollution concentration and lot of other factors are very different from developing countries. Air pollution is a very serious problem especially in Asian countries and it has very serious impact on health. According to the world health organization (WHO) 4.6 million healthy life-years lost and 865,000 deaths each year worldwide is contribution of urban air pollution, approximately 60% of lost life-years and deaths occurs in the Asia's developing countries which depicts that the burden is not distributed equally. Throughout Asian countries high concentration of pollutants were found especially in Malaysia, India, Indonesia, Bangladesh, china, Philippine, Korea, Thailand and Vietnam. Six cities of Asia (Chennai, Hanoi, Bangkok, Manila, Bandung, Beijing) having high levels of particulate matters (pm10, pm2.5) were reported by (Oanh et al. 2006). Cairo, Dhaka, Karachi and Beijing are major Asian cities having the highest MPI (multi pollution index).

Pakistan is one of the urbanize country in the South Asia with 35% approximately of population living in cities and towns. As compare to global average Pakistan's per capita pollution emission are far below. Pollution is more national concern than global because of its impact on locals. One of the major concerns of environment in Pakistan is ambient air quality degradation which has been identified by international organization and most of government departments. Key sources which are contributing in degradation of air quality in the country are suspended particulate, increasing traffic trends, indoor air pollution and industrial pollution (Pak-EPA 2005). Mass-transit system is very poor in urban areas and it is also play an important role in degradation of air quality in urban areas. Economic Survey Report of Pakistan 2006-2007 stated that Increase in vehicles, absence of public transport and high population growth are major reason from which Pakistan is suffering for its poor air quality. Pollution emission in Pakistan sharply increased over two decades 1977-

78 and 1997-98 in major producing sectors like industry, power, agriculture and transport etc over these two decades average 23- fold of sulfur dioxide increased across all sectors similarly, fourfold of average carbon dioxide increased, in power sector 25- folds of nitrogen oxides has been increased. The amount of carbon monoxide (CO), sulfur dioxide (SO_2) and Ozone (O_3) are below than hazardous level in atmosphere. On other hand, Lahore and Karachi's carbon monoxide levels exceeded WHO's levels showed by National conservation strategy data (Colbeck et al., 2009). Atmospheric Particulate matter data is more uniform. It is estimated that PM10 and (TSP) total suspended particulate matter levels are extremely above safety level across major cities and industrial areas in Punjab. In Karachi, Rawalpindi, Peshawar and Lahore concentration of lead in ambient air is very high as compared to WHOs limit. The most polluted city in world is Karachi which is one of the most populated and mega city of Pakistan with respect to total suspended particulate and fourth one on MPI-based ranking. This shows that how much serious is the condition of Pakistan's air pollution, and so for very little work has been done on the management of air quality. Pakistan clean air program (PCAP) is published by the government of Pakistan for ambient air quality improvement from 2005 to 2010 as 5 year plans. Burning of solid waste, Industrial emissions, natural dust and vehicular emissions are Pakistan's major sources of air pollution in urban area highlighted by PCAP they also proposed long and short term measures which requires action at all government levels.

1.2 Oxides of nitrogen

On local, regional and global scale in atmospheric chemistry nitrogen plays an important role. Oxides of Nitrogen are collectively called as (NOx). During the combustion at high temperature NOx is produced from a reaction of oxygen and nitrogen in air. Air pollution can be noteworthy in areas where large amount of nitrogen oxides released in atmosphere especially in large cities because of heavy vehicle traffic. In simple words when ever in the presence of nitrogen combustion occurs NOx gases will be formed. NOx major sources are on-road mobile sources (39%), industrial sources (11%), electric utilities which combusts fossil fuel (25%) and off-road mobile sources (e.g. railroads, logging, garden and lawn equipment and pleasure craft; 15%) (EPA, 1998). Naturally occurring organic nitrogen have also several sources including plant pollen and sea-spray (Prospero et al., 1996). The

importance of nitrogen as air pollution arise from its role as a contributor to dry and wet acid deposition (Hsu et al., 2007; EPA, 1986). Airways in respiratory system of humans can irritate by breathing air having high concentration of nitrogen dioxide. Exposure of NOx over short time period can cause respiratory diseases like asthma, leading towards respiratory symptoms (such as wheezing, coughing and difficulty in breathing). Acid rain is formed when NOx interacts with other chemicals, oxygen and water in atmosphere. Forest and lakes are sensitive ecosystem and it can be harm by Acid rain. Particulate matters are also formed with the help of NOx which is one of major environmental pollutants and it can cause adverse health effect. NOx is also responsible for production of photochemical ozone (O_3) in the troposphere that causes crop damage (Ettouney et al., 2009). NOx high level can have adverse effects on the vegetation including reduce growth and leaf damage. It contributes to greenhouse effect and it also damages the forest and makes vegetation susceptible to disease (Pitarma et al., 2016; Rao Amaraneni et al., 2004). The particles of nitrate results from NOx reduce visibility and makes air hazy.

1.3 Oxides of sulfur

SOx forms when oxides of sulfur combine. In ambient air sulfur dioxide (SO_2) is pollutant of environmental importance. SO_2 has both anthropogenic and natural sources like most of other pollutants. Some of major natural sources are volcanic eruption, sulfur gasses oxidation and sea-salt emissions while sources of anthropogenic SOx are industrial combustion, biomass combustion and burning coal (Speidel et al., 2007; Kawamoto et al., 2004; Sun et al., 2013). Latter SO_2 emissions occur predominantly as industrial facilities (20%) power plants fossil fuel combustion (73%). Earths radiation budget and albedo of earth is also known to exert influence by sulfur dioxide (Książek, 2017). Sulfur dioxide contributes in alteration of atmospheric chemistry and regional and global climate condition through the process of chemical transformation and dilution/diffusion into sulphate aerosols (Ali and Athar, 2008). Solar radiation reflects back to space by increase of sulphate particles in atmosphere (Kaufman et al., 2002). Intensification of scattering albedo increases becauses in atmosphere particles of sulphate turn as cloud condensation nuclei (Manktelow et al., 2009). SO_2 exposure for a short-term can make difficulties in breathing and also can harm respiratory system of humans. Elderly, children and asthma patients are sensitive to the effects of sulfur dioxide. SO_2 can cause cardiovascular abnormalities

(e.g. heart rate decrease), broncho-constrictor and respiratory irritation (Tunnicliffe et al., 2001). Small particle forms in atmosphere when SOx reacts with other compounds. Particulate matter pollution increases with the help of these particles and these small particles penetrates deep into the lungs towards sensitive parts and cause health problems. SOx in gaseous form can harm plants and trees by decreasing growth and damaging foliage. Acid rain forms from sulfur dioxide harming ecosystem. Fine particles forms when oxides of sulfur react with other compounds that help them in reduce visibility (haze) in atmosphere.

1.4 Carbon monoxide

Carbon monoxide is odourless, colourless gas if that can be inhaled in large amount so it can be harmful. In many developing countries carbon monoxide is one of the important causes of poisoning mortality and morbidity. When something is burn in an absence of air CO is released. Two common sources of carbon monoxide are car engine exhaust fumes (when catalytic converters are not present) and fire smoke. Other sources include use of charcoal fire in confined place like tents (International programme on chemical safety, 1999). Variety of items in our home such as gas space heaters and unvented kerosene, furnaces and leaking chimneys and gas stoves release carbon monoxide and through this way air quality of indoor can be effected. Propane and butane (in caravans) incomplete combustion and domestic heating appliances which are badly installed may lead to chronic, occult or sub-acute poisoning.

In several ways CO reduces tissues oxygen delivery.

1) Carboxyhaemoglobin (COHb) forms when CO combines with haemoglobin, which reduces haemoglobin availability amount to carry oxygen (the affinity of CO has 240 times then O2).

2) Oxyhaemoglobin dissociation curve shifts to the left when COHb forms, which impairs oxygen liberation to the cells (Cheung and Wang, T., 2001).

CO can cause unconsciousness, dizziness, confusion and death at extremely high levels which are normally present in enclosed environments or indoor.

Mostly CO dose not occurs outdoor at a very high level. However when carbon monoxide concentration elevates in an open environment then it becomes a matter of concern for the surrounding people because high concentration is one the major causes of heart disease. These people have already reduced ability for carrying oxygenated blood to their heart in situations where heart need more than usual oxygen. Whenever these kinds of people are under increase stress or exercising then they are more vulnerable to CO effects. In this situation elevated CO short-term exposure may cause reduced oxygen to heart patients and can cause angina (Chest pain).

CO poisoning early features are non-specific and it may include vomiting, dizziness, nausea and headache. Prolong CO interaction can cause Progressive impairment of consciousness. It has also described in literature that acute gastroenteritis can cause syndrome. Hyper reflexia, extensor planter responses, hyperventilation, increased muscle tone, hypotension and clonus develops as poison severity increases.

1.5 Ozone

Three atoms of oxygen combine to form Ozone (O_3) gas. Ozone occurs both on ground which is anthropogenic and at stratosphere which is natural. Ozone is beneficial or harmful it depends on where it found. Stratospheric ozone which is also called good ozone occurs naturally in atmosphere protects us from ultraviolet rays coming out from sun light by forming protective layers that reflects harmful radiation. Unfortunately manmade chemicals are destroying beneficial ozone known as "Ozone hole". (Nagendra et al., 2018).

Ground or tropospheric ozone, dose not emits directly into the atmosphere rather it is created by help of chemical reaction between volatile organic compounds (VOC) and oxides of nitrogen (NOx). This happens when cars emit pollutants, industrial boilers, chemical plants, power plants, refineries and other sources react chemically in the presence of sunlight. Ozone on a ground is very hazardous pollutant, because it effects environment and people, and it is also one of main smog ingredients. (Liu et al., 2019).

Ozone concentration increases in urban areas on a hot summer days, but it can also increase its concentration during winters. Sometimes rural areas also experience high levels of ozone because it also travels from one area to another by convection. Most of the people breathing air containing ozone is at high risk including outdoor workers who are very actively working outdoor, children, asthma patients and older adults. In addition, people with fewer intakes of nutrients like vitamin E and C and people containing certain genetic characteristics are at high risk from the exposure of ozone. Ozone breathing can cause various health problems like airway inflammation, coughing, throat irritation and chest pain. It also harms lung tissue and reduces lung function. Ozone can worsen asthma, emphysema and bronchitis leading towards increased medical care. (Rosaria and Francesco, S.P., 2016).

Ozone affects vegetation and ecosystem such as parks, wilderness areas, wildlife refuges and forests. Ozone gas also affects Sensitive vegetation during their growing season.

1.6 Carbon dioxide

Carbon dioxide contains one carbon and two oxygen atoms is a naturally occurring, very common molecule. CO_2 is one of those commonly occurring gas that is every day around us. It is naturally present odourless, colourless gas in atmosphere and plays an important role in earth's carbon cycle. All animals and human beings when breath they exhale carbon dioxide and plants utilize it during process of photosynthesis. (Liu et al., 2019).

Carbon dioxide both occurs naturally and by human activities. Anthropogenic sources of carbon dioxide are livestock, deforestation, fertilization, burning of fossil fuels and land use changes etc. they all results in increase emissions. On the other side natural sources include hot geysers and springs, volcanoes because CO_2 is water soluble so it occurs naturally in seawater, ice caps, rivers, lakes, groundwater and glaciers.

Carbon dioxide is called GHG (greenhouse gas) because it traps the sun radiations entering the earth and maintains the earth temperature and provides live able conditions. But the problem occurs when CO_2 concentration in the atmosphere increase due to anthropogenic activities for example fossil fuel burning release carbon

dioxide in the atmosphere (along with other GHG) and on the other hand tress are absorbing less CO_2 due to increase in deforestation etc. this causes increase in the concentration of CO_2 in the atmosphere and increase instability in the climate which causes global warming. (Song et al., 2019).

1.7 Particulate matter

Among the major air pollutants categories particulate matter is considered to be the most harmful pollutant. Generally particulate matter is a mixture of liquid droplets and solid particles present in air (Vassilakos et al., 2005). In past, scientists were focusing on quantification and characterization of particulates, to understand atmospheric chemical phenomena and to find their appropriate sources that help in its removal and transport. Particulate matter consists of some major components representing main part of particles total mass and trace components represents less than 1% of TPM.

Particulate matter in atmosphere is generally a mixture of organic and elemental carbon, mineral dust, ammonium, water, sulphates, nitrates and trace elements. PM is a pollutant that emits directly through anthropogenic activities into atmosphere including combustion from industrial activities, house hold, car-engines and natural processes like windblown dust, wildfires, volcanic eruption etc. they can also be created by the emission of polluted gasses from industry or traffic due to chemical transformation known as secondary aerosols.(Feng et al., 2018)

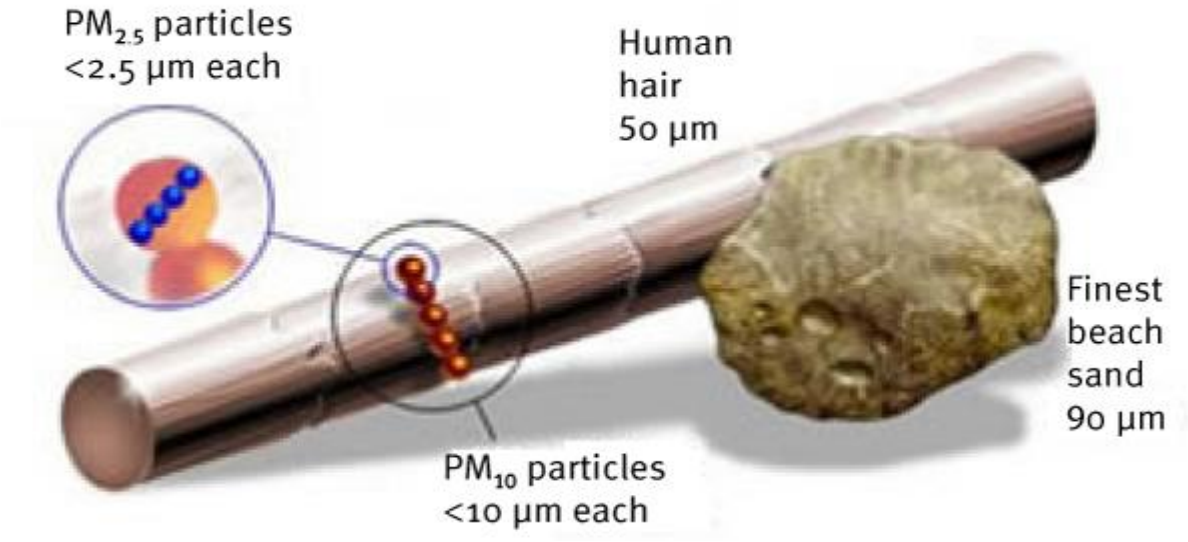

Figure 1.1 Different size of particulate matter.

1.7.1 PM_{10} and $PM_{2.5}$

PM_{10} incorporates regularly re-suspended dust from industries, streets and organic material like pollen grains and bacterial fragments. PM_{10} also include the world's crustal materials like wind-blown from agricultural forms, mining operations, unpaved streets or revealed soil. PM_{10} produce from the burning procedure of non-flammable materials for example fly slag (Krzyzanowski et al., 2008). The main concern about PM_{10} is that it helps in environmental change and it also has unfriendly impacts on human beings as well (Kappos et al., 2004).

The $PM_{2.5}$ breaks down into particles of an extremely small size (2.5 μm) which enable it to spread far and wide through air and become cause of various medical issues (MEP, 2012; WHO, 2005). It has been found that with spread of $PM_{2.5}$, many individuals would become powerless to various ailments and intense respiratory side effects such as asthma, myocardial localized necrosis, lung tumor and even mortality (Deng et al., 2013; Goss et al., 2004; Laden et al., 2006). As China has experienced rapid development and financial growth in all areas, this has also come with an ever increasing rise in number of motor vehicles, further growing ecological issues caused by $PM_{2.5}$. According to research conducted in Pakistan by National Bureau of Statistics (2013), the number of vehicles has increased from 1358400 units in the year 1978 to 93563200 units in 2011. Looking at this increase from a yearly perspective, it comes down to a growth of around 20.87% each year.

1.8 Literature review

A research conducted by (Oanh et al., 2006) in framework of regional Asian air pollution research network. In this study high level of ($PM_{2.5}$, PM_{10}) were reported in six cities of Asia (Bangkok, Chennai, Hanoi, Bandung, Beijing, Manila) and their results were that average concentration of PM2.5 were range from 44-168 $\mu g/m^3$ in dry season and 18-104 $\mu g/m^3$ in wet season and concentration of PM_{10} were range from 54-262 $\mu g/m^3$ in dry season and 33-180 $\mu g/m^3$ in wet season.

Analysis of the particulate matter on a per city basis suggests that it is a pollution of concern in lot of cities. A research conducted by (Gurjar et al., 2008) in which they evaluate air quality of eighteen mega cities all over the world (with the population of 10 million or more) and in results they categorized five cities having

"fair" quality of the air and thirteen cities as "poor" quality. They also suggested (MPI) multi pollution index in which they measure the combine level of WHO three criteria pollutants total suspended particles (TSP), sulfur dioxide ($S0_2$), and nitrogen dioxide ($N0_2$). Beijing, Karachi, Dhaka and Cairo emerged as mega cities having highest MPI.

Research conducted by Global environmental monitoring system (GEMS) from 1978 till 1980 and they found that suspended particulate matter (SPM) annual mean level in commercial city centre were 332 $\mu g/m^3$ in 1978 and in suburban residential site concentration in 1979 were 749 $\mu g/m^3$ and in 1980 were it was 690 $\mu g/m^3$ (WHO 1984). Later GEMS extended their research in pollution monitoring in other mega cities and one of the research published in 1992 by (WHO/UNEP, 1992) in which the annual mean suspended particulate matter concentration in Karachi was 239 $\mu g/m^3$ in 1985 and the concentration of SPM rise continuously 265, 275 and 328 $\mu g/m^3$ in 1986, 1987 and in 1988 respectively.

Some other researches have also being done on particulate matter in Karachi. The research was about annual mean SPM concentration in Sindh industrial estate and Sadar and their results were in 1987 PM concentration were 254 $\mu g/m^3$ in industrial estate and 459 $\mu g/m^3$ in sadar and in 1988 it was 333 $\mu g/m^3$ in industrial estate and 397 µg/m3 in Sadar. Another research in Karachi on ambient air pollution were conducted in 1990 by (Ghauri et al. 1992a, 1994) and this research was carried out for 15 consecutive days at thirteen different sites in karachi and they found that daily mean total suspended particles (TSP) were 240 in the month of March 230 in May and 260 $\mu g/m^3$ in June. (Parekh et al., 2001) also conduct a research in Karachi and Islamabad on TSP from December 1998 to January 1999 and according to them the average daily concentration of TSP at karachi ranges from 627-928 $\mu g/m^3$ while in Islamabad it was range from 428-998 $\mu g/m^3$. The average taken every hour at Qasim port in karachi of PM_{10} concentration for the seven days in the month of November and their finding was 123.49 $\mu g/m^3$ (Hashmi et al., 2005a).

