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ASSESSMENT OF HEAVY METALS FROM RESPIRABLE SUSPENDED PARTICULATE MATTER (PM_{10}) IN THIRUVOTTIYUR, CHENNAI, INDIA

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Abstract-*This study assesses the heavy metal levels in ambient air PM_{10} component in Thiruvottiyur (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} filter papers during 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 fibre filter paper (EPM 2000). PM_{10} concentrations ranges from 13-93µg/m³.These concentrations are complying with the National Ambient Air Quality Standards (NAAQS) during the entire monitoring period.Highest concentrations were found 0.449, BDL, 0.209, 1.58, 0.019, 0.82, 0.192, 16.3, 0.829 and 0.011 µg/m³ for Copper, Cadmium, Total Chromium, Ferrous, Manganese, Nickel, Lead, Zinc, Cobalt and Arsenic respectively. Concentrations of Lead (Pb) were found to be far below the Standard limits prescribed by NAAQS (2009) and Arsenic 12.5% of times and Nickel 18.8% of times are not complying with the Standard and other metals (Zn, Mn, Cd, T.Cr and Cu) compared with International Standards, World Health Organization, Texas Commission on Environmental Quality and European Environmental Agency. 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.*

***Key* Words:** **Ambient Air, Pollution, Particulate Matter, Heavy Metals, Chennai, India**.

1.INTRODUCTION

The atmosphere is a blanket of air that surrounds the Earth. This 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, it can be defined as combination of gaseous matter that forms the stratosphere or the invisible gaseous substances surrounding the Earth. 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. 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, Thiruvottiyur (Industrial area) Chennai, Tamil Nadu was selected. The samples were analyzed for Heavy Metals after acid digestion. The present study was 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.

2.STUDY AREA

Thiruvottiyur Sub district (Tiruvotriyur) is an effective suburb in North Chennai administered by the Chennai Corporation. According to 2011 sensus, Thiruvottiyur had a population of 249,446 and situated at 13.16°N and 80.3°E. Thiruvottiyur is one of the oldest habitations nearthe sea, has a diverse residential population due to the industrial units, trading activity and nearby fishing activities. Thiruvottiyur is one ofthe heavily polluted area where medium and small scale level of industries

are present such as Mohan Rubber Industries, Bharat Steel Industries, Saravana Industries etc. The location map is shown in Fig-1.

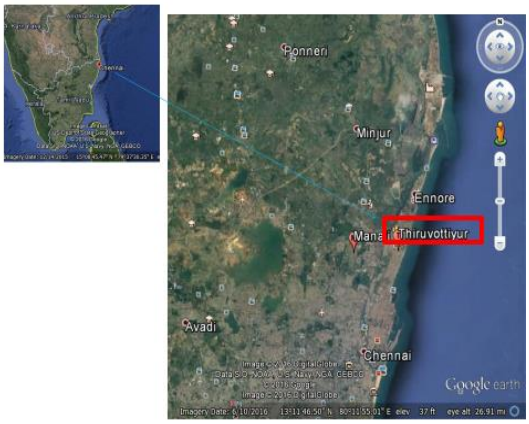

Fig-1: Location of Study Area in Chennai

3.METHODOLOGY

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

3.1 Sampling and Concentration of PM_{10}1

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. These protective 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 Fig-2.

3.2 Digestion of Samples2

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 awatch 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. A series of blanks were prepared using the same digestion method. Step by step procedure for digestion of sample shown in Fig-3.

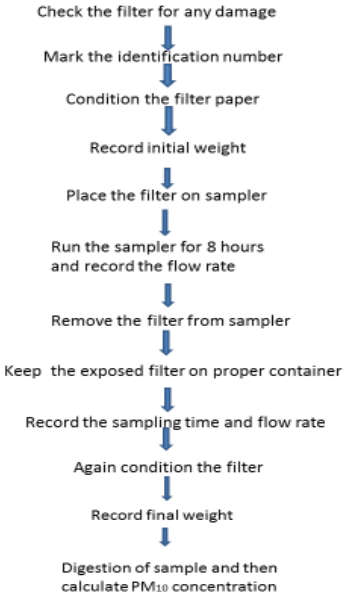

Fig-2: Flow Diagram for Procedure of PM_{10}

Fig-3: Digestion of Samples

3.3 Analysis of digested samples by ICP-OES 3

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 the sample was obtained. Process of ICP-OES are follows as

- Aspiration:where a high speed gas flow is directed across an open tube, creating a negative pressure and drawing solution through the tube.
- Nebulization:Creating an aerosol from a liquid by the use of pneumatic or mechanical forces.
- Desolvation:Remove solvent molecules from a sample droplet, resulting in a dried sample.

