

Identifying Knowledge Gaps in Incorporating Toxicity of Particulate Matter Constituents for Developing Regulatory Limits on Particulate Matter

Ananya Das, Arun Kumar, Gazala Habib, Vivekanandan Perumal

Abstract—Regulatory bodies has proposed limits on Particulate Matter (PM) concentration in air; however, it does not explicitly indicate the incorporation of effects of toxicities of constituents of PM in developing regulatory limits. This study aimed to provide a structured approach to incorporate toxic effects of components in developing regulatory limits on PM. A four-step human health risk assessment framework consists of - (1) hazard identification (parameters: PM and its constituents and their associated toxic effects on health), (2) exposure assessment (parameters: concentrations of PM and constituents, information on size and shape of PM; fate and transport of PM and constituents in respiratory system), (3) dose-response assessment (parameters: reference dose or target toxicity dose of PM and its constituents), and (4) risk estimation (metric: hazard quotient and/or lifetime incremental risk of cancer as applicable). Then parameters required at every step were obtained from literature. Using this information, an attempt has been made to determine limits on PM using component-specific information. An example calculation was conducted for exposures of PM_{2.5} and its metal constituents from Indian ambient environment to determine limit on PM values. Identified data gaps were: (1) concentrations of PM and its constituents and their relationship with sampling regions, (2) relationship of toxicity of PM with its components.

Keywords—Air, component-specific toxicity, human health risks, particulate matter.

I. INTRODUCTION

AIR pollutants such as PM are a well-recognized human health risk factor. Its health effect from both indoor and outdoor environments is matter of concern even in low concentration. However these studies were conducted in countries like Germany, USA, Finland, Netherland, Mexico, etc. where the concentration and composition of aerosol are expected to be very different than India [1]. Urban air pollution in under developed countries in the world possess much threat, indoor smoke from solid fuels, is recognised as a major contributor to the worldwide burden of disease [2]. PM_{2.5} is described as the tiny killer (with diameter of 2.5 μm and less than that); it is responsible for approximately 0.8 million premature deaths and 6.4 million years of life lost [3].

Many Indian cities are facing acute air pollution due to industrial activity, population growth, construction booms for

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housing and infrastructure, increased vehicular traffic, congested streets, poorly maintained vehicles, limited access to clean fuel and lack of effective control programmes [4]. Indian epidemiological studies [5], [6] also linked respirable PM concentration with respiratory symptoms and pulmonary function. However, it is expected that PM_{2.5} that basically comes from anthropogenic sources will show stronger relationship with respiratory symptoms and pulmonary function. These associations have subsequently proven to be robust in epidemiological studies conducted globally including rural areas in developing countries [6]-[11].

International Agency for Research on Cancer (IARC), classified outdoor air pollution as Group 1 carcinogenic to humans. In India, numerous research were done across the country regarding PM of $d \leq 2.5 \mu\text{m}$ and PM of $d \leq 2.5 \mu\text{m}$ [12]-[14]; and pollutant concentrations were found to be much more above the permissible national standards. Transition metals, such as iron, vanadium, nickel, chromium, copper, zinc, have been cited to be most toxic on the basis of their ability to support electron exchange [15] and catalyse and generate ROS (Reactive oxygen species) in biological tissues [12], [16]. These issues indicate the need for conducting quantitative analysis of health risk. In addition, there is also a need for including toxicity of exposure of mixture of two or more metals at a single time, as PM is a mixture of several chemical constituents and heavy metals [18].

The objective of this study was to understand data gap in literature to assess inhalation risks of exposures of PM - associated heavy metals. This aspect was illustrated using three heavy metals (As, Cr, Cd). A brief study on mixture toxicity of the metals is done (Table I).

II. METHODOLOGY

A four-step human risk assessment framework, consist of hazard identification, exposure assessment, dose response assessment, and risk characterization was developed as per the USEPA methodology. PM-associated metals were selected and calculation of both cancerous risk and non-cancerous risk due to inhalation of these three their metals were conducted. arsenic, cadmium & chromium were chosen for the example calculations because inhalation-based RfD of these three heavy metals were found to be much low which indicated their high toxicity. Same criteria were used for determining toxic reference values for cancerous risk [27]. Parameters required at every step were compiled and literature review was conducted to obtain the values [12]. Fig. 1 shows schematic of

steps used in assessing risks due to inhalation exposure of single type of metal ions.