Some of the research has also being conducted in Pakistan capital city Islamabad on particulate matter. (Wasim et al., 2003) collected a baseline data from industrial area of the Islamabad and this research was conducted from October 1998 to June 1999 and they reported highest concentration of TSP occurred in December

and it was approximately 350 µg/m^3 (Shaheen et al. 2005a) which was conducted from June to September 2002 on TSP and their findings were range from 18.5 to 218.6 µg/m^3 with mean of 150.5 µg/m^3. (Rajput et al., 2005) carried out an investigation on TSP concentration and their composition in residential and industrial areas of Islamabad in 1995 and they reported that the level of TSP in residential area were 133 µg/m^3 and in industrial area it was more than double 297 µg/m^3.

Pakistan environmental protection agency (Pak-EPA) has carried out a study with the collaboration with Japan international collaboration agency (JICA) on quality of air in various cities of Pakistan (Lahore, Rawalpindi and Islamabad). In 2001 they reported (Pak-EPA/JICA 2001a) that highest average hourly levels of SPM were in Lahore city (895 µg/m^3) then Rawalpindi (709 µg/m^3) and then Islamabad which was (520 µg/m^3). Ali and Athar (2008) monitored ambient air quality of national highway of Pakistan. They divided highway in 3 different sections and select 3 sampling sites in each section and their findings of PM_{10} varied from 123-443 µg/m^3.

A research conducted by (Hopke et al., 2008) from 2002 to 2005 at Nilore (Islamabad) and they measure the $PM_{2.5}$ and PM_{10} for four years and their mean concentration of $PM_{2.5}$ were 15 and for PM_{10} were 68 µg/m^3 and its standard deviation were 10 and 50 respectively. GEMS also measures the SO_2 concentration in Lahore city at two different sites in 1978 to 1979 and the concentration of city centre which they find out was 49 µg/m^3 and for the suburban residential area it was 40 µg/m^3 (WHO, 1984). Later research conducted on SO_2 shows that the concentration of SO_2 in the suburban residential area were varied from 25-67 µg/m^3 and for the city center it was 67-134 µg/m^3.

A research was conducted on concentration of SO_2 in five different sites of Karachi (Hashmi et al., 2005) in which three sites were in industrial area and one each was in residential area and down town. They evaluated time-weight average value for 1 and 24 hour and maximum 24 hour average value was reported in industrial site which was 9.30 µg/m^3 the downtown which was 0.98 µg/m^3 and then residential area 0.24 µg/m^3.

Study in Kosan, Cheju Island Korea from 11 March to 19 April in 1994 monitored different air pollutants (Kim et al., 1994). The island was not heavily populated and it is tourist spot but its atmosphere is being affected by its neighbouring

countries like China and Japan. Sampling was being done in the trailer containing all of gas analysers. The sampler inlet height was above 6 m and sampling was being done for 6 to 24 hours and the average was calculated after every 6 hours for more than a month and their findings were that the sea salt fraction of sulphate was more than 6%, the concentration of SO_2 and NOx were 0.97 and 3.5 ppb respectively which was lower as compare to other cities of Korea but higher then remote areas. O_3 concentration was 55 ppb which was comparable and half of the air particles were from china during the period which shows China is affecting their atmosphere.

NOx, CO, black carbon and particulate matter was monitored by (Martinez et al., 2012) with help of mobile monitoring platform to collect spatial and temporal data of pollution in Somerville, Massachusetts (USA) near interstate highway (i-93) for 55 days from September 2009 to August 2010. In this research they collect the air pollutants data from the both sides of the highway from 0 to 2.3 km distance in 4 to 6 hours and their findings were that all selected air pollutants concentration decreases as moving away from the either sides of highway maximum concentration in morning than rest of the day, higher on weekdays than weekends and the concentration was highest in winters as compare to other seasons.

Statistical models developed by (Dignon and Hameed, 1989) in which they can relate rate of pollution emission to rate of fuel consumption. They run this model in the populated continents like North America, Asia, Africa, South America, Europe and Oceania to estimate rate of Nitrogen and Sulfur oxide emissions from fossil fuel from 1860 to 1980 at ten year interval and their findings were sulfur emission has been increased at rate of 2.9% per year and nitrogen emissions at rate of 3.4% per year. Global sulfur emission ratio to nitrogen emissions has declined it was 5% in 19th century and becomes 3% by 1980. Most rapid emissions have been registered in South America, Asia and Africa after Second World War. If the fossil fuel consumption data is available these relations can be used to estimate pollution emission in other regions.

Ozone and trace gases (NOx, SO_2 and CO) were measured at rural site having intensive anthropogenic activity at Yangtze Delta, China by (Cheung and Wang, T., 2001) from June 1999 to July 2000. The instrument used for the detection of pollutant was ambient air sampler drawn through Teflon line at an elevation of five meter

above laboratory. UV photometry analyser was used to measure Ozone. Elevated ozone levels were observed during the study with highest frequency in early summer and late spring. In 1 year research period 21 days were found to have ozone concentration overreached new US 8-h 80 ppb health standard. Calculation also showed that ozone concentration was higher in all seasons except winter. Metrological data showed that high ozone days were associated with intense solar radiation and minimum rainfall. High level of CO and NOx was also detected during study which was a major reason in the formation of tropospheric ozone.

Exposure of respire able suspended particulate matters (PM_{10}, $PM_{2.5}$) and carbon monoxide in public transports of Guangzhou, China was examined by (Chan et al., 2002) in 2001. Sampling was conducted for 5 consecutive weekdays in May and December and selected pollutant level were measured in both afternoon and evening. 80 Carbon monoxide, 80 PM_{10}, and 50 $PM_{2.5}$ samples were placed in four different transportation modes (subway, texi, air conditioned bus and non-air conditioned bus). The highest mean of carbon monoxide and PM_{10} level was obtained in non-air conditioned and in air conditioned bus serves and the overall PM_{10} and $PM_{2.5}$ ratio in public transports was high, ranging from 76% to 83%. Subway exposure level was lower than taxi and the exposure level were only slightly lower in afternoon than in evening. Poor emission controls, poor maintenance and slow moving traffic with frequent stops are believed to be a major cause of high pollution level.

Oxides of nitrogen, sulphur and carbon monoxide ascending from combustion of old tyres in slaughterhouse environment was monitored by (Dibofori-orji and Braide, 2013) with the help of flue gas analyser by the method used by American society for testing and materials. Air samples emitting from slaughterhouse were drawn and quantified by means of modules and result showed that concentration of NOx and SOx was ($0.73mg/m^3$) and ($0.11mg/m^3$) respectively which were higher than WHO Allowable limits however carbon monoxide emission ($0.67mg/m^3$) was below then the allowable limit. They also recommended that the use of tyres should be avoided and use other sustainable energy production methods.

From November 2015 to January 2016 (Nagendra et al., 2018) monitored air quality of Chennai, India by developing an air sampling device which was a

combination of a commercially available CO, O_3, NO_2, PM, humidity and temperature sensors along with GPRS and microcontroller known as Smart personal air quality monitoring system (SPAMS) and it was calibrated in laboratory. They performed field measurement by selecting 3 different spots (busy traffic road, urban background site and beach side road) for consecutive 3 months at various times of day and different days in a week and their result indicates that $PM_{2.5}$ was highest in busy traffic site and lowest in urban background which was (mean = 22.7 ± 8.45 μg/m^3) and (mean = 9.3± 5.75 μg/m^3) respectively whereas carbon monoxide concentration was lowest at beach road (mean = 0.26 ± 0.01ppm). While traveling in buses higher concentration were observed during morning and evening of NO_2 and CO due to peak traffic. During afternoon O_3 concentration was found to be highest due to photochemical reaction.

(Ambade, 2018) studied short term measurements of trace gasses (NO_2, O_3 and SO_2), PM_{10} and heavy metals during Diwali in a moderately polluted site in city Jamshedpur (India) from 21st October to 26th October 2014 and they found that on Diwali day 12-h PM10 concentration were extremely high (500.5 μg/m^3) which was > 5 times to the WHO standards. Other pollutants level were also very high like ozone (53.33 μg/m^3), NO_2 (73.32 μg/m^3) and SO2 (8.6 μg/m^3) and they exceeded the prescribe limit of National Ambient Air Quality Standard. The concentration of heavy metals Fe, Zn, Pb, Mn, Cu, Cd, Be and Ni were 2.2, 1.5, 2.8, 1.6, 2.2, 1.2, 5.9 and 3.3 which is very high as compare to the normal days. They also find out that fire work on Diwali day contributes 21 to 27% of PM_{10} aerosol and all these results indicates that the fire work during Diwali event is one of the major contributor in affecting the air quality of ambient air due to emission of PM_{10}, O_3, NO_2 and trace metals.

Fluctuations in air pollution of Romania was studied by (Nastase et al., 2018) using 142 Romania's national air pollution monitoring stations after Romania joined the European Union on 1st January 2007, use of fossil fuel was enormous, but shift to biomass or natural gas from consumers decreased use of fossil fuels. Their result indicates that CO annual average mass emission has decreased from 3,186 to 774 Gg from 1990 to 2014 respectively (decrease by <76%), decrease of SOx was from 1,311 to 176 Gg (decrease by ~60%), NOx decreased from 546 to 218 Gg (decrease by ~87%) and CO_2 was decreased from 66.226 to 38.916 Gg/year from 2007 to 2014 respectively (decrease by <41%).

From December 2015 to November 2016 (Aliyu et al., 2018) conducted a research in northern Nigeria to evaluate the local and global impacts of the air pollution using cost-effective device (MSA Altair 5× gas detector and the CW-HAT200 particulate counter) and they finds out in one year day time sampling that average concentration of CO, $PM_{2.5}$, PM_{10} and SO_2 were 29.22 ppm, 219.73 µg/m^3, 451.96 µg/m^3 and 0.32 ppm respectively. The concentration level of their findings were higher than national and international air quality standards and concentration of particulate matter pollutants ($PM_{2.5}$ and PM_{10}) were so high to place Zaria, Nigeria among the WHO list of polluted cities.

Another research on air pollution in Nigeria has been done by (Sonibare, 2010) regarding pollution produce from thermal electric plants for electricity generation. They collect samples from all proposed and existing thermal plants in the country and calculates the emissions of oxides of nitrogen (NOx), sulphur dioxide (SO_2), carbon monoxide (CO), particulate matters (PM) and volatile organic compounds (VOCs) and their emissions range were 1635–41,148, 19–472, 978–24,607, 37–924, and 11–286 ton/annum respectively. As these results are very harmful for environment and health so they also suggested different sustainable means of electricity production to reduce air pollution.

To determine effect of open burning of rice crop residue (Singh et al., 2010) conducted a research in which they monitored air quality at five different locations in Patiala city of India. They monitored concentration of nitrogen dioxide (NO_2), sulfur dioxide (SO_2) and suspended particulate matter (SPM) and performed their sampling in different locations like residential, commercial, agricultural, sensitive and urban areas using high level sampling technique combined with gaseous sampling from August 2006 to January 2007 and August 2007 to January 2008 covering two rice crop burning periods. The findings of SO_2, SPM and NO_2 concentration in their (24 hour) sampling were 5±4 µg/m^3 to 55±34 µg/m^3, 100±11 µg/m^3 to 547±152 µg/m^3 and 9±5 µg/m^3 to 91±39 µg/m^3 respectively. According to the results the concentration of pollutants were higher in commercial area as compare to other sampling sites and selected pollutants showed clear increase concentration in the residue burning month (October–November) with the incorporation of metrological parameters like precipitation, wind direction and atmospheric temperature.

Continues measurements of air pollutants like NO_2, SO_2 and CO were carried out in rural area of Anantapur, India by (Lingaswamy et al., 2017) using multi gas analyzer (Model APMA-370, HORIBA) from January to December 2012 and what they find out was that the maximum concentration of CO was measured in winter (310±17ppbv) followed by summer and post monsoon while lowest in monsoon (72±9 ppbv). The average concentration of NOx in winter, monsoon, post monsoon and summer were 0.76, 0.88, 0.91 and 0.80 respectively and lowest concentration of SOx was found in monsoon (0.46 ±0.02 ppbv) and highest in winter (2.42 ±0.21ppbv). The level of air pollutants (CO, NOx and SOx) were influenced by urban effect, meteorology and trans-boundary transport in troposphere.

(Shabbier et al., 2015) conducts a research in which they monitored spatial distribution of tropospheric NO_2 along National highway N5 from Islamabad to Lahore (300 km long) from 13 to 14 November 2012 with the help of first car MAX-DOAS (multi axis differential optical absorption spectroscopy). Source identification revealed that the concentration of NO_2 was high in major cities along the national highway and the highest density of NO_2 vertical column was detected in two major cities of Rawalpindi and Lahore. They also present the comparison of NO_2 measured with car MAX-DOAS and ozone monitoring instrument (OMI) and both of the instruments showed the same results but car MAX-DOAS shows more detailed spatial distribution of NO_2.

The air pollution status due to large air pollutants emission from highly industrialized city of Visakhapatnam is monitored by (Suneela and Rekha, 1999). Rain water composition and air quality were monitored with help of 16 during post monsoon from October to January 1998. Their results indicated that pollution level of Visakhapatnam were so high that in future it will be one of the most polluted cities of India. Industrial zone emissions of criteria pollutants like sulfur dioxide, particulate matter and nitrogen dioxide were high among different monitoring stations and Air Quality Exposure Index (AQEI) computed that out of 16 stations four of them fall in highly polluted category, six of them were moderately polluted and only one in a clean category. Total deposition of NO_2 and SO_2 was estimated 149.7, 43.95, 92.98 meq/m^2/yr in industrial, residential and commercial areas, respectively.

(Rosario and Scandura, 2016) measured air quality of Catania city (Italy) from 2003 to 2012 to drawn a comparison of change in air quality using four air monitoring stations of city known as Air Quality Monitoring Network (AQMN). Pollutants impact was drawn from analysis of daily concentration of NO_2, SO_2, CO, PM_{10} and O_3 and then data has been assembled into classes by applying Sturge's rule. The results obtained from station (S1) showed reduction in pollution like NO falls from class 2 (18.55–35.80μg/m^3) to class 1 (1.29–18.54μg/m^3). NO_2 falls from class 5 (55.00–66.35μg/m^3) to class 3 (32.28–43.63μg/m^3). CO falls from class 3 (1.14–1.64mg/m^3) to class 1 (0.12–0.62mg/m^3). SO2 uniquely remains in class 1 with concentration interval of 0,18 and 1,08 μg/m^3. Results obtained from station (S2) shows increase in concentration of pollution. O_3 concentration rise from class 1 to class 3 (4.24–14.49μg/m^3) to (32.28–43.63μg/m^3) respectively. CO falls from class 2 (0.52– 0.82mg/m^3) to class 1 (0.21–0.51mg/m^3). PM_{10} rise from class 2 (9.81–16.21μg/m^3) to class 4 (22.63–29.03μg/m^3). Results of station (S3) were little different. In this station concentration of NO_2 and CO has reduced. NO_2 falls from class 5 to class 4 and CO falls from class 4 to class 2. NO and SO_2 were stable and placed in a class 2 and class 1 respectively. PM_{10} concentration rise from class 2 to class 3. Concentration of pollutants over the ten years from station (S4) showed that O_3 rise from class 2 (13.61–24.96μg/m^3) to class 6 (59.05–70.40μg/m^3) and PM_{10} rise from class 2 to class 3. CO and NO showed stability and it remains in class 2 and class 1 respectively. NO_2 falls from class 5 to class 2.

Samples of ambient air and atmospheric precipitation were collected for 7 months (ambient air) and for 1 year (wet deposition) at a single site in Washington, USA by (Melaku et al., 2008) to analyze lead, cadmium, chromium and arsenic. The wet deposition ranges of heavy metal concentration for 1 year were 0.11-3.2 mg/l, 0.060-5.1 mg/l, 0.062-4.6 mg/l and 0.20-1.3 mg/l for lead, cadmium, chromium and arsenic respectively. With the precision of 5% for measurements more than 95%. The heavy metals range for ambient air were 2.90-137 ng/m3, 1.50-30.0 ng/m3, 16.8-112 ng/m3 and 0.800-15.7 ng/m3 for lead, cadmium, chromium and arsenic respectively with the 10% precision. In both the samples (wet deposition and ambient air) there was high seasonal variation observed for heavy metals

1.9 Objectives

1. To assess pollutant gasses (SO_2, NO_2, O_3, CO and CO_2) in ambient air in the vicinity of Hattar Industrial estate.

2. To monitor the concentration of coarse PM_{10} and fine $PM_{2.5}$ particulate matter in the vicinity of Hattar Industrial estate.

3. To determine chemical qualitative analysis of PM_{10} and $PM_{2.5.}$

CHAPTER 2

MATERIALS AND METHODS

2.1 Sampling site

Hattar is an industrial estate and it is one of 44 union councils, administrative subdivision of District Haripur in the province of Khyber Pakhtunkhwa, Pakistan. It is located at 33° 51'1N 72° 51'8E and share its border with the Punjab province Tehsil 'Taxila'. It is at the distance of about 55 km from Islamabad (capital of Pakistan) and about 145 km away from Peshawar city (Provincial capital). Hattar is a mountainous range having planes at the elevation of 500 m altitude. This industrial state was established in 1985-86 covering total area of about 4.18 km^2 (1,032 acres) of land. As it is established over last two decades there are around 400+ operational units mainly composed of textile, paper printing, cement, rubber, leather products, food and beverage, crockery, chemical, publishing, carpets and pharmaceuticals. These units produce a lot of hazardous waste and a survey of hazardous waste producing industries in Khyber Pakhtunkhwa lists 348 industries and most of them were located in Hattar (Rasheed et al., 2013). Effluents from industries are discharge independently and there is no proper waste treatment facility. These industries also produce lot of hazardous gasses and do not contain any type of gas filtration system so that the gasses enters in the environment directly and these industries are the major sources of Smog causing environmental problems in the area. (Rasheed et al., 2013)

Fine particulate matter $PM_{2.5}$, coarse particulate matter PM_{10}, carbon dioxide, carbon monoxide, oxides of sulfur, oxides of nitrogen and ozone sampling were performed with in the vicinities of Hattar (industrial area) at six different locations, covering industrial and residential area. Sampling areas were selected and marked on map with the help of GIS on sadia cements (cement factory), Gold roofs (pre-feb house factory), 600 quarters labour colony (residential area), Nasir advertisers (billboard factory), Wah noble acetates (Chemicals Company), 400 quarters colony (residential area), shown in Figure 2.1. These sites were selected on the basis of the large amount of greenhouse gasses emissions and heavy traffic flow (trucks, trollies and bulldozer's with produce large amount of gasses and particulate matters) which impacts the air quality of the Hattar and its surrounding residential area. (Cheng et al., 2010; Ho et al., 2006).

