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Health Risks Associated with Heavy Metals in Fine Particulate Matter: A Case Study in Delhi City, India

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Abstract

The concentrations of twenty five heavy metals adsorbed to fine fraction of particulate matter, $PM_{2.5}$ ($d \leq 2.5$ μm) have been experimentally analysed at a sampling site located at the kerbside along a National Highway in Delhi city, India. The sampling has been carried out for 12-hour using Ecotech Intruments, APM550. The $PM_{2.5}$ has been collected on PTFE filter papers for the winter season. Later, the filter papers have been analysed for various heavy metal concentrations using ED-XRF. It has been observed that the metals concentrations are in this trend: Si > K > S > Ca = Fe > Zn = Pb > Br. it is observed that Si has high co-relation with Ca, Fe and K, which may be due to crustal origin of all three elements; while S, Br and Pb may be from vehicular exhaust emissions and/or abrasions due to brake and tyre wear. The potential health risks associated with different carcinogenic heavy metals have also been calculated. One of the health risk indicators, the excess cancer risk (ECR), is found to be in the order as As > Cd > Pb > Cr > Ni.

Keywords

Fine PM, Heavy Metals, Excess Cancer Risk, Kerbside, National Highway

1. Introduction

Air quality has been a cause of concern all over the world because concentrations of various *criteria* pollutants frequently violate the ambient standards, particularly in developing countries. Particulate matter (PM), one of the six criteria pollutants, comprises a complex mixture of different elements and compounds. $PM_{2.5}$ (diameter < 2.5 μm) can penetrate into the lungs more readily and are therefore more likely to have short- and long-term effects such as decreased lung functions and alterations in lung tissues, premature death and increased respiratory symptoms and disease [1]. Fine PM ($PM_{2.5}$) typically contains wide range of chemical species, ranging from metals to organic and inorganic compounds [2]. Among inorganic compounds, most important ones are the trace metals, which are emitted by various sources such as road dust, geogenic materials, motor vehicles, coal and oil combustion, construction activities, incineration and other industrial activities [3] [4].

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Delhi, the capital city of India with over 14 million populations is experiencing health risks from various such pollutants, especially the respirable particulate matters. There are many different sources of PM like road side dust, vehicles, industries, trans-boundary migrations, power plants, solid waste and local sources. Particulate matters from these sources may contain hazardous pollutants and can have carcinogenic and mutagenic effects. Thus, identification of the sources and estimating their contributions to the ambient environment seem to be a paramount task for air quality management [5]. The study in 2010 has indicated that 223,000 deaths from lung cancer worldwide resulted from air pollution [6]. International Agency for Research on Cancer (IARC), specialized cancer agency of the World Health Organization classified outdoor air pollution as *Group* 1 *carcinogenic* to humans in October 2013 [7]. Against this background, a study has been carried out to determine the atmospheric concentrations of heavy metals in $PM_{2.5}$ and their associated health risks (excess cancer risks) at one of the sampling sites located at the kerbside along a National highway in the Delhi city, India.

2. Methodology

2.1. Sample Collection

Delhi, the Capital of India is situated between latitudes 28˚24'17" and 28˚53'00N and longitudes 76˚50'24" and 77˚20'37"E at 216 meters above the mean sea level (MSL). It is spread over an area of approximately 1500 sq. km. The site on NH-2, a "kerbside", is in proximity of one of the busiest traffic intersections (Ashram Chowk) in Delhi. It is surrounded by ring roads connecting to Sarai Kale Khan, Mathura road, Lajpat nagar and Nizamuddin area, in different directions with a flyover on outer ring road (Sarai Kale Khan–Lajpat Nagar). The junction connects two States, namely UP (through Noida Toll Bridge) and Haryana (through Mathura road leading to Faridabad and to Gurgaon via Dhaula Kuan). Nizamuddin railway station and Sarai Kale Khan bus stand are about 2 km away from the Ashram Chowk. Overall, the study zone can be defined as high activity zone with very high traffic activity throughout day and night. There are several small scale industries, Okhla Industrial Area, a waste management plant and slumps nearby.

Sampling has been conducted for 24-hour duration for a sampling cycle of 12 - 12 hrs (*i.e.*, morning sampling 8 am to 8 pm and night 8 pm to 8 am) using $PM_{2.5}$ Sampler (Ecotech Instruments Pvt. Ltd., APM 550) which works on WINS impactor and runs at a constant flow rate of 16.67 L/min during December 2013–January 2014 for alternate weeks. The sampling details and average flow rate have been recorded and carefully maintained throughout the study. Field blank samples are collected by mounting blank filters onto the sampler for about 10 min without pumping any air. The polytetrafluoroethylene (PTFE) filters are pre-conditioned for 2 days in a controlled room (temperature: 20˚C ± 1˚C, relative humidity: 50% ± 5%) before and after the sampling and then weighed using an analytical balance (Sartorius, CPA2PF). After sampling, the sampled filters are sealed in aluminum foil bags and stored in a freezer (−20˚C) prior to analysis.

