# Assessment and evaluation of ambient PM$_{2.5}$ in relation to its health effects in mineral-based coal-fired areas

*Shamsh Pervez[1], Rakesh Kumar Sahu[1], Mamta Tripathi[1], Shahina Bano[1], Jeevan Lal Matawle[2], Suresh Tiwari[3], Manas Kanti Deb[1] and Yasmeen Fatima Pervez[4]*

[1] School of Studies in Chemistry, Pt. Ravishankar Shukla University, Raipur, Chhattisgarh, India

[2] Directorate of Geology and Mining, Chhattisgarh, Regional Laboratory, Bilaspur, Chhattisgarh, India

[3] Indian Institute of Tropical Meteorology Pune, New Delhi, India

[4] Ashoka Institute of Technology and Management, Rajnandgaon, Chhattisgarh, India

Atmospheric PM$_{2.5}$ pollution, has shown potential impact on the human health in general, thus it requires to look into the chemical characteristics of PM$_{2.5}$ masses for designing effective policies to reduce health risks amongst public under exposure. The study carried out, here, has presented the ambient PM$_{2.5}$ concentrations, concentrations of chemical components and associated health risks over rural and urban environments in the area of mineral based coal-fired industrial areas of central India for a period of one year (2015–16). Overall 260 PM$_{2.5}$ samples, collected from rural, urban and industrial sites, were analyzed for various elements Al, As, Ca, Hg, Cr, Co, Cu, Fe, Mn, K, Cd, Mo, Ni, Pb, Se, Sb, Na, Mg, K, V and Zn, ions such as Na$^+$, Mg$^{2+}$, K$^+$, Ca$^{2+}$, F$^-$, Cl$^-$, NH$_4^+$, NO$_3^-$, SO$_4^{2-}$ and carbonaceous matter. The annual average PM$_{2.5}$ mass concentrations were found to be ~2 to ~6 folds higher than the annual National Ambient Air Quality standard (40 µg m$^{-3}$). Further this study also evaluates, carcinogenic and non-carcinogenic health risks associated with ambient PM$_{2.5}$ exposures (via ingestion, inhalation and dermal). The elemental species that have shown non-carcinogenic risks for both children and adults of all three sites are: Co, Mn, Ni (rural), As, Cd, Cr, Mn, Ni, V (urban and industrial sites). Similarly, the excess carcinogenic risks, in total, from Cd, Co, Cr, Ni, Pb was found to be higher than acceptable limits (10$^{-6}$ to 10$^{-4}$).

*Keywords*: ambient PM$_{2.5}$, chemical characteristics, ion balance, mass reconstruction, health risks

## 1. Introduction

PM$_{2.5}$, a potential carrier of large number of toxic species, is one among the most harmful atmospheric contaminants for human health (Tchounwou et al., 2012). These absorbed toxic species on PM$_{2.5}$ particles, entered in human body through inhalation, dermal contact and ingestion exposure routes (Cao et al., 2014; Ferreira-Baptista and De Miguel, 2005; Lu et al., 2010). Fine particulates with decreasing particle size are known for increased surface area for absorbing trace elements and eventually posed more hazardous threat to human health (Slezakova et al., 2013). The tiny sized particles (less than 2.5 µm) penetrates deeper into the lungs as they have decreased diameter of aerodynamic particulate matter (PM) which increases the risk of cancer in lungs and also in other organelles (Akyüz and Çabuk, 2009; Cassee et al., 2013; Fajersztajn et al., 2013; Harrison and Yin, 2000; Pui et al., 2014; Wang et al., 2002; Kampa and Castanas; 2008; Weijers et al., 2011). This hazardous condition increases, even more, when the heavy metals (metals having specific weight more than $5\,\mathrm{g\,cm^{-3}}$) component is increases in absorbed trace content of particulate matter. Major heavy metals (Co, Mg, Cu, Fe, Mo, Cr, As, Hg, Mn, Ni, Pb, Zn and Sn) are known to be proven toxic species for human target organs and biological fluids (Crisponi, 2014; Govind, 2014; Mani and Kumar, 2014). Some heavy metals like Cu, Fe, Zn, Mo and Co are vital for plant species, and micro amounts of Cr, Ni and Sn are necessary for animals (Pandey and Madhuri, 2014; Yu et al., 2017). But Cd, Hg and Pb are neither necessary for plants nor for animals. Apart from this, Cr, Cu, Fe and V are essential for proper operation of the metabolic processes of the body, but if concentrations of these metals exceed the maximum permissible limit, then these metals could be proven toxic for bio-systems.

Emissions of many toxic elements from coal-burning practices have been reported in last few decades (French and Maxwell, 1998; Rubin, 1999; Färe et al., 2010). Several studies were performed either with lesser number of species or with short duration of the air sampling (Sharma and Maloo, 2005; Kulshrestha et al., 2009; Deshmukh et al., 2011; Kothai et al., 2011; Zhang et al., 2014; Pant et al., 2015). In India, few studies have addressed the health risk assessments for PM$_{2.5}$ chemical components and all of that confined to specific urban environments viz. Excess Lifetime Cancer Risks (ELCR) evaluation for particulate PAH emissions from Indian cooking activities (See et al., 2006), Cancer risks of bio-accesible fractions of indoor PM$_{2.5}$ toxic elements in Pune (Satsangi et al., 2014), Health risk factors and disease burden of respiratory and cardio-pulmonary health problems due to ambient PM$_{10}$ in Thar Desert, Western Rajasthan (Rumana et al., 2014), assessment of hazardous quotiens and cancer risks from ambient PM$_{2.5}$ and PM$_{10}$ toxic elements in Pune (Jan et al., 2016), Health risks from indoor PM$_{2.5}$ in Raipur-Bhiali (Matawle et al., 2017), Health risk assessment for ambient PM$_{10}$ and SPM in mining areas Ganjam, Odisha (Yadav et al., 2019) and Health risk assessment from ambient PM$_{2.5}$ toxic elements in Dhanbad City (Jena et al., 2019), While surveying literature, it was

observed that the mass and chemical composition of ambient $PM_{2.5}$ vary with distance and time (Yu et al., 2013).

The findings presented in this study are based on measurements and chemical characterization of ambient $PM_{2.5}$, made during a comprehensive ambient $PM_{2.5}$ monitoring and analysis program under the SERB sponsored project which was carried out in rural, urban and industrial environments of central India. Previously, the ambient $PM_{2.5}$ mass and associated carbonaceous matter concentrations, measured in this program, was described by Sahu et al. (2018). In continuation, evaluation of spatiotemporal variability in the major inorganic constituents and trace elements of ambient $PM_{2.5}$ and associated health risks has been taken into account in the present study. Day and night variation in ionic and elemental component of ambient $PM_{2.5}$ in urban site was also aimed to investigate. Ion balance and mass closure approaches have been applied to validate the chemical database of $PM_{2.5}$ masses. This study depicts an appropriate picture of ambient $PM_{2.5}$ toxic component for the scientific community and useful in designing the effective policy to minimize the health risks in the inhabitants of heavy industrial areas.

## 2. Materials and methods

### 2.1. Study area and air sampling

Three different environments namely, rural (Kosmarra, District Dhamtari), urban (Raipur City, District Raipur) and industrial (Bhilai City, District Durg) have been chosen within an area of 400 $km^2$ in central India for air
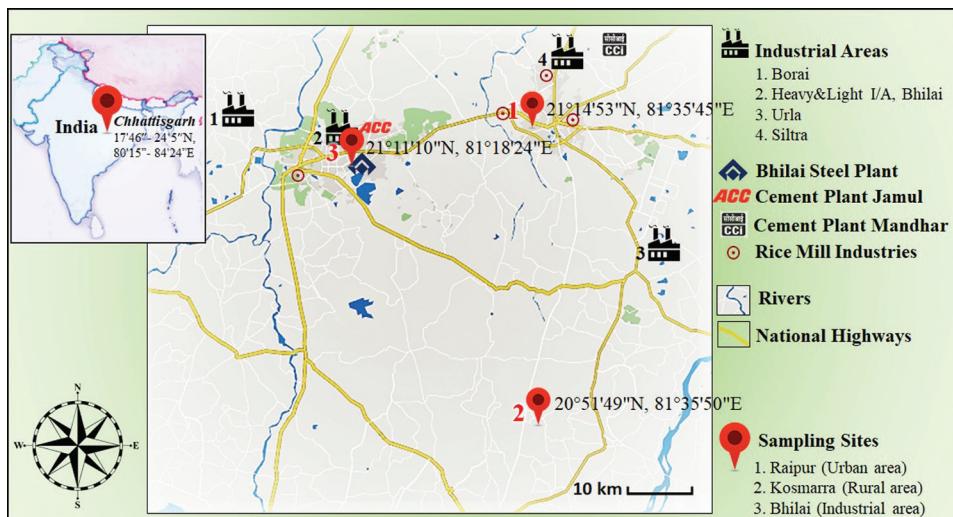


**Figure 1.** Location of sampling sites in Central India.

sampling program. Three major coal-fired industries (7 Mt steel production, cement manufacturing and 500 MW power generation) are located in the industrial site, which, collectively, emit ~25 tonnes of atmospheric particulate matter every year (Matawle et al., 2014; Guttikunda et al., 2015; Dewangan et al., 2016, Dubey and Pervez, 2008; Balakrishna and Pervez, 2009; Balakrishna et al., 2010). Rural site is about 100 km away from both urban and industrial site and free from any major coal-fired industries. Few small-scale rice milling plants are located in nearby areas of rural site. Figure 1 shows the monitoring sites of rural, urban and industrial area on GPS location of 21° 14´ N, 81° 38´ E; 21° 17´ N, 81° 33´ E and 20° 86´ N, 81° 59´ E, respectively. Furthermore, details of study area and air sampling plan have been reported in our earlier published research work (Sahu et al., 2018).