Major sources of emission at sampling location (SL1) were smoke coming out of machinery from fuel burning, heavy vehicles and generators. Major sources of sampling location (SL2) were smoke coming out of chimney, dust, Fumes and heavy vehicles. (SL3) sources are construction activities, generators, and residential activities. Sampling location (SL4) emissions consist of chemical fumes, traffic, and other sources of transportation. Location (SL5) emissions consist of residential activities, construction activity and generators etc. (SL6) location contains printing fumes, dust, welding smoke, heavy vehicles etc.

Table 2.1 Detail of sampling sites with coordinates

NO	Sampling location	Sampling design	Coordinates		Category	Human activities
			North	East		
1	Gold wing roofs (pre-fabricated house factory)	SL1	33º53’16	72º50’36	Vehicular/ industrial	Heavy vehicles/ industrial activity
2	Sadia cement (cement factory)	SL2	33º54’00	72º51’47	Vehicular/ industrial	Construction/ heavy vehicles/ industrial activities
3	Labour colony 600 quarters	SL3	33º54’45	72º50’37	Vehicular/ Industrial/ Residential	Heavy vehicles/residential activities/industrial activities
4	Wah noble acetate’s	SL4	33º54’50	72º50’07	Industrial/ Chemicals	Industrial activities/ light transporting vehicles
5	Labour colony 400 quarters	SL5	33º54’38	72º51’28	Vehicular/ industrial/ residential	Industrial activities/ Residential activities/ heavy traffic flow
6	Nasir advertisers	SL6	33º53’20	72º50’06	Industrial/ Vehicular	Metal processing/ heavy vehicles flow/ other industrial activities

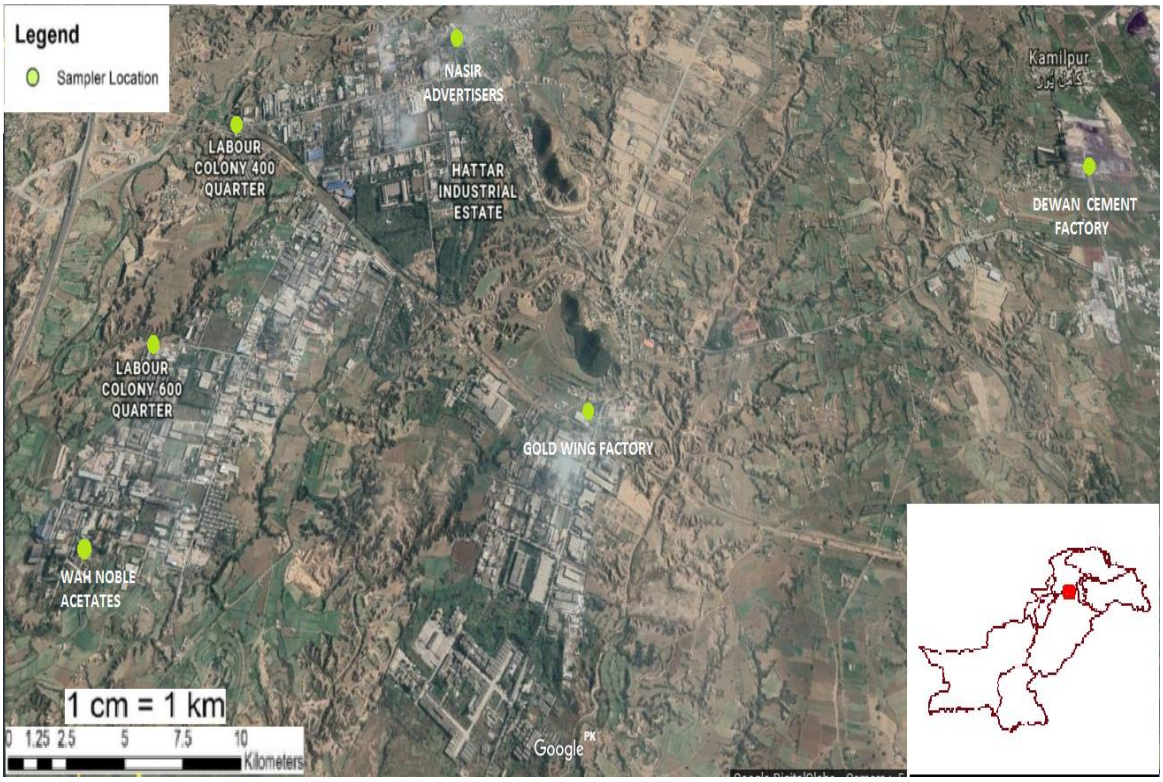

Figure 2.1 Sampling areas sampling point map.

2.2 Sampling technique

Ambient air gasses were analysed with the help of portable ambient air analysers which was placed at roof top in open air at six selected sampling sites for one hour a day and at each location sampling was performed for 3 days. For the sampling of CO_2 Telaire T7001, for CO Smart Sensor AS8700A, for SO_2, NO_2 and O_2 MRU Vario Plus and coarse and fine particulate matter were analysed from low volume duel air sampler. This air sampler is capable of sampling the air at low flow rate (0.016 m^3/min) for consecutive 24 hours. Sampler will be placed on roof top at six selected locations of Hattar to assess the particulate pollution. The sampling will be performed for consecutive 3 days at each sampling site. Low volume $PM_{2.5}$ and PM_{10} sampler draws air inside at low flow rate. Micro fibre filters were used for 24 hour $PM_{2.5}$ and PM_{10} collection at each point. Quarts filters were pre and post weighed while sampling to determine the mass of particulate matters of both size. Concentration of particulate matter will be finding out by subtracting the initial weight with the final one gained from $PM_{2.5}$ and PM_{10}.

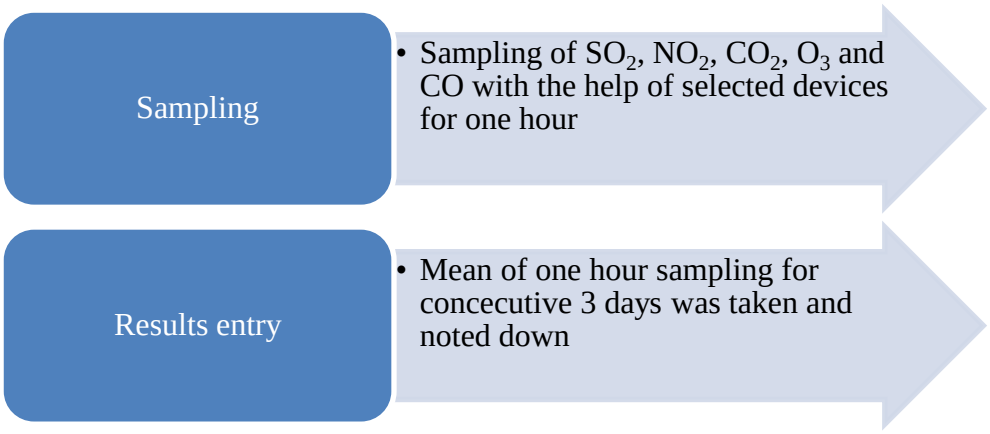

Figure 2.2. Show methodology followed for ambient gas sampling.

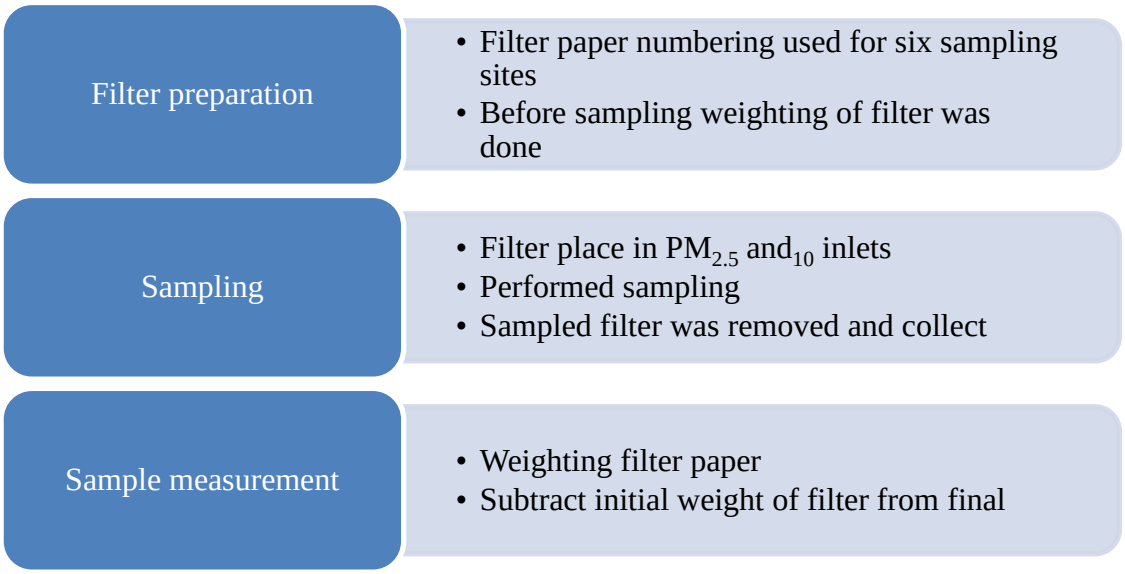

Figure 2.3. Methodology followed for $PM_{2.5}$ and PM_{10} sampling.

2.3 Apparatus description

2.3.1 Telaire 7001

To measure CO_2 in the ambient air we use portable equipment Telaire 7001 as shown in figure 2.4. This equipment measures CO_2 with the method of duel beam absorption infrared technology which is planted in its CO_2 sensors. The sensors in this equipment measures both temperature and CO_2 and calculates and display real-time ventilation. It takes warm up time of about <60 seconds and it's capable of displaying carbon dioxide from the rage of 0 to 10,000 ppm with the accuracy of ±50 ppm. Data of CO_2 in this equipment can be recorded and transfers to the computer.

Figure 2.4 Telaire 7001 for carbon dioxide sampling

2.3.2 Vairo plus MRU

To measure SO_2, NO_2 and O_3 Vairo plus MRU air fair as shown in Figure 2.5 was used which is suitable for ambient air quality analysis and it is equipped with combined infrared technology (NDIR) and for maximum versatility electrochemical sensors are installed, complies with the method of USEPA CTM-030 and CTM-034. It stores internal data of about 8,500 measurements.. It is capable of measuring Nitrogen dioxide from 0 to 200µg/m^3 with an accuracy of ±5µg/m^3 and sulfur dioxide from 0 to 2,000µg/m^3 with an accuracy of ±10µg/m^3.

Figure 2.5 Vairo plus MRU for SO_2, NO_2 and O_3 sampling

2.3.3 Smart sensor AS8700a

To measure the concentration of CO in the ambient air Smart sensor AS8700a as shown in figure 2.6 has been used. It is a portable device to detect the concentration of carbon monoxide in its surrounding environment containing the alarm system because when the CO concentration increases then alarm rings. It is a device with high precision and extremely light weight so it is very easy to operate and carry. It is normally used in chemical, metallurgy, fire, telecommunication, textile, coal, paper, municipal, food, petroleum and other industries. It displays CO concentration ranging from 0 to 1000PPM with an accuracy of ±5% or ±10PPM and displays resolution of 1PPM.

Figure 2.6 Smart sensor AS8700a for carbon monoxide sampling

2.3.4 Low volume duel air sampler

To collect the air born small particles from the atmosphere we use low volume samplers shown in Figure 2.7. In this sampler there are lot of option available and it is very versatile so with the help of this user can easily develop information about size and quantity of airborne particulate. In low volume samplers air is drawn inside with the help of powerful motor through selective inlets and air passes from filters leaving behind particulate matter on the filter paper. Micro fiber quartz filter collects $PM_{2.5}$ and PM_{10} with the help of their own size inlets. Sensors that monitor pressure and temperature also maintain flow of air. Low volume sampler draws low volume of air normally over 24 hours. This sampler commonly consists of following components.

1. Covering for the protection.

2. Low volume blower/electric motor.

3. Control of flow rate which controls the flow of air at 0.016 m^3/min.

For the sampling of $PM_{2.5}$ and PM_{10} selective inlet is use which is of design-size. Cyclone inlet is the size-selected for $PM_{2.5}$ and PM_{10} measurement. To allow the particles to enter from all angles through inlets omnidirectional cyclone design is used. To remove the large size particles inner collection tube is placed. This tube contains an oil-coated surface which is a 'perfect absorber' and that helps to eliminate particle bounce. After the removal of large particles air enters in upward direction trajectory contain small particles. These small particles are then passes from downward trajectory so that they deposited on a filter paper for analysis. Flow rate of 0.016 m^3/min has design generally for popular cyclonic impaction.

Figure 2.7 Low volume duel air sampler for particulate matter sampling

2.4 Filter medium

Proper analytical technique is pre-assured, appropriate filter and monitoring of time-integrated ($PM_{2.5}$ and PM_{10}) and ensures knowledge of predicted properties.

• Particle sample efficiency

Filter capable of removing 99% of the particle present in the inlet when air is draws from it.

• Mechanical stability

To minimize leakage and wear during handling filter enough to be substantial.

• Chemical stability

There will be no chemical reaction between the trapped particles and filter paper.

• Temperature stability

Filter must hold the original structure and porosity during sampling. Quartz fiber filter is the most common filter used for the sampling of coarse and fine

particles. Quartz filters are prepared by the process in which spun glass fibre by inclusion of the fibre with organic binder and then compressing this material in paper machine. On the basis of following qualities quartz filter were used.

1. Works accurately with in high temperature.

2. They resist high humidity level so they are used in humid environment.

3. Their collection efficiency is very high.

4. Other filter are very fragile and must handle with care then Quartz filter because Quartz filter are extremely difficult to ash by the chemicals or heat

2.4.1 Pre weighing of filters

Filter paper will weighed on an analytical weighing balance before the sampling to examine the initial weight of filter paper under approved humidity and temperature so through this way we can calculate the weight of a particulate matter after sampling. The temperature must be around 20 to 25 °C (±2 °C) while the humidity must be around 50 to 55% during sampling.

2.4.2 Filter loading procedure

Micro fibre filter must be placed in the selective inlets of the gasket with proper handling for the sampling of PM_{10} and $PM_{2.5}$. The filter paper should not be loaded with the bare hands to avoid blockage of pores and to avoid contamination filter paper must be carry and loaded in the gasket with proper technique.

2.4.3 Removal of used filter

Checking of gasket of both panels that whether it is in a good condition or not and then wipe cleaning the screen is the first step. Then we check the filter paper by removing it from gasket and if any unusual condition was found that might affect the sample then they were noted down. As shown in figure 2.8. The filter paper after the removal from gasket was then folded down in a way that the particulate-coated surface were in contact and then folded filter was weighed in the same lab under the same conditions. Filter paper must be placed in a zip lock bag after weighting.

Figure 2.8 Filter paper before and after sampling

2.5 Calculation of PM_{10}

By using following formula PM_{10} concentration is calculated:

Particulate matter Concentration C ($\mu g/m^3$).

PM_{10} = (Wf –Wi) X 106/ V ---------- (i)

Where, initial weight of clean filter is 'Wi', Wf is the exposed filters final weight, 106 is used to convert µg from g, V is the sampled air volume (m^3) and PM_{10} is the particulate matters total mass concentration ($\mu g/m^3$).

2.6 Calculation of $PM_{2.5}$

By using following formula $PM_{2.5}$ concentration is being calculated:

Particulate matter Concentration C ($\mu g/m^3$)

$PM_{2.5}$ = (Wf –Wi) X 106/ V---------- (ii)

Where, initial weight of clean filter is 'Wi', Wf is the exposed filters final weight, 106 is used to convert µg from g, V is the sampled air volume (m^3) and $PM_{2.5}$ is the particulate matters total mass concentration ($\mu g/m^3$).

2.7 Siting requirement

During sampling the entire sampling sites requirement meets according to sampler protocol. The sampler must place on a high roof of building and away from the plantation site for consecutively 24 hours. For low volume duel sampler following rules must be followed.

1. Continual electricity supply for the sampler.

2. Near the sampler there should be no interference like trees and buildings.

3. There should be no vent or exhaust near the sampler.

2.8 Conversions

Conversion from ppm to µg/m^3

Conversion is required to compare the values with Pak-NEQS.

$$\mu g/m^3 = \frac{ppm \times Molecular\ weight\ of\ gas}{PV=nRT} \times 1000$$

PV = nRT

P (Atmospheric pressure) = 101.325 KPa

V (Volume of gas) = ?

n (Number of moles of gas = 1

R (Gas constant) = 8.314 j/mol.K

T (Temerature in Kelvin) = 273+ ^oC

2.9 Atomic Absorption Spectroscopy (AAS)

For the quantitative analysis of metals present in the particulates atomic absorption spectroscopy is the standard analytical technique used most commonly. In this study atomic absorption spectroscopy is used for the analysis of different metals like Zn, Ni, Pb, Cr, Cd and Cu in selected samples. Metal (salt) was used as standard to generate the calibration curves over metal concentration which ranges from 0 to 10

mg/L. After calibration curve preparation, the filter paper containing field samples were digested for their analysis on AAS.

2.9.1 Sample preparation for atomic absorption spectroscopy

Aqueous medium sample can only be analysed in atomic absorption spectroscopy and to fulfil this requirement filter containing sample must be digested. For digestion each filter paper is divided into small pieces and transfer into a beaker then we add 10ml of aqua regia which is prepared from 1:3 nitric acid and Hcl respectively and then cover the container with the help of lid for 24 hours for maximum metal extraction. After 24 hours we place beaker on hot plate for 1 hour to evaporate aqua regia, after evaporation 25 ml of distilled water is added in that beaker containing sample and then pass it from the Whatman 41 filter paper. After completing the digestion process aqueous medium sample was stored in a sterilized polyethylene bottle and then analysed on atomic absorption spectroscopy.

2.9.2 The Atomic Absorption Spectrometry (AAS) working principle

The working principle of atomic absorption spectroscopy depends on "Matter emits the light at same wavelength at which it absorbs light''. Atom absorbs radiation of same amount in ground state as it emits in the excited state. Sample solution is vaporised first and then atomized in a flame, it is transformed to unexcited ground state that at specific wavelength absorbs light. Than lamp emits the light beam whose cathode is made up of the element of concern, that light passes through the flame. Atom absorbs the radiation and transforms ground state atom to an excited state. At selected wavelength absorption is measured by change in the intensity of light striking the detector, which is directly related to elements amount in sample.

