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# Chemical Fraction and Health Effect of Size Segregate PM at National Highway of Northern India

**Rahul Tiwari[1,2] | Akshay Botle[3] | Kalpana Rajouriya[2] | Prabal P Singh[1] | Ajay Taneja[2]✉**

1. Department of Chemistry GLA University Mathura, 281406 India
2. Department of Chemistry, Institute of Basic Science, Dr. B. R. Ambedkar University, Agra 282002 India
3. Department of Environmental Science, The Institute of Science Dr. Homi Bhabha State University, Mumbai 400032 India

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## ABSTRACT

Sampling was conducted on Agra-Delhi national highway NH-2. Samples were collected with the help of Sioutas cascade impactor. During the sampling, $PM_{1.0-0.5}$ (255.85μg/m$^3$) was higher than $PM_{2.5-1.0}$ (218.96μg/m$^3$). The AQI value for the average $PM_{2.5}$ concentration also exceeded the severe AQ limit (401-500). These results showed that $PM_{2.5}$ pollution has a significant influence on the site as a result of a variety of anthropogenic activities. During the summer season, for $PM_{1.0-0.5}$ and $PM_{2.5-1.0}$ highest values (μg/m$^3$) of metals followed the same trend and it was observed as Mg(6.52)> Ca(5.89)> Al(3.64)> while for $PM_{2.5-1.0}$ it was as Mg(10.12)> Ca(9.5)> Al(5.95) respectively. At roadside, most of these metals are emitted from the resuspension of dust and vehicle activities which causes serious diseases to the human being. Cd, Cr, Cu, Pb, and Zn were highly enriched at national highway sampling sites, highlighting the crustal source, which has a major impact on metals concentration, followed by anthropogenic sources. The present research was conducted to find out the concentration level of metals in $PM_{2.5-1.0}$ and $PM_{1.0-0.5}$ particles in Agra, India to find out the health risk assessment at highway site.From the results, it was observed that all metals bound to larger size PM has high bioavailability. From the health risk assessment, it was found that all the metals bound smaller size particles showed higher HQ except in the case of Ni and Al. Cr, Pb showed carcinogenic risk to children and adults in both size fraction of PM except in the case of Ni.

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## INTRODUCTION

Since India suffers from some of the most polluted air in the entire globe, the Indian government has declared it a vital objective to address it, as indicated by the introduction of the National Clean Air Programme in January 2019 (MoEFCC, 2019). Over 99% of the nation's population is regularly subjected to ambient $PM_{2.5}$ concentrations higher than the average yearly ambient concentration recommendations established by the World Health Organization, which is 10 μg/m$^3$. Furthermore, over half of the population is subjected to concentrations higher than India's yearly National Ambient Air Quality Standard (NAAQS), which is 40 μg/m$^3$ (Purohit et al., 2019). According to the World Health Organization, India comprises the most polluted metropolitan areas globally and is the most significant contributor to the yearly particle concentration worldwide (WHO, 2016). According to the Health Effects Institute (2018), more than 90% of India's population inhales air higher than the recommended intermediate target-1

*Corresponding Author Email: *ataneja5@hotmail.com*

set by the World Health Organization (WHO), which is 35 μg/m$^3$. According to Balakrishnan et al. (2019), the overall number of people who passed away in India due to air pollution (including ambient and household) in 2017 was 1.24 million. Considering criteria related to poor air quality, author attempted PM monitoring on highway and tried to evaluate health risk assessment in size segregated PM from traffic. Significant causes of poor air quality are the massive uncontrolled emissions from automobiles, factories, solid waste burning, urbanization, and population expansion (Shrivastava et al., 2018). According to the findings, $PM_{2.5}$ and $PM_{10}$ particles may induce acute respiratory symptoms, wheezy bronchitis in newborns, and a slower rate of lung expansion in children (Tiwari et al., 2022). Children and the elderly who live near vehicle traffic are particularly prone to such infections. As a result of the elevated concentrations of fine and ultrafine particles in the urban environment, everyday commuters, including children, the elderly, and city inhabitants, face substantial health risks (Tiwari et al., 2020; Tiwari et al., 2022).

Traffic activities are critical contributors to metals being released into the atmosphere, these metals pose substantial health concerns by entering the body via soil, dust, skin contact, or inhalation (Tiwari et al., 2020). Complicated metal size distribution in indoor and outdoor aerosol particles found by Rohra et al., (2018b), provides problems for managing pollution produced by the elements. The investigation stipulated that the health risk of inhaling PM of various sizes is not insignificant. Because particle size impacts toxicity, the computed findings revealed that finer particles offer a larger non-carcinogenic (2.5 times) and carcinogenic (14.8 times) risk than coarser particles. The investigation also found that the posed health risk of inhaling various PM sizes is insignificant. Masih et al., (2019) investigated submicron particles in indoor and outdoor air, which pose an increased cancer risk in two separate microenvironments in western India. According to epidemiological research, rising levels of air pollution have increased respiratory ailments and mortality (Tiwari et al., 2020; Tiwari et al., 2022). In 2012, the death of 3.7 million people resulted from ambient air pollution worldwide (WHO, 2014). Some studies have been undertaken, such as Gao (2021); Colbeck et al., (2011), to quantify the mass concentrations of distinct fractions of PM along the roadside. Humans are in danger of severe respiratory and cardiovascular problems due to substantial amounts of tiny particulate matter ($PM_{1.0}$ and $PM_{2.5}$) (Lee et al., 2011). These microscopic particles are produced through myocardial infarction, cardiovascular disorders, lung cancer, and other respiratory illnesses (Gao, 2021). A small number of fascinating published studies (Izhar et al., 2016; Tiwari et al., 2022) have proposed a statistical association between health effects and ambient fine particulate matter concentration levels, particularly submicron particulate matter that can easily reach deep into the alveolar region of the respiratory system, remain there for prolonged periods, and then enter the blood circulation system. Asia has limited research, particularly in rapidly developing countries, this study thoroughly explains the health issues linked with PM and heavy metals. PM emissions are increasingly concerning nowadays since they are pervasive and exist in minute quantities, causing major health problems in humans, agriculture, and the environment. This research is being conducted to investigate the worsening air quality caused by PM in the form of heavy metals created by vehicles on highways which will aid in gathering critical data for research into the impact of PM on health. The current research aims to offer data on the concentration of size-segregated PM at traffic intersections. The present research was conducted to find out the concentration level of metals in size segregated PM in Agra, India. The main objectives of the research are (i) to investigate the size distribution and related metal constituent concentration in $PM_{2.5\text{-}1.0}$ and $PM_{1.0\text{-}0.5}$ particle fractions at highway site. (ii) To assess the particle size effect on elemental bioavailability and (iii) to evaluate the carcinogenic and non-carcinogenic risk of particle size-segregated metal constituents through inhalation pathway. Notably, the risk assessment performed in the present study is one of its kinds study in size segregated PM. Thus, the results of this study will give a better view of the outdoor air quality with reference to size resolved particulate concentrations at highway site which could help the health officials and general public to gain insight into the toxicity of metal bound particles.