2.2. Chemical Analysis

Elemental compositions of the TSP samples have been determined by Energy Dispersive X-Ray Fluorescence (ED-XRF) spectrometry (Epsilon 5 ED-XRF, PANalytical B. V.). The X-ray source is a side window X-ray tube with a gadolinium anode and operated at an accelerating voltage of 25 - 100 kV and a current of 0.5 - 24 mA (maximum power: 600 W). The characteristic X-ray radiation is detected by a germanium detector (PAN 32). Each sample is analyzed for 30 min to obtain a spectrum of X-ray counts versus photon energy with the individual peak energies matching specific elements and peak areas corresponding to elemental concentrations. In this study, 25 elements (*i.e.*, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Cd, In, Sn, Sb, Ba, Pb) have been determined. Blank correction is performed for QA/QC purposes.

2.3. Excess Cancer Risk Assessment

Excess cancer risks (ECRs) have been calculated using the unit risk and the PM-bound concentration of the metals which represents the total ambient concentration of the metals. ECRs can be calculated simply by using the following formula [8]-[10]:

$$ECR = CA \times IUR \quad (1)$$

where CA is the concentration of the pollutant ($\mu g/m^3$) and IUR is the inhalation unit risk $(\mu g/m^3)^{-1}$. The infor-

mation on the carcinogenic types and the unit risks of the metals is obtained from the US EPA database for IRIS (Integrated Risk Information System) [11].

3. Results and Discussions

3.1. $PM_{2.5}$ Concentrations

The daily mean $PM_{2.5}$ concentration at the sampling site has been observed to be 286.23 (±41.1) μg/m^3. Observed concentrations are three to four times higher as compared to the air quality standard for $PM_{2.5}$ of 60 μg/m^3 [12] and 35 μg/m^3 [13]. This is because the selected sampling site is *stop-and-go* site at a national highway which has high traffic volume of approximately 170,000 vehicles per day [14].

Concentrations were found to be higher during night time as compared to daytime (**Figure 1**). This can be attributed to the movement of inter-state diesel-fueled heavy duty vehicles whose entry is allowed in the city from the national highway during the nighttime (after 8 pm). Also, due to the inversion conditions that prevail during the night in winters, fine PM particles remain suspended in the atmosphere for a very long time. During weekends, the concentrations of $PM_{2.5}$ are again increasing when compared to weekdays. It may be due to additional *weekend trips*.

3.2. Heavy Metals Concentrations

Si, being the crustal element, is found to be maximum *i.e.* 33%, followed by K, 21% and S, 20%. The concentration trend shows Si > K > S > Ca = Fe > Zn = Pb > Br (**Figure 2**). However, it is observed that Si has high co-relation with Ca, Fe and K, which may be due to crustal origin of all three elements; while S, Br and Pb may be from vehicular exhaust emissions and/or abrasions due to brake and tyre wear.

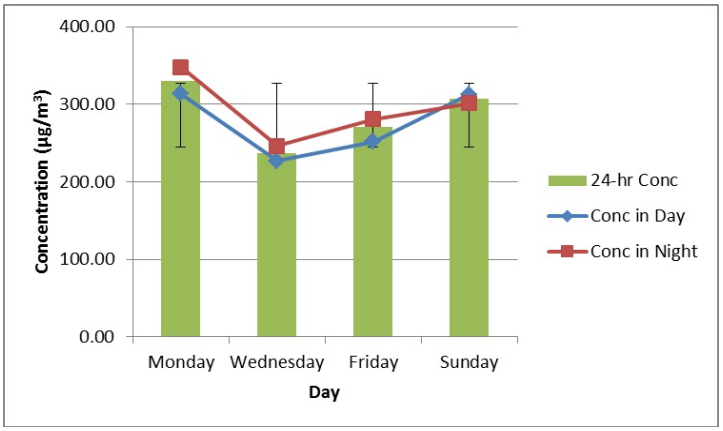

Figure 1. Diurnal variations in $PM_{2.5}$ concentrations at the sampling site.