2.9.3 Heavy metals calculation formula

By using following formula heavy metals concentration can be calculated:

Concentration in ppm

$$\text{Ppm} = \frac{V}{W} \times \text{AAS}$$

Where ‘V’ is final volume after digestion (ml), ‘W’ is sample weight (g), ‘AAS’ is AAS metal concentration result in [ppm = mg/l]

2.10 Statistical Analysis

The obtained data was tabulated in MS Excel, formula sheet was used to measure PM

Heavy metals data was tabulated means were calculated with replication value in MS Excel

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Particulates and gasses concentration

Pollution in the atmosphere of industrial areas is extremely harmful for both environment and human health and it has also great impact of economics as well (Gulia et al., 2015). Emissions from the road traffic are one of the major contributors to air pollution (Mukerjee et al., 2015). The problem of air pollution was widely observed in urban centres and industrial area due to the massive increase in traffic in past few years, adding elevated level of pollution (Franco et al., 2013).

As we all know that air pollution is capable of causing health issues and environmental problems including acid rain, secondary pollutants production, problems of fine and ultrafine particulates and increase in vehicles (Yu et al., 2009). Environmental standards are less stringent, weak vehicular emission quantification and understandings are the major problems in the developing countries and increasing vehicles also enhancing this problem too (Guo et al., 2007). Air pollution formation and particulate matter frequent occurrence in atmosphere have gained lot of attention.

Industrial activity produces large amount of particulate matter varying in different sizes as shown in Table 3.1. Fossil fuel burning produces small particles and they are likely to be the most dangerous because deep into the lungs they can be inhaled and then they settles in the body from where body's mechanism of natural clearance cannot remove them easily (Krzyzanowski et al., 2008). Small particulate constituents also tend to be acidic and chemically active as well and therefore can be more harmful. Particulate pollution can cause respiratory illness and lung function acute changes (Douglas et.al 1996), and these problems lead towards admission in hospital for heart and respiratory disease. Respiratory infections can also lead towards job and school absence or chronic conditions augmentation can cause bronchitis and asthma (Deborah, 1996).

Table 3.1. Different size of particulate and sources coming out of industries.

Sr. No	Type of particulate	Diameter
1	Cement dust	80-90% > 30 um
2	Motor vehicle	0.01-5000 um
3	Urban road dust	3-100 um
4	Fly Ash	1-2000 um
5	Coal Dust	3-100 um

The health effects of gaseous pollutants are extremely negative. Their role is also very important in atmospheric chemistry because of environmental changes. NO_2 and SO_2 chemically reacts in an atmosphere and forms different acid with ultimately deposits on oceans and land in the form of acid rain. Various health effects are caused by NOx which emits from the cement kilns by the high temperature combustion of fuel. After power generation cement industry is the second most largest CO_2 emitting industry. Nearly about 5% of manmade global CO_2 emits from cement industry, of which 40% is from fuel burning and 50% from chemical process.

Table 3.2.Total concentration of pollutant gasses

Sr. no	Sampling location	Days	SO_2 ($\mu g/m^3$)	NO_2 ($\mu g/m^3$)	O_3 ($\mu g/m^3$)	CO_2 (ppm)	CO (mg/m^3)
1	Gold wing roof (SL1)	1st day	41.3	51.3	25	435	2.3
		2nd day	38.4	59.7	28	410	3.1
		3rd day	43.8	48.1	24	429	3.9
2	Dewan Cement factory (SL2)	1st day	50.1	65.5	19	452	5.2
		2nd day	53.3	61.9	21	461	4.4
		3rd day	49.6	66.3	23	449	5.8
3	Labour colony 600 quarters (SL3)	1st day	81.4	108.3	54	480	12.3
		2nd day	86.8	96.2	50	493	10.6
		3rd day	80.7	101.8	55	460	13.1
4	Wah noble acetates (SL4)	1st day	69.3	69.1	49	450	8.2
		2nd day	65.1	73.4	41	437	5.9
		3rd day	70.5	75.7	46	441	6.7
5	Labour colony 400 quarters (SL5)	1st day	51.6	58.4	32	439	5.8
		2nd day	53.9	63.9	36	442	6.3
		3rd day	54.2	56.2	40	451	6.8
6	Nasir advertisers (SL6)	1st day	72.4	81.4	51	440	11.4
		2nd day	77.7	76.9	43	455	9.5
		3rd day	70.4	71.5	52	449	8.9

Table 3.3 Total concentration of $PM_{2.5}$

Sr.no	Sampling location	No of days	Initial weight Wi in grams (g)	Final weight Wf in grams (g)	Daily $PM_{2.5}$ Concentration $\mu g/m^3$
1	Gold wing roof (SL1)	1st day	0.1448	0.1488	173.611
		2nd day	0.1441	0.1484	181.632
		3rd day	0.1463	0.1500	168.590
2	Dewan Cement factory (SL2)	1st day	0.1459	0.1503	192.368
		2nd day	0.1455	0.1501	199.681
		3rd day	0.1468	0.1511	186.291
3	Labour colony 600 quarters (SL3)	1st day	0.1457	0.1494	160.590
		2nd day	0.1440	0.1472	138.889
		3rd day	0.1449	0.1483	147.569
4	Wah noble acetates (SL4)	1st day	0.1439	0.1480	175.951
		2nd day	0.1449	0.1488	169.271
		3rd day	0.1430	0.1473	186.632
5	Labour colony 400 quarters (SL5)	1st day	0.1454	0.1479	108.507
		2nd day	0.1440	0.1468	121.528
		3rd day	0.1409	0.1436	117.188
6	Nasir advertisers (SL6)	1st day	0.1458	0.1499	177.951
		2nd day	0.1435	0.1474	169.271
		3rd day	0.1441	0.1483	182.292

Table 3.4 Total concentration of PM_{10}

Sr no	Sampling Location	No of days	Initial weight Wi in grams (g)	Final weight Wf in grams (g)	Daily PM_{10} Concentration $\mu g/m^3$
1	Gold wing roofs (SL1)	1st day	0.1420	0.1483	273.438
		2nd day	0.1462	0.1527	282.118
		3rd day	0.1436	0.1497	264.654
2	Dewan cement factory (SL2)	1st day	0.1441	0.1511	301.174
		2nd day	0.1422	0.1489	291.862
		3rd day	0.1461	0.1536	312.631
3	Labour colony 600 quarters (SL3)	1st day	0.1438	0.1487	212.674
		2nd day	0.1436	0.1508	225.694
		3rd day	0.1461	0.1518	247.396
4	Wah Nobel acetates (SL4)	1st day	0.1446	0.1511	282.118
		2nd day	0.1450	0.1519	299.479
		3rd day	0.1458	0.1522	277.778
5	Labour colony 400 quarters (SL5)	1st day	0.1438	0.1471	143.229
		2nd day	0.1423	0.1463	173.611
		3rd day	0.1450	0.1485	151.910
6	Nasir advertisers (SL6)	1st day	0.1442	0.1491	212.674
		2nd day	0.1452	0.1510	251.736
		3rd day	0.1460	0.1513	230.035

3.1.1 Gold wing roof (SL1)

The results of 3 days sampling for 24 hours of PM10 and PM2.5 vary from 264.6541µg/m3 to 282.1181µg/m^3 and 168.5901µg/m^3 to 181.6321µg/m^3 with mean concentration of 273.4031µg/m^3 and 174.6111µg/m^3 respectively.

The results of SO_2, NO_2, O_3, CO_2 and CO of 3 days sampling for 1 hour shows the mean concentration of 41.11µg/m^3, 53.031µg/m^3, 25.61µg/m^3, 424.6 ppm and 3.1 mg/m^3 respectively from the respective Gold wing roof factory (SL1) in Hattar industrial estate.

The impact of pollution on the particulate matter and gasses is explored in this study. Gold wing roof is prefab house factory inside the factory machine use for the compaction of thermocol and welding of sheets produce lot of smoke which is the major cause gaseous pollutants and the cutting of sheets and thermocol produce large number of particulate matters. The factory is also surrounded by some other factories like chicken feed factory which also contributes in producing harmful gasses and particulate matters. Although sampling was carried out during wet season as we know that in the start of 2019 there was massive rain fall from January till May but still the study revealed that the amount of gasses and especially particulates were very high.

3.1.2 Dewan Cement factory (SL2)

The sampling revealed that the concentration of PM_{10} and $PM_{2.5}$ vary from 291.862 µg/m^3 to 312.631 µg/m^3 and 199.681 µg/m^3 to 186.291 µg/m^3 with mean concentration of 301.889 µg/m^3 and 192.78 µg/m^3 respectively which is extremely higher than normal.

The results shows that the mean concentration of SO_2, NO_2, O_3, CO_2 and CO at sampling site was 51 µg/m^3, 64.5 µg/m^3, 21 µg/m^3, 454 ppm and 5.1 mg/m^3 respectively from the respective Dewan cement factory (SL2) in Hattar industrial estate.

The sampling was performed for consecutive 3 days for 24 hours for particulates and the study revealed that their concentration was extremely high. The concentration of gasses was also very high except carbon dioxide which was within the limits. Sampling was performed in April 2019 higher precipitation rate were

observed. Sampling site contains massive amount of heavy transporting vehicles for the loading of cement and road condition was also not so good because of constant traffic flow, loading procedure of cement bags also contributes in the production of particulate matter and the amount of vegetation were also very low, while the cement production process and heavy transporting vehicles also contributes in harm full gasses production like SO_2 and NO_2. NO_2 release when fuel is combusted in the cement kilns at high temperature. From the processing of sulfur and pyrite in raw material and combustion of compounds which bears sulfur e,g oil, coal and petroleum contributes in SO_2 emission. When calcium carbonate in cement factory is heated so CO_2 is directly releases in the atmosphere.

3.1.3 Labour colony 600 quarters (SL3)

During sampling period the results of PM_{10} and $PM_{2.5}$ vary from 212.674µg/m^3 to 247.396µg/m^3 and 138.889µg/m^3 to 160.590µg/m^3 with the mean concentration of 228.588µg/m^3 and 149.016µg/m^3 respectively which is higher than the permissible limits.

The results of pollutant gasses SO_2, NO_2, O_3, CO_2 and CO with the mean concentration was 82.9µg/m^3, 102.1µg/m^3, 53µg/m^3, 477.6 ppm and 12 mg/m^3 respectively of Labour colony 600 quarters in Hattar industrial estate.

Sampling revealed that concentration of particulate matter of PM_{10} and $PM_{2.5}$ was higher than the permissible limits because of the transporting vehicles, residential activities, less vegetation and industrial activities of surrounding factories. 600 quarters colony is in the heart of Hattar industrial estate and surrounded by many pollution emitting factories like TOPS juice factory, Horizon paper and board mills and Cider foods and their chimney emits huge amount of smoke which is major coz of SO_2, NO_2 and CO. That is the reason the concentration of SO_2, O_3 and especially NO_2 is very high then the permissible limits and it is extremely unhealthy for the residents living in this colony and daily interacts with these pollutants. Concentration of pollutants is very high in this sampling site even the sampling was performed during rainy season which helps in cleaning the atmosphere.

3.1.4 Wah Nobel acetates (SL4)

In this sampling point the concentration of PM_{10} and $PM_{2.5}$ varies from 277.778 µg/m^3 to 299.479 µg/m^3 and 169.271 µg/m^3 to 186.632 µg/m^3 with mean concentration of 286.458 µg/m^3 and 177.284 µg/m^3 respectively.

The mean concentration of pollutant gasses SO_2, NO_2, O_3, CO_2 and CO was 68.3 µg/m^3, 72.7 µg/m^3, 45.3 µg/m^3, 442.6 ppm and 6.9 mg/m^3 respectively of Wah Nobel acetates in Hattar industrial estate.

Sampling of this site revealed that the impacts of pollution increase the particulate matter in the atmosphere. It was observed that the concentration of both size particulates were above the permissible limits even it was wet season which normally effects the PM concentration in the atmosphere. It was also revealed that the concentration of pollutant gasses like SO_2, NO_2 and O_3 were comparatively higher then CO_2 and CO which is very harmful for the health of labours. The factory is surrounded by other industries like crescent textile mills, Amin paper and AR processing industries which helps in increasing the particulates and gaseous pollutants. Wah Nobel acetates itself manufacture lot of hazardous chemicals including Butyl Acetate, Acetaldehyde, Acetic Acid, Ethyl Acetate and other Acetate which also helps in the production of hazardous gasses.

3.1.5 Labour colony 400 quarters (SL5)

During sampling the concentration of PM_{10} and $PM_{2.5}$ vary from 143.229µg/m^3 to 173.611µg/m^3 and 108.507µg/m^3 to 121.528µg/m^3 with the mean concentration of 156.25µg/m^3 and 115.741µg/m^3 respectively.

The mean concentration of pollutant gasses SO_2, NO_2, O_3, CO_2 and CO finding was 53.2µg/m^3, 59.5µg/m^3, 36µg/m^3, 444 ppm and 6.3 mg/m^3 respectively at Labour colony 400 quarters in Hattar industrial estate.

The sampling revealed that concentration of particulates was higher than permissible limits even 400 quarters colony is surrounded by vegetative area. The concentration of gasses were also very high except CO_2 and CO and major reason for this might be residential activities of residents, heavy transporting vehicles as this colony is adjacent to Hattar main high way and the factories in its surrounding like

Frontier paper products, Gul banaspati ghee mill and Waheed hafeez ghee industries. Railway track also passes from this colony which helps in increasing the particulates and gaseous pollutants.

3.1.6 Nasir advertisers (SL6)

The concentration of PM_{10} and $PM_{2.5}$ sampling varies from 212.674 µg/m^3 to 251.736 µg/m^3 and 169.271 µg/m^3 to 182.292 µg/m^3 with the mean concentration of 231.481 µg/m^3 and 176.504 µg/m^3 respectively.

Mean concentration of pollutant gasses SO_2, NO_2, O_3, CO_2 and CO was 73.5 µg/m^3, 76.6 µg/m^3, 48.6 µg/m^3, 448 ppm and 9.9 mg/m^3 respectively at Nasir advertisers in Hattar industrial estate.

This study explores pollution impacts on level of atmospheric particulate matters and gaseous pollutants for this sampling of particulate matters was done and it was observed that both PM_{10} and $PM_{2.5}$ were higher than the permissible limits and also pollutant gasses were sampled and their concentration were above then the given standards. Major reason for this high concentration might be the lack of vegetation, the condition of roads was not so good and there was high traffic flow also in that area for carriage purpose. Nasir advertising agency itself emits huge amount of pollutants in atmosphere particulates were produced while welding of bill board rods and gaseous pollutants were produce while printing of Pena flex. Sampling site was also surrounded by other industries like Pakistan steel re-rolling mills and Bloom pharmaceuticals also contributes a lot in the production of environmental pollutants.

3.2 Particulate matter (PM_{10})

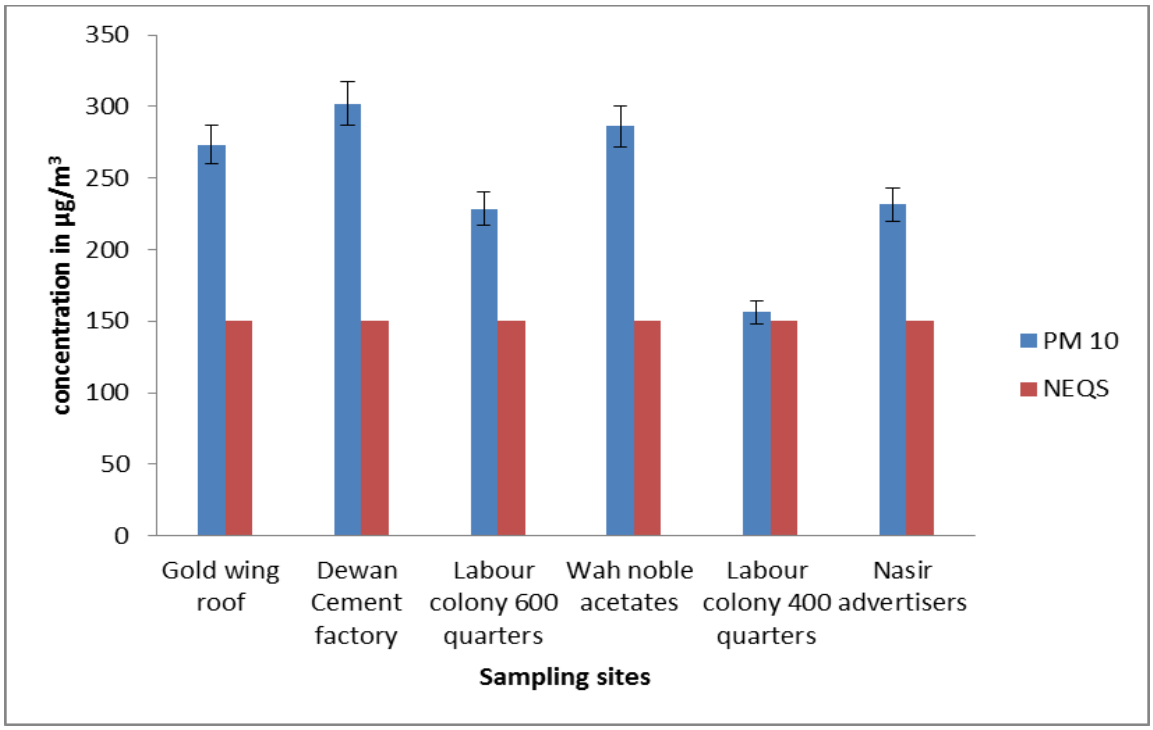

Figure 3.1 Mean concentration of PM_{10} at selected sampling sites

The study reveals that PM_{10} concentration was highest in Dewan cement factory even it is far away from the main industrial estate but the reason for high concentration of PM_{10} might be the heavy traffic flow because it is close to the main road of Hattar and road condition is not appropriate so it is the main source of dust in that area along with so other cement factories adjacent to it. Fuel burning loading and unloading of cement bags also contributes in PM_{10} pollution.