## ENVIRONMENTAL EFFECT OF PM

Historical and cultural monuments across the world are damaged due to air pollution. Building materials like marble and calcarenite are devastated due to PM-containing mineral fractions (Tidblad et al., 2009). India has many historical monuments dating back to the Black Carbon (BC) period. Pollution of air has led to the degradation of architectural monuments. A classic example is the Taj Mahal, made of marble which has lost its lustre due to generators operating in Agra, three-wheelers running on diesel, emissions from petroleum refineries, and coal plants (https://www.downtoearth.org.in/indepth/doomed-tomb-31109 visited on 26/4/2018), brick kilns and combustion of wood (Kulshrestha et al., 2009). Reduced visibility in areas like national parks and forests is the significant effect of $PM_{2.5}$ pollution. Wind acts as a carrier for these particles, which then settle on the ground or water. This setting can lead to a nutrient imbalance in the river basins and coastal waters, acidity in the lakes and streams, nutrient depletion in soil, adverse effects on forests and crops, and may affect the ecosystem diversity (Katsouyanni et al., 2001). The absorption and scattering of light caused by PM lead to reduced visibility Tiwari et al., 2020; Tiwari et al., 2023). Particulate matter soils the artificial surfaces, due to which the economic burden incurs as the cleaning and repairing processes are undertaken. Air pollution also affects vegetation depending on the concentration of the pollutants and environmental conditions. The process of photosynthesis is hindered due to the dust and smoke particles, which settle on the stomata of the leaves and reduce light absorption (WHO, 2002). Sodium (Na), Magnesium (Mg), Potassium (K), and Calcium (Ca) are also included in $PM_{2.5}$. These species are soluble in water and can enter human bodies quickly, leading to adverse health effects (Tiwari et al., 2020). Due to the emission control policies on heating, vehicles, and power generation industry, the particulates, carbon monoxides, and sulphur oxides have declined in developed countries like Western Europe and the US (WHO, 2005).

### *Health Effects of PM*

The intensity of health problems caused depends upon the size of PM. The size of PM (less than 10μm) can enter the lungs and bloodstream, which poses a severe health risk. These particles also enter the bloodstream (Prüss-Üstün et al., 2003; Tiwari et al., 2020). Exposure to these particles affects both lungs and the heart (Nelin et al., 2012). According to the studies, exposure to PM leads to the death of thousands of elderly people every year. According to the studies, thousands of hospital admissions result from exposure to fine particles. These fine particles have an adverse effect on individuals already suffering from diseases like emphysema, chronic bronchitis, or heart disease. Deaths and hospital admissions increase in the case of sensitive populations due to PM (Tiwari et al., 2020a,b). Children are more susceptible to such threats than adults, as their respiratory system is still developing. The frequency of childhood illnesses increases in children exposed to particulate matter and can lead to impaired lung development in children (Penner et al., 1993). Difficulties in breathing and aggravated coughing are other symptoms seen in children due to particulate matter, which can hinder normal school activities (Michelson & Tourin, 1967). Asthma cases have increased over some time. 40% of the total asthma cases are reported in children. Other pollutants and fine particles can aggravate asthma, leading to increased medication (Haywood & Boucher, 2000). Numerous studies link particulate pollution exposure to numerous problems (Tiwari et al., 2020ab; Tiwari et al., 2022; Tiwari et al., 2023). There is no specific definition of short-term exposure as opposed to long-term exposure; short-term exposure is viewed hours today while long-term exposure ranges over the year. A few diseases occurring from the PM are summarized.

*Short-Lasting / Short-term Effect of $PM_{2.5}$*

Short-term exposure causes nausea, headaches, and irritation of the throat, nose, and eyes, as well as aggravates asthma (Ghio et al., 2000; Tsai et al., 2003; Gallus et al., 2008) respiratory illness suddenly, the higher chance of heart attack (Norris et al., 1999).

*Long-Lasting/Long-term Effect of $PM_{2.5}$*

Several research studies have shown the long-term effects of PM particles on people, including impaired lung function (D'Ippoliti et al., 2003), increased chronic bronchitis (Tolbert et al., 2000), a decrease in life probability (Hackshaw et al., 1997), and elevated lung cancer risks (Pope III et al., 2004).

*Human Health Affected by Metals*

Heavy metal pollution is a chief health apprehension in elderly people and children as it is a leading cause of many diseases (www.drugs.com/Health-guide/pneumoconiosis.html visited on 12/12/2018). Heavy metals are toxic, and this harmfulness owes to fertilisers, insecticides, vehicular traffic, automotive exhaust, industrial dumps, and many human activities **(**Aikpokpodion et al., 2012; Li et al., 2009**)**. Tremendous research worldwide is carried out to analyse the health risks to human health as they are inhaled, ingested, and absorbed by dermal layers of the skin. Heavy metals are transported to the soil by traffic activity. Heavy metals enter the body via breathing, soil, dust, and cutaneous contact. They can also be transported through the food chain by which they enter the human body and thus prove toxic. In small quantities, heavy metals like Cu and Zn act as micronutrients and are not toxic to humans. However, As, Hg, Pb, and Cd, even at minimum concentrations, prove extremely harmful and toxic to humans **(**Khairiah et al., 2012; Khairy et al., 2011**)**. Heavy metals have an adverse effect on the circulatory, cardiovascular, nervous, reproductive, and renal systems. Heavy metals also act as promoters or initiators for various diseases. Attention deficiency, reduced intelligence, and behavioural abnormality are some of the negative impacts of heavy metals on humans (Abbasi et al., 2012; Zheng et al., 2010).

