Assessment of Heavy Metals from Respirable Suspended Particulate Matter (PM_{10}) in Manali, Chennai, India

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Abstract- *This study assesses the heavy metal levels in ambient air PM_{10} component in Manali (Industrial area) Chennai, Tamil Nadu, India. Under National Ambient Air Quality Monitoring Program (NAMP), this area is monitored continuously on 24-hours and twice in a week. In case of PM_{10} monitoring, the conventional Gravimetric Method is followed. For study purpose, we collected the PM_{10} samples (Filter papers) for the period of April to November 2015 for analysis of heavy metals. The analysis of heavy metals, was carried out by Inductively Coupled Plasma- Optical Emission Spectrometer instrument (ICP-OES) after digestion of micro glass fiber filter paper (EPM 2000). PM_{10} concentrations at the Manali ranged from 11 -90µg/m³. These concentrations are complying with the National Ambient Air Quality Standards (NAAQS) during the entire monitoring period. Highest concentrations were found 0.628, BDL, 0.064, 2.39, 0.016, 0.956, 0.21, 14.4, 0.44 and 0.03 µg/m³ for Cu, Cd, T. Cr, Fe, Mn, Ni, Pb, Zn, Co and As respectively Main sources of PM_{10} and heavy metals at the site were resuspension of road dust, traffic exhaust, tyre abrasions, naturally occurring suspended dust and emissions from industrial processes. Concentrations of Lead (Pb) were found to be far below the Standard limits prescribed by NAAQS (2009) and Arsenic 37.5% of times and Nickel 37.5% of times are not complying withthe Standard and other metals (Zn, Mn, Cd, Cr and Cu) compared with International Standards, World Health Organization (WHO), Texas Commission on Environmental Quality (TCEQ) and European Environmental Agency (EEA). Therefore, there is a scope to carry out an in-depth further study and integrated assessment of air pollution and associated health risk in these areas.*

Keywords- Ambient Air, Chennai, Heavy Metals, Particulate Matter, Pollution

I. INTRODUCTION

The atmosphere is a blanket of air that surrounds the whole Earth. It is a mixture of gases that contains a huge number of solid and liquid particles [1]. It is a source of essential gases, temperature, rain, air and protect from UV rays and meteors [2]. Air can be defined as combination of gaseous matter that forms the stratosphere or the invisible gaseous substances surrounding the Earth. One can live easily for five weeks without food, one week without water but no one can live without air for more than three minutes. This implies the importance of air. Therefore, it is the primary duty of everyone to maintain the Air Quality to its pristine quality.

Air quality is determined by the level of pollutants in the ambient air. Growth in population, rapid growth in urbanization and industrialization, raising demands for energy and motor vehicles are affecting the Air Quality [3]. The main aspect of Air Quality Management is to monitor the pollution level and take efficient preventive and control measures. As per Air (Prevention and Control of Pollution) Act, 1981, "Air pollution" means the presence in the atmosphere of any air pollutants. Air pollution may come from anthropogenic or natural sources. Different activities such as transportation, burning, drilling, blasting, and industries etc. are carriedout and generating considerable amount of air pollution. Polluted air contents one, or more, hazardous substance, pollutants or contaminant that creates a hazard to general health. Continuous surveillance of air quality is most important in Air Quality Management. In this study, Manali, Chennai, Tamil Nadu was selected. The samples were analyzed for Heavy Metals after acid digestion. The present studywas intended to find out the concentrations of Respirable Suspended Particulate Matter and heavy metals concentration in the PM_{10} fraction of dust in ambient air.

II. STUDY AREA

Manali is an Industrial area and a zone in Corporation of Chennai and located in Thiruvallur district in the Indian state of Tamil Nadu. It is located in North of Chennai City, the town had a population of 35,248 and situated at 13.163°Nand80.258°E. It borders Thiruvottiyur to the east. Chennai Petroleum CorporationLimited (CPCL) (formerly MRL) is the largest company in Manali and is one of the mostcomplex refineries in India with Fuel, Lube, Wax and Petrochemical feedstocksproduction facilities. The main products of the company are LPG, Motor Spirit,Superior

Kerosene, Fuel Oil, Hexane and Petrochemical feed stocks etc.Ambient air monitoring was done within the premises of a Government High School. Location of the study area are shown in Figure 1.