Second highest concentration of PM_{10} was observed in Wah Nobel acetates as shown in Figure 3.1 which is located in the heart of industrial estate and concentration was more than 146 then the given NEQS which is almost double and reason of high concentration is the adjacent factories and the fuel burning with in the factory. The 3rd highest reading was observed in Gold wing roof factory which is pre-fabricated house factory and it produce lot of dust while cutting thermacol and metal sheets other possible reason might be heavy traffic dust along with the factory generators and dust produce from factories in its surrounding. Concentration of PM_{10} was 125µg/m^3 higher than NEQS in Gold wing roof factory which is very high. The next highest concentration of PM_{10} was observed in Nasir advertisers which was 231.48µg/m^3

which is 80µg/m^3 higher than permissible limits. The reason for high concentration in this area might be pharmaceutical companies, agricultural activities, heavy transporting vehicles, printing of Pena flex, billboard welding, cutting and grinding. Following Nasir advertisers the 5th highest concentration was observed in 600 quarters colony which was 228.588µg/m^3 and that is 78 higher than the given NEQS. Reason for high concentration in this area might be the residential activities of residents like using generators, cars for transportation etc and major cause of particulates are factories in its surrounding which produce lot of smoke and cause pollution. Lowest concentration was observed in 400 quarters colony which was 156.25µg/m^3 and only 6 higher than the limits. The reason for average concentration as compare to other industrial area is because 400 quarters colony is a residential area and it is outside from the rest of the industries.

3.3 Particulate matter $PM_{2.5}$

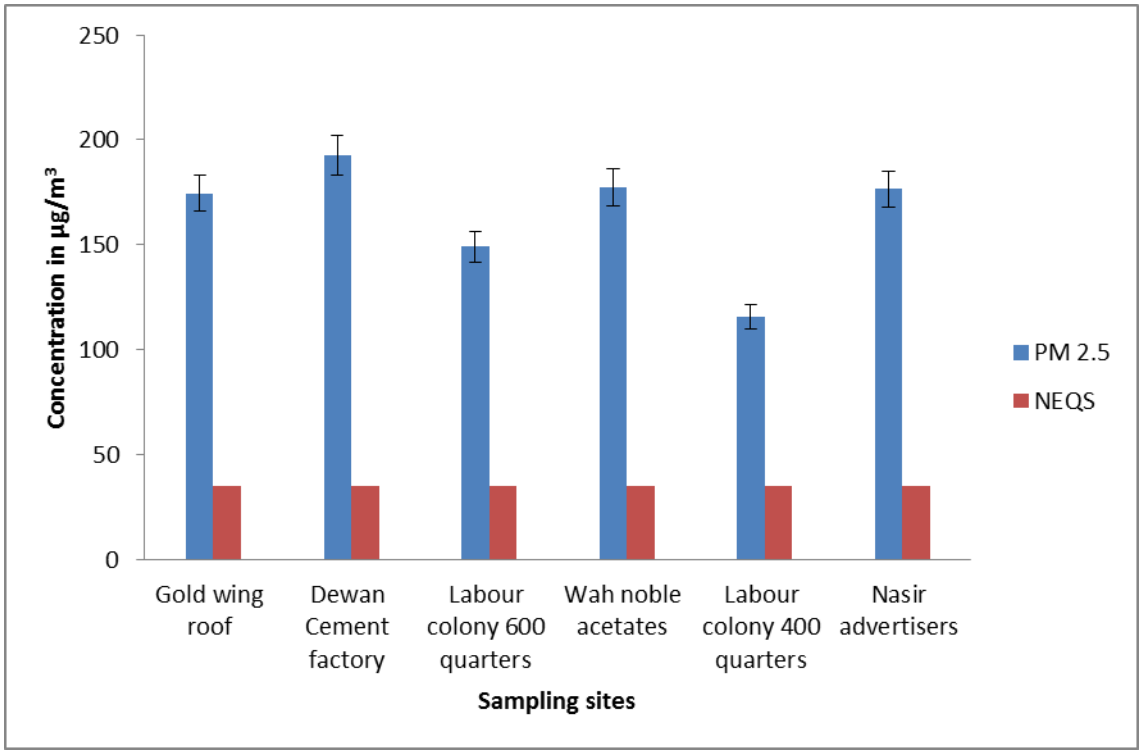

Figure 3.2 Mean concentration of $PM_{2.5}$ at selected sampling site

The concentration of $PM_{2.5}$ is more harmful than the PM_{10} because of its size and it can be inhaled easily. As shown in figure 3.2 Dewan cement factory contains the highest concentration of $PM_{2.5}$ (192.78µg/m^3) which is 157µg/m^3 higher than the permissible limits. As discussed earlier the reason for high concentration might be

heavy vehicles movement in the vicinity of cement factory because diesel engines produce lot of particulate matters and other cement making activities also. The second highest concentration was observed in Wah noble acetates which was 177.284µg/m^3 and that is 142µg/m^3 higher than permissible limits of Pakistan. The reason for high concentration in this sampling site was the process of producing harmful chemicals by factory itself and rest of factories in its surrounding. The 3rd highest concentration of $PM_{2.5}$ was observed in Nasir advertisers (176.504µg/m^3) which is 141µg/m^3 higher than limits and reason for high concentration might be the burning of fuel for the generators in the factory and welding process which is widely used in the factory. Surrounding pharmaceutical factories also play its part in the contribution of particulates. Gold wing roof factory contains the 4th highest concentration of $PM_{2.5}$ according to sampling (174.611µg/m^3) which is 139µg/m^3 higher than permissible limits and reason for high concentration might be the process of cutting and assembling of thermacol and metal sheets. Rest of the activities also play its part like loading un-loading process of pre-fabricated sheets and the movement of trucks in vicinity of factory. The 5th highest concentration of $PM_{2.5}$ was found in 600 quarters colony (149.016µg/m^3) which is 114µg/m^3 higher than NEQS the reason of high concentration in the residential area is because it is surrounded by other factories and paper mills. Residential activities also play its part in contribution of particulates. Lowest concentration of $PM_{2.5}$ was found in 400 quarters colony (115.741µg/m^3) which is 80µg/m^3 higher than the limits. The reason for high concentration in residential area is because it is close to main highway of Hattar and little contribution from train because railway track also passes from this colony.

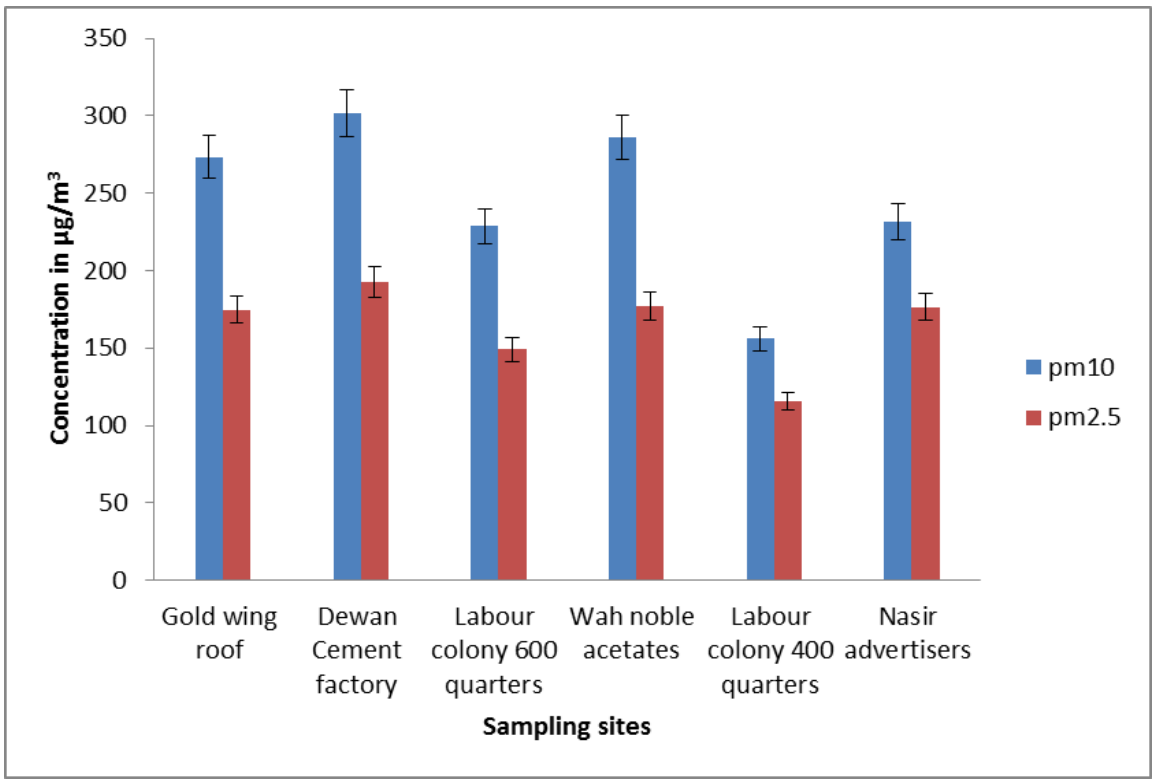

Figure 3.3 Comparison of PM_{10} and $PM_{2.5}$ in Hattar industrial area

The concentration of $PM_{2.5}$ and PM_{10} shown in figure 3.3 shows that the overall concentration of both particulates are very high in Hattar as compare to permissible limits by WHO as well as Pak-NEQS air quality standards with the mean concentration of 163.833 µg/m^3 and 245.833 µg/m^3. The attained result of $PM_{2.5}$ and PM_{10} shows that other industrial estates of Pakistan also might contain high concentration of particulates.

Some of the reasons responsible for high concentration of PM_{10} and $PM_{2.5}$ in Hattar are system of poor mass-transit, substantial rise in vehicles, lack of vegetation in roadside and paved areas; soil erosion, dry climate and automobile emission from poorly maintained and old vehicles have been responsible for increase in particulates. PM is high generally in summer than winters. Movement of trucks are extremely high in hattar for transportation of material and goods and according to research truck emits highest quantity of smoke (0.56 g/s) (Ilyas et al 2006).

3.4 Sulfur dioxide

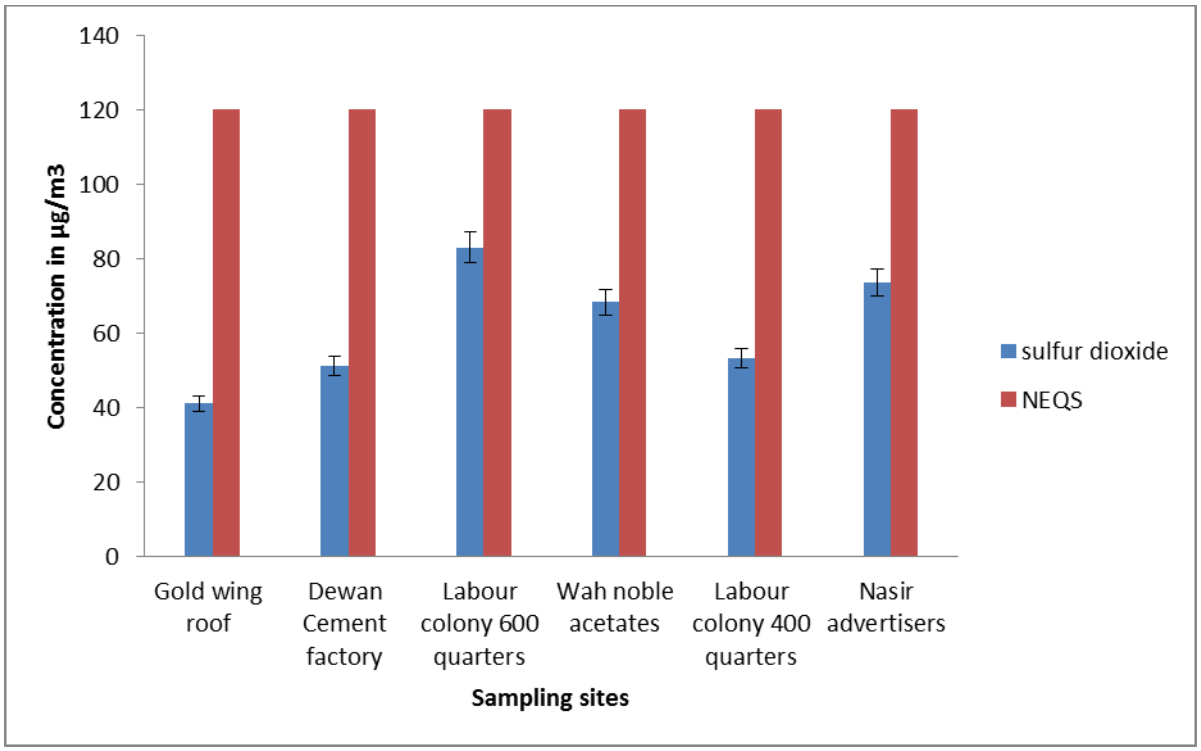

Figure 3.4 Mean concentration of sulfur dioxide on a sampling site

According to the results as shown in figure 3.4 the highest concentration of sulfur dioxide was observed in labour colony 600 quarters with the mean concentration of 82.9µg/m^3 because of the factories in its surroundings the second highest concentration was observed in Nasir advertisers which was 73.5µg/m^3 and it is because of the pollution in its surrounding area. The 3rd highest concentration of sulfur dioxide was observed in Wah Nobel acetates which was approximately 68.3µg/m^3 and major reason is production of chemicals in factory. Fourth highest concentration of SO_2 was observed in labour colony 400 quarters with mean concentration of 53.2µg/m^3 because of main highway. After 400 quarters colony the highest concentration of sulfur dioxide was observed in Dewan cement factory with mean concentration of 51µg/m^3. The factory is outside from main industrial estate but has a potential of producing harmful gasses. Least high concentration of SO_2 was observed in Gold wing roof factory with the average concentration of 41.1 µg/m^3 it is comparatively low because factory is located comparatively in less polluted environment and emission of gasses are low.

Over all the concentration of SO_2 was below than the Pak-NEQS 24 hours limit (120µg/m^3) but higher than the WHO ambient air quality guideline value which is 20 for 24 hour (WHO 2006). Sulfur dioxide main sources according to research conducted in 2005 industrial process, power generation plants and diesel engines, as compare to 1980 diesel engines were 3 times higher in 2005 (World, 2006a).

3.5 Nitrogen dioxide

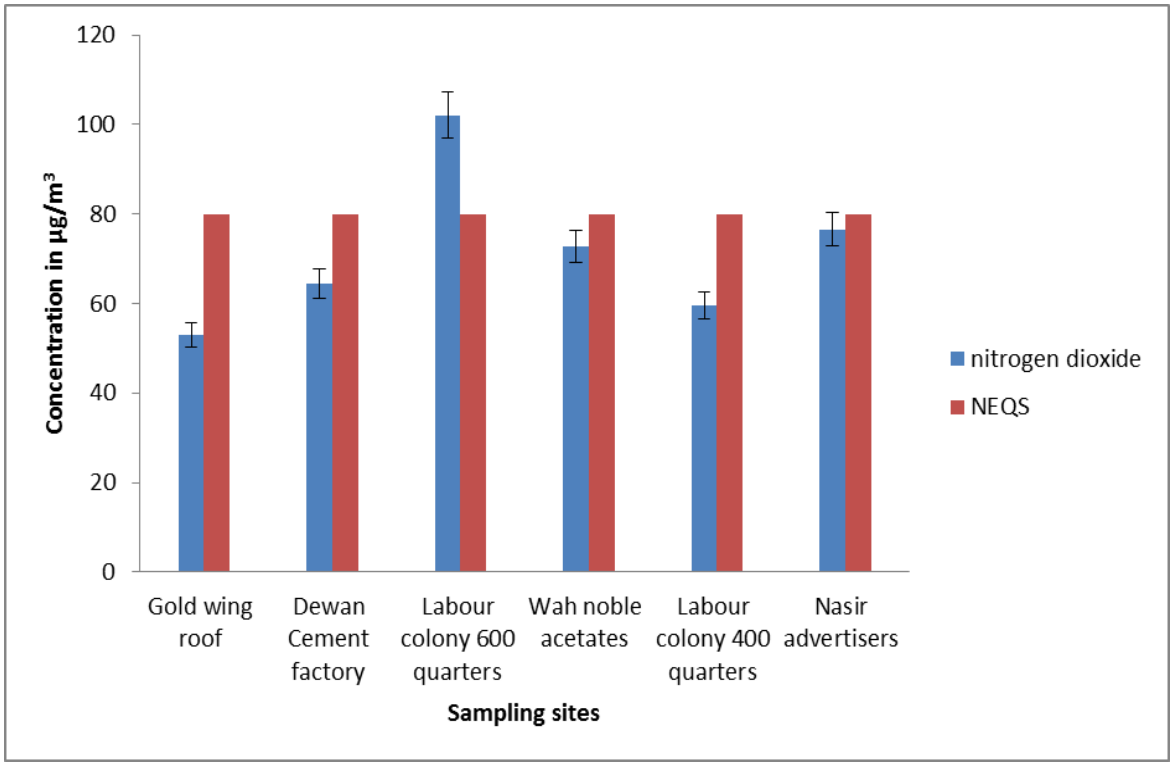

Figure 3.5 concentration of nitrogen dioxide on a sampling site

According to the research the highest concentration of NO_2 was observed in Labour colony 600 quarters which was more than 100µg/m^3 as shown in Figure 3.5. The reason for the high concentration in residential area is because of the surrounding factories specially tops food factory which produce lot of smoke from its boiler and this high concentration shows that how much harmful it will be for the residents of this colony. The 2nd highest concentration was observed in Nasir advertisers which was approximately 76.6µg/m^3. The reason for high concentration was the movement of trucks and surrounding factories. The 3rd highest concentration was observed in Wah Nobel acetates which was approximately 72.7µg/m^3 and the reason for high concentration in this area is because of the chemicals production in this factory and Wah Nobel is also surrounded by some of the paper mills which also contribute in the

production of gasses. After Wah Nobel acetates the highest concentration was observed in Dewan cement factory with mean concentration of 64.5µg/m^3 and the reason for NO_2 production in this area is the massive movement of trucks for the transportation of cement nags and cement factory is on a road side so other vehicles also contributes in the production of NO_2 gas. The 5^{th} highest concentration of NO_2 was observed in Labour colony 400 quarters with the mean concentration of 59.5µg/m^3 and the reason of NO_2 high concentration is also the same as of Dewan cement that this residential area is on the road side of Hattar main road. The least high concentration was observed in Gold wing roof factory and the reason for production of NO_2 in this area is because of the fuel burning for generators and surrounding factories.

Over all the levels of NOx are below than permissible limits of Pak-NEQS 24 hours except labour colony 600 quarters but these values are slightly higher than the WHO ambient air quality guideline 40µg/m^3. According to the research CNG vehicles are main responsible for the increase of NOx in the ambient air (Ghauri et al. 2007).