## MATERIAL & METHODS

*Description of Study Area*

Uttar Pradesh is one of the Northern states of India. The state has many historical, natural, and religious tourist spots **(**https://en.wikipedia.org/wiki/Uttar_Pradesh**)**. The state has seventy-five districts, and Mathura is one of them. Sampling was done at GLA University, Mathura which is situated on Agra-Delhi national highway NH-2 (renumbered as NH-19). Mathura city comprises a total population of 4,41,894 with a density of about 761 persons/$km^2$. The national highway is around 67 km from the city of Agra (27.28°N 77.41°E). NH-19 is one of India's busiest highways; where approximately 14-15 thousand vehicles pass per day on this highway, which makes a big concern about air pollution impact. At this site, the traffic is mainly on the highway. Some greenery, restaurants, and dhabas surround this sampling site. Hindustan petroleum corporation limited's oil refinery has an 8.0 MMTPA capacity is located nearby the area while Mathura refinery is also 15 km far away from the location. Moreover, other prominent industrial contributors like textile industries indulge in printing, including sari-printing, fabric dyeing, and silver ornaments present in this area (Fig. 1).

*Climatology*

Climatic conditions are continental, subtropical, and dry. The climate of Mathura has three seasons; summer consists of (April, May, and June) followed by monsoon consisting (July, August, and September), and winter consists (December, January, and February). Post-monsoon, which some people consider the fourth season, overlaps the characteristic of monsoon and the

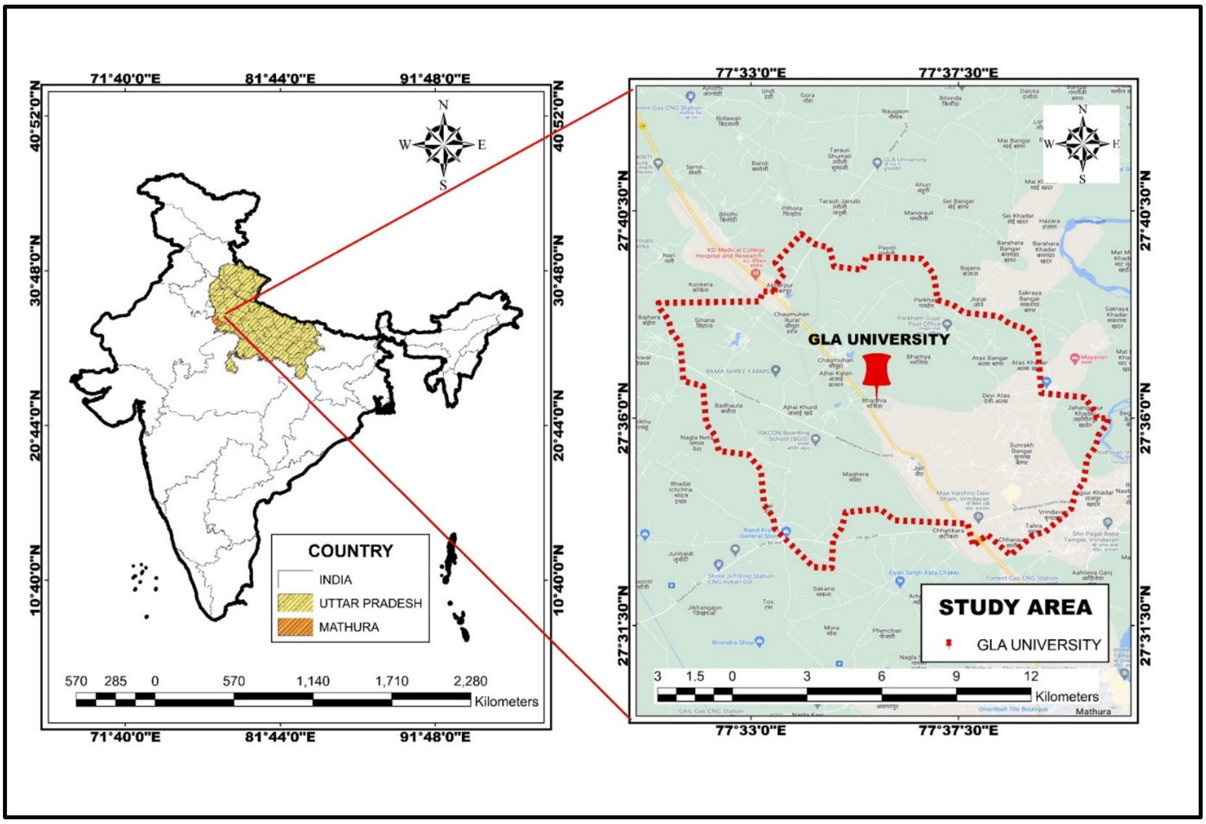


**Fig. 1.** Study Area at Highway (GLA) site India.

winter season. Sometimes monsoon extends to October and winters, as early as the last week of October. Winters are freezing, with temperatures falling up to 10-25$^{o}$ C during the daytime and reaching 5$^{0}$ C at night. The rainy season comprises an annual rainfall of 26 inches (660mm) and relative humidity of 60% to 90%. Temperatures during these months are between 26$^{o}$ C to 37$^{o}$ C. Summer is consisting hot, dry westerly winds with temperatures reaching up to 48$^{0}$ C fall in relative humidity is seen during this season where humidity levels are between (25%-40%).

*Sample Collection*

A Leland legacy pump (skc Inc. 84 PA USA) coupled with Sioutas cascade impactors was used to collect 2.5-1.0µm and 1.0-0.5µm particles on 25 mm filters of Poly Tetra Fluoro Ethylene (PTFE) (Whatman; pore size 0.5µm) for size fraction of $PM_{2.5-1.0}$ and $PM_{1.0-0.5}$. The impactor can collect fine particles up to 3.16 mg (Singh et al., 2003; Sioutas, 2004). Cascade was placed on an average height, i.e. 5.5 feet (flow rate 9L/min). Sampling was conducted for 4 hours/day, which was depends on collection efficiency of cascade impactor, higher concentrations of particles chock the pump in lesser time limit. Samples from the GLA NH-2 traffic junction were collected from April to June 2018 (Summer season). Weighing of filter paper was done thrice before and after the sampling to check the accuracy with a four-digit microbalance (Wensar MAB 120) with a sensitivity range of ±2 mg. (range 220-200mg). Samples were equilibrated in desiccators at 20-30$^{o}$ C with 30-40% relative humidity for 24-48 hours.