## 2.2. Experimental method

Post-sampling treatment of PM$_{2.5}$ sampled Teflon (Pall Corporation, Catalogue No. R2PJ047) and quartz fiber filters (Whatman, Catalogue No. 1851-047) has been described in the first part of the study (Sahu et al., 2018). Quartz filters were used for the determination of ionics along with carbonaceous matter (Sahu et al., 2018). Teflon filters were subjected to acid digestion for elemental analysis after gravimetric analysis for mass measurements. For elemental analysis: Teflon filters were kept in Teflon digestion bomb for acid digestion using 3:1 ratio of HNO$_3$ and H$_2$O$_2$ in an oven at 200 °C for 6 to 8 hours, cooled and filtered using 0.001 M perchloric acid through Whatman No.42 filter paper (Committee, 1977; Envirotech, 2000). Seventeen elemental species (Al, Zn, Co, Cu, Fe, Cr, Ni, Cd, Mn, Hg, Mo, Pb, S, As, Se, Sn, and V), known for the potential and moderate source markers (Matawle et al., 2015), were analyzed by double beam Atomic Absorption Spectroscopy (AAS) by following standard protocol of analyses (DRI, 2011; Thermo Fisher, 2011).

For quantifying ionic component, the remnant portion of quartz filters after the analysis of carbonaceous matter (Sahu et al., 2018), were subjected to sonication with 10 ml double distilled water (DDW) for about 90 minutes. The extracts were, then, filtered via filter paper (Whatman No.42, UK) with maintaining the final volume of 25 ml by DDW in a volumetric flask. Nine ionic species (five cations: Ca$^{2+}$, K$^+$, Mg$^{2+}$, NH$_4^+$ Na$^+$, and four anions: Cl$^-$, F$^-$, NO$_3^-$ and SO$_4^{2-}$) were quantified by Ion Chromatographically (Dionex ICS-2000&ICS-1000, USA) using reported standard procedures (Chow and Watson, 1999; Thermo Scientific, 2005, 2006). Moreover, the acid digested samples were also exposed to ion chromatography analysis for four cations (Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$) to quantify its concentration, in total, including water soluble and insoluble fractions (Chow and Watson, 1999).

## 2.3. Human health exposure assessment

US Environmental Protection Agency (USEPA) developed the health risk estimation method for PM$_{2.5}$ and same technique is adopted in the present study

(US EPA, 2010). Three different exposure assessments, namely; (1) ingestion (Chemical Daily Intake – *CDI*); (2) dermal contact (Dermal Absorbed Dose – *DAD*); (3) inhalation Exposure Concentration (*EC*) inhalation exposure concentration (*EC*) were conducted to address the human health risks from ambient $PM_{2.5}$ toxic elements. Formulas used to evaluate human health exposure in this study are:

$$CDI = \frac{C \times IngR \times EF \times ED \times CF}{BW \times AT} \qquad (1)$$

$$DAD = \frac{C \times SL \times SA \times ABN \times EF \times ED \times CF}{BW \times AT} \qquad (2)$$

$$EC = \frac{C \times InhR \times EF \times ED}{BW \times AT} \qquad (3)$$

where, $C$ is the concentration of the elements in $PM_{2.5}$ ($\mu g\,m^{-3}$), $IngR$ is ingestion rate ($mg\,day^{-1}$), $EF$ is relative exposure frequency ($days\,year^{-1}$), $ED$ is the exposure duration (years), $CF$ is conversion factor (unit less), $BW$ is the average body weight (kg), $AT$ is the average time (days), $SL$ is the skin adherence factor ($mg\,cm^{-2}\,day^{-1}$), SA is contacted skin area ($cm^2$), $ABS$ is dermal absorption factor (unitless), $InhR$ is the inhalation rate ($m^3\,day^{-1}$). Factor values of the different parameters, used for health exposure calcu-lations are represented in Tab. 1.

For concentrations, the 95% upper confidence limit for the arithmetic mean was calculated as follows:

$$C_{95\%} = \exp\left( X + 0.5 \times s^2 + \frac{s \times H}{\sqrt{n-1}} \right) \qquad (4)$$

Table 1. Factor values of different parameters used for calculation of exposure assessment.

| Parameter | Value | | Reference |
|---|---|---|---|
| | Children | Adult | |
| $IngR$ | 200 mg day$^{-1}$ | 100 mg day$^{-1}$ | US EPA, 2011 |
| $EF$ | 350 days year$^{-1}$ | 350 days year$^{-1}$ | US EPA, 2013 |
| $ED$ | 6 year | 30 year | US EPA, 2011 |
| $CF$ | $10^{-6}$ | $10^{-6}$ | US EPA, 2011 |
| $BW$ | 15 kg | 70 kg | US EPA, 2011 |
| $AT$ | $ED \times 365$ day (non-carcinogen) $70 \times 365 = 25{,}550$ days (carcinogen) | | US EPA, 2011 Agarwal et al., 2017 |
| $ATn$ | $AT \times 24$ h | | US EPA, 2011 |
| $InhR$ | 7.6 m$^3$ day$^{-1}$ | 20 m$^3$ day$^{-1}$ | Man et al., 2010; Zheng et al., 2010 |
| $SA$ | 1800 cm$^2$ | 4350 cm$^2$ | US EPA, 2011 |
| $SL$ | 0.2 mg cm$^{-2}$ | 0.07 mg cm$^{-2}$ | US EPA ,2011 |
| $ABS$ | 0.03 for As and 0.001 for other elements | | Hu et al., 2012 |

where, $s$ is standard deviation, $n$ is the $n^{th}$ number of samples, $H$ is the $H$-statistic and $X$ is the arithmetic mean of log-transformed data (Gilbert, 1987).

The non-cancer exposure risk of sixteen species (Al, Se, Zn, Co, Ni, Cu, NO$_3^-$, Fe, Mn (diet), Cr (IV), Pb (acetate), Hg (element), V, Cd (diet), As (inorganic) and F (soluble fluoride)) and cancer exposure risk of six elements (As (inorganic), Cd (diet), Co, Cr (IV), Ni, Pb (acetate)) were estimated, independently, using above mentioned pathways and evaluated by cancer risk (*CR*), hazard index (*HI*) and hazardous quotient (*HQ*) parameters using the given equations:

$$HQ = \frac{CDI}{RfDo} = \frac{DAD}{(RfDo \times GIABS)} = \frac{EC}{(RfCi \times 1000 \; \mu g \; mg^{-1})} \tag{5}$$

$$HI = \Sigma HQi \tag{6}$$

$$CR = CDI \times SFo = DAD \times \left(\frac{SFo}{GIABS}\right) = EC \times IUR \tag{7}$$

where, *RfCi* is inhalation reference concentrations ($\mu g \; m^{-3}$), *RfDo* is the oral reference dose ($mg \; kg^{-1} \; day^{-1}$), *SFo* is the oral slope factor (($mg \; kg^{-1} \; day^{-1})^{-1}$), *GIABS* is gastrointestinal absorption factor, *IUR* is inhalation unit risk (($\mu g \; m^{-3})^{-1}$). $i$ shows different toxic chemical species.

### 2.4. Quality control (QC)

To improve accuracy and precision, the quality control is given a lot of attention. The sampled filters collected were sealed pack in a filter cassette covered with a polyethylene zip bag and placed in an airtight box prior to shipment from the sampling site. The samples were, then, shifted to a temperature-controlled box and kept in a refrigerator in the research laboratory. Field blank samples were also collected, separately, and subjected to chemical analysis for target species using similar protocol of analysis for making blank corrections of chemical concentrations of measured PM$_{2.5}$. All polypropylene glassware and bottles used for sample preparation were pre-treated with 2% HNO$_3$ for overnight and then washed three-times by DDW and dried in the oven at 20–25 °C. For AAS analysis, standard dilution series of targeted elemental species in different concentration ranges has been applied for calibration with minimum $R^2$ value equal to 0.95. In Ion Chromatography, the minimum limits of detection (MLD) for Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, NH$_4^+$, F$^-$, Cl$^-$, SO$_4^{2-}$ and NO$_3^-$ were < 0.01 ppm with 0.3 ml min$^{-1}$ eluent flow rate.

## 3. Results and discussion

### 3.1. Characterisation of elements in PM$_{2.5}$

Table 2 shows the concentration of selected ionic and elemental species in ambient PM$_{2.5}$ samples of all sites. Levels of PM$_{2.5}$ mass and carbonaceous mat-

ter, reported in the first part of the study (Sahu et al., 2018), were also included in the Tab. 2 to address the issue of mass closure.