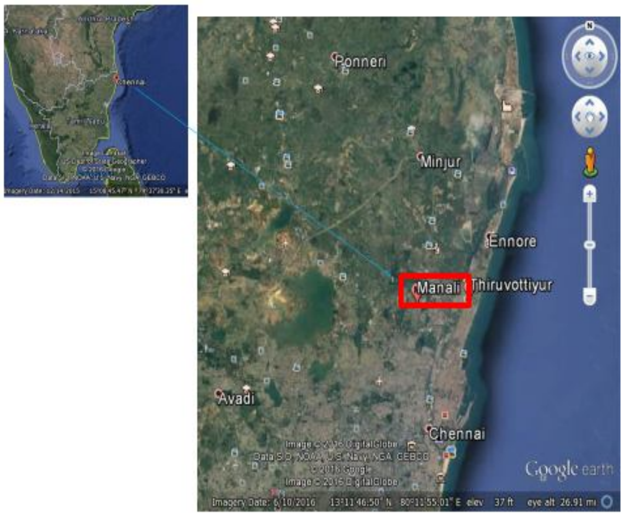

Figure 1: Location of Study Area in Chennai

III. METHODOLOGY

Determination of concentration of PM_{10} and characterization of heavy metals was carried out as per guidelines given by CPCB (2009) India.

A. Sampling and Concentration of PM_{10}

PM_{10} samples were collected on pre-weighed EPM 2000 filter paper using a Respirable Dust Sampler (APM 460 BL, Envirotech Instruments Pvt. Ltd) from April to November 2015.Average flow rate during the sampling was 1–1.2 m^3/min. After collecting samples, the filters were transported to the laboratory in a shipping envelope, taking care to minimize contamination and loss of the sample. Theseprotective envelopes stored at 30°C until analysis. The concentration of PM_{10} was calculated by dividing mass of the collected particulates by volume of air sampled. Flow diagram for procedure for PM_{10} shown in Figure 2.

B. Digestion of Samples

Acid digestion was performed in Teflon beaker with the extraction solution (3% HNO_3 & 8% HCl). Beakers were placed on the hot plate, contained in a fume hood and refluxed gently while covered with a watch glass for 30 minutes. The content was filtered through a Whatman Filter 42 and the final volume was adjusted to 100 ml by adding distilled water. Step by step digestion of samples shown in Figure 3. A series of blanks were prepared using the same digestion method.

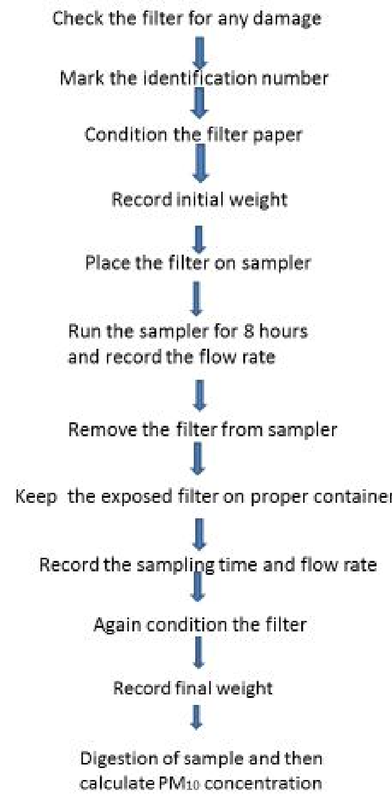

Figure 2: Flow Diagram for Procedure of PM_{10}

C. Analysis of digested samples by ICP-OES

Analysis of acid digested samples was carried out with the ICP-OES (Perkin Elmer make Optima 7000 DV model) instrument. Digested samples were aspirated into the flame, using nebulizer and concentration of element in thesample was obtained. Process of ICP-OES are follows as:

- *Aspiration:*A process where a high speed gas flow is directed across an open tube, creating a negative pressure and the drawing solution through the tube.
- *Nebulization:*This is a process of creating an aerosol from a liquid by the use of pneumatic or mechanical forces.
- *Desolvation:*Process of removing the solvent molecules from a sample droplet, resulting in a dried sample particle.
- *Vaporization:*Breaking down of dissolved sample particles into gas molecules.
- *Atomization:*Process of dissociating vaporized sample molecules into free atoms.
- *Excitation:*Process in which an electron is page 7 promoted to a higher energy level, resulting in an atom or ion said to be in an excited state.
- *Ionization:*Process where a neutral atom is converted to a charged ion through the gain or loss of an electron.

Figure 3: Digestion of Samples

D. Standards for National Ambient Air Quality

National Ambient Air Quality Standards Notified by Government of India are placed in Table 1.