TABLE I
SUMMARY OF STUDIES ON PM-ASSOCIATED RISK ASSESSMENT

| Name of paper | Type of metals in PM | Mixture toxicity | Reference |
|--|--|-------------------|-----------|
| Pollution and health risk of potentially toxic metals in urban road dust in Nanjing, a mega-city of China. | Pb, Cr, Cu | No study was done | [17] |
| Risk assessment of heavy metals in road and soil dusts within PM _{2.5} , PM ₁₀ and PM ₁₀₀ fractions in Dongying city, Shandong Province, China. | Ni, As, Pb | No study was done | [18] |
| Sources and risk assessment of heavy metals in ambient PM _{2.5} during Youth Asian Game period in Nanjing | V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Sn, Sb and Pb | No study was done | [19] |
| Assessment of Public Health Risk associated with Atmospheric Exposure to PM _{2.5} Washington DC, USA. | Ar, Cr | No study was done | [20] |
| Assessing the Hazardous Risks of Vehicle Inspection Workers' Exposure to Particulate Heavy Metals in Their Work Places | V, Cr, Mn, Co, Ni, Cu, Zn, As, Cd and Pb | No study was done | [21] |
| PM ₁₀ and PM _{2.5} and health risk assessment for heavy metals in a typical factory for cathode ray tube television recycling. | Cr, Ni, Pb, Cd. | No study was done | [25] |

A. Allowable Concentrations of Heavy Metal

Allowable concentration of heavy metals resulting in non-cancerous risk was calculated using (1) where 'C_a' is the concentration of metals (that are selected) in mg/kg; ADD_{inh} is daily allowable dose of inhaled metal (mg/kg of body weight/day) (for ADD_{inh}=Reference dose, i.e., RfD for hazard quotient equals to 1), 'InhR' is the inhalation rate (m³/day); 'EF' is the Exposure frequency (days/year); 'ED' is the Exposure duration (year); 'BW' is the body weight (kg); AT is the averaging time for non-carcinogens (days/year); 'PEF' is the Particle Emission fraction (m³/kg). Values for different parameters were obtained from published reports by US EPA [26]. Here, HQ is the ratio of the potential exposure to the substance and the level at which no adverse effects are expected. If the HQ is calculated to be equal to or less than 1, then no adverse health effects are expected as a result of exposure. If the HQ is greater than 1, then adverse health effects are possible. Recommended values of Reference Doses (RfD) of three selected metals are presented in Table II.

$$C_a = \frac{ADD_{inh} * BW * AT * PEF}{InhR * EF * ED} \quad (1)$$

In addition, allowable concentration of heavy metals resulting in cancerous risk was calculated using (2) where 'C_a' is the concentration of metals resulting in cancerous risk (mg/kg); ECR is maximum allowable lifetime incremental risk of cancer; AT is the averaging time for carcinogens (days); ET is exposure time (h/day); EF is exposure frequency (days/year), ED is exposure duration and IUR is inhalation unit risks. Values of IUR were obtained from (1/(μg/m³)) [17] and presented in Table II. The value of ECR was fixed as 10⁻⁶ to calculate maximum allowable metal concentration:

$$C_a = \frac{ECR * AT}{ET * EF * ED * IUR} \quad (2)$$

TABLE II
RECOMMENDED VALUES OF REFERENCE DOSES (RfD) (mg/kg/day) [RfD INHALATION: INHALATION REFERENCE DOSE; IUR (1/(μg/m³))] [27]

| Heavy metal | As | Cd | Cr |
|------------------------------|--------|--------|-----------|
| RfD inhalation(mg/kg/day) | 0.0003 | 0.001 | 0.0000286 |
| IUR (1/(μg/m ³)) | 0.0043 | 0.0018 | 0.012 |

IUR: Inhalation Risk Factor

B. Allowable Concentrations of PM as per Maximum Allowable Value of Heavy Metals

Value of maximum allowable PM based on allowable concentration of metal ions (PM_{metal_a}) (as calculated in (1) and (2)) was calculated using (3) where f_{metal} represents fraction of metals in PM. This value was obtained from published report for different metals found on PM. Then, ratio (R) of PM_{metal_a} to maximum value of allowable PM values as per regulation (PM_{reg}) was calculated in (4) where R greater than 1 indicates need for revision of regulatory limit and R lesser than 1 does not indicate the need for revision. PM_{reg} was taken to be 40 μg/m³ [27].