Group of elements (Al, Ca, Fe, Mg, Na, K, S) constituted major fraction of $PM_{2.5}$ elemental components in all three different locations with 9.79%, 10.90%

Table 2. Annually averaged concentrations (geomean ± standard deviation) of $PM_{2.5}$ mass and chemical species for rural, urban and industrial sites (units - $\mu g\,m^{-3}$; *$ng\,m^{-3}$).

| Species | Rural | Urban | Industrial |
|---|---|---|---|
| #$PM_{2.5}$ | 71.82 ±27.27 | 133.49 ± 51.15 | 240.40 ± 61.18 |
| #Carbon | | | |
| OC | 17.76 ± 6.13 | 36.39 ± 15.45 | 57.11 ± 13.80 |
| EC | 4.51 ± 2.22 | 10.35 ± 8.31 | 30.58 ± 7.77 |
| Ions | | | |
| $F^-$ | 1.38 ± 0.87 | 1.01 ± 0.31 | 3.18 ± 2.20 |
| $Cl^-$ | 2.83 ± 1.81 | 4.41 ± 3.35 | 9.88 ± 4.56 |
| $NO_3^-$ | 1.45 ± 0.87 | 4.60 ± 2.42 | 10.32 ± 1.60 |
| $SO_4^{2-}$ | 2.14 ± 1.03 | 4.10 ± 1.34 | 12.32 ± 4.00 |
| $Na^+$ | 0.60 ± 0.17 | 1.40 ± 0.86 | 2.61 ± 0.97 |
| $NH_4^+$ | 1.54 ± 1.03 | 1.84 ± 0.92 | 4.24 ± 2.08 |
| $K^+$ | 0.74 ± 0.15 | 2.06 ± 1.20 | 2.55 ± 1.55 |
| $Ca^{2+}$ | 1.74 ± 0.41 | 1.25 ± 0.58 | 2.43 ± 0.96 |
| $Mg^{2+}$ | 0.17 ± 0.13 | 0.61 ± 0.27 | 3.52 ± 0.76 |
| Elements | | | |
| Al | 0.94 ± 0.51 | 0.96 ± 0.57 | 1.92 ± 0.34 |
| As* | **0.03 ± 0.02** | **5.67 ± 1.20** | **8.84 ± 0.62** |
| Ca | 2.47 ± 0.47 | 1.49 ± 0.62 | 2.63 ± 1.06 |
| Cd | 0.00 ± 0.00 | 0.27 ± 0.27 | 0.31 ± 0.20 |
| Co | 0.01 ± 0.01 | 0.15 ± 0.14 | 0.65 ± 0.19 |
| Cr | 0.02 ± 0.01 | 1.66 ± 0.99 | 5.35 ± 1.55 |
| Cu | 0.28 ± 0.10 | 2.46 ± 1.62 | 1.69 ± 0.36 |
| Fe | 0.83 ± 0.56 | 2.93 ± 1.72 | 2.53 ± 0.70 |
| Hg* | **4.51 ± 5.09** | **12.54 ± 9.88** | **54.00 ± 10.28** |
| K | 0.80 ± 0.18 | 2.32 ± 1.27 | 4.17 ± 1.69 |
| Mg | 0.22 ± 0.19 | 0.75 ± 0.32 | 3.76 ± 0.84 |
| Mn | 0.07 ± 0.05 | 1.12 ± 0.31 | 2.45 ± 0.71 |
| Mo | 0.01 ± 0.00 | 0.36 ± 0.74 | 1.73 ± 0.18 |
| Na | 0.70 ± 0.20 | 1.56 ± 0.91 | 2.83 ± 0.96 |
| Ni | 0.02 ± 0.01 | 1.53 ± 1.00 | 1.61 ± 0.71 |
| Pb | 0.02 ± 0.01 | 0.24 ± 0.18 | 0.36 ± 0.11 |
| S | 1.08 ± 0.32 | 3.03 ± 1.03 | 8.63 ± 4.50 |
| Se* | **1.41 ± 0.79** | **17.53 ± 9.86** | **23.16 ± 17.86** |
| Sn | 0.03 ± 0.03 | 0.51 ± 0.47 | 0.93 ± 0.18 |
| V* | **0.70 ± 0.40** | **7.05 ± 3.12** | **51.71 ± 13.69** |
| Zn | 0.25 ± 0.13 | 0.19 ± 0.16 | 0.64 ± 0.27 |

# Published in previous works (Sahu et al., 2018).

and 11.01% of PM$_{2.5}$ and 90.81%, 63.37% and 68.45% of the total elemental component for rural, urban and industrial sites, respectively. Similarly sum of the measured toxic elements (As, Se, Co, Zn, Cd, Cu, Cr, Mn, Ni, Hg, Pb and V) have shown 0.94%, 5.92% and 5.69% of PM$_{2.5}$ and 8.75%, 34.40% and 29.13% of total elemental component in rural, urban and industrial sites, respectively. These findings indicate nearly seven-fold higher PM$_{2.5}$ toxic elemental fraction in urban/industrial sites, compared to those found in rural site and comparable to those reported earlier for other urban centres across the world (Chan et al., 1997; Marcazzan et al., 2001; Lin, 2002; Ho et al., 2003; Kang et al., 2004; Hueglin et al., 2005; Sun et al., 2006; Aldabe et al., 2011; Tiwari et al., 2013; Pant et al., 2015; Liang et al., 2018). Among the measured species, sulphur content has been found to be 1.50%, 3.40% and 3.59% of PM$_{2.5}$ of rural, urban and industrial environments, respectively. Similar concentration levels of sulphur in urban and industrial sites might be due to close proximity of both sites (~45 km distance between urban and industrial sites) and emissions from major coal-fired industries are affecting both sites in a uniform scale. As far as source marker species are concern, Ni, V, Cu and Mo are classified as vehicular components; Zn, Pb are known for road dust sources; Ca, Mg, Na and Al represent natural dust components; As, S, and Se indicate coal power plant emission components and Cd, Zn, Cr, Fe and As address other industrial emissions (Cao et al., 2005; Duan et al., 2006; Balakrishna and Pervez, 2009; Balakrishna et al., 2010; Chakraborty and Gupta, 2010; Matawle et al., 2014, 2015; Agarwal et al., 2017; Liang et al., 2018).

Day/night variability in PM$_{2.5}$ elemental concentrations of urban site (Raipur) has also been investigated. Meteorological conditions, emission sources and solar radiation varies with time and specially differed during day and night time measurements (Jalava et al., 2015). Figure 2 has shown the wind roses of day and night time for urban site for a period of October 2015– September 2016

Percentage of total elemental component in PM$_{2.5}$ has been found to be relatively higher by a factor of 1.24 in day time, compared to those observed for nighttime measurements. Two elements Fe and Hg have shown 2-fold higher concentra-
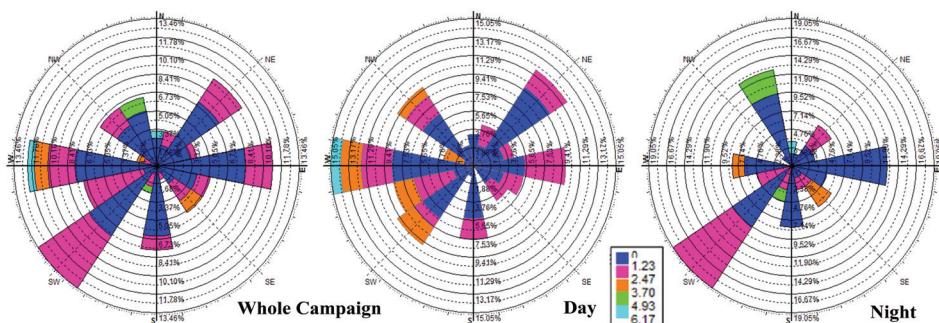


**Figure 2.** Wind rose at day and night time in Raipur.

tion (percent by weight of $PM_{2.5}$) during daytime measure-ments than those observed for night time measurements. On contrary, Mg has shown 2-fold higher percent by weight value in night time $PM_{2.5}$ than those observed for daytime $PM_{2.5}$.