Table 1: National Ambient Air Quality Standards [4,5]

Pollutants	Average Time	Concentration in Ambient Air	
		Industrial, Residential and Rural Areas	Ecologically Sensitive Area (Notified by Government)
Particulate Matter (<10µm) or PM_{10} µg/m³	Annual* 24 Hours**	60 100	60 100
Lead (Pb) µg/m³	Annual* 24 Hours**	0.50 1.0	0.50 1.0
Arsenic (As), ng/m³	Annual*	06	06
Nickel (Ni), ng/m³	Annual*	20	20

* Annual Arithmetic mean of minimum 104 measurements in a year at a particular site taken twice a week 24 hourly at uniform intervals.

** 24 hourly or 8 hourly or 1 hourly monitored values, as applicable, shall be complied with 98% of the time in a year. 2% of the time, that may exceed the limits but not on two consecutive days of monitoring.

Wherever National Standards are not available, International Standards are adopted as reference (In case of Zn, Mn, Cd, Cr and Cu) placed in below Table 2.

Table 2: International Standards for Zn, Mn, Cd, Cr and Cu [6]

Pollutants	Concentration	References
Zinc (Zn), µg/m³	100	World Health Organization, Geneva[7]
Manganese (Mn), µg/m³	0.15	European Environmental Agency[8]
Cadmium (Cd), µg/m³	0.005	European Environmental Agency[8]
Chromium (Cr), µg/m³	0.01	Texas Commission on Environmental Quality
Copper (Cu), µg/m³	1	Texas Commission on Environmental Quality

E. Air Pollution

Air pollution is one such form that refers to the contamination of the air. A physical, biological or chemical alteration to the air in the atmosphere can be termed as pollution. It occurs when any harmful gases, dust, smoke enters into the atmosphere and makes it difficult for plants, animals and humans to survive as the air becomes dirty.

Air pollution is a gas (or a liquid or solid dispersed through ordinary air) released in such quantity to harm the health of people or animals, kill plants or stop them growing properly, damage or disrupt the environment or cause some other kind of nuisance.

Table 3: Sources and Effects of Common Air Pollutants[9]

Pollutants	Sources	Health Effects
PM	Burning of wood, diesel and other fuels	Eye, nose, throat irritation, lung damage, cancer Bronchitis
Pb	Combustion of fossil fuels and leaded gasoline, paint, battery, smelters	Brain and nervous system damage, cause cancer in animals.
Mn	Ferrous and non-ferrous metal casting, chemical industries, additive in petrol.	Respiratory disease.
Cr	Iron works, rubber works.	Can alter genetic materials and cause cancer.
Cd	Tobacco smoke, combustion of fossil fuels, fertilizers and fungicide	Bone damage, affects liver and kidney. Itai-Itai disease
Zn	Smelters and welding activity	Respiratory problems
Ni	wind-blown dust, weathering of rocks and soils, volcanic emissions, forest fires and vegetation.	dermatitis produces erythema, eczema and lichenification

F. Particle Size Classification

The dust particle is mainly divided into different categories namely Suspended Particulate Matter (SPM), Respirable Suspended Particulate Matter (PM_{10} or RSPM), $PM_{2.5}$, PM_1 and Ultrafine particles.The classification and size of particles is at Table 4.

Table 4: Classification and Size of Particles [10]

Fraction	Size range
SPM	0.01-100 µm in diameter
RSPM or PM_{10} (Thoracic fraction)	<=10µm diameter, 2.5-10 µm is called coarse fraction.
Fine particles or $PM_{2.5}$	<=2.5 µm in diameter composed mainly of carbonaceous materials, inorganic compounds, and trace metals
PM_1	<=1 µm in diameter
Ultrafine particles	<=0.1 µm in diameter

G. Calculation

Calculation of volume of air sampled:

V= (Q). (t)

where, V = volume of air, m^3

Q = average sampling rate, m^3/min,

t = time in minutes.

- Calculation of PM_{10} concentration in ambient air:

$PM_{10} = [(W2 - W1) * 10^6] / V$

where,

PM_{10} = mass concentration of PM_{10} in µg/m^3.