*QA/QC (Quality Analysis/ Quality Control) procedure*

Blank field filters were also collected to minimise gravimetric bias from sampling and handling. Pincers were glazed with Teflon to reduce any contamination chances during the handling of filters. After post-weighing, samples were preserved by refrigeration at 4$^{o}$ C to halt the evaporation of any volatile compounds present (Tiwari et al., 2022; Varshney et al., 2015). 2% $HNO_3$ was used for rinsing all plastic and other glassware used for the storage and extraction, where all apparatus was soaked overnight before the extraction process, followed by rising the whole apparatus with de-ionised and double-distilled water (Tiwari et al., 2023).

*Element Extraction Process*

Extraction was performed to determine the heavy metal concentration with the acid extraction method using aqua-regia in 1:3 proportions. Acid extraction was carried out for 30 min, using a hot plate at a controlled temperature of 40º C to 45º C in a 50ml measuring beaker using double distilled water and aqua-regia (Parveen et al., 2018; Tiwari et al., 2023). The susceptible filter paper was divided in two parts by cutting it into two halves, where one part of it was again divided into two strips which were transferred into pre-washed 100ml borosil beakers in such a manner that cut filter papers faced toward the bottom of the beaker, to the beaker 5ml aqua regia was added. The beaker was kept at 20-30˚C on a hot plate for one and a half hours with a slowly increasing temperature. Covering the beakers with a lid (watch glass) prevents volatile compounds from evaporation. Aliquots were obtained from the extracted filters with pre-washed Whatman filter paper. Distilled water was used to rinse the wall of the beakers 2-3 times and was allowed to stand for 30 min and then filtered without shaking. An extracted aliquot was diluted up to 40ml with de-ionized water, and the sample was kept below 4ºC in refrigerators (Parveen et al., 2018).

*Statistical Analysis*

*Air quality assessment*

The term "Air Quality Index" (AQI) refers to a single phrase used during reporting air quality in terms of its impact on human health (CPCB, 2015).

$$I_p = \frac{I\,high - I\,low}{Bp\,High - Bp\,Low}\left(Cp - Bp\,Low\right) + I\,Low \ldots \quad (1)$$

Where,

| | |
|---|---|
| $I_p$: | Contaminant AQI value for ($PM_{2.5}$) |
| $C_p$ | Pollutant's absolute concentration. |
| $BP_{high}$ | Break Point Value ($\geq C_p$) |
| $BP_{Low}$ | Break Point Value ($\leq C_p$) |
| $I_{High}$ | Equivalent AQI value to ($BP_{High}$) |
| $I_{Low}$ | Equivalent AQI value to ($BP_{Low}$) |
| AQI | (Good AQ): 0-50,<br>(Satisfactory AQ): 51-100,<br>(Moderately Polluted AQ): 101-200,<br>(Poor AQ): 201-300,<br>(Very Poor AQ): 301-400,<br>(Severe AQ): 401-500 |

*Enrichment Factor (EF) Calculation*

In EF, a reference element that is exclusively crustal in origin is chosen to represent the extent of metal enrichment in an air sample (Rahn, 1976). Its computation is performed using the following formula (Wedepohl, 1995).

$$EF=\frac{\left(\frac{C_x}{C_{ref}}\right)_{sample}}{\left(\frac{C_x}{C_{ref}}\right)_{crust}}\ldots \quad (2)$$

Where Cx is the present concentration of metal in the air and Cref is the elemental reference concentration in the crust.

*Health Risk Assessment*

A model given by United State Environmental Protection Agency (USEPA) for the health risk assessment was used in this study. Firstly, Exposure Concentration (EC) through the inhalation pathway was calculated given in equation 3. Risk characterization through the inhalation pathway, at last, involved the estimation of the Hazard Quotient (HQ) and Excess Lifetime Cancer Risk (ELCR).

$$EC=\left(c\times ET\times EF\times ED\right)/\,AT\ldots \quad (3)$$

Hazard Quotient is the ratio of exposure to an appropriate reference dose depicted in equation 4. It is an additional risk that someone might have of getting non-cancerous disease if that person is exposed to disease-causing materials for a longer time (Rohra et al., 2018a)

$$HQ=EC/\left(RfC\times 1000\right)\ldots \quad (4)$$

The incremental possibility that a person would acquire cancer during their lifetime as a result of cumulative exposure to the possible carcinogen has been calculated as an excess cancer risk. ECR is determined using the provided formula 5 (Niu et al., 2015; Rohra et al., 2018a; Tiwari et al., 2022; Tiwari et al., 2023).

$$ELCR=EC\times IUR\ldots \quad (5)$$

Where,

| | |
|---|---|
| IUR | Inhalation unit risk (µg/m$^3$) |
| AT: Average time for carcinogens | (70year×365days/year×24h/days) |
| ET: Exposure time | 8h/day |
| EF: Exposure Frequency | 350 Days/Year |
| ED: Exposure Duration | 6Years for Child 24Years For Adult |

Since carcinogens are non-threshold substances, acquaintance to any quantity of them increases the risk of developing cancer; the safe level is “Zero.” The USEPA’s Integrated Risk Information System (IRIS) database is where the information on metals’ inhalation unit risks and carcinogen kinds may be found (USEPA, 1993). According to Tiwari et al. (2022), contamination is unlikely to pose a danger for cancer if the risk value is within the ranges of $10^{-6}$-$10^{-4}$ (USEPA 2009, Taner et al., 2013).

## RESULTS AND DISCUSSIONS

*PM Concentration at National Highway Sampling Site*

During the sampling event, $PM_{1.0-0.5}$ (255.85µg/m$^3$) was higher than $PM_{2.5-1.0}$ (218.96µg/m$^3$). Mathura national highway is one of the bustling highways (NH-2) where nearly 14-15 thousand vehicles cross the road, including 50 buses and 100 cars of GLA university at the sampling point could be a possible source of $PM_{1.0-0.5}$ size fraction. Burning fossil fuel by nearby dhabas/restaurants is another contributor to PM at the sampling site.

The AQI reading (1121.75) for average $PM_{2.5}$ also surpassed the severe AQ limit (401-500). These findings imply that the sampling site is heavily impacted by PM pollution as a sign of an extensive series of human events, including automotive emissions and restaurant operations in the neighbourhood, A bridge construciotn acitiy was also performing nearby the site which could be a reason for sever AQI.