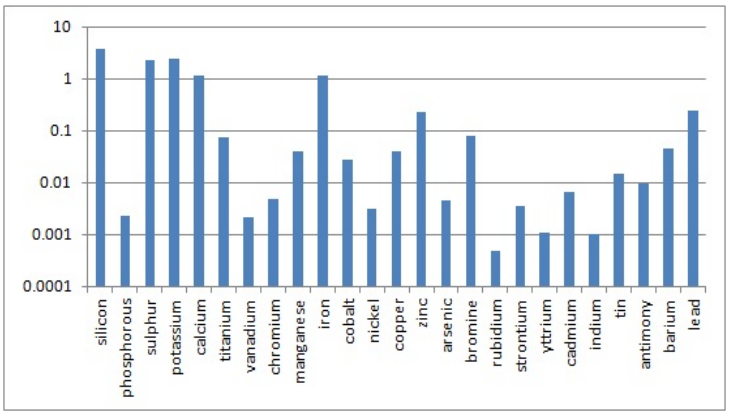

Figure 2. Metals concentrations in ambient $PM_{2.5}$ samples.

The high concentrations of Zn may have its origin from automotive sources *i.e.* lubricating oil, wear and tear of vulcanized rubber tyres and corrosion of galvanized vehicular parts but it is considered to be a good marker for tyre wear [15] [16]. Although direct emissions of Pb from vehicular exhausts ceased as leaded gasoline was banned in Delhi but lead is still persistent in dust from earlier emissions because of its long residence time in theenvironment [17]. Copper is observed to be coming from brake wear, tyre wear and wheel bearing [18]. Copper can be attributed to solid waste dumping and incineration also [19]. Apart from road dust Mn is mostly emitted by automobile exhaust [20] [21]. It is used as an additive in unleaded gasoline and Manganese tricarbonyl compound in unleaded petrol is used to enhance automobile performance but they have toxicological significance [22].

3.3. Excess Cancer Risk Assessment

The elements of As, Cd, Cr, Ni and Pb are the known carcinogenic metals among the twenty-five metals investigated in this study and are introduced by exposure through the inhalation pathway. The IARC [23] [24] has classified Cd and Ni are classified as Class 1 carcinogenic elements and Pb as Class 2B carcinogenic element. The chromium identified in this study included Cr (III), however, it is known that the concentration ratio of carcinogenic Cr (VI) to non-carcinogenic Cr(III) in ambient air is about 1:6. Therefore, the concentration of Cr (VI) used for the carcinogenic risk assessment was calculated as one seventh of the total concentration [9] [10] [25]. There are different forms of nickel including nickel refinery dust, nickel subsulfide (Ni_3S_2), nickel carbonyl and nickel-soluble salts (nickel chloride, nickel sulfate). The US EPA has classified nickel refinery dust and nickel subsulfide as group A materials, known human carcinogens. Lead is classified as Group B2, but human evidence is inadequate in IRIS thus, values for IUR were selected from California Environmental Protection Agency.

Table 1 shows the estimated ECR of PM-bound carcinogenic elements for the average values of As, Cd, Cr, Ni and Pb. As has the highest ECR followed by Cd. Cr(VI) has high ECR than Ni and Pb even though its concentration in the PM is lowest and Pb has the highest, because of the much higher unit risk of Cr (VI), ranging from 7 to 50 times, compared to the unit risk of the Ni or Pb forms. The total ECRs based on the average values of As, Cd, Cr, Ni and Pb in $PM_{2.5}$ is 4.34×10^{-5}. These results indicate that 4 or 5 people out of 100,000 could get cancer after exposure to the toxic trace metals in ambient $PM_{2.5}$ residing or working near to a national highway.

4. Conclusion

The daily mean $PM_{2.5}$ concentration at the sampling site has been observed as 286.23 (±41.1) μg/m^3, which is three to four times higher as compared to the air quality standard for $PM_{2.5}$. Concentrations have been found to be higher during night time as compared to daytime and during weekends than weekdays. The metal concentrations are in this trend: Si > K > S > Ca = Fe > Zn = Pb > Br. It is observed that Si has high co-relation with Ca, Fe and K, which may be due to crustal origin of all three elements; while S, Br and Pb may be from vehicular exhaust emissions and/or abrasions due to brake and tyre wear. The potential health risks associated with different carcinogenic heavy metals have also been calculated. One of the health risk indicators, the excess cancer risk (ECR), is found to be in the order as As > Cd > Pb > Cr > Ni. According to health risk assessment, 4 or 5 people out of 100,000 could get cancer after exposure to the toxic trace metals in ambient $PM_{2.5}$ residing or working near to a national highway.

Table 1. ECR of PM-bound carcinogenic elements.

Elements	CA, mg/m^3	IUR, (mg/m^3)$^{-1}$	ECR
As	4.62E−03	4.30E−03[a]	1.99E−05
Cd	6.52E−03	1.80E−03[a]	1.17E−05
Cr (VI)	6.74E−04	1.20E−02[a]	8.09E−06
Ni	3.14E−03	2.40E−04[a]	7.55E−07
Pb	3.10E−01	1.20E−05[b]	2.95E−06
Total ECR			**4.34E−05**

[a]Values taken from IRIS (Integrated Risk Information System). [b]Values taken from Cal EPA (California Environmental Protection Agency).

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