3.6 Ozone

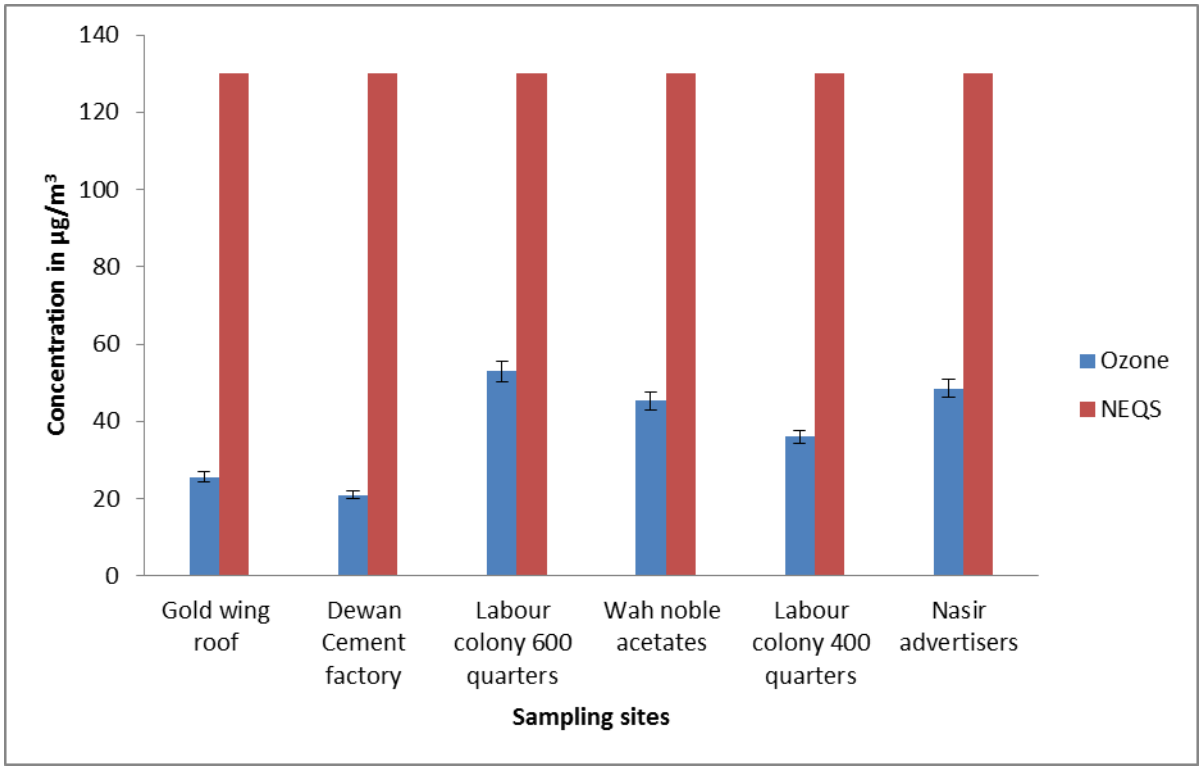

Figure 3.6 Mean concentration of ozone in a sampling site

According to the sampling the highest concentration of Tropospheric ozone was observed in Labour colony 600 quarters with the mean concentration of 53µg/m^3. The reason for the presence of ozone in this area is because high level of smoke and pollution is present in this area. The second highest concentration of ozone was observed in Nasir advertisers with the mean concentration of 48.6µg/m^3. Pollution from the surrounding pharmaceutical companies might be the reason of ozone in this area. The 3rd highest concentration was observed in Wah Nobel acetates with the mean concentration of 45µg/m^3 and the reason for the presence of ozone in this area might be the surrounding factories like textile and paper mills and the production of pollutant gasses by the factory itself might contributes in the production of ozone. After Wah Nobel acetates the highest concentration was observed in labour colony 400 quarters with the mean concentration of 36µg/m^3 and the reason for the presence of ozone in this area might be the same as discuss earlier that it is surrounded by number of factories which produces pollution. The 5th highest concentration of ozone was observed in Gold wing roof factory with the mean concentration of 25.61µg/m^3 and the reason for the presence of ozone in this area might be the surrounding chicken feed factories. The least high concentration was observed in Dewan cement with the mean concentration of 21µg/m^3 and reason for such concentration is because this factory is outside from the rest of industrial estate.

Over all the sampling revealed that the concentration of ozone in the ambient air of Hattar is much lower than the permissible limits of Pak-NEQS and WHO standards but still there are some chances of increase in ozone concentration in future because of increase in NO_2 emitting vehicles.

3.7 Carbon monoxide

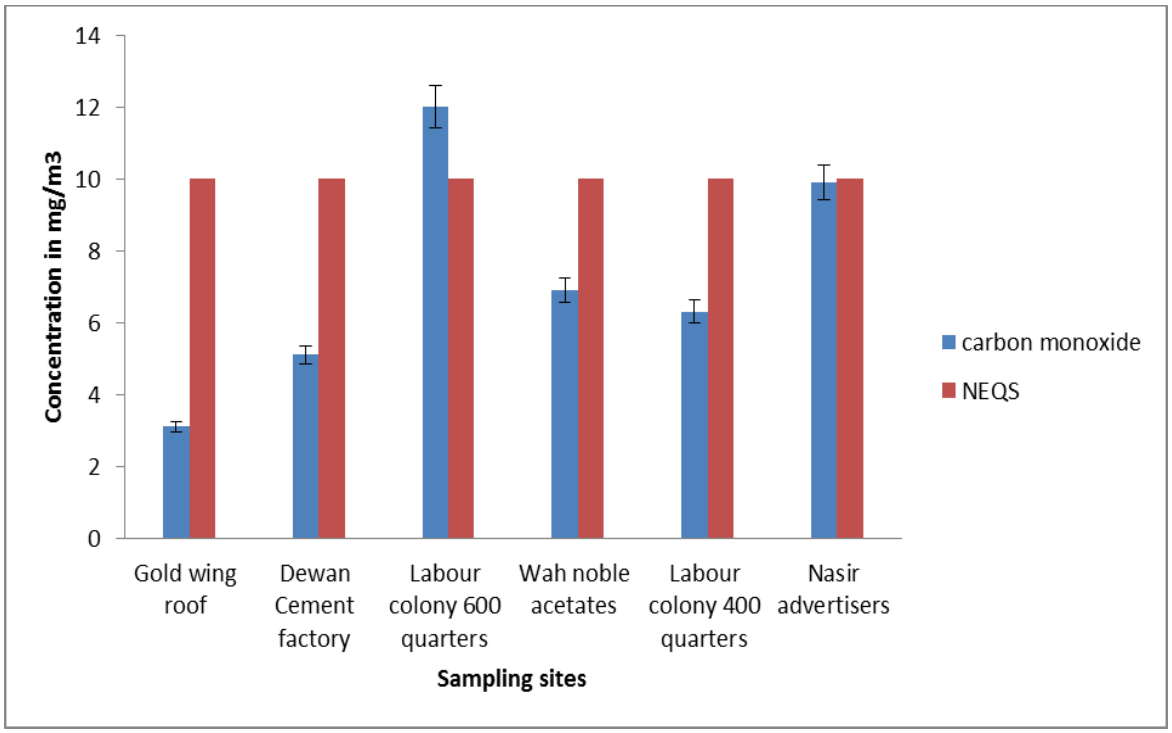

Figure 3.7 Concentration of carbon monoxide on a sampling site

As shown in figure 3.7 the sampling revealed that the highest concentration of carbon monoxide was observed in Labour colony 600 quarters with mean concentration of 12 mg/m^3 which is 2 mg/m^3 higher than the limits of Pak-NEQS. The reason for such high concentration of CO at Labour colony 600 quarters is because this colony is in the heart of Hattar and different food processing factories are in its surrounding which produce lot of unburned gasses from their burner and pollute the area. The second highest concentration of CO was observed in Nasir advertisers with the mean concentration of 9.9 mg/m^3 and reason for the emission of CO from this sampling site is because of metal welding for billboards. The 3rd highest concentration was observed in Wah Nobel acetates with the average value of 6.9mg/m^3 and reason for the production of CO in this area might be the production of chemicals by the factory itself as well as surrounding factories like textile and paper mills also contributes in the production of CO in the surrounding environment. After Wah Nobel acetates the highest concentration of CO was observed in Labour colony 400 quarters with the mean concentration of 6.3 mg/m^3. The passage of train surrounding Ghee Mills and Hattar's main highway traffic contributes in the production of CO in its surrounding area. The 5th highest concentration was observed in Dewan cement

factory with the mean concentration of 5.1 mg/m^3. The main reason for the production of CO in this area might be the gasses emitting from the chimney of the factory and the main road traffic as well. The least high concentration was observed in Gold wing roof factory with the mean concentration of 3.1 mg/m^3 which is quite safe for the ambient air.

Over all the concentration of CO was below than the Pak-NEQS and WHO standards (10 mg/m^3 for 1 hour and 30 mg/m^3 for 1 hour) except the observed concentration in 600 quarters colony which was higher than the limits. Poor mass transit system, increase in the number of vehicles and burning of solid waste are some of principal contributing factors to increase CO in the atmosphere.

3.8 Carbon dioxide

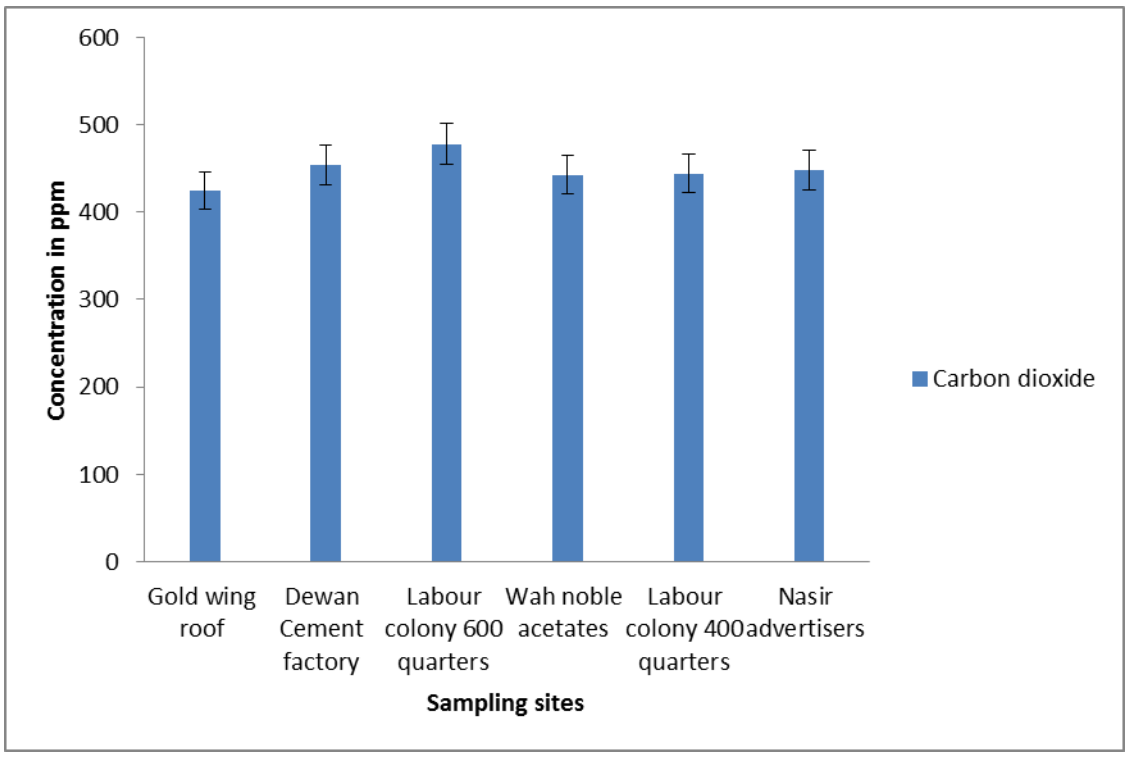

Figure 3.8 Concentration of carbon dioxide on a sampling site

Sampling revealed that as shown in figure 3.8 that the highest concentration of carbon dioxide was observed in Labour colony 600 quarters with the mean concentration of 477.6ppm. The second highest concentration was observed in Dewan cement factory with mean concentration of 454 ppm and some of reasons are that with factory when calcium carbonate is heated so CO_2 directly emits in the air from factory

chimney and factory is located on a road side so heavy traffic vehicles increase the concentration of carbon dioxide in the atmosphere. The 3rd highest concentration was observed in Nasir advertisers agency and the reason for high concentration is the surrounding pollution in the atmosphere. After Nasir advertisers highest concentration of CO_2 was observed in Labour colony 400 quarters with the mean concentration of 444 ppm and its reason is also the Hattar's main road heavy vehicles traffic after them the highest concentration was observed in Wah Nobel acetates with an average concentration of 442 ppm and reason for high concentration is the surrounding factories chimney smoke. Least high concentration of CO_2 was observed in Gold wing roof factory with mean concentration of 424.6 ppm and reason for high concentration is use of generators and fuel consumption with in factory.

Over all concentration of CO_2 was low except Labour colony 600 quarters and Dewan cement factory. The main reason for CO_2 concentration in Hattar industrial estate is the use of old engine trucks and diesel generators which produce smoke and increases CO_2.

3.8 Air quality index for Particulates and Gasses

For better demonstration of associated concerns of elevated levels of particulates and gasses, for this level of gasses and particulates were compared with Air quality Index. Levels of particulates and gasses were compared with the levels of AQI so that the pollution level is known in Hattar industrial estate which is in return affecting the human health very badly. Furthermore it is mentioned that quality of air contains different colour levels from 0 to 500 ppm and µg/m3 therefore the greater level of air pollution have higher AQI value. For example AQI value of 50 represents good quality with less capacity of affecting public health. On the other side AQI value grater then the 300 represents hazardous air quality. AQI value less than 100 represents satisfactory and above than that shows that air quality is carcinogenic and toxic for particular age groups. Particulates and gasses calculated were compared with AQI, which shows that particulates concentration falls in Hazardous (maroon colour) part of AQI and Gasses falls in unhealthy (red colour). It was revealed that Hattars air quality is hazardous and toxic in most cases to breath and it will also be harmful for the people who are already lungs patients. Surrounding area population and labours

working in the factories should take precautionary measures to avoid unhealthy and hazardous risk.

Table 3.5 Comparison of PM_{10} with Air Quality Index (AQI)

AQI VALUES	AIR QUALITY DESCRIPTOR	HEALTH CONCERN PM_{10}	AQI comparison with PM_{10} measured	
			Sampling site and day of sampling	Total concentration ($\mu g/m^3$)
0-50	Good	None		None
51-100	Moderate	None		None
101-150	Unhealthy for Sensitive Groups	People with respiratory disease like asthma,	SL5- 1st day	143.229
151-200	Unhealthy	People with respiratory disease like asthma, avoid outdoor exertion; Especially the children and elders should avoid outdoor exertion	SL5- 3rd day SL5- 2nd day	151.910 173.611

201-300	Very unhealthy	People with respiratory disease like asthma people must avoid outdoor activity; children and elders must avoid outdoor activity	SL3- 1st day SL3- 2nd day SL3- 3rd day SL4- 3rd day SL4- 1st day SL4- 2nd day SL1- 3rd day SL1- 1st day SL1- 2nd day SL2- 2nd day SL6- 1st day SL6- 3rd day SL6- 2nd day	212.674 225.694 247.396 277.778 282.118 299.479 264.654 273.438 282.118 291.862 212.674 230.035 251.736
301>	Hazardous	Everyone should avoid any outdoor exertion specially people with asthma and other respiratory disease	SL2- 1st day SL2- 3rd day	301.174 312.631

Table 3.6 Comparison of $PM_{2.5}$ with Air Quality Index (AQI).

AQI VALUE	AIR QUALITY DISCRIPTION	HEALTH CONCERN $PM_{2.5}$	AQI comparison with $PM_{2.5}$ measured	
			Sampling site and day of sampling	Total concentration ($\mu g/m^3$)
0-12	Good	None		None
12-35.4	Moderate	Sensitive people avoids heavy exertion		None
35.5-55.4	Unhealthy for Sensitive Groups	People with respiratory or heart disease avoid heavy exertion		None
55.5-150.4	Unhealthy	Children and adults with heart and lungs disease must avoids heavy exertion	SL3- 2nd day SL3- 3rd day SL5- 1st day SL5- 2nd day SL5- 3rd day	138.889 147.569 108.507 121.528 117.188
150.5-250.4	Very Unhealthy	Active children and adults, asthma patients should limit outdoor exertion	SL1- 2nd day SL1- 1st day SL1- 3rd day SL2- 1st day SL2- 3rd day SL2- 2nd day SL3- 1st day	181.632 173.611 168.590 192.368 186.291 199.681 160.590

			SL4- 1st day SL4- 2nd day SL4- 3rd day SL6- 1st day SL6- 2nd day SL6- 3rd day	175.951 169.271 186.632 177.951 169.271 182.292

Table 3.7 Comparison of SO_2 with Air Quality Index (AQI).

AQI VALUE	AIR QUALITY DISCRIPTION	HEALTH CONCERN FOR SO_2	AQI comparison with SO_2 measured	
			Sampling site and day of sampling	Total concentration ($\mu g/m^3$)
0-50	Good	None	SL1-1st day SL1-2nd day SL1- 3rd day SL2-1st day SL2- 3rd day	41.3 38.4 43.8 50.1 49.6
51-100	Moderate	Sensitive people avoids heavy exertion	SL2- 2nd day SL3-1st day SL3-2nd day SL3- 3rd day SL4-1st day SL4-2nd day SL4- 3rd day SL5-1st day SL5-2nd day SL5- 3rd day SL6-1st day SL6-2nd day	53.3 81.4 86.8 80.7 69.3 65.1 70.5 51.6 53.9 54.2 72.4 77.7

			SL6- 3rd day	70.4
101-150	Unhealthy for Sensitive Groups	People with respiratory or heart disease avoid heavy exertion		None

Table 3.8 Comparison of NO_2 with Air Quality Index (AQI).

AQI VALUE	AIR QUALITY DISCRIPTION	HEALTH CONCERN FOR NO_2	AQI comparison with NO_2 measured	
			Sampling site and day of sampling	Total concentration ($\mu g/m^3$)
0-40	Good	None		None
41-80	Moderate	Sensitive people avoids heavy exertion	SL1-1st day SL1-2nd day SL2-1st day SL2-2nd day SL2- 3rd day SL4-1st day SL4-2nd day SL4- 3rd day SL5-1st day SL5-2nd day SL5- 3rd day SL6-2nd day	51.3 59.7 65.5 61.9 66.3 69.1 73.4 75.7 58.4 63.9 56.2 76.9

			SL6- 3rd day SL1-3rd day	71.5 48.1
80-150	Unhealthy for Sensitive Groups	People with respiratory or heart disease avoid heavy exertion	SL3-1st day SL3-3rd day SL3-2nd day SL6-1st day	108.3 101.8 96.2 81.4

Table 3.9 Comparison of O_3 with Air Quality Index (AQI).