*Metal Concentrations at the National Highway site*

Natural water, air, dust, soil, and sediment all contain heavy metals. A lot of heavy metals are considered hazardous to living organisms. Subsequently, in the past few decades, Public and scientific attention has shifted to heavy metal contamination and its human effects (Tiwari et al., 2020a,b). The heavy metals emitted through traffic activity are an essential pollution source; heavy metals directly affect public health by entering the body. Specific elements such as Cd, Pb, Zn, and Cu are present in the roadside soils due to the discharges from various automotive sources, such as traffic which can be transferred indirectly through the food chain (Tiwari et al., 2022).

The total concentration of metals at the national highway site was found as 33.72µg/m$^3$ in $PM_{2.5-1.0}$ size fraction, while for $PM_{1.0-0.5}$, it was found as 26.78µg/m$^3$. (Table 1 & Fig. 2). During summer season for $PM_{1.0-0.5}$ the trend was followed as Mg(6.52)> Ca(5.89)> Al(3.64)> Ba(2.82)> Pb(2.67)> Cr(1.95)> Cu(1.54)> Fe(0.82)> Mn(0.21)> Cd(0.04)= Fe(0.04) while for $PM_{2.5-1.0}$ it was observed as Mg(10.12)> Ca(9.5)> Al(5.95)> Pb(2.18)>Ba (2.08)>Cr (1.22)> Fe(1.00)> Cu(0.98)> Zn(0.45)> Mn(0.09)> Ni(0.06)> Cd(0.01). The total concentration for $PM_{2.5-1.0}$ (33.7 µg/m$^3$) size fraction was higher than $PM_{1.0-0.5}$ (26.7 µg/m$^3$). Ambade, (2014) found the trend of heavy metals concentration as Fe > Zn > Pb > Cu > Ni > Cr > Cd. In the results, it was inferred that Fe and Zn bound fine PM was highest as compared to other metals.

**Table 1.** Metal Concentration (µg/m$^3$) at national highway

| | Metal Concentration bound PM | |
|---|---|---|
| **Metals** | **$PM_{2.5-1.0}$** | **$PM_{1.0-0.5}$** |
| Al | 5.95 | 3.64 |
| Ba | 2.08 | 2.82 |
| Ca | 9.56 | 5.89 |
| Cd | 0.03 | 0.02 |
| Cr | 1.22 | 1.95 |
| Cu | 0.98 | 1.54 |
| Fe | 1 | 0.82 |
| Mg | 10.12 | 6.52 |
| Mn | 0.09 | 0.21 |
| Ni | 0.06 | 0.04 |
| Pb | 2.18 | 2.67 |
| Zn | 0.45 | 0.66 |
| Total | 33.72 | 26.78 |

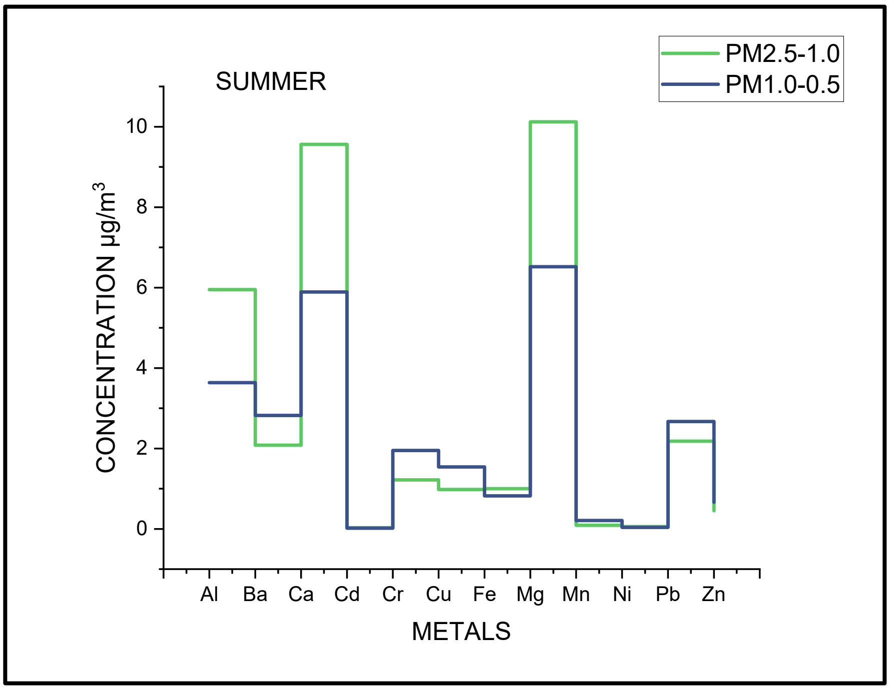


**Fig. 2.** Concentration of metals during the summer season.

(Srivastava & Jain, 2007) found that traffic sites were most affected by metals bound PM pollution as compared to non-traffic sites. Pant et al., (2017) revealed that Cu, Ba, and Sb were found to have the characteristic of non-exhaust (brake wear) emission peaks in the coarse size range in the tunnel. Fomba et al., (2018) found that Sr, Ti, and Ca concentration arises from road resuspension and traffic sources. Rajaram et al., (2014) revealed that vehicular traffic consider to be a major source of Zn, Ba, Cu, and Pb in road dust. Arruti et al., (2010) concluded that Cu and Mo are used as tracers of traffic emissions.

Ba, Mg, and Fe are emitted at the roadside from the resuspension of dust and vehicle activities (Tiwari et al., 2022). Na, Cu, and Zn are attributed to resuspension to road dust (Noonan & Ward, 2007). Cr is attributed to heating (Celo & Dabek-Zlotorzynska, 2010). Mn attributed to smoking (Chan & Yao, 2008). Fe and Mn comprise anthropogenic activities such as wood-burning at nearby dhabas/ restaurants and roadside activities (Chan & Yao, 2008; Lai, 2002). Ca, Ba, and Cu are attributed to resuspension to road dust (Chan & Yao, 2008). Pb, Cr, and Zn are attributed to solid waste incineration (Noonan, 2007). Mg can be attributed to vehicular emissions (Chan & Yao, 2008).