Ions are one of the major parts of atmospheric aerosols and it were analysed and presented in Tab. 2 in this study. It has been observed that the sum of ions contributed 17.53%, 15.94% and 21.24% of the total $PM_{2.5}$ mass concentration in rural, urban and industrial sites respectively. Among all the nine ions, three ions (sum of $SO_4^{2+}$, $NO_3^+$ and $Cl^-$) contribute more than 50% of total ionic contribution. The total ionic species have been found highest in industrial site than urban and rural sites. The concentrations of the ions has been ranked in the order : $Cl^->SO_4^{2-}$ $>Ca^{2+}>NH_4^+> NO_3^->F^->K^+>Na^+>Mg^{2+}$ at rural site; $NO_3^->Cl^-> SO_4^{2-}> K^+> NH_4^+>$ $Na^+> Ca_2^+ >F^->Mg^{2+}$ in urban site and $SO_4^{2-}>NO_3^->Cl^->NH_4^+>Mg^{2+}>F^-$ $>Na^+>K^+>Ca^{2+}$ in industrial site. Previous studies of other urban locations have shown similar trend of relative occurrences of $SO_4^{2-}$ and $NO_3^-$ (Sanhueza and Rondón, 1988; Wang et al., 2006; Chakraborty and Gupta, 2010). $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$ are classified among secondary aerosol components; $Na^+$ and $Cl^-$ marin components; $K^+$ and $NO_3^-$ agricultural components as well as among municipal waste components and $Mg^{2+}$, $SO_2^{2-}$ and $Ca^{2+}$ among industrial elements (Cao et al., 2005; Duan et al., 2006; Balakrishna and Pervez, 2009; Balakrishna et al., 2010; Chakraborty and Gupta, 2010; Matawle et al., 2014, 2015; Agarwal et al., 2017; Liang et al., 2018). As far as day/night variability in ions at urban site is concern, ions have shown relatively higher association with $PM_{2.5}$ by a factor of 1.12, compared to $PM_{2.5}$ measured in night time. Fluoride in percent by weight of $PM_{2.5}$ has shown 1.53 times higher during daytime than those observed for night-time $PM_{2.5}$. Similar to day/night variability pattern of elemental magnesium, ionic magnesium ($Mg^{2+}$) has also shown 2.57-fold higher associations with night-time $PM_{2.5}$ than those observed for daytime.

### 3.2. Mass reconstruction

Mass closer or mass reconstruction (MR) is used for data validation (Chow et al., 2015), it is a statistical formula which is multiplied to several measured species and estimates unmeasured species (Chow et al., 1994; Malm et al., 2011; Watson et al., 2012). Chow et al. (2015) has summarized different PM mass reconstruction methods and explained that MR is submission of seven of its corresponding chemical components: inorganic ions, organic matter (OM), elemental carbon (EC), Geological minerals, salts, trace elements and others). For this paper, *MR* of $PM_{2.5}$ has been carried out using IMPROVE methods which is:

*[MR]=Inorganic ions (1.375 $SO_4^{2-}$ + 1.29 $NO_3^-$) + OM(1.8 OC) + EC +*
*+ Geological minerals (2.2 Al + 2.49 Si + 1.63 Ca + 1.49 Ti + 2.42 Fe) +*
*+ Salt (1.8 $Cl^-$) +*
*+ Trace elements (all elements measured excluding Na, Mg, Al, S, K Ca, and Fe) +*
*+ Others (none)*
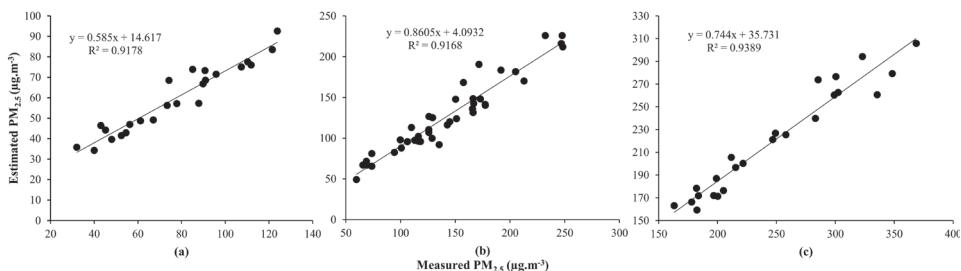
**Figure 3.** PM$_{2.5}$ mass reconstruction: correlation between estimated and measured PM$_{2.5}$ in (*a*) rural; (*b*) urban and (*c*) industrial sites.

Silica (Si) and Titanium (Ti), two major geological elements depicted in *MR* equation, are not chemically analysed and implied to the lower estimation of mass reconstruction values, which were $79.70 \pm 11.90\%$; $89.11 \pm 9.66\%$ and $89.47 \pm 5.50\%$ of PM$_{2.5}$ masses in rural, urban and industrial sites, respectively. Higher correlation ($R^2$) between measured PM$_{2.5}$ and Estimated PM$_{2.5}$ mass for rural (0.92), urban (0.92) and industrial (0.94) sites were observed (Fig. 3).

The fractional percentage contribution of chemical components to recon-structed mass of PM$_{2.5}$ for all three sites of sampling has been depicted in
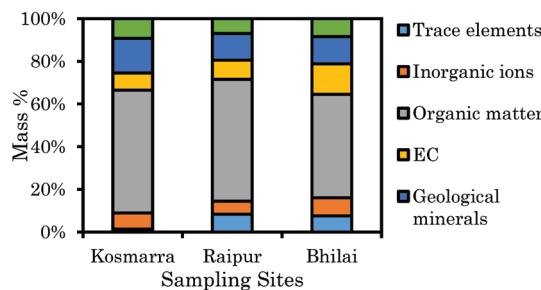


**Figure 4.** PM$_{2.5}$ mass reconstruction: % contribution of different species to PM$_{2.5}$ mass.

Fig. 4. Organic matter (*OM*) has shown major contributor ($\geq 50\%$) of PM$_{2.5}$ Masses. Elemental carbon (*EC*) has shown ~2-times higher contribution to PM$_{2.5}$ of industrial site, as correlated to those found for rural and urban sites. This might be due to emissions from high temperature combustions in an integrated steel plant, located in industrial site. Salt and geological components have shown nearly similar contribution to ambient PM$_{2.5}$ across the three sites. As far as contribution of the component of trace elements to ambient PM$_{2.5}$ is concern, sharp decrease (1.37%) in rural site, compared to urban (8.42%) and industrial (7.58%) sites has been observed.

### 3.3. Ion balance

Ion balance act as indicator for acid–base property of $PM_{2.5}$ fractions (Wang et al., 2005; Xu et al., 2012). Conversion of ion mass concentration into both cation equivalents ($C$) and anion equivalents ($A$) was implemented to calculate the $PM_{2.5}$ anion/cation balance (Cao et al., 2005; Zhang et al., 2011; Tao et al., 2013). Cation and anion equivalents are explained by following equations:

$$C = \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39} + \frac{Mg^{2+}}{12} + \frac{Ca^{2+}}{20} \qquad (8)$$

$$A = \frac{F^-}{19} + \frac{Cl^-}{35,5} + \frac{NO_3^-}{62} + \frac{NO_4^{2-}}{48} \qquad (9)$$

The ratio of anion and cation equivalents with a value of one ($A/C = 1$) describes good balance electro- neutrality condition, whereas $A/C$ ratio $<1$ and $>1$ addresses the basic and acidic nature of $PM_{2.5}$ in the atmosphere (Kerminen et al., 2001; Cao et al., 2005; Shen et al., 2007, 2009). Figure 5 shows the correlation graph between Σ anion equivalent and Σ cation equivalent in (a) rural (b) urban and (c) industrial sampling site, which has shown good $R^2$
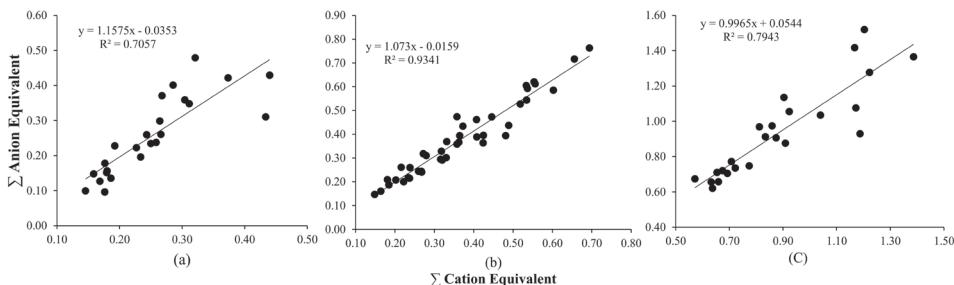


**Figure 5.** $PM_{2.5}$ ion balance: correlation between anion and cation equivalents of $PM_{2.5}$ in (*a*) rural, (*b*) urban and (*c*) industrial sites.

values 0.71, 0.93 and 0.79 respectively. The annually averaged values of $A/C$ ratios for rural ($0.96 \pm 0.24$), urban ($1.02 \pm 0.11$) and industrial ($1.06 \pm 0.11$) sites address the nearly neutral character of ambient $PM_{2.5}$ in both rural and urban environment. However, $PM_{2.5}$ samples collected during August–September 2016 in rural site have shown strong basic character with $A/C$ ratio in the ranges of 0.62–0.75. Most of the $PM_{2.5}$ samples were received from urban and industrial sites during winter season have shown slightly acidic character with $A/C$ values ranges from 1.13–1.26.