W1= Initial weight of the filter in g

W2 = Final weight of the filter in g

V= Volume of air sampled in m^3

10^6 = Conversion factor of g to µg

IV. RESULTS AND DISCUSSIONS

A. PM_{10} concentrations

Concentration of PM_{10} for Manali (industrial area) of Chennai are given in Table 5 and Figure 4 for the period summer, pre-monsoon and monsoon (April-November 2015). PM_{10} concentrations varied from 11-73µg/m^3 (summer), 13-90µg/m^3 (pre-monsoon) and 28-71µg/m^3 (monsoon) The minimum monthly mean value of 33µg/m^3 was recorded in the month of August, 2015 and the maximum monthly mean value of 47µg/m^3 was recorded in the month of July. The slightly higher value may be due to heavy wind (Audi Kaaththu), which is common in Tamil Nadu. Sources ofParticulate matter are generators, dust, vehicles, industries, burning wastes etc.

Table 5: RSPM Values in Manali

Months (2015)	RSPM, µg/m^3 (monthly mean)
April	41
May	34
June	41
July	47
August	33
September	39
October	45
November	45

Table 6: Seasonal Variation of PM_{10} Range and Mean Concentration

Seasons (2015)	Manali		National Standard 100 (µg/m³)
	Range (µg/m³)	Mean (µg/m³)	
Summer	11-73	38.7	Complied with
Pre-Monsoon	13-90	40.5	Complied with
Monsoon	28-71	44.7	Complied with
Study Period	11-90	41.3	Complied with

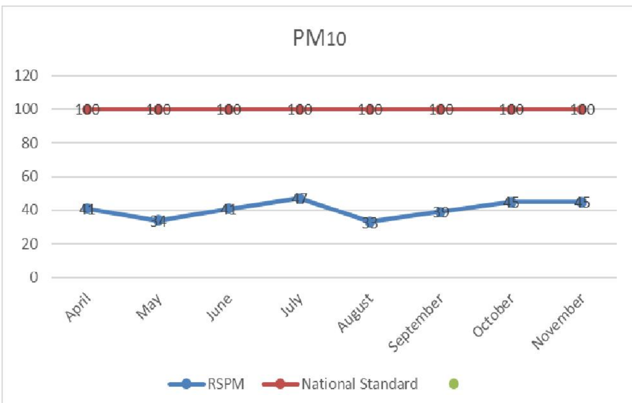

Figure 4: Monthly Variation of PM_{10} (2015)

Figure 4 shows that RSPM is complied with the National Standards (100µg/m^3) during the entire study period and the level of PM_{10} is at 41% of National Standards. Thedata shows that RSPM is complied with the National Standards 100%. The highest concentration of RSPMwas found in the month of July (47µg/m^3) followed by October and November (45 µg/m^3). The minimum value of 33 µg/m^3 was found in the month of August. There is no significant dispersion of data and the data are hovering around 41 µg/m^3.

B. Heavy Metals Concentrations

Results of heavy metals in PM_{10} fraction of suspended dust samples are collected from the Manali presented in Table 7. Concentration of Cu, Cd, T.Cr., Fe, Mn, Ni, Pb, Zn, Co and As in the RSPM samples were found in the range of 0.062-0.628, BDL, BDL-0.15, 0.844-2.39, BDL-0.016, BDL- 0.956, BDL-0.244, 1.75-14.4, 0.006-0.044 and BDL-0.024 µg/m^3 for Manali samples in the year 2015. The mean concentration of heavy metals found in the order of Zn> Fe> Cu> Ni>Pb> Co>T.Cr>Mn> As> Cd.

Table 7: PM_{10} bound Heavy Metals (2015)

Location		Manali
Coppper (Cu)	Range	0.062-0.628
	Mean	0.238
Cadmium (Cd)	Range	BDL
	Mean	BDL
Total Chromium (T.Cr)	Range	BDL-0.15
	Mean	0.018
Ferrous (Fe)	Range	0.844-2.39
	Mean	1.656
Manganese (Mn)	Range	BDL-0.016
	Mean	0.009
Nickel (Ni)	Range	BDL-0.956
	Mean	0.192
Lead (Pb)	Range	BDL-0.244
	Mean	0.096
Zinc (Zn)	Range	1.75-14.4
	Mean	9.05
Cobalt (Co)	Range	0.006-0.044
	Mean	0.025
Arsenic (As)	Range	BDL-0.024
	Mean	0.006

Out of 10 heavy metals (Cu, Cd, T.Cr, Fe, Co, Mn, Ni, Pb, Zn, Co and As) studied, Standards are notified for 3 metals only (Ni, As and Pb).Therefore, much emphasis has been given to these three metals and analyzed exclusively. The same is presented below as figures:

Figure 5: Monthly Variation of Lead Concentration

Figure 5 shows that the maximum concentration of Lead was found in April and November. It is observed that Lead concentration in study area complied with NAAQS (1 µg/m^3). Mean concentration of Lead is 0.096 µg/m^3.