AQI VALUE	AIR QUALITY DISCRIPTION	HEALTH CONCERN FOR O_3	AQI comparison with O_3 measured	
			Sampling site and day of sampling	Total concentration ($\mu g/m^3$)
0-50	Good	None	SL1-1st day SL1-2nd day SL1- 3rd day SL2-1st day SL2-2nd day SL2- 3rd day SL3-2nd day SL4-1st day SL4-2nd day SL4- 3rd day SL5-1st day SL5-2nd day SL5- 3rd day SL6- 2nd day	25 28 24 19 21 23 50 49 41 46 32 36 40 43

51-100	Moderate	Sensitive people avoids heavy exertion	SL3-1st day SL3- 3rd day SL6-1st day SL6- 3rd day	54 55 51 52
101-150	Unhealthy for Sensitive Groups	People with respiratory or heart disease avoid heavy exertion	None	None

Table 3.10 Comparison of CO with Air Quality Index (AQI).

AQI VALUE	AIR QUALITY DISCRIPTION	HEALTH CONCERN FOR CO	AQI comparison with CO measured	
			Sampling site and day of sampling	Total concentration (mg/m^3)
0-4.4	Good	None	SL1-1st day SL1-2nd day SL1- 3rd day SL2-2nd day	2.3 3.1 3.9 4.4
4.5-9.4	Moderate	Sensitive people avoids heavy exertion	SL2-1st day SL2- 3rd day SL4-1st day SL4-2nd day SL4- 3rd day SL5-1st day SL5-2nd day SL5- 3rd day SL6- 3rd day	5.2 5.8 8.2 5.9 6.7 5.8 6.3 6.8 8.9

9.5-12.4	Unhealthy for Sensitive Groups	People with respiratory or heart disease avoid heavy exertion	SL3-1st day SL3-2nd day SL6-1st day SL6-2nd day	12.3 10.6 11.4 9.5
12.5-15.4	Unhealthy	Children and adults with heart and lungs disease must avoids heavy exertion	SL3- 3rd day	13.1

3.10 Chemical characterization by Atomic Absorption Spectroscopy

To find out the chemical composition and concentration of elements within Particulate matters $PM_{2.5}$ and PM_{10} samples, qualitative and quantitative analysis of all the samples will be performed with the help of Atomic Absorption Spectroscopy. All 32 samples taken from selected sites were analysed by AAS for selected elements. Result showed the presence of Zn, Cr, Pb, Cu, Ni and Cd for both $PM_{2.5}$ and PM_{10} with different concentration. As we know that most of the samples contain dust elements and some of them form from anthropogenic activities.

Anthropogenic origin trace metals, like Pb, Cr, Ni, Cd and Cu were present in a low concentration at selected locations. Concentration of these metals is due to anthropogenic activities (e.g oil and coal combustion, industries, vehicles, etc.) (Mijic et al.,2012).

3.10.1 Heavy metal concentration in PM_{10} and $PM_{2.5}$

3.10.1.1 Zinc (Zn)

The study showed that the concentration of Zinc in PM_{10} samples were 3.5, 7.4, 6.618, 7.12, 4.39 and 6.83 µg/m^3 at Gold wing roof, Dewan Cement factory, Wah noble acetates, Labour colony 600 quarters, Labour colony 400 quarters and Nasir advertisers respectively. Highest concentration of Zinc was observed in Dewan cement factory with the concentration of 7.4 µg/m^3 and reason might be the cement

production process and heavy traffic on the adjacent road. Lowest concentration of Zn was observed in Gold wing roof factory (3.5 µg/m^3). The overall mean concentration of Zinc was 5.976 µg/m^3.

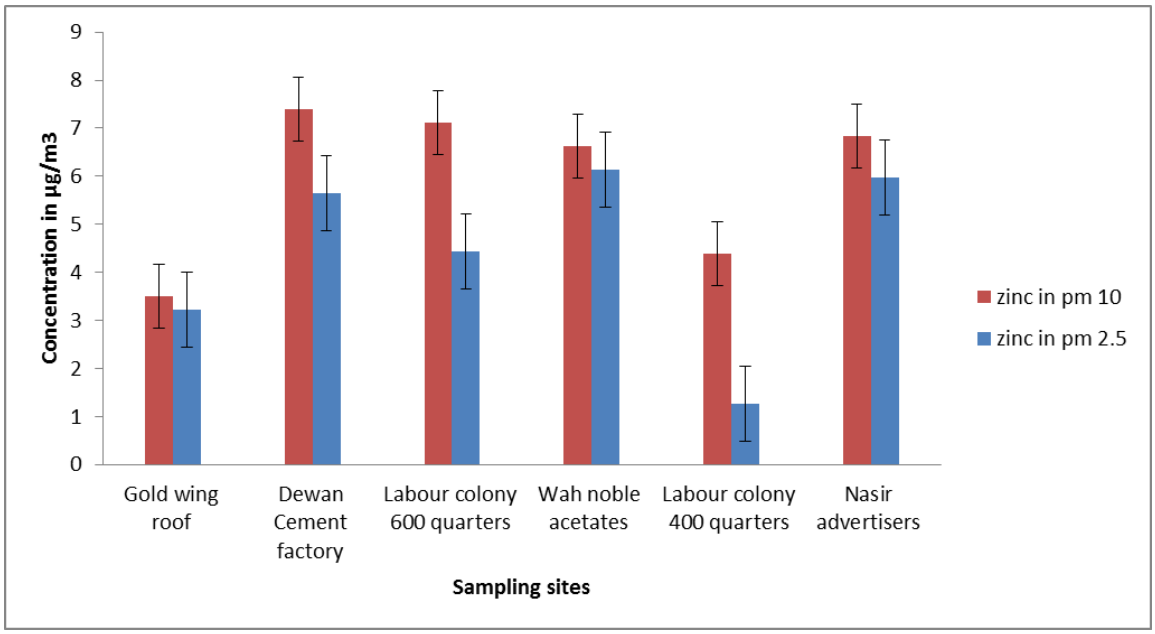

Figure 3.9 Zinc (Zn) Concentration in PM_{10} and $PM_{2.5}$ within Sampled sites.

The study also discusses the presence of Zinc in a $PM_{2.5}$ samples and the results shows that the highest concentration of Zn was observed in Wah Nobel Acetates and Nasir advertisers which was 6.13 and 5.98 µg/m^3 respectively and lowest concentration was observed in Gold wing roof and 400 quarters colony which was 3.21 and 1.26 µg/m^3 respectively. The overall mean concentration of $PM_{2.5}$ ambient air samples was 4.4425 µg/m^3.

Industries are one of major sources of zinc presence in the air borne particles (Lin et al., 2005) and it is most bioactive element known to be present in particulates (Moreno et al 2004). Zinc/brass production facilities and metallurgical plants might release Zn containing particles in the atmosphere. Two stroke emissions, galvanizing operations and municipal solid waste also contributes their part in the emission of Zinc. All of the industries surrounded by sampling site were main sources of Zinc. Zinc is immeasurable in high and chilly temperature of water and it is dissolvable in acidic corrosive, alkalise and corrosive (Merck, 1989) and inside the particulate contamination Zinc is the component which is extremely proactive (Lu 2003, Moreno et al., 2004). Zinc concentration in Hattar is comparatively higher as compared to the

previous studies. Research conducted at Islamabad in 2007 shows that mean concentration of Zn in particulate matters were 2.311 µg/m^3 (Shah and Shaheen, 2008). Another research conducted in Delhi, India shows that mean concentration of zinc was about 4.67 µg/m^3 (Shridhar et al., 2010) which shows that concentration of zinc in Hattar is higher than in its surrounding areas.

3.10.1.2 Chromium (Cr)

The study showed that the concentration of Chromium in PM_{10} samples were 0.208, 0.3236, 0.301, 0.265, 0.216 and 0.1792 µg/m^3 at Gold wing roof, Dewan Cement factory, Wah noble acetates, Labour colony 600 quarters, Labour colony 400 quarters and Nasir advertisers respectively. Highest concentration of Chromium was observed in Dewan cement factory containing the concentration of 0.3236 µg/m^3 and reason might be the cement factory fumes and traffic smoke. Lowest concentration of Cr was observed in Nasir Advertisers (0.1792 µg/m^3). The overall sampling sites mean concentration of Chromium was 0.2488 µg/m^3.

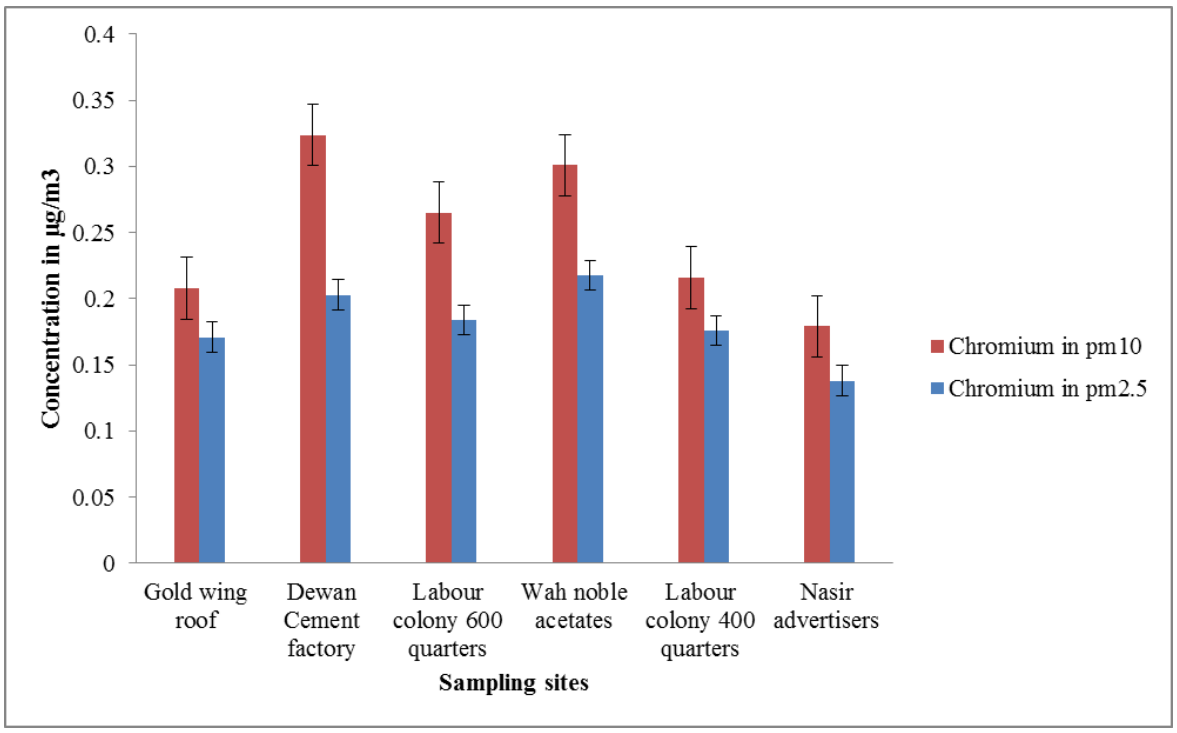

Figure 3.10 Chromium (Cr) Concentration in PM_{10} and $PM_{2.5}$ within Sampled sites.

The results of $PM_{2.5}$ ambient air samples showed that the sampling site Wah Noble acetates and Dewan cement factory contains the highest concentration of Chromium 0.2176 and 0.203 µg/m^3 respectively. The lowest concentration was

observed in Gold wing roof and Nasir advertisers which was 0.171 and 0.138 µg/m^3 respectively. The overall mean concentration of Cr in Hattar ambient air was 0.1816 µg/m^3.

Chromium mostly originates from industrial activities and combustion of fossil fuel. The chromium chemical form depends on source. Respiratory system irritation, lung cancer and nasal passage perforation can be cause by chromium long term exposure. Kidney and liver damage can be cause by chronic exposure (Khillare et al., 2004). A research conducted in Delhi, India shows that mean concentration of Cr was about 0.35 µg/m^3 (Shridhar et al., 2010) another research conducted in Faislabad shows that mean concentration of Cr was about 0.0309 µg/m^3 (Qadir and Zaidi, 2006) which shows hattar concentration of Cr is higher than it surroundings.

3.10.1.3 Lead (Pb)

According to the results the concentration of lead in PM_{10} samples were extremely high in Dewan cement factory, Gold wing roof and Wah Noble acetates which was about 0.9521, 0.9136 and 0.892 µg/m^3 respectively. The lowest concentration was observed in Labour colony 600 quarters, Labour colony 400 quarters and Nasir advertisers which was 0.883, 0.724 and 0.683 µg/m^3. Overall the mean concentration of lead was 0.841 µg/m^3.

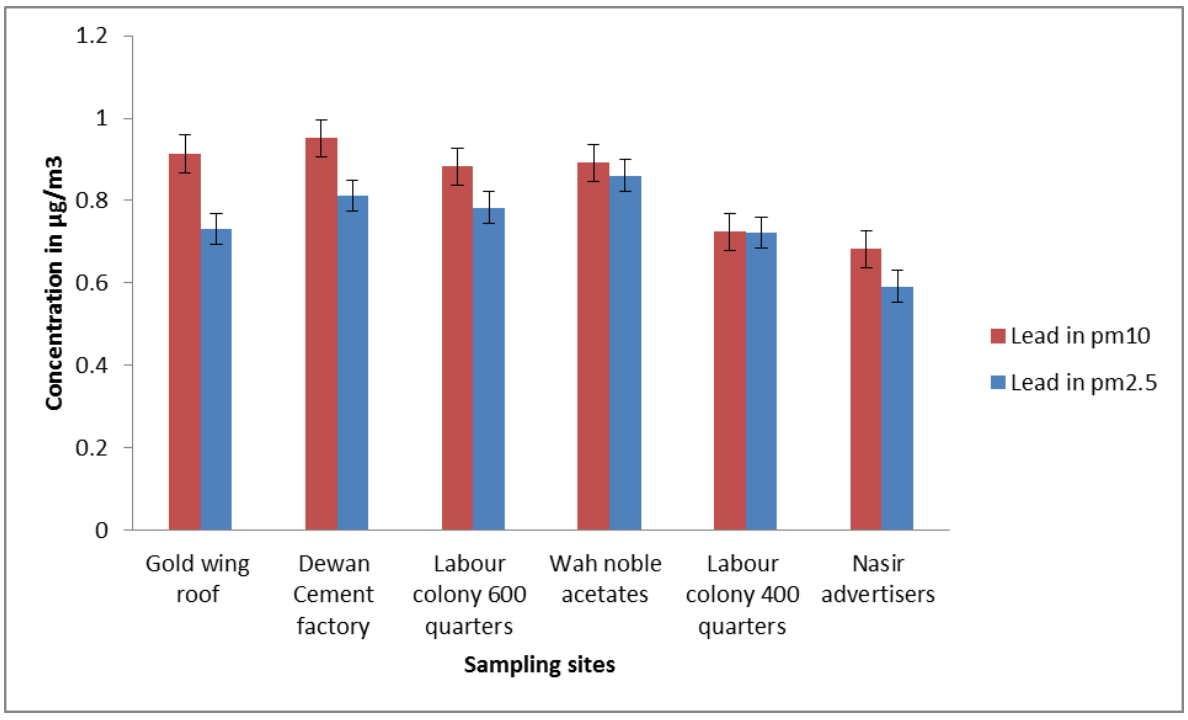

Figure 3.11 Lead (Pb) Concentration in PM_{10} and $PM_{2.5}$ within Sampled sites.

The results of $PM_{2.5}$ shows that the highest observed concentration of lead was 0.861, 0.811 and 0.783 µg/m^3 at Wah Noble acetates, Dewan cement factory and Labour colony 600 quarters respectively and the lowest was 0.7312, 0.722 and 0.592 µg/m^3 at Gold wing roof, Labour colony 400 quarters and Nasir advertisers respectively. The overall mean concentration of Pb in $PM_{2.5}$ sample was 0.750 µg/m^3.

According to a research conducted in 2002 approximately 391 metric tons/year lead is emitted directly into the atmosphere (Parekh et al., 2002). Pakistani government in the year 2001 encourages all the oil refineries to remove the lead from petrol by July 2002 (Paul et al., 2003). A research conducted by (Shah et al., 2004) from March to May 2002 in Islamabad and they find out that the mean concentration of lead in rural side was 505 ng/m^3 and mean concentration of lead in the urban site was 185 ng/m^3. Another research conducted by (Shaheen et al., 2005) from June to September 2002 in Islamabad and they find out the mean concentration of lead was 146 ng/m^3 ranging from 12-481 ng/m^3. These results show that the concentration of lead in Islamabad was comparatively lower than the concentration of lead in Hattar industrial estate and concentration of lead is also below than the Pak-NEQS permissible limits (1.5µg/m^3). USEPA showed that battery plants and smelters are the main fountains of lead precipitation. Lead introduction in body can cause various damages starting from internal breath white wash and can damage fragile tissue and bone. Lead deposits in the body and can also impacts diverse organs, liver, kidneys and tactile framework.

3.10.1.4 Copper (Cu)

The study showed that the concentration of Copper in PM_{10} samples were 0.0955, 0.1732, 0.2386, 0.203, 0.08 and 0.115 µg/m^3 at Gold wing roof, Dewan Cement factory, Wah noble acetates, Labour colony 600 quarters, Labour colony 400 quarters and Nasir advertisers respectively. Highest concentration of Copper was observed in Wah Noble acetates containing the concentration of 0.2386 µg/m^3 and reason might be the dust blown from its surrounding area. Lowest concentration of Cu was observed in Labour colony 400 quarters (0.08 µg/m^3). The overall mean concentration of Copper was 0.15 µg/m^3.