### 3.4. Health risk assessment of $PM_{2.5}$ chemical component

The carcinogenic and non-carcinogenic risks from $PM_{2.5}$ chemical component, evaluated through exposure dose calculation via ingestion, dermal and inhalation routs, have been assessed for children and adult age group people in all three sampling locations (rural, urban and industrial) and detailed calculated values of dose exposure and hazardous quotient (*HQ*) were summarized in Supplementary Tabs. S2–S4. The hazardous index (*HI*) to address the non-carcinogenic risk for sixteen chemical species of ambient $PM_{2.5}$ have been presented in Fig. 6 and Tabs. S2–S4. Similarly, the values of carcinogenic risk (*CR*) from six toxic elements of ambient $PM_{2.5}$, evaluated through exposure dose calculation via ingestion, dermal and inhalation routs (Tabs. S2–S4), have been plotted in Fig. 7. The inhalation rout of exposure has been found as a most responsible way of exposure
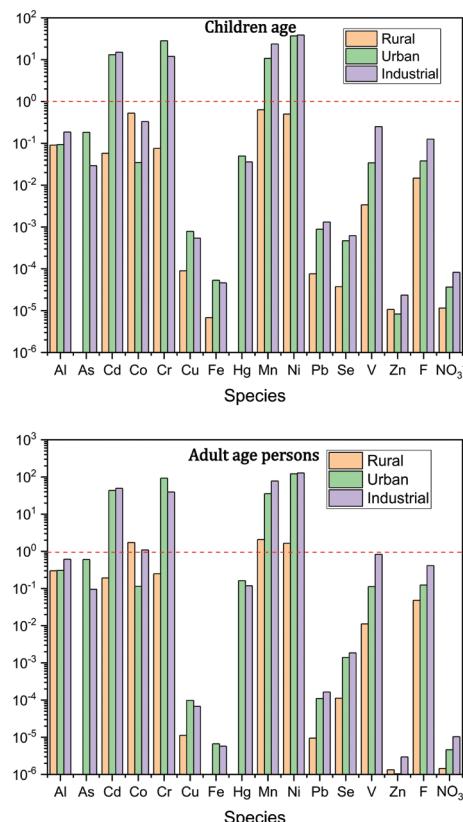


**Figure 6.** Non-carcinogenic risks and exposure pathways of $PM_{2.5}$ toxic component in Adult and Children at Rural, Urban and Industrial sites; dotted line represent the safe level for hazardous Index for non-carcinogenic risks.

for different carcinogenic and non-carcinogenic chemical species in human health of both age groups. Cr, Mn, Ni and Cd have shown non-carcinogenic risk with multi-fold higher hazardous index (*HI*) values, compared to *HI* value (01) for safe level. In case of rural site, only Mn and Ni have shown ~ two-fold higher *HI* values for adult age group people. *HI* value for adult is higher than children of all sampling sites. Cr and Cd have shown highest level of non-carcinogenic health risks among the people of urban site, compared to Industrial and rural sites. On contrary, Mn has shown highest *HI* value for adult aged group of industrial sites. Interestingly, nickel's highest *HI* value was observed for children aged groups of urban sites. The carcinogenic risk through ingestion exposure and Dermal Absorbed Dose in $PM_{2.5}$ for young ones and adults is lower than permissible limit $(1 \times 10^{-4}$ to $1 \times 10^{-6})$ of all sites which is acceptable for a health. The carcinogenic risk through inhalation shown higher $CR_{inh}$ value for adult age group people. The
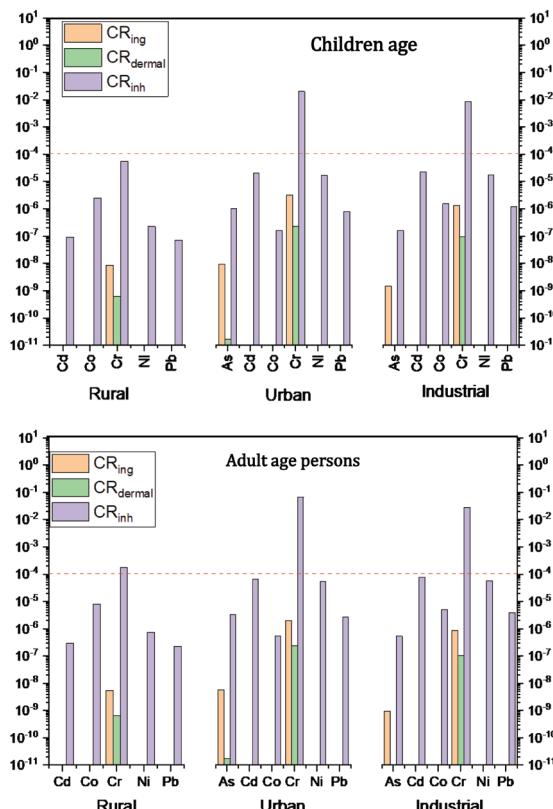


**Figure 7.** Cancer risks (*CR*) and exposure pathways of $PM_{2.5}$ toxic component values with the help of different pathways (inhalation, ingestion and dermal) in adult and children at rural, urban and Industrial sites; dotted line represent the safe level for hazardous Index for carcinogenic risks.

carcinogenic risk through inhalation have shown carcinogenic risk with multi-fold higher Sum of $CR_{inh}$ value, compared to value $CR_{inh}$ (1×10$^{-4}$ to 1×10$^{-6}$) for safe level. Element Cr has shown the highest carcinogenic risk than other elements at all sampling sites for both adult and children age groups in all sampling sites (Tabs. S2–S4). The elements Cd, Co, Ni and Mn were also found within the range of cancer risk threshold limit value for both age group at urban and Industrial sites, except as in children age group for industrial site. However, Co and Ni were also found within the cancer risk range for rural site. These all described elements were found higher or within the range of threshold limit value of US EPA which means these elements poses a potential carcinogenic health risk in both younger generation and adult age group people of the respective study area.

## 4. Conclusions

Estimates of mass reconstruction (*MR*) was approximately 80 to 90% of the PM$_{2.5}$ mass in all selected sites and it is observed to be good *MR* value in the absence of Si and Ti. *OM* is the major contributor of *MR* at all sampling sites which is approximately half of the total estimated mass. Annually averaged ambient PM$_{2.5}$ levels of rural, urban and industrial sites that found in a relative scale of 1:2:3, respectively, have shown major elemental content (percent by weight of PM$_{2.5}$) in a close equivalence. On contrary, trace elemental content (percent by weight of PM$_{2.5}$) was found in a relative scale of 1:5:5 for rural, urban and industrial sites, respectively. Similarity in the concentrations (percent by weight) of major elemental constituents and total carbonaceous matter, reported by Sahu et al. (2018), across the three sites clearly indicate that it is the trace elemental component that actually contrast the PM$_{2.5}$ chemical character between rural and urban environment. This might be due to close proximity of coal-fired industrial emissions to urban and industrial sites, which were the sources of 32 toxic trace elements (Block and Dams, 1975). Highest PM$_{2.5}$ ionic component has been observed in industrial site. As and Co concentrations (percent by weight of PM$_{2.5}$) have shown inverse relation on evaluating day/night variations in urban site. Ionic component has not shown significant variation between day and night time urban PM$_{2.5}$ measurements. Annually averaged anion/cation ratios (*A*/*C* ratio) were found in the ranges 0.96 to 1.06 in all monitoring sites which indicates the neutral nature of PM$_{2.5}$. The average daily exposure doses were comparatively higher in children than for adults for each exposure pathways. The elemental order of non-carcinogenic risk has been found in order; Mn > Co > Ni for rural site and Ni > Cr > Cd > Mn for urban site and Ni > Mn > Cd > Cr for industrial monitoring site. The non-carcinogenic risks for elements As, Cd, Cr, Mn, Ni, and V have been found to be greater than 1 for both young ones and adults for urban and industrial sites while Co, Mn, and Ni were found more than 1 for both children and adults in case of rural site. The total excess carcinogenic risk was found to be higher than the acceptable limits (10$^{-6}$ to 10$^{-4}$). On the basis of assessment and

evaluation, serious efforts should be implemented and needed to reduce ambient pollution of $PM_{2.5}$ in all study areas. $PM_{2.5}$ measured data and its chemical speciation will be highly useful and contributory for further health risk assessments and source apportionment studies for study areas.