*Enrichment Factor Calculation*

Metals viz. Al, Ca, Fe, Mg, and Mn were closer to a non-enriched or crustal source, indicating a natural contribution. Ba and Ni having 10-100 were thus termed “moderately enriched”, while Cd, Cr, Cu, Pb, and Zn were found highly enriched at national highway sampling sites (Table 2 & Fig. 3). Results of the current study found similar to an earlier study (Lee & Hieu, 2011), which highlights that both crustal and anthropogenic sources affect metal concentration. Fomba et al., (2018) found that Sr, Ti, and Ca concentration arises from road resuspension and traffic sources. Rajaram et al., (2014) revealed that vehicular traffic consider to be a major source of Zn, Ba, Cu, and Pb in road dust. Arruti et al., 2010 concluded that Cu and Mo are used as tracers of traffic emissions.

**Table 2.** EF Values at national highway sampling site.

| GLA | Enrichment Factor Values for Metals bound PM | |
|---|---|---|
| | $PM_{2.5-1.0}$ | $PM_{1.0-0.5}$ |
| **Al** | 1 | 1 |
| **Ba** | 40.52 | 89.81 |
| **Ca** | 4.22 | 4.25 |
| **Cd** | 3827.95 | 4171.51 |
| **Cr** | 453.67 | 1185.30 |
| **Cu** | 891.94 | 2291.12 |
| **Fe** | 0.42 | 0.56 |
| **Mg** | 9.74 | 10.26 |
| **Mn** | 2.22 | 8.47 |
| **Ni** | 41.98 | 45.75 |
| **Pb** | 1668.99 | 3341.38 |
| **Zn** | 112.63 | 270.02 |

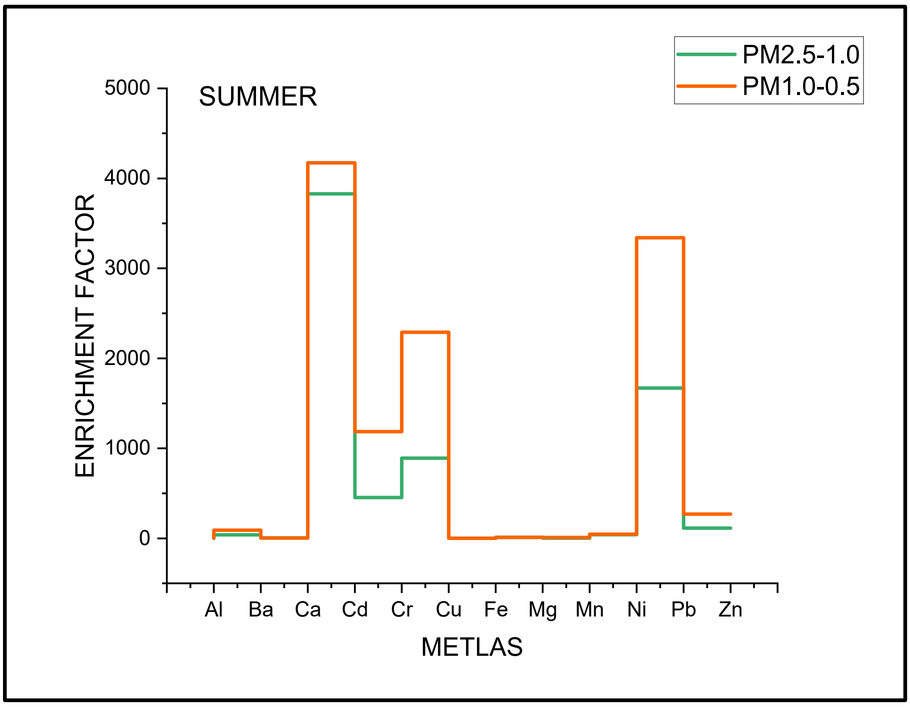


**Fig. 3.** Enrichment factor of elements during the summer season.

*Bioavailability of Metals*

The proportion of total element concentration in PM, the soluble element content retrieved by water, is referred to as elemental bioavailability. The extent of metal solubility, as well as their responsiveness, may determine the toxicity of a specific PM. The bioavailability (BI) of metals was estimated by determining the quantity of soluble portion that transfers it across the cell membrane through the inhaling route (Smichowski, 2013). Some elements are more bioavailable than others. It can be shown that all metals in larger size particles ($PM_{2.5-1.0}$) had greater BI; comparable findings were obtained for Ni, Cr, Mg, Al, Ba, Cd, and Fe in $PM_{2.5-1.0}$ size fractions compared to $PM_{1.0-0.5}$ in earlier research (Rohra et al., 2018a,b).

*Bioavailability of Metals at GLA*

Total BI at the GLA site for summer seasons was found as 34.66%, while the concentration of bioavailable metals in $PM_{2.5-1.0}$ and $PM_{1.0-0.5}$ trend followed by 54.66% and 42.88%, respectively. Mn and Al are referred to as medium BI metals, whereas Mg was found to be the same for $PM_{1.0-0.5}$ size fraction. Results found similar to the previous study that reported that at traffic sites, BI of metals was found higher, nearly 45.2 to 92.5%, while it was found lowest in fly ash particles, 3.3-21% (Julien et al., 2011; Hu et al., 2012). Physiochemical factors can affect the BI of metals at different sites or locations **(**Espinosa et al., 2002**)**. Bigger particles showed higher bioavailability compared to small-size fractions. A higher concentration of BI poses more risks to humans. Values of Zn(60%), Pb(59.9%), Cu(29%), and Cd(61.9%) were almost found to be three times higher than in the present study, while Cr (11.7%) and Mn (32.9%) were found to similar with the present study (Hu et al*.,* 2012). Cr, Mn, and Ca results mirrored Jiang et al. (2015), although Cd BI matched a 2002 Spanish research (Espinosa et al., 2002). Cu, Cd, Pb, and Zn results were identical (Rohra et al., 2018a). The current research's results for Cr, Cd, Fe, Pb, Ni, Zn, and Mn were comparable to those of a preceding study (Sah et al., 2019), whereas Zn and Cu were lower. However, previous investigations refuted the conclusions of Fe, Cu, Al, Ba, and Mn (Espinosa et al., 2002; Jiang et al., 2015; Rohra et al., 2018a). This could be due to the investigation's acid extraction and digestion methodologies, culminating in variations in the ability to retrieve metals in different chemical states (Sah et al., 2019). Metals that are bioavailable to humans have a more harmful impact on their biological systems. Mn brings on different psychological and motor issues. Lung and pulmonary fibrosis injuries are linked to long-term exposure to Al. Anaemia, liver and renal failure, nausea, and diarrhoea are all linked to Cu, Zn. Pb exposure over an extended period is linked to renal failure, nervous system damage, and heme biosynthesis (Varshney et al., 2016).