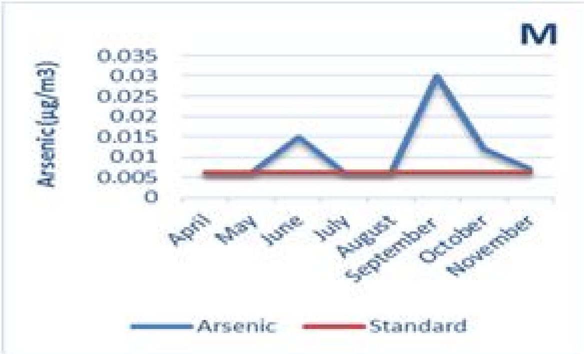

Figure 6: Monthly Variation of Arsenic Concentration

Figure 6 shows the maximum concentration of Arsenic found in the month of September 2015, whereas minimum concentration found in the month of April, May, July, August and November.Arsenic 37.5% of times not complied with National Standard. Arsenic were found much below the standard limit.

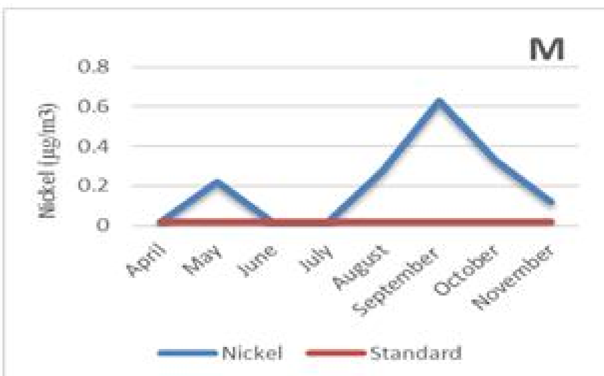

Figure 7: Monthly Variation of Nickel Concentration

Figure 7 shows the maximum concentration of Nickel was in the month of September 2015, whereas minimum concentration observed in the month of April, June &July. From the observed data, it was found that Nickel concentration is not complied with the National Standard ($0.02 \mu g/m^3$) by 37.5% of times. Mean Concentration of Nickel found in the present study was $0.192 \mu g/m^{3.}$

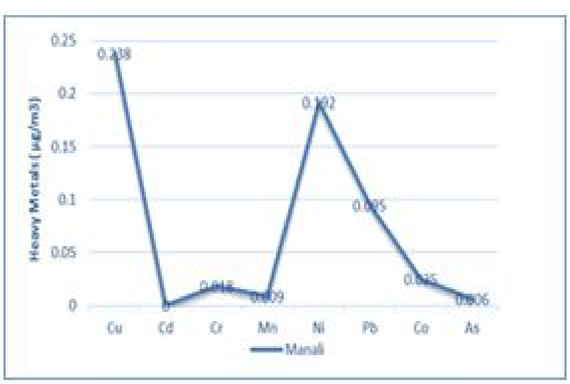

Figure 8: Variation of Mean Concentration of Heavy Metals.

Figure 8 shows that the concentration of 8 heavy Metals only except Zinc and Ferrous which are relatively more than the other elements. These two metals are intentionally excluded so as to show the level of other elements distinguish. These two significant metals are followed by Copper, Nickel and Lead. Concentration of Cadmium, Chromium, Manganese, Cobalt and Arsenic are found relatively less i.e. below $0.05 \mu g/m^3$.

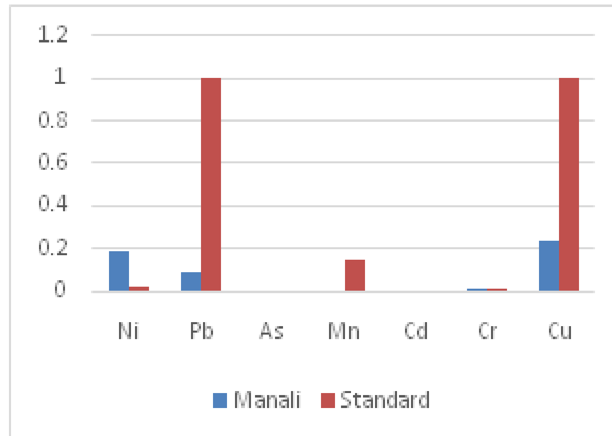

Figure 9: Comparison of Ni, Pb, As (CPCB), Cd, Mn (EEA) and Cr, Cu (TCEQ) with Standards.