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SAŽETAK

# Procjena i vrednovanje PM$_{2.5}$ u vanjskom okolišu u odnosu na njegove zdravstvene učinke u industrijskim područjima u kojima se koristi mineralni ugljen

*Shamsh Pervez, Rakesh Kumar Sahu, Mamta Tripathi, Shahina Bano, Jeevan Lal Matawle, Suresh Tiwari, Manas Kanti Deb i Yasmeen Fatima Pervez*

Onečišćenje atmosfere lebdećim česticama (PM$_{2.5}$) pokazalo je potencijalni utjecaj na zdravlje ljudi općenito. Stoga je potrebno sagledati kemijska svojstva čestica PM$_{2.5}$ kako bi se postiglo učinkovito smanjenje zdravstvenih rizika izložene populacije. U ovome radu prikazuju se rezultati studije koncentracija PM$_{2.5}$ i koncentracija kemijskih sastojaka u lebdećim česticama za jednogodišnje razdoblje (2015.–2016.) koji su povezani sa zdravstvenim rizicima u ruralnim i urbanim sredinama u industrijskim područjima u središnjoj Indiji u kojima se koristi mineralni ugljen kao pogonsko industrijsko gorivo. Ukupno je analizirano 260 uzoraka PM$_{2.5}$ s ruralnih, urbanih i industrijskih lokacija za različite elemente: Al, As, Ca, Hg, Cr, Co, Cu, Fe, Mn, K, Cd, Mo, Ni, Pb, Se , B, Na, Mg, K, V i Zn, ione poput Na$^+$, Mg$^{2+}$, K$^+$, Ca$^{2+}$, F$^-$, Cl$^-$, NH$_4^+$, NO$_3^-$, SO$_4^{2-}$ i spojeve ugljika. Utvrđeno je da su prosječne godišnje masene koncentracije PM$_{2.5}$ od ~2 do ~6 puta više od dopuštenih godišnjih vrijednosti prema indijskom Nacionalnom standardu kvalitete zraka (40 µg m$^{-3}$). Nadalje, ova studija također ocjenjuje kancerogene i nekancerogene rizike za zdravlje povezane s izloženošću česticama PM$_{2.5}$ u okolišu (putem gutanja, udisanja i dodira s kožom). Elementi koji su pokazali nekancerogene rizike i za djecu i za odrasle na sve tri lokacije su: Co, Mn, Ni (ruralno područje), As, Cd, Cr, Mn, Ni i V (urbano i industrijsko područje). Slično, utvrđen je povećan kancerogeni rizik za Cd, Co, Cr, Ni i Pb, koji je veći od prihvatljivih granica (10$^{-6}$ do 10$^{-4}$).

*Ključne riječi*: okolni PM$_{2.5}$, kemijska svojstva, ionska ravnoteža, masena rekonstrukcija, zdravstveni rizici

*Corresponding author's address*: Dr. Shamsh Pervez, ORCID 0000-0001-8334-9387; cell phone: +91 94 252 42 455; e-mail: shamshpervez@gmail.com

# Supplementary materials

*Table S1: Summary of annual concentration (GM ± SD) of chemical species associated with compare day and night time in Raipur (units: µg m⁻³; \*ng m⁻³).*

| Species | Raipur | |
|---|---|---|
| | Day | Night |
| $PM_{2.5}$# | 115.39 ± 51.65 | 147.90 ± 69.63 |
| Carbon# | | |
| OC | 34.52 ± 14.52 | 37.21 ± 18.48 |
| EC | 8.69 ± 5.74 | 11.45 ± 11.38 |
| Ions | | |
| $F^-$ | 1.04 ± 0.36 | 0.87 ± 0.51 |
| $Cl^-$ | 3.75 ± 2.98 | 4.68 ± 4.47 |
| $NO_3^-$ | 4.36 ± 2.90 | 4.59 ± 2.47 |
| $SO_4^{2-}$ | 3.58 ± 1.69 | 4.36 ± 1.58 |
| $Na^+$ | 1.36 ± 0.93 | 1.27 ± 1.09 |
| $NH_4^+$ | 1.56 ± 0.98 | 1.98 ± 1.14 |
| $K^+$ | 1.98 ± 0.97 | 1.98 ± 1.76 |
| $Ca^{2+}$ | 1.20 ± 0.47 | 1.18 ± 0.90 |
| $Mg^{2+}$ | 0.27 ± 0.23 | 0.89 ± 0.45 |
| Elements | | |
| Al | 0.86 ± 0.68 | 0.85 ± 0.87 |
| As* | 0.29 ± 0.13 | 7.24 ± 6.03 |
| Ca | 1.46 ± 0.49 | 1.38 ± 0.97 |
| Cd | 0.25 ± 0.26 | 0.26 ± 0.31 |
| Co* | 0.52 ± 1.97 | 0.18 ± 0.29 |
| Cr | 4.97 ± 5.84 | 5.42 ± 3.98 |
| Cu | 2.11 ± 1.84 | 2.43 ± 2.51 |
| Fe | 3.33 ± 2.04 | 2.30 ± 1.99 |
| Hg* | 33.16 ± 54.74 | 23.58 ± 15.38 |
| K | 2.21 ± 1.17 | 2.24 ± 1.82 |
| Mg | 0.38 ± 0.25 | 1.06 ± 0.51 |
| Mn | 1.13 ± 0.36 | 1.07 ± 0.35 |
| Mo | 0.31 ± 0.69 | 0.24 ± 0.86 |
| Na | 1.51 ± 0.96 | 1.45 ± 1.12 |
| Ni | 1.54 ± 1.23 | 1.44 ± 1.04 |
| Pb | 0.19 ± 0.14 | 0.28 ± 0.25 |
| S | 4.01 ± 1.86 | 4.80 ± 1.83 |
| Se* | 15.72 ± 10.45 | 18.43 ± 11.30 |
| Sn | 0.56 ± 0.63 | 0.39 ± 0.39 |
| V* | 4.36 ± 24.57 | 7.47 ± 42.27 |
| Zn | 0.18 ± 0.14 | 0.20 ± 0.21 |

# published in previous works (Sahu et al., 2018)

*Table S2. Average daily dose of each element from different exposure pathways: $D_{ing}$, ingestion; $D_{inh}$, inhalation; $D_{dermal}$, dermal contact; HQ, hazard quotient; HI, hazard index in rural site.*