$$PM_{metal_a} = \frac{C_a}{f_{metal}} \quad (3)$$

$$R = \frac{PM_{metal_a}}{PM_{reg}} \quad (4)$$

C. Example Calculation of Allowable Concentration of PM as per Maximum Allowable Values of Arsenic (As), Cadmium (Cd), Chromium (Cr)

Values of different parameters used for estimating allowable concentration of PM as per maximum allowable values of As, Cd, Cr are presented in Table III. Data were also collected to know co-occurrence of metals in PM using published reports [19]-[21] (Table IV). Reference values for cancerous and non-cancerous effects were obtained from USEPA. Using this information, values of PM_{metal_a} and R were calculated for both cancerous and non-cancerous effects.

TABLE III
 SUMMARY OF PARAMETERS REQUIRED FOR CALCULATING MAXIMUM ALLOWABLE CONCENTRATION OF METAL

| Parameter | Description | Value and source |
|--|---|---|
| HQ (Hazard Quotient) | A metric to represent non-carcinogenic health risk of heavy metals in ambient particles | Literature data [12] (assumed to be 1, i.e., worst-case scenario) |
| RfD (Reference Dose) (mg/kg/day) | Concentration of a chemical at which adverse effect(s) on human health are known to occur | Recommended values taken from USEPA [12] |
| InhR (m ³ /day) | Inhalation rate | 7.63 (Adults) [26], [12] |
| ED (exposure duration)(years) | Duration of acute and chronic effects | 1 year [27] |
| BW (Body weight) (kg) | Weight of person body | 70 kg [27] |
| EF(exposure Frequency) (days/year) | Average days of annual exposure | 180 days/year [12] |
| AT (Average time) (days) | Average time of exposure of non-carcinogens | ED*365 days/year [12] |
| PEF (particle emission factor) (m ³ /kg) | The average amount of a specific pollutant or material discharged into the atmosphere by a specific process, fuel, equipment, or source. | 1.36*10 ⁹ m ³ /kg [12] |
| ECR (Excess cancer risk) (μg/m ³) | An incremental probability of a person developing cancer over a lifetime as consequences of total exposure to potential carcinogens. | 10 ⁻⁶ [26], [8] |
| IUR (Inhalation unit risk factor) (1/(μg/m ³)) | An estimate of the increased cancer risk from inhalation exposure to a concentration of 1 mg/m ³ for a lifetime. The IUR can be multiplied by an estimate of lifetime exposure (in mg/m ³) to estimate the lifetime cancer risk. | Values taken from [27] |
| ET (Exposure Time) (hour/day) | It is the time duration in hours within a day when the exposure is occurring. | 8 hour/day (Literature data's which are collected from US EPA [12]) |
| Fraction of metal content (μg/m ³) | Presence of each heavy metal in PM | Literature data [14] |