- Vaporization:Breaking down the dissolved sample particles into a gas of sample molecules.
- Atomization:Dissociating vaporized sample molecules into free atoms.
- Excitation:An electron is promoted to a higher energy level, resulting in an atom or ion said to be in an excited state.
- Ionization:A neutral atom is converted to a charged ion through gain or loss of an electron.

3.4 Standards for Ambient Air Quality 4

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	
		Industrial, Residential, Rural and other Areas	Ecologically Sensitive Area (Notified by Government)
Particulate Matter or PM_{10} µg/m^3	Annual * 24 Hours **	60 100	60 100
Lead (Pb) µg/m^3	Annual * 24 Hours **	0.50 1.0	0.50 1.0
Arsenic (As), µg/m^3	Annual *	0.006	0.006
Nickel (Ni), µg/m^3	Annual *	0.02	0.02

* 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.

(*NOTE: Whenever and wherever monitoring results on two consecutive days of monitoring exceed the limits specified above for the respective category, it shall be considered adequate reason to institute regular or continuous monitoring and further investigations*)

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/m^3	100	World Health Organization, Geneva [7]
Manganese (Mn), µg/m^3	0.15	European Environmental Agency [8]
Cadmium (Cd), µg/m^3	0.005	European Environmental Agency [8]
Chromium (Cr), µg/m^3	0.01	Texas Commission on Environmental Quality
Copper (Cu), µg/m^3	1	Texas Commission on Environmental Quality

3.5 Air Pollution 5

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 Air Pollutants [9]

Pollutants	Sources	Health Effects	Environmental Effects
PM	Burning of wood, diesel and other fuels, industrial processes	Eye, nose and throat irritation, lung damage, Bronchitis, cancer	Reduces visibility, discolor structures and property.
Lead	Combustion of fossil fuels and leaded gasoline, paint, smelters, battery manufacturing units	Brain and nervous system damage, cause cancer in animals.	Harm to wildlife and livestock.
Chromium	Iron works,	Can alter genetic	Accumulates in food chain

	rubber works.	materials and cause cancer.	
Cadmium	Tobacco smoke, combustion of fossil fuels, fertilizers and fungicide	Bone damage, affects liver and kidney. Itai-Itai disease	Accumulates in food chain

3.6 Particle Size Classification 6

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 2.3.

Table-4: Classification and Size of Particles [10]

Fraction	Size range
SPM	0.01-100µm in diameter
RSPM or PM_{10} (Thoracic fraction)	<=10µm diameter and diameter ranges from 2.5-10 µm is called coarse fraction.
Fine particles or $PM_{2.5}$	<=2.5 µm in diameter
PM_1	<=1 µm in diameter
Ultrafine particles (UFP)	<=0.1 µm in diameter

3.7 Calculation 7

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

4. RESULTS AND DISCUSSIONS

4.1 PM_{10} Concentrations 1

Concentration of $PM_{10}$are given in Table-5 and Fig-4 for the period summer, pre-monsoon and monsoon (April-November 2015). PM_{10} concentrations varied from 17-76µg/m^3 (summer), 13-83µg/m^3 (pre-monsoon) and 21-93µg/m^3 (monsoon) The minimum monthly mean value of 38µg/m^3 was recorded in the month of April, 2015 and the maximum monthly mean value of 51µg/m^3 was recorded in the month of November. The higher value may be due to heavy wind (Audi Kaaththu), which is common in Tamil Nadu. Sources of Particulate matter are generators, dust, vehicles, industries, burning wastes etc.

Table-5: RSPM Values

Months (2015)	RSPM, µg/m^3 (monthly mean)
April	38
May	42
June	43
July	49
August	41
September	43
October	44
November	51

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

Seasons (2015)	Thiruvottiyur		National Standard 100 (µg/m^3)
	Range (µg/m^3)	Mean (µg/m^3)	
Summer	17-76	40.8	Complied with
Pre-Monsoon	13-83	44.2	Complied with
Monsoon	21-93	47.2	Complied with
Study period	13-93	44.1	Complied with

Table-6 shows that the PM_{10} is fully complied with the National Standards throughout the study, there is no significant trend and the values are almost flat. The monthly average is around 44µg/m^3 with marginal fluctuation.