*Health Risk Assessment*

Assessment of Human health risk is based upon USEPA methodology applied to determine the nature of adverse health effects in humans. For this estimation, IUR and reference concentration (R*f*c) values will be used from the literature to calculate cancer and non-cancerous risk in terms of HQ and ELCR, respectively (USEPA, 1993).

*Hazard Quotient for GLA*

Results of HQ for $PM_{2.5-1.0}$ in the summer season found as Cr (11.69), Ni (4.10), Al (1.14), and Mn (1.72). Results of HQ for $PM_{1.0-0.5}$ for the summer season were observed as Cr (18.69), Ni (2.73), Al (0.69) and Mn (4.02). The results inferred that Cr and Ni bound $PM_{2.5-1.0}$ cause Non-Carcinogenic risk in humans while $PM_{1.0-0.5}$ Cr and Mn showed higher Non-Carcinogenic risk followed by Ni. In the case of metals, the HQs trend for $PM_{2.5-1.0}$ and $PM_{1.0-0.5}$ was found as Cr>Ni>Mn >Al and Cr>Mn>Ni>Al, which corresponds to (Khan et al., 2016), where Ni was observed higher than Mn. Cr was shown to be more abundant than Al (Rohra et al., 2018a) (Niu et al., 2015). Moreover, it is required to highlight that commuters, pedestrians, and those working in nearby business enterprises are all at risk from prolonged vehicular exhaust exposures and re-suspended road dust.

*Excess Lifetime Cancer Risk (ELCR)*

The metal carcinogenic risk was determined in ($PM_{2.5\text{-}1.0}$ and $PM_{1.0\text{-}0.5}$) size fractions. Cr presented the most significant non-carcinogenic risk for adults and children and the highest ELCR value compared to the permitted baseline (USEPA 2009). Including both fractions $PM_{2.5\text{-}1.0}$ and $PM_{1.0\text{-}0.5}$, the metal trend for carcinogenicity was Cr (VI)>Pb>Ni. This study's findings were consistent with previous research (Hieu & Lee, 2010; Pandey et al., 2013; Sah et al., 2019).

The HQ value (Table 3 & Fig. 4) and ELCR (Table 4 & Fig. 5) were found to vary by various size fractions. For GLA sample locations, HQ and ELCR values were observed to be more significant as $PM_{1.0\text{-}0.5}$>$PM_{2.5\text{-}1.0}$. The shift of an overall average of carcinogenic risk factors was observed to be elevated two folds than the pre-determined limit ($1\text{x}10^{-6}$) implemented by USEPA guidelines. Additionally, adults were found to be more susceptible to cancer risk than children (2 times). The current research estimated HQ and ELCR to determine the impact of metals on adults and children. The findings show that smaller particles are more hazardous or have higher HQ and ELCR values. Cr had the highest value, followed by Ni, Mn, and Al. For both adults and children, the risk assessment value for all metals was substantially higher than

**Table 3.** Non-Carcinogenic Health Risk (HQ) Values

| Hazard Quotient Or HQ | | | |
|---|---|---|---|
| **S.No.** | **Metal** | **$PM_{2.5\text{-}1.0}$** | **$PM_{1.0\text{-}0.5}$** |
| **1.** | **Cr** | 11.69±9.53 | 18.69±11.23 |
| **2.** | **Ni** | 4.10±3.69 | 2.73±1.02 |
| **3.** | **Mn** | 1.72±1.02 | 4.02±1.98 |
| **4.** | **Al** | 1.14±0.91 | 0.69±0.36 |

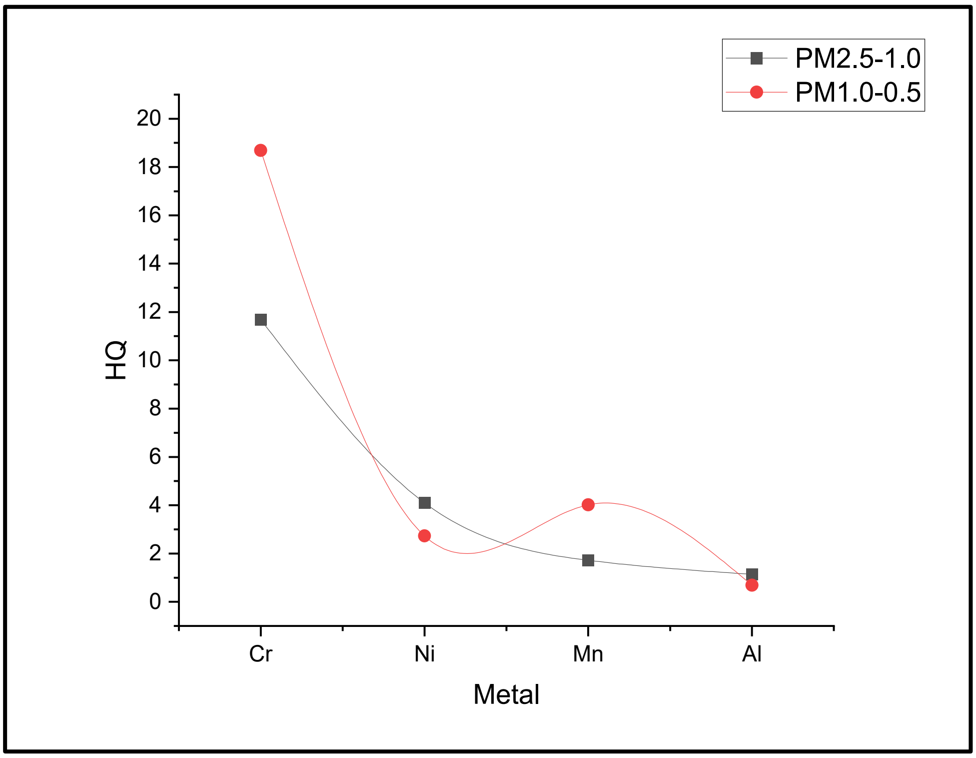


**Fig. 4.** Hazard Quotient Index at Highway site.

**Table 4.** Carcinogenic Health Risk (ELCR) Values

| S.No. | Metals | ELCR | | | |
|---|---|---|---|---|---|
| | | $PM_{2.5\text{-}1.0}$ | | $PM_{1.0\text{-}0.5}$ | |
| | | Adult | Child | Adult | Child |
| **1.** | **Ni** | 3.94E-06 | 1.18E-06 | 2.63E-06 | 7.89E-07 |
| **2.** | **Cr** | 3.91E-03 | 1.17E-03 | 6.21E-03 | 7.59E-03 |
| **3.** | **Pb** | 7.16E-06 | 2.15E-06 | 8.77E-06 | 2.63E-06 |