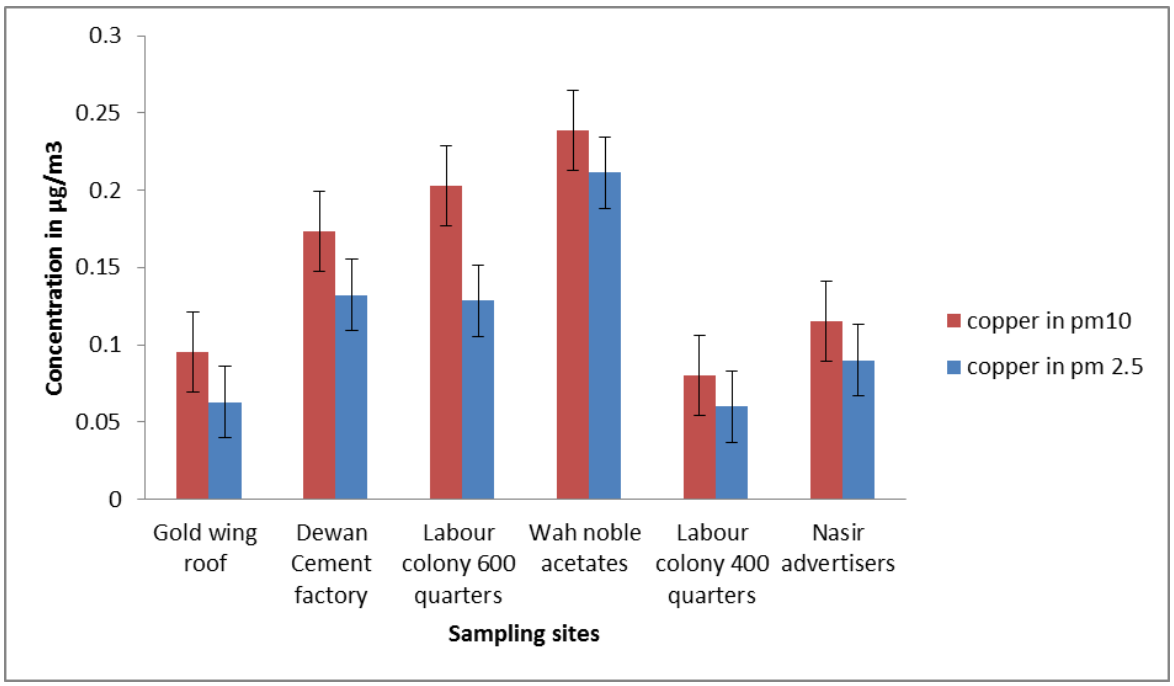

Figure 3.12 Copper (Cu) Concentration in PM_{10} and $PM_{2.5}$ within Sampled sites.

The results of $PM_{2.5}$ ambient air samples showed that the sampling site Wah Noble acetates and Dewan cement factory contains the highest concentration of Copper 0.2113 and 0.1321 µg/m^3 respectively. The lowest concentration was observed in Gold wing roof and Labour colony 400 quarters which was 0.063 and 0.06 µg/m^3 respectively. The overall mean concentration of Cu in Hattar ambient air was 0.114 µg/m^3.

Road side environment is the place where copper mostly founds. Some of the major sources of copper in air is burning fuel, corrosion of batteries, metallic parts like radiators and wearing out of tyres (Akbar et al., 2006). Concentration of Copper varies with the location, in Islamabad the concentration of Cu was about 0.306 µg/m^3 (Shah and Shaheen, 2008). Another research shows that mean concentration of Cu in Delhi was about 3.690 µg/m^3 (Shridhar et al., 2010) which shows that the concentration on Copper in Hattar is lower than its surrounding areas

3.10.1.5 Cadmium (Cd)

According to the results the concentration of Cadmium in PM_{10} samples were extremely high at Dewan cement factory, Labour colony 600 quarters and Wah Noble acetates which was about 0.035, 0.0268 and 0.0247 µg/m^3 respectively and reason of high concentration in these areas were the burning of fossil fuel in surrounding

industries and the Volta battery Factory between 600 quarters colony and Wah Noble acetates. The lowest concentration was observed in Gold wing roof, Labour colony 400 quarters and Nasir advertisers which was 0.01, 0.0175 and 0.0211 µg/m^3 respectively. Overall the mean concentration of Cadmium was 0.022 µg/m^3.

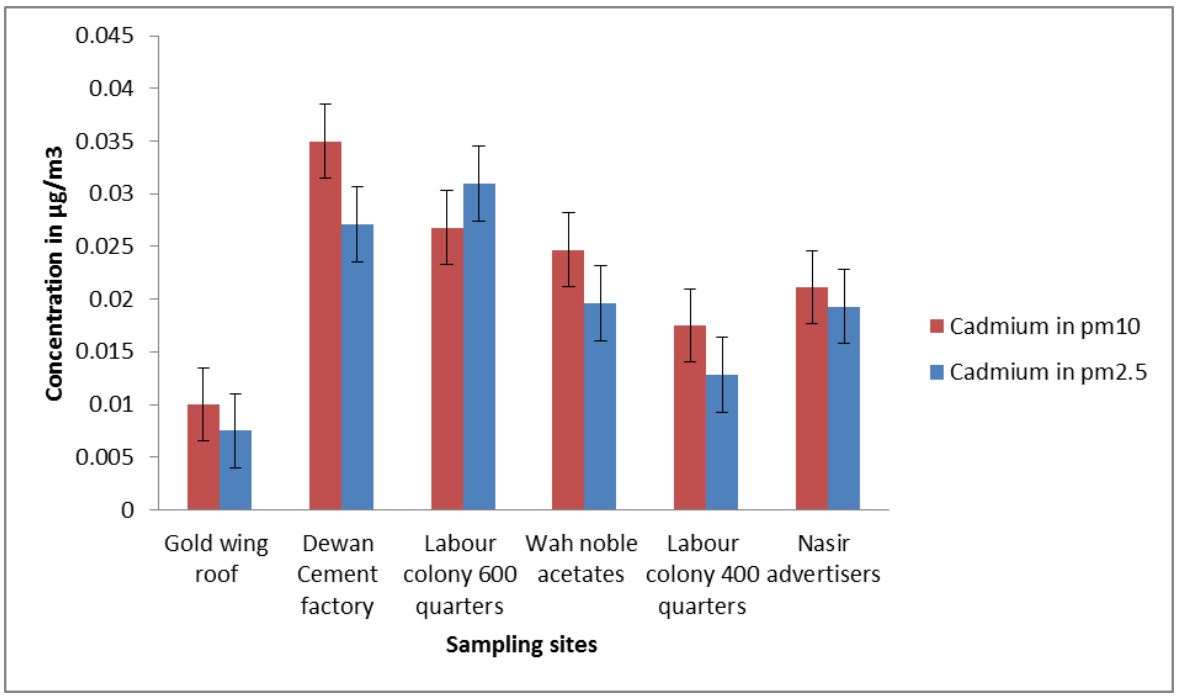

Figure 3.13 Cadmium (Cd) Concentration in PM_{10} and $PM_{2.5}$ within Sampled sites.

The results of $PM_{2.5}$ show that the concentration of Cadmium was highest at Labour colony 600 quarters (0.031 µg/m^3) and lowest at Gold wing roof (0.0075 µg/m^3). The concentration of Cadmium on other sampling sites were 0.0271, 0.0196, 0.0128 and 0.0193 µg/m^3 at Dewan cement factory, Wah Noble acetates, Labour colony 400 quarters and Nasir advertisers respectively. Overall the mean concentration of Cd was 0.019 µg/m^3.

The reason for Cadmium presence in the PM samples might be the industrial activities in industrial estate. Some of Cadmium anthropogenic sources in environment are non-ferrous production of metal, steel and iron production, waste incineration and fossil fuel combustion, paints, pigment, plastic stabilizers manufacturing units, photovoltaic devices and batteries manufacturing industries, coating and cement production (ATSDR, 2008c; WHO, 2007). A research conducted in Luanda/Angola by Baptista and E. DeMiguel (2005) they find out that mean concentration of Cd was 1.15 mg/kg. Cadmium mean concentration in Kayseri city

located in Turkey was 2.53 mg/kg (Tokalioglu and S.Kartal, 2006). According to the research in Faisalabad the mean concentration of Cd was about 0.0205µg/m^3 (Qadir and Zaidi, 2006). In Kolkata, India the mean concentration of Cd was 0.0396µg/m^3 (Gupta et al., 2007) which shows that concentration in Hattar is lower than the other places in the world.

3.10.1.6 Nickel (Ni)

The results show that concentration of Nickel in PM_{10} sample varies from 0.3836 to 0.09 µg/m^3 at Labour colony 600 quarters and Gold wing roof respectively. The concentration of Dewan cement factory, Wah Noble acetates, Labour colony 400 quarters and Nasir advertisers was 0.2143, 0.1983, 0.163 and 0.114 µg/m^3 respectively. The mean concentration of sampling site was 0.194 µg/m^3.

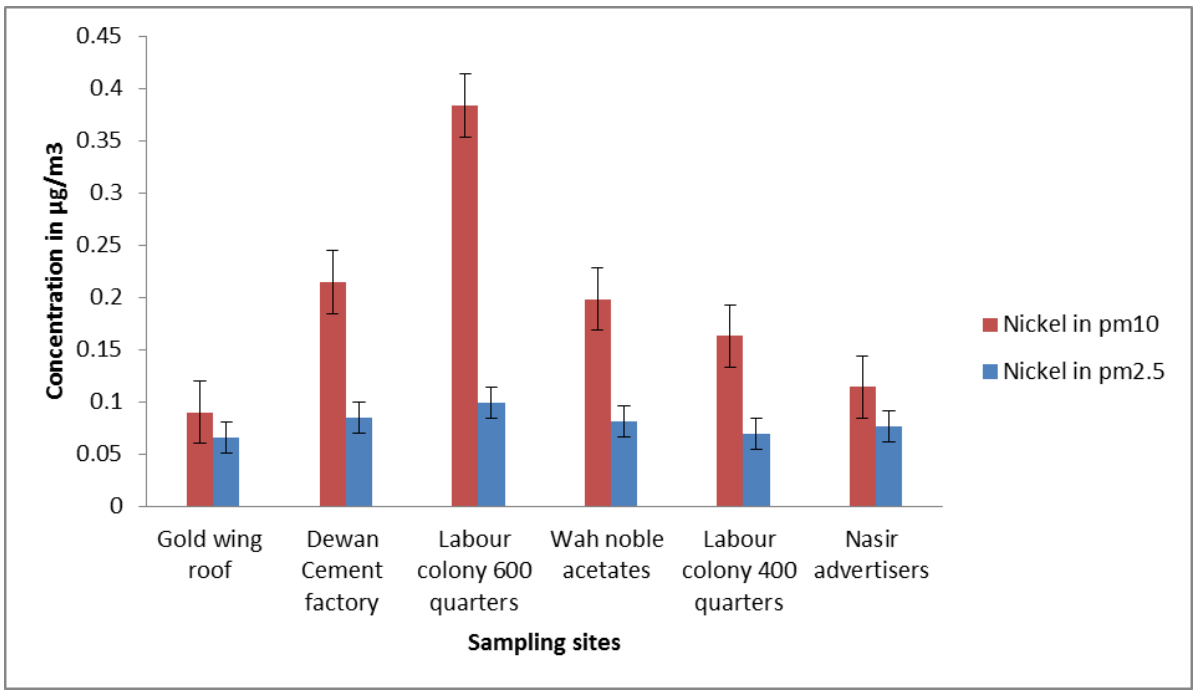

Figure 3.14 Nickel (Ni) Concentration in PM_{10} within Sampled sites.

The concentration of Nickel in $PM_{2.5}$ sample shows that the highest concentration observed was 0.098 µg/m^3 at Labour colony 600 quarters and the lowest one was 0.066 µg/m^3 at Gold wing roof. The concentration of Dewan cement factory, Wah Noble acetates, Labour colony 400 quarters and Nasir advertisers was 0.085, 0.0812, 0.069 and 0.076 µg/m^3 respectively. The overall mean concentration of Nickel in Hattar ambient Particulate $matter_{2.5}$ was 0.0793 µg/m^3.

Nickel often presents in air and can cause reaction of skin (Cempel et al., 2005). Some of the sources of Nickel are batteries manufacturing industries, paint and coating of paint, colour glass, incinerators and ceramics etc (Pandey et al., 2017). Nickel threshold level varies from 0.1 mg/m^3 to 1 mg/m^3 at working place for 8 hours (Mishra et al., 2017). The concentration of Nickel in Shanghai/China in the year 2008 was about 83.98 mg/kg (Shi et al., 2008). Another research conducted by (DeMiguel et al., 1997) in Madrid/Spain and they finds out the mean concentration of Nickel was 44 mg/kg.

CONCLUSIONS

Current research was conducted in six different sites of the Hattar industrial Estate i.e. Dewan cement factory, Gold wing factory, Labour colony 600 quarters, Wah Noble acetates, Labour colony 400 quarters and Nasir advertisers. Following are the study conclusion.

1 Sampling was performed for one hour at each location for 3 consecutive days and there is no proper limit of Sulfur dioxide and Nitrogen dioxide for one hour but if we compare to 24 hours limits of NEQS. According to NEQS Sulfur dioxide and Nitrogen dioxide values are within the permissible limits for ambient air in the entire sampling site except for NO_2 at Labour colony 600 quarters. Ozone and Carbon monoxide values were also within the one hour limit of NEQS except for the carbon monoxide at Labour colony 600 quarters. There is no proper limit for CO_2 because it is a greenhouse gas. According to the calculations the highest mean concentration was observed in Labour colony 600 quarters.

2 The results of 24 hour particulate matter PM_{10} and $PM_{2.5}$ sampling in all six sampling sites were much higher than NEQS. The results were expected because Hattar industrial estate contains lot of dust and smoke, road side dust and heavy traffic vehicles contributes a lot. Even in some sampling sites like Dewan cement and Gold wing roof the concentration reaches 2 to 4 times higher than permissible limit.

3 In quantitative analysis of all six metals i.e. Zinc, Nickel, Lead, Cadmium, Chromium and Copper PM_{10} and $PM_{2.5}$ samples contains the highest concentration of Zinc follow up by Lead. Copper and Cadmium contains the lowest concentration in the PM_{10} sample whereas Nickel and Cadmium contains the lowest concentration in $PM_{2.5}$ sample.

4 Out of all six sampling sites pollution concentration was observerd in order of Labour colony 600 quarters > Nasir advertisers > Wah Nobel accetates > Dewan cement factory > Labour colony 400 quarters > Gold wing factory. Major particulate matter sources are road side dust and heavy vehicles wear as major reason of gaseous pollution is the industrial activities and fuel burning.

RECOMMENDATIONS

Following are the proposed recommendations from this study.

1. Air quality monitoring station must be installed for air quality continues checking in Pakistan.
2. Monitoring of gasses and particulate matter concentration on seasonal basis.
3. It is needed to introduce comprehensive air quality plans.
4. Consultant authorities must raise awareness among the people of Hattar about air pollution.
5. Use of Alternate energy (Bio-gas and Solar panels) and low emission fuel must be introduced.
6. Cement factories shell avoid the source generation of gasses and particulates (fire places, wood burning stoves).

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Appendix 1- Ambient air quality NEQs for Paki

National Environmental Quality Standards for Ambient Air

Pollutants	Time-weighted average	Concentration in Ambient Air		Method of measurement
		Effective from 1st January 2009	Effective from 1st January 2012	
Sulphur Dioxide (SO_2)	Annual Average*	80 µg/m^3	80 µg/m^3	-Ultraviolet Fluorescence method
	24 hours**	120 µg/m^3	120 µg/m^3	
Oxides of Nitrogen as (NO)	Annual Average*	40 µg/m^3	40 µg/m^3	- Gas Phase Chemiluminescence
	24 hours**	40 µg/m^3	40 µg/m^3	
Oxides of Nitrogen as (NO_2)	Annual Average*	40 µg/m^3	40 µg/m^3	- Gas Phase Chemiluminescence
	24 hours**	80 µg/m^3	80 µg/m^3	
O_3	1 hour	180 µg/m^3	130µg/m^3	-Non dispersive UV absorption method
Suspended Particulate Matter (SPM)	Annual Average*	400µg/m^3	360µg/m^3	- High Volume Sampling, (Average flow rate not less than 1.1 m3/minute).
	24 hours**	550µg/m^3	500µg/m^3	
Respirable Particulate Matter. PM_{10}	Annual Average*	200µg/m^3	120µg/m^3	-β Ray absorption method
	24 hours**	250µg/m^3	150µg/m^3	
Respirable Particulate Matter. $PM_{2.5}$	Annual Average*	25µg/m^3	15µg/m^3	-β Ray absorption method
	24 hours**	40µg/m^3	35µg/m^3	
	1 hour	25µg/m^3	15µg/m^3	
Lead (Pb)	Annual Average*	1.5µg/m^3	1 µg/m^3	- ASS Method after sampling using EPM 2000 or equivalent Filter paper
	24 hours**	2 µg/m^3	1.5µg/m^3	
Carbon Monoxide (CO)	8 hours**	5 mg/m^3	5 mg/m^3	- Non Dispersive Infra Red (NDIR) method
	1 hour	10 mg/m^3	10 mg/m^3	
*Annual arithmetic mean of minimum 104 measurements in a year taken twice a week 24 hourly at uniform interval.				
** 24 hourly /8 hourly values should be met 98% of the in a year. 2% of the time, it may exceed but not on two consecutive days.				

Appendix 2- Sampling sites photographs

Wah Nobel Acetates

Labour colony 400 quarters

Gold wing roof

Nasir Advertisers

Dewan cement factory

Labour colony 600 quarters

Appendix 3-Temperature and Humidity of Hattar in March and April 2019

Date	Temperature	Humidity	Date	Temperature	Humidity
1st March	17 ºC	70%	1st April	32 ºC	30%
2nd March	13 ºC	73%	2nd April	33 ºC	28%
3rd March	15 ºC	62%	3rd April	34 ºC	32%
4th March	20 ºC	72%	4th April	35 ºC	36%
5th March	22 ºC	60%	5th April	34 ºC	40%
6th March	22 ºC	46%	6th April	34 ºC	39%
7th March	20 ºC	65%	7th April	35 ºC	32%
8th March	21 ºC	45%	8th April	32 ºC	42%
9th March	23 ºC	42%	9th April	35 ºC	36%
10th March	24 ºC	32%	10th April	33 ºC	29%
11th March	16 ºC	81%	11th April	32 ºC	62%
12th March	22 ºC	38%	12th April	32 ºC	63%
13th March	20 ºC	64%	13th April	29 ºC	50%
14th March	19 ºC	86%	14th April	31 ºC	76%
15th March	22 ºC	41%	15th April	33 ºC	56%
16th March	25 ºC	35%	16th April	26 ºC	80%
17th March	26 ºC	34%	17th April	22 ºC	81%
18th March	26 ºC	43%	18th April	27 ºC	72%
19th March	21 ºC	83%	19th April	30 ºC	47%
20th March	21 ºC	58%	20th April	32 ºC	51%
21st March	25 ºC	30%	21st April	33 ºC	44%
22nd March	26 ºC	38%	22nd April	35 ºC	42%
23rd March	22 ºC	51%	23rd April	36 ºC	40%
24th March	26 ºC	45%	24th April	31 ºC	73%
25th March	28 ºC	37%	25th April	34 ºC	49%
26th March	29 ºC	32%	26th April	34 ºC	48%
27th March	30 ºC	32%	27th April	35 ºC	42%
28th March	31 ºC	34%	28th April	36 ºC	36%
29th March	29 ºC	44%	29th April	36 ºC	42%
30th March	27 ºC	60%	30th April	32 ºC	52%

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