| Species | $CDI_{ing}$ (mg (kg day)$^{-1}$)$^{-1}$ Children | Adult | $DAD_{dermal}$ (mg (kg day)$^{-1}$)$^{-1}$ Children | Adult | $EC_{inh}$ (µg m$^{-3}$)$^{-1}$ Children | Adult | $HQ_{ing}$ Children | Adult | $HQ_{dermal}$ Children | Adult | $HQ_{inh}$ Children | Adult | $HI$ Children | Adult |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Al | $1.20\times10^{-05}$ | $1.50\times10^{-06}$ | $2.16\times10^{-08}$ | $4.56\times10^{-09}$ | $4.55\times10^{-01}$ | $1.50\times10^{+00}$ | $1.20\times10^{-08}$ | $1.50\times10^{-06}$ | $2.16\times10^{-08}$ | $4.56\times10^{-09}$ | $9.11\times10^{-02}$ | $3.00\times10^{-01}$ | $9.11\times10^{-02}$ | $3.00\times10^{-01}$ |
| As (Inorganic) | – | – | – | – | – | – | – | – | – | – | – | – | – | – |
| Cd (Diet) | $1.53\times10^{-08}$ | $1.92\times10^{-09}$ | $2.76\times10^{-11}$ | $5.84\times10^{-12}$ | $5.83\times10^{-04}$ | $1.92\times10^{-03}$ | $1.53\times10^{-05}$ | $1.92\times10^{-06}$ | $1.10\times10^{-06}$ | $2.34\times10^{-07}$ | $5.83\times10^{-02}$ | $1.92\times10^{-01}$ | $5.83\times10^{-02}$ | $1.92\times10^{-01}$ |
| Co | $8.31\times10^{-08}$ | $1.04\times10^{-08}$ | $1.50\times10^{-10}$ | $3.16\times10^{-11}$ | $3.16\times10^{-03}$ | $1.04\times10^{-02}$ | $2.77\times10^{-04}$ | $3.46\times10^{-05}$ | $4.99\times10^{-07}$ | $1.05\times10^{-07}$ | $5.26\times10^{-01}$ | $1.73\times10^{+00}$ | $5.27\times10^{-01}$ | $1.73\times10^{+00}$ |
| Cr (IV) | $2.01\times10^{-07}$ | $2.51\times10^{-08}$ | $3.61\times10^{-10}$ | $7.64\times10^{-11}$ | $7.63\times10^{-03}$ | $2.51\times10^{-02}$ | $6.69\times10^{-05}$ | $8.36\times10^{-06}$ | $4.82\times10^{-06}$ | $1.02\times10^{-06}$ | $7.63\times10^{-02}$ | $2.51\times10^{-01}$ | $7.63\times10^{-02}$ | $2.51\times10^{-01}$ |
| Cu | $3.59\times10^{-06}$ | $4.49\times10^{-07}$ | $6.47\times10^{-09}$ | $1.37\times10^{-09}$ | $1.37\times10^{-01}$ | $4.49\times10^{-01}$ | $8.98\times10^{-05}$ | $1.12\times10^{-05}$ | $1.62\times10^{-07}$ | $3.42\times10^{-08}$ | – | – | $9.00\times10^{-05}$ | $1.13\times10^{-05}$ |
| Fe | $4.80\times10^{-06}$ | $5.99\times10^{-07}$ | $8.63\times10^{-09}$ | $1.83\times10^{-09}$ | $1.82\times10^{-01}$ | $5.99\times10^{-01}$ | $6.85\times10^{-06}$ | $8.56\times10^{-07}$ | – | – | – | – | $6.85\times10^{-06}$ | $8.56\times10^{-07}$ |
| Hg (Elemental) | – | – | – | – | – | – | – | – | – | – | – | – | – | – |
| Mn (Diet) | $8.37\times10^{-07}$ | $1.05\times10^{-07}$ | $1.51\times10^{-09}$ | $3.19\times10^{-10}$ | $3.18\times10^{-02}$ | $1.05\times10^{-01}$ | $5.98\times10^{-06}$ | $7.48\times10^{-07}$ | $2.69\times10^{-07}$ | $5.69\times10^{-08}$ | $6.36\times10^{-01}$ | $2.09\times10^{+00}$ | $6.36\times10^{-01}$ | $2.09\times10^{+00}$ |
| Ni | $2.65\times10^{-07}$ | $3.31\times10^{-08}$ | $4.76\times10^{-10}$ | $1.01\times10^{-10}$ | $1.01\times10^{-02}$ | $3.31\times10^{-02}$ | $2.41\times10^{-05}$ | $3.01\times10^{-06}$ | $1.08\times10^{-06}$ | $2.29\times10^{-07}$ | $5.03\times10^{-01}$ | $1.65\times10^{+00}$ | $5.03\times10^{-01}$ | $1.65\times10^{+00}$ |
| Pb (Acetate) | $2.65\times10^{-07}$ | $3.31\times10^{-08}$ | $4.76\times10^{-10}$ | $1.01\times10^{-10}$ | $1.01\times10^{-02}$ | $3.31\times10^{-02}$ | $7.56\times10^{-05}$ | $9.45\times10^{-06}$ | $1.36\times10^{-06}$ | $2.88\times10^{-08}$ | $7.58\times10^{-05}$ | $9.48\times10^{-06}$ | $7.58\times10^{-05}$ | $9.48\times10^{-06}$ |
| Se | $1.79\times10^{-08}$ | $2.24\times10^{-09}$ | $3.22\times10^{-11}$ | $6.81\times10^{-12}$ | $6.80\times10^{-04}$ | $2.24\times10^{-03}$ | $3.58\times10^{-06}$ | $4.47\times10^{-07}$ | $6.44\times10^{-09}$ | $1.36\times10^{-09}$ | $3.40\times10^{-05}$ | $1.12\times10^{-04}$ | $3.76\times10^{-05}$ | $1.12\times10^{-04}$ |
| V | $8.95\times10^{-09}$ | $1.12\times10^{-09}$ | $1.61\times10^{-11}$ | $3.41\times10^{-12}$ | $3.40\times10^{-04}$ | $1.12\times10^{-03}$ | $1.79\times10^{-06}$ | $2.24\times10^{-07}$ | $1.24\times10^{-07}$ | $2.62\times10^{-07}$ | $3.40\times10^{-03}$ | $1.12\times10^{-02}$ | $3.40\times10^{-03}$ | $1.12\times10^{-02}$ |
| Zn | $3.20\times10^{-06}$ | $4.00\times10^{-07}$ | $5.76\times10^{-09}$ | $1.22\times10^{-09}$ | $1.22\times10^{-01}$ | $4.00\times10^{-01}$ | $1.07\times10^{-05}$ | $1.33\times10^{-06}$ | $1.92\times10^{-08}$ | $4.06\times10^{-09}$ | – | – | $1.07\times10^{-05}$ | $1.34\times10^{-06}$ |
| F (Soluble fluoride) | $5.03\times10^{-06}$ | $6.29\times10^{-07}$ | $9.05\times10^{-09}$ | $1.91\times10^{-09}$ | $1.91\times10^{-01}$ | $6.29\times10^{-01}$ | $8.38\times10^{-05}$ | $1.05\times10^{-05}$ | $1.51\times10^{-08}$ | $3.19\times10^{-08}$ | $1.47\times10^{-02}$ | $4.84\times10^{-02}$ | $1.48\times10^{-02}$ | $4.84\times10^{-02}$ |
| NO$_3^-$ | $1.85\times10^{-05}$ | $2.31\times10^{-06}$ | $3.33\times10^{-08}$ | $7.05\times10^{-09}$ | $7.03\times10^{-01}$ | $2.31\times10^{+00}$ | $1.16\times10^{-05}$ | $1.45\times10^{-06}$ | $2.08\times10^{-08}$ | $4.40\times10^{-09}$ | – | – | $1.16\times10^{-05}$ | $1.45\times10^{-06}$ |
| **Sum** | $\mathbf{4.88\times10^{-05}}$ | $\mathbf{6.10\times10^{-06}}$ | $\mathbf{8.78\times10^{-08}}$ | $\mathbf{1.86\times10^{-08}}$ | $\mathbf{1.85\times10^{+00}}$ | $\mathbf{6.10\times10^{+00}}$ | $\mathbf{6.85\times10^{-04}}$ | $\mathbf{8.56\times10^{-05}}$ | $\mathbf{8.41\times10^{-06}}$ | $\mathbf{1.78\times10^{-06}}$ | $\mathbf{1.91\times10^{+00}}$ | $\mathbf{6.28\times10^{+00}}$ | $\mathbf{1.91\times10^{+00}}$ | $\mathbf{6.28\times10^{+00}}$ |

**Carcinogenic risks**

| Species | $CDI_{ing}$ (mg (kg day)$^{-1}$)$^{-1}$ Children | Adult | $DAD_{dermal}$ (mg (kg day)$^{-1}$)$^{-1}$ Children | Adult | $EC_{inh}$ (µg m$^{-3}$)$^{-1}$ Children | Adult | $CR_{ing}$ Children | Adult | $CR_{dermal}$ Children | Adult | $CR_{inh}$ Children | Adult |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| As (Inorganic) | – | – | – | – | – | – | – | – | – | – | – | – |
| Cd (Diet) | $1.32\times10^{-09}$ | $8.22\times10^{-10}$ | $2.37\times10^{-12}$ | $2.50\times10^{-12}$ | $5.00\times10^{-05}$ | $1.64\times10^{-04}$ | – | – | – | – | $9.00\times10^{-08}$ | $2.96\times10^{-07}$ |
| Co | $7.12\times10^{-09}$ | $4.45\times10^{-09}$ | $1.28\times10^{-11}$ | $1.36\times10^{-11}$ | $2.71\times10^{-04}$ | $8.90\times10^{-04}$ | – | – | – | – | $2.44\times10^{-06}$ | $8.01\times10^{-06}$ |
| Cr (IV) | $1.72\times10^{-08}$ | $1.08\times10^{-08}$ | $3.10\times10^{-11}$ | $3.27\times10^{-11}$ | $6.54\times10^{-04}$ | $2.15\times10^{-03}$ | $8.60\times10^{-09}$ | $5.38\times10^{-10}$ | $6.19\times10^{-10}$ | $6.55\times10^{-10}$ | $5.49\times10^{-05}$ | $1.81\times10^{-04}$ |
| Ni | $2.27\times10^{-08}$ | $1.42\times10^{-08}$ | $4.08\times10^{-11}$ | $4.32\times10^{-11}$ | $8.62\times10^{-04}$ | $2.84\times10^{-03}$ | – | – | – | – | $2.24\times10^{-07}$ | $7.37\times10^{-07}$ |
| Pb (Acetate) | $2.27\times10^{-08}$ | $1.42\times10^{-08}$ | $4.08\times10^{-11}$ | $4.32\times10^{-11}$ | $8.62\times10^{-04}$ | $2.84\times10^{-03}$ | – | – | – | – | $6.90\times10^{-08}$ | $2.27\times10^{-07}$ |
| **Sum** | $\mathbf{7.10\times10^{-08}}$ | $\mathbf{4.44\times10^{-08}}$ | $\mathbf{1.28\times10^{-10}}$ | $\mathbf{1.35\times10^{-10}}$ | $\mathbf{2.70\times10^{-03}}$ | $\mathbf{8.88\times10^{-03}}$ | $\mathbf{8.60\times10^{-09}}$ | $\mathbf{5.38\times10^{-09}}$ | $\mathbf{6.19\times10^{-10}}$ | $\mathbf{6.55\times10^{-10}}$ | $\mathbf{5.77\times10^{-05}}$ | $\mathbf{1.90\times10^{-04}}$ |

*Table S3. Average daily dose of each element from different exposure pathways: $D_{ing}$, ingestion; $D_{inh}$, inhalation; $D_{dermal}$, dermal contact; HQ, hazard quotient; HI, hazard index in industrial site.*