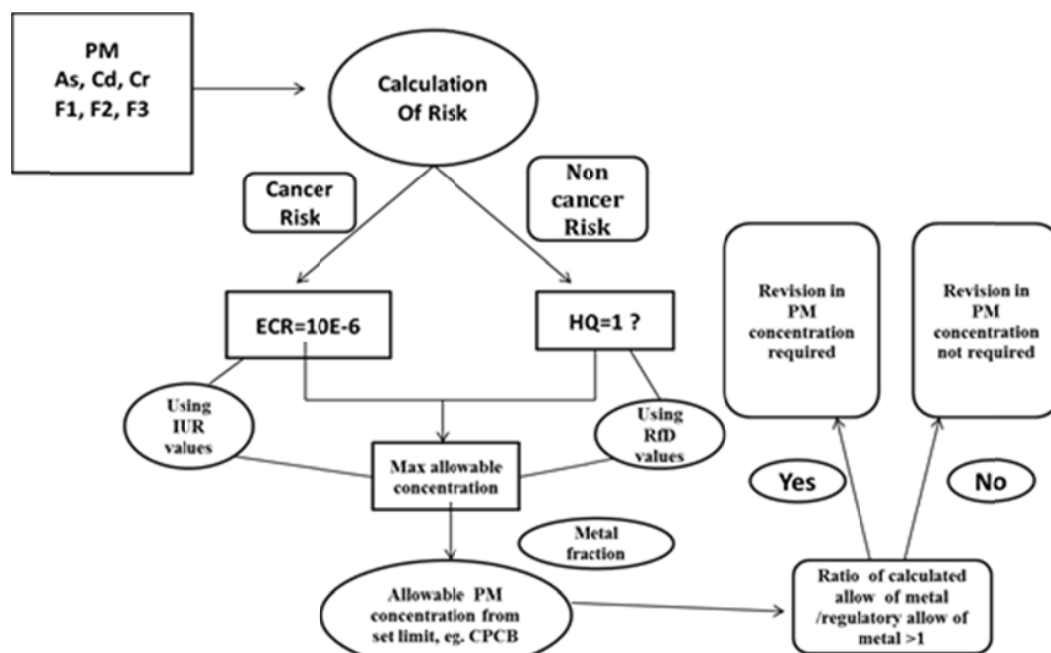


Fig. 1 The methodology of calculation of maximum allowable concentration of metal to see if any revision required (single metal at a time)

 TABLE IV
 REPORTED CO-OCCURRENCE OF SELECTED THREE HEAVY METALS IN PM (GLOBALLY)

| | As | Cd | Cr |
|----|----------------------|-----------------|----|
| As | | | |
| Cd | Yes [15], [16], [22] | | |
| Cr | Yes [14],[22], [23] | Yes; [22], [14] | |

III. RESULTS AND DISCUSSION

For both types of effects, allowable concentrations of PM as per maximum allowable value of heavy metals were found to be lower than the regulatory PM value (Tables V, VI), indicating that regulatory PM value is sufficient to reduce risk of non-cancerous and/or cancerous due to exposure of PM-associated PM one-at-a-time. This estimate was not calculated for scenario where receptor is simultaneously exposed to PM associated different metals and organic compounds.

During method development, following data gaps were identified: (1) information on concentrations of different constituents of PM, (2) information on relationship of toxicity of PM with its components. As and Cd were seen to be present together in most cases, where Cr was found to be absent in the presence of as and Cd in majority of the cases. There was no

availability of data in case of binary toxicity [19]-[24]. Even there is no availability of dose-response data of inhalation of mixture of metals to lung [19]-[24]. More efforts are required to systematically obtain this information using field and laboratory studies to protect human health.