4.2 Heavy Metals Concentrations2

Concentration of Cu, Cd, T.Cr, Fe, Mn, Ni, Pb, Zn, Co and As in the RSPM samples were found in the range of 0.077-0.449, BDL, 0.009-0.209, 1.14-1.58, 0.01-0.019, BDL-0.82, 0.08-0.192, 9.42-16.3, 0.033-0.829 and BDL-0.011 µg/m^3 in the year 2015 placed in Table-7. The mean concentration of heavy metals found in the order of Zn> Fe> Cu>Pb> Co> Ni>T.Cr>Mn> As> Cd.

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

Location		Thiruvottiyur (µg/m³)
Copper (Cu)	Range	0.077-0.449
	Mean	0.190
	IS = 1µg/m³	Complied with
Cadmium (Cd)	Range	BDL
	Mean	BDL
	IS=0.005 µg/m³	Complied with
T.Chromium (T.Cr)	Range	0.009-0.209
	Mean	0.064
	IS=0.01 µg/m³	87.5% of times not complied
Ferrous (Fe)	Range	1.14-1.58
	Mean	1.275
	IS=NA*	NA
Manganese (Mn)	Range	0.01-0.019
	Mean	0.015
	IS=0.15 µg/m³	Complied with
Nickel (Ni)	Range	BDL-0.82
	Mean	0.076
	IS=0.02 µg/m³	18.8% of times not complied
Lead (Pb)	Range	0.08-0.192
	Mean	0.096
	IS=1 µg/m³	Complied with
Zinc (Zn)	Range	9.42-16.3
	Mean	11.7
	IS=100 µg/m³	Complied with
Cobalt (Co)	Range	0.033-0.829
	Mean	0.090
	IS=NA	NA
Arsenic (As)	Range	BDL-0.011
	Mean	0.001
	IS=0.006 µg/m³	12.5% of times not complied

*(*NA= Not available)*

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 beengiven to these three metals and analyzed exclusively. The same is presented below:

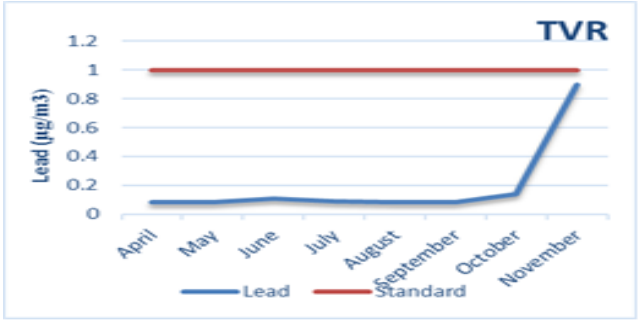

Fig-4: Monthly Variation of Lead Concentration (2015).

Fig-4 shows that the maximum concentration of Lead in October month. Concentration of Lead from April to October is almost same. Although it is observed that Lead concentration is complied with NAAQS (1µg/m³). Mean concentration of Lead is 0.096 µg/m³.

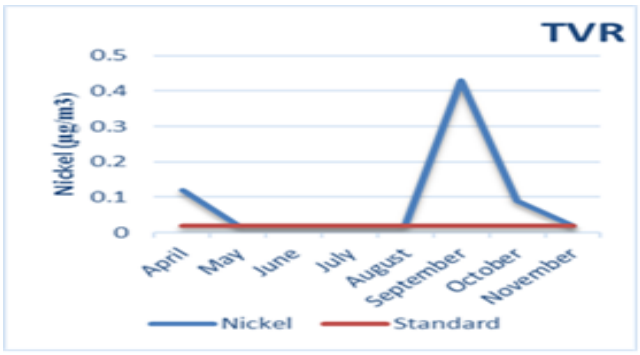

Fig-5: Monthly Variation of Nickel Concentration (2015)

Fig-5 shows the maximum concentration of Nickel was in the month of September 2015 whereas minimum concentration observed in the month of May to August and November 2015. From the observed data, it was found that Nickel concentration is not complied with the National Standard (0.02µg/m³) by 18.9% of times. Mean Concentration of Nickel found in the present study was 0.076µg/m³.

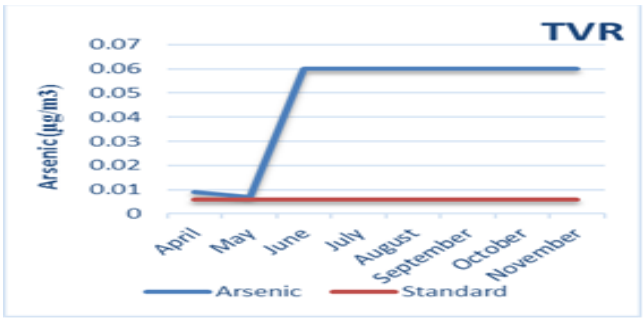

Fig-6: Monthly Variation of Arsenic Concentration (2015)

Fig-6 shows the maximum concentration of Arsenic found in the month of June to November, it is observed that concentration of Arsenic is constant from June to July. Minimum concentration found in the month of May 2015. Arsenic 12.5% of times not complied with National Standard. Arsenic mean concentration 0.001 µg/m³ were found much below the standard limit.