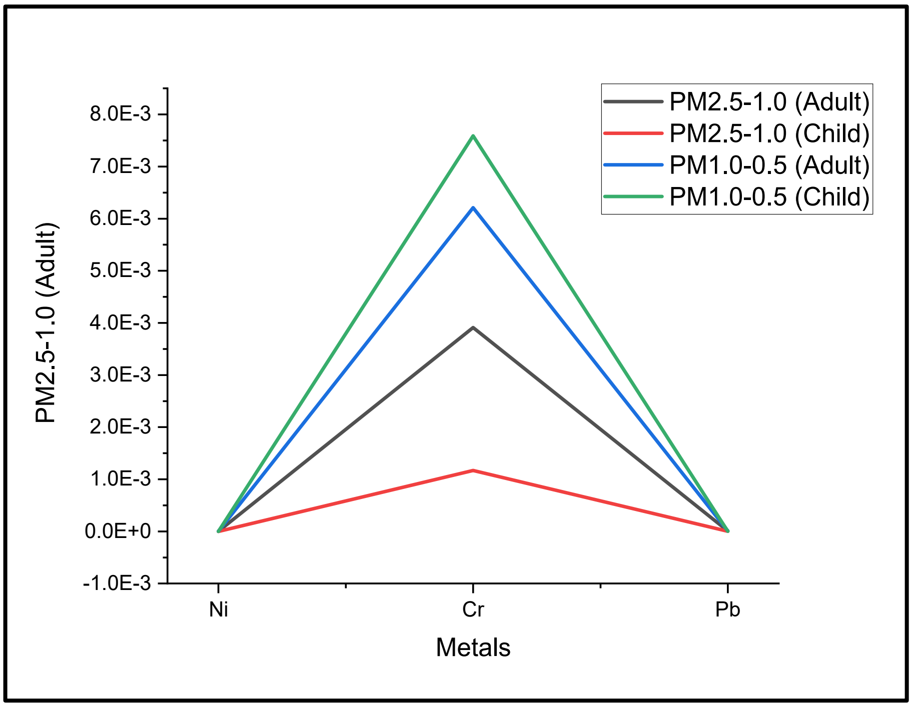


**Fig. 5.** ELCR value at Highway site.

the permitted benchmark level (USEPA, 2009).

## CONCLUSION

During the summer sampling event, Particulate Matter concentration was higher for $PM_{1.0\text{-}0.5}$ (255.85g/m$^3$) than $PM_{2.5\text{-}1.0}$ (218.96g/m$^3$). The Air Quality Index results (1121.75) indicated that traffic sites have severe air quality according to AQ limits given by CPCB (401-500). These findings imply that $PM_{2.5}$ highly pollutes the traffic site due to numerous human-induced activities, like road and bridge construction on national highway sites. During summer season for $PM_{1.0\text{-}0.5}$ the trend was followed as Mg(6.52)> Ca(5.89)> Al(3.64)> Ba(2.82)> Pb(2.67)> Cr(1.95)> Cu(1.54)> Fe(0.82)> Mn(0.21)> Cd(0.04)= Fe(0.04) while for $PM_{2.5\text{-}1.0}$ it was observed as Mg(10.12)> Ca(9.5)> Al(5.95)> Pb(2.18)>Ba (2.08)>Cr (1.22)> Fe(1.00)> Cu(0.98)> Zn(0.45)> Mn(0.09)> Ni(0.06)> Cd(0.01). The findings revealed that most metals arise from the resuspension of dust and vehicle activities and cause severe disease in the human being. Cd, Cr, Cu, Pb, and Zn were highly enriched at GLA sampling sites, highlighting that crustal source significantly impacts metals concentration and anthropogenic sources. Results inferred that Cr and Ni bound $PM_{2.5-1.0}$ to produce non-carcinogenic risk in humans. However, $PM_{1.0-0.5}$ Cr and Mn exhibited greater non-carcinogenic risk, followed by Ni. Cr, Pb showed the carcinogenic risk to children and adults in both size PM except for Ni. The findings show that smaller particles are more hazardous or have higher HQ and ELCR values. Overall, the value, including both size fractions, is more significant. Cr had the highest value, followed by Ni, Mn, and Al. The risk assessment value for all metals was substantially more significant for adults and children than the tolerable benchmark level ($1x10^{-6}$).


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## CONFLICT OF INTEREST

The authors declare that there is not any conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/ or falsification, double publication and/or submission, and redundancy has been completely observed by the authors.

## LIFE SCIENCE REPORTING

No life science threat was practiced in this research.

## LIST OF ABBREVIATIONS

| Full Form | Abbreviation |
|---|---|
| Particulate Matter | PM |
| Air Quality Index | AQI |
| Air Quality | AQ |
| Black Carbon | BC |
| Poly Tetra Fluoro Ethylene | PTFE |
| Pollutant's absolute concentration. | $C_p$ |
| Break Point Value ($\geq C_p$) | $BP_{high}$ |
| Break Point Value ($\leq C_p$) | $BP_{Low}$ |
| Equivalent AQI value to ($BP_{High}$) | $I_{High}$ |
| Equivalent AQI value to ($BP_{Low}$) | $I_{Low}$ |
| Enrichment Factor | EF |

| | |
|---|---|
| Present Concentration of Metal x | Cx |
| Elemental reference concentration | Cref |
| United State Environmental Protection Agency | USEPA |
| Exposure Concentration | EC |
| Excess Lifetime Cancer Risk | ELCR |
| Hazard Quotient | HQ |
| Reference Concentration | RfC |
| Inhalation unit risk | IUR |
| Average time for health risk assessment | AT |
| Exposure time | ET |
| Exposure Frequency | EF |
| Exposure Duration | ED |
| Integrated Risk Information System | IRIS |
| bioavailability | BI |

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