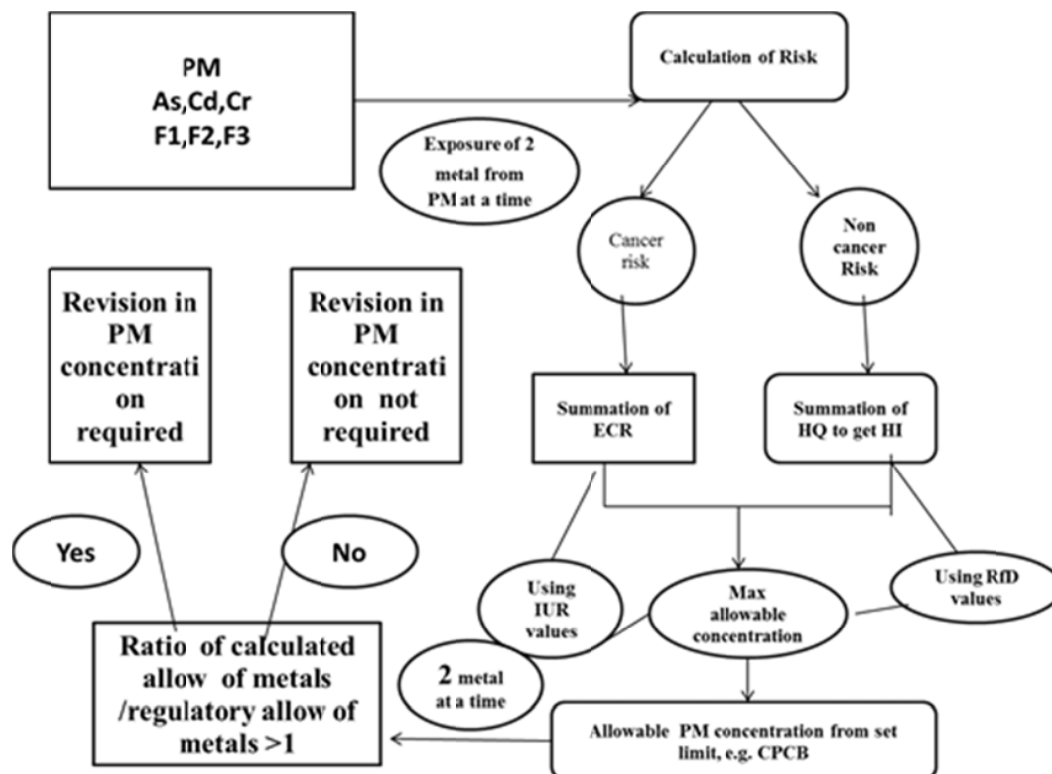


Fig. 2 Schematic showing the methodology of calculation of maximum allowable concentration of metal (mixture of metal at a time)

TABLE V
CALCULATION OF RATIO OF MAXIMUM VALUE OF PM BASED ON MAXIMUM ALLOWABLE METAL CONTENTS TO REGULATORY ALLOWABLE PM FOR NON-CANCEROUS EFFECTS

| Heavy Metals | Maximum allowable metal concentration ($\mu\text{g}/\text{m}^3/\text{day}$) (col.1) | Metal fraction in PM [14] (col.2) | Maximum allowable PM value based on maximum allowable metal concentration ($\mu\text{g}/\text{m}^3/\text{day}$) (col.3=col.1/col.2) | Ratio (col.3/regulatory maximum allowable PM value) | Need revision (ratio>1) |
|--------------|---|-----------------------------------|---|---|-------------------------|
| As | 49512159604 | 1.10E-05 | 4.51E+15 | 1.10E-05 | No |
| Cd | 16504053201 | 3.30E-05 | 5.01E+14 | 3.30E-05 | No |
| Cr | 47201592156 | 1.94E-04 | 2.43E+14 | 1.94E-04 | No |

TABLE VI
CALCULATION OF RATIO OF MAXIMUM VALUE OF PM BASED ON MAXIMUM ALLOWABLE METAL CONTENTS TO REGULATORY ALLOWABLE PM FOR CANCEROUS EFFECTS

| Heavy Metals | Maximum allowable metal concentration (col.1) | Metal fraction in PM [14] (col.2) | Maximum allowable PM value based on maximum allowable metal concentration ($\mu\text{g}/\text{m}^3/\text{day}$) (col.3=col.1/col.2) | Ratio (col.3/regulatory maximum allowable PM value) (col.4) | Need revision (ratio>1) |
|--------------|---|-----------------------------------|---|---|-------------------------|
| As | 0.000271318 | 1.10E-05 | 2.47E+01 | 1.10E-05 | No |
| Cd | 0.000648148 | 3.30E-05 | 1.97E+01 | 3.30E-05 | No |
| Cr | 9.72222E-05 | 1.94E-04 | 5.01E-01 | 1.94E-04 | No |

IV. SUMMARY AND CONCLUSIONS

The study presented a structured approach for incorporating component-specific information in estimating risk and in determining limit on PM concentration based on mass

concentration. An example calculation illustrating the application of proposed approach was presented. For cancerous and non-cancerous effects, allowable concentrations of PM as per maximum allowable value of heavy metals were found to be lower than the regulatory PM value (Tables V,

VI), indicating that regulatory PM value is sufficient to reduce risk of non-cancerous and/or cancerous due to exposure of PM-associated metals one-at-a-time and no revision is required.

Following data gaps were identified: (1) information on concentrations of different constituents of PM, (2) information on relationship of toxicity of PM with its components. Fig. 2 presents a schematic of steps for including toxicity of mixture of PM-associated metals in estimating risk of cancerous and non-cancerous effects. In this regard, hazard index (i.e., summation of hazard quotient values for inhalation exposure of different metals) can be calculated and used to estimate allowable concentrations of PM as per maximum allowable value of heavy metals. For cancerous effects also, this method can be used as per given steps in Fig. 2. More efforts are required to systematically obtain this information using field and laboratory studies for explicitly acknowledge effects of mixture of metals and other constituents in estimate health risks due to inhalation exposure of PMs.

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