| Species | $CDI_{ing}$ (mg(kg·day)⁻¹) | | $DAD_{dermal}$ (mg(kg·day)⁻¹) | | $EC_{inh}$ (µg·m⁻³)⁻¹ | | $HQ_{ing}$ | | $HQ_{dermal}$ | | $HQ_{inh}$ | | $HI$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult |
| Al | $2.45\times10^{-05}$ | $3.06\times10^{-06}$ | $4.41\times10^{-08}$ | $9.33\times10^{-09}$ | $9.32\times10^{-01}$ | $3.06\times10^{+00}$ | $2.45\times10^{-05}$ | $3.06\times10^{-06}$ | $4.41\times10^{-08}$ | $9.33\times10^{-09}$ | $1.86\times10^{-01}$ | $6.13\times10^{-01}$ | $1.86\times10^{-01}$ | $6.13\times10^{-01}$ |
| As (Inorganic) | $1.15\times10^{-08}$ | $1.44\times10^{-09}$ | $6.21\times10^{-10}$ | $1.31\times10^{-10}$ | $4.37\times10^{-04}$ | $1.44\times10^{-03}$ | $3.84\times10^{-05}$ | $4.79\times10^{-06}$ | $2.07\times10^{-06}$ | $4.38\times10^{-07}$ | $2.92\times10^{-02}$ | $9.59\times10^{-02}$ | $2.92\times10^{-02}$ | $9.59\times10^{-02}$ |
| Cd (Diet) | $3.96\times10^{-06}$ | $4.95\times10^{-07}$ | $7.13\times10^{-09}$ | $1.51\times10^{-09}$ | $1.51\times10^{-01}$ | $4.95\times10^{-01}$ | $3.96\times10^{-03}$ | $4.95\times10^{-04}$ | $2.85\times10^{-04}$ | $6.03\times10^{-05}$ | $1.51\times10^{+01}$ | $4.95\times10^{+01}$ | $1.51\times10^{+01}$ | $4.95\times10^{+01}$ |
| Co | $5.24\times10^{-08}$ | $6.55\times10^{-09}$ | $9.44\times10^{-11}$ | $2.00\times10^{-11}$ | $1.99\times10^{-03}$ | $6.55\times10^{-03}$ | $1.75\times10^{-04}$ | $2.18\times10^{-05}$ | $3.15\times10^{-07}$ | $6.65\times10^{-08}$ | $3.32\times10^{-01}$ | $1.09\times10^{+00}$ | $3.32\times10^{-01}$ | $1.09\times10^{+00}$ |
| Cr (IV) | $3.15\times10^{-05}$ | $3.93\times10^{-06}$ | $5.67\times10^{-08}$ | $1.20\times10^{-08}$ | $1.20\times10^{+00}$ | $3.93\times10^{+00}$ | $1.05\times10^{-02}$ | $1.31\times10^{-03}$ | $7.55\times10^{-04}$ | $1.60\times10^{-04}$ | $1.20\times10^{+01}$ | $3.93\times10^{+01}$ | $1.20\times10^{+01}$ | $3.93\times10^{+01}$ |
| Cu | $2.17\times10^{-05}$ | $2.71\times10^{-06}$ | $3.90\times10^{-08}$ | $8.25\times10^{-09}$ | $8.23\times10^{-01}$ | $2.71\times10^{+00}$ | $5.42\times10^{-04}$ | $6.77\times10^{-05}$ | $9.75\times10^{-07}$ | $2.06\times10^{-07}$ | — | — | $5.43\times10^{-04}$ | $6.79\times10^{-05}$ |
| Fe | $3.23\times10^{-05}$ | $4.04\times10^{-06}$ | $5.81\times10^{-08}$ | $1.23\times10^{-08}$ | $1.23\times10^{+00}$ | $4.04\times10^{+00}$ | $4.61\times10^{-05}$ | $5.77\times10^{-06}$ | — | — | — | — | $4.61\times10^{-05}$ | $5.77\times10^{-06}$ |
| Hg (Elemental) | $2.85\times10^{-07}$ | $3.56\times10^{-08}$ | $5.13\times10^{-10}$ | $1.09\times10^{-10}$ | $1.08\times10^{-02}$ | $3.56\times10^{-02}$ | — | — | — | — | $3.61\times10^{-02}$ | $1.19\times10^{-01}$ | $3.61\times10^{-02}$ | $1.19\times10^{-01}$ |
| Mn (Diet) | $3.13\times10^{-05}$ | $3.91\times10^{-06}$ | $5.64\times10^{-08}$ | $1.19\times10^{-08}$ | $1.19\times10^{+00}$ | $3.91\times10^{+00}$ | $2.24\times10^{-04}$ | $2.80\times10^{-05}$ | $1.01\times10^{-05}$ | $2.13\times10^{-06}$ | $2.38\times10^{+01}$ | $7.83\times10^{+01}$ | $2.38\times10^{+01}$ | $7.83\times10^{+01}$ |
| Ni | $2.05\times10^{-06}$ | $2.57\times10^{-07}$ | $3.69\times10^{-08}$ | $7.81\times10^{-09}$ | $7.80\times10^{-01}$ | $2.57\times10^{+00}$ | $1.87\times10^{-03}$ | $2.33\times10^{-04}$ | $8.40\times10^{-05}$ | $1.78\times10^{-05}$ | $3.90\times10^{+01}$ | $1.28\times10^{+02}$ | $3.90\times10^{+01}$ | $1.28\times10^{+02}$ |
| Pb (Acetate) | $4.60\times10^{-06}$ | $5.75\times10^{-07}$ | $8.28\times10^{-09}$ | $1.75\times10^{-09}$ | $1.75\times10^{-06}$ | $5.75\times10^{-07}$ | $1.31\times10^{-03}$ | $1.64\times10^{-04}$ | $2.37\times10^{-06}$ | $5.00\times10^{-07}$ | $1.32\times10^{-03}$ | — | $1.32\times10^{-03}$ | $1.65\times10^{-04}$ |
| Se | $2.97\times10^{-07}$ | $3.71\times10^{-08}$ | $5.34\times10^{-10}$ | $1.13\times10^{-10}$ | $1.13\times10^{-02}$ | $3.71\times10^{-02}$ | $5.93\times10^{-05}$ | $7.42\times10^{-06}$ | $1.07\times10^{-07}$ | $2.26\times10^{-08}$ | $6.23\times10^{-04}$ | $1.85\times10^{-03}$ | $6.23\times10^{-04}$ | $1.86\times10^{-03}$ |
| V | $6.61\times10^{-06}$ | $8.26\times10^{-07}$ | $1.19\times10^{-09}$ | $2.52\times10^{-10}$ | $2.51\times10^{-02}$ | $8.26\times10^{-02}$ | $1.32\times10^{-04}$ | $1.65\times10^{-05}$ | $9.15\times10^{-06}$ | $1.94\times10^{-06}$ | $2.51\times10^{-01}$ | $8.26\times10^{-01}$ | $2.51\times10^{-01}$ | $8.26\times10^{-01}$ |
| Zn | $7.06\times10^{-06}$ | $8.83\times10^{-07}$ | $1.27\times10^{-08}$ | $2.69\times10^{-08}$ | $2.68\times10^{-01}$ | $8.83\times10^{-01}$ | $2.35\times10^{-05}$ | $2.94\times10^{-06}$ | $4.24\times10^{-08}$ | $8.96\times10^{-09}$ | $2.36\times10^{-05}$ | — | $2.36\times10^{-05}$ | $2.95\times10^{-05}$ |
| F (Soluble fluoride) | $4.30\times10^{-05}$ | $5.37\times10^{-06}$ | $7.74\times10^{-08}$ | $1.64\times10^{-08}$ | $1.63\times10^{+00}$ | $5.37\times10^{+00}$ | $7.17\times10^{-04}$ | $8.96\times10^{-05}$ | $1.29\times10^{-06}$ | $2.73\times10^{-07}$ | $1.26\times10^{-01}$ | $4.13\times10^{-01}$ | $1.26\times10^{-01}$ | $4.13\times10^{-01}$ |
| NO₃⁻ | $1.32\times10^{-04}$ | $1.65\times10^{-05}$ | $2.37\times10^{-07}$ | $5.02\times10^{-08}$ | $5.01\times10^{-01}$ | $1.65\times10^{+00}$ | $8.25\times10^{-05}$ | $1.03\times10^{-05}$ | $1.48\times10^{-05}$ | $3.14\times10^{-08}$ | — | — | $8.26\times10^{-05}$ | $1.03\times10^{-05}$ |
| Sum | $3.54\times10^{-04}$ | $4.42\times10^{-05}$ | $6.37\times10^{-07}$ | $1.35\times10^{-07}$ | $1.34\times10^{-01}$ | $4.42\times10^{+01}$ | $1.97\times10^{-02}$ | $2.46\times10^{-02}$ | $1.15\times10^{-03}$ | $2.43\times10^{-04}$ | $9.08\times10^{+01}$ | $2.99\times10^{+02}$ | $9.08\times10^{+01}$ | $2.99\times10^{+02}$ |

### Carcinogenic risks

| Species | $CDI_{ing}$ (mg(kg·day)⁻¹) | | $DAD_{dermal}$ (mg(kg·day)⁻¹) | | $EC_{inh}$ (µg·m⁻³)⁻¹ | | $CR_{ing}$ | | $CR_{dermal}$ | | $CR_{inh}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult |
| As (Inorganic) | $9.86\times10^{-10}$ | $6.16\times10^{-10}$ | $1.78\times10^{-12}$ | $1.88\times10^{-12}$ | $3.75\times10^{-05}$ | $1.23\times10^{-04}$ | $1.48\times10^{-09}$ | $9.25\times10^{-10}$ | $2.66\times10^{-12}$ | $2.82\times10^{-12}$ | $1.61\times10^{-07}$ | $5.30\times10^{-07}$ |
| Cd (Diet) | $3.40\times10^{-07}$ | $2.12\times10^{-07}$ | $6.11\times10^{-10}$ | $6.46\times10^{-10}$ | $1.29\times10^{-02}$ | $4.25\times10^{-02}$ | — | — | — | — | $2.32\times10^{-05}$ | $7.64\times10^{-05}$ |
| Co | $4.49\times10^{-09}$ | $2.81\times10^{-09}$ | $8.09\times10^{-12}$ | $8.55\times