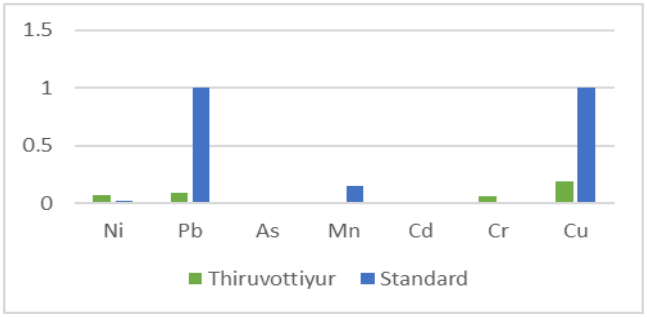

Fig-7: Comparison of Ni, Pb, As (CPCB), Cd, Mn (EEA) and Cr, Cu (TCEQ) with Standards.

Fig-7 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 0.076µg/m³ against the National Standard of 0.02µg/m³ which is not complied with standard. Lead is fully complied with the National Standard 1µg/m³. Arsenic not complied with Standard by 12.5% of times. Cadmium, Manganese and Copper complied with the EEA standard 0.005µg/m³, 0.01µg/m³ and 1µg/m³ respectively. Chromium not complied with International Standard 0.01 µg/m³.

Table-8: Total and Percentage of Heavy Metals in PM_{10}

Months (2015)	THM	PM_{10}	% of HM
April	14	38	36.8
May	12	42	28.6
June	20	43	46.5
July	14	49	28.6
August	15	41	36.6
September	15	43	34.9
October	17	44	38.6
November	20	51	39

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

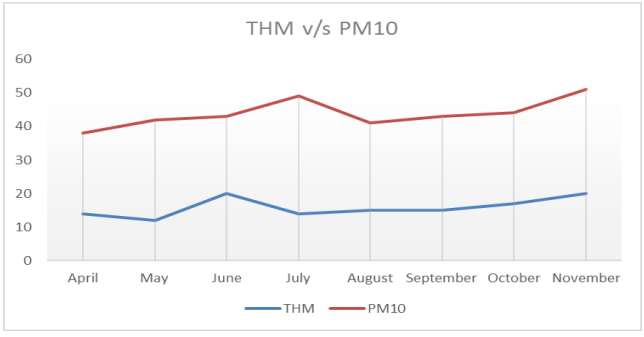

Fig-8: Total Heavy Metals in PM_{10} against PM_{10} (2015)

Table-8 shows the total Heavy metals present in PM_{10} and its percentage. Heavy metals percentage ranges from 28.6% to 46.5% and in an average it is 36.2% of PM_{10}. Minimum percentage of heavy metals found in May whereas maximum in June,2015. Total Heavy Metals in PM_{10} against PM_{10} during the study period of 2015 are shown in Fig-8.

5.CONCLUSIONS

The conclusions are summarized below:

- ✓ RSPM were compared with the National Standard and found that it was complying with Thiruvottiyur during the study period.
- ✓ In case of Lead (Pb), it was complied with the National Standard (1µg/m³) during the entire study period.
- ✓ It is concluded that the observed parameter in this study area of Thiruvottiyur are generally complied with except Nickel and Arsenic. Concentration of Nickel (Ni) and Arsenic (As) are not complied with and 18.9% and 12.5% of times in Thiruvottiyur respectively with the National Standard (Ni= 0.02 µg/m³ and As=0.006 µg/m³). The extent of violation in case of Ni and As were 0.382 and 0.004 µg/m³.

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

- Nickel and its compounds have many industrial and commercial uses. Most Nickel is used for the production of stainless steel and other Nickel alloys with high corrosion and temperature resistance. Nickel metal and its alloys are used widely in the metallurgical, chemical and food processing industries, especially as catalysts and pigments. The sources of nickel content are coal and crude oil.The highest concentration of nickel was found in the smallest particles emitted from a coal - fired plant and 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, 22% in agricultural chemicals, and the rest in glass, pharmaceuticals and metallic alloys. The use of Arsenic in the preservation of timber has led to contamination of the environment. 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 in this study area are complied with the International Standard (100µg/m³) 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 related,

industrial and residential activities. Breathing large amounts of Zn as dust or fumes can cause specific short-term disease.

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