Figure 9, shows that the comparison for observed data with National and International Standards whether it is complied with or not. Mean Concentration of Nickel found in the present study was 0.192 $\mu g/m^3$ against the National Standard of 0.02 $\mu g/m^3$. Lead is complied with the National Standard 1 $\mu g/m^3$. Arsenic not complied with Standard by 37.5% of times. Cadmium, Manganese and Copper complied with the EEA standard 0.005 $\mu g/m^3$,0.01 $\mu g/m^3$ and 1 $\mu g/m^3$ respectively. Chromium not complied with International Standard 0.01 $\mu g/m^3$.

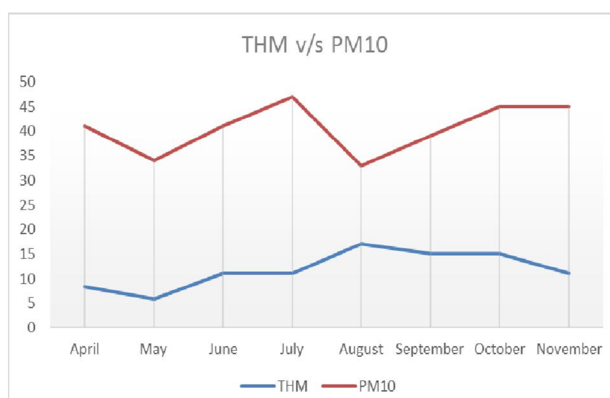

Figure 10: Total Heavy Metals in PM_{10} against PM_{10} (2015)

Table 9: Total and Percentage of Heavy Metals in PM_{10}

Months (2015)	THM	PM_{10}	% of HM
April	8.3	41	20.24
May	5.8	34	17
June	11	41	26.8
July	11	47	23
August	17	33	51.5
September	15	39	38.5
October	15	45	33
November	11	45	24

(Note: THM= Total Heavy Metals; HM= Heavy Metals)

Table 9, shows the total Heavy metals present in PM_{10} and its percentage. Heavy metals percentage ranges from 17% to 51.5% and in an average it is 29.3% of PM_{10}. Minimum percentage of heavy metals found in May whereas maximum in the month of August, 2015. Total Heavy Metals in PM_{10} against PM_{10} in Manali during the study period of 2015 are shown in Figure 10.

4.3 Control Measures

The measures taken for controlling air pollution from industries are as follows:

- Emission standards have been notified under the Environment (Protection) Act, 1986 to check pollution.
- Industries have been directed to install necessary pollution control equipment and legal action has been initiated against the defaulting units.
- Action Plan has been formulated for restoration of environmental quality in polluted areas.
- Environmental audit in the form of environmental statement has been made mandatory for all polluting industries.

V. CONCLUSIONS

The conclusions are summarized below:

✓ RSPM were compared with the National Standard and found that it was complying with, during the entire study period.

✓ In case of Lead (Pb), it was complied with the National Standard (1µg/m^3) during the entire study period.

✓ It is concluded that the observed parameter in this study area are generally complied with except Nickel and Arsenic. Concentration of Nickel (Ni) and Arsenic (As) are not complied with 37.5% (Ni and As) of times with the National Standard (Ni=0.02 µg/m^3 and As=0.006 µg/m^3). The extent of violation in case of Ni and As were 0.43 µg/m^3 and 0.012 µg/m^3.

✓ Reasons for non-compliance of Nickel and Arsenic in the study area:

- Nickel and its compounds have many industrial and commercial uses. Nickel metal and its alloys are used widely in the metallurgical, chemical and food processing industries, catalysts and pigments. The highest concentration of Nickel was found in the smallest particles emitted from a coal - fired plant and crude oil combustion.

- Arsenic is produced commercially from arsenic trioxide. Arsenic trioxide is a by-product of metal smelting operations. About 70% of the world production of Arsenic is used in timber treatment led to contamination of the environment, 22% in agricultural chemicals, and the rest in glass, pharmaceuticals and metallic alloys. Mining, metal smelting, coal-fired power plants and burning of fossil fuels are the major industrial processes that contribute to Arsenic contamination of air.

✓ It is concluded that the Zinc concentration are complied with the International Standard (100µg/m^3) given by WHO, Geneva. Zinc is not so harmful in nature. The presence of Zn in the atmosphere could be attributed to wind-blown soil, road dust, zinc production facilities, foundries, traffic, industrial and residential activities. Breathing large amounts of Zn as dust or fumes can cause specific short-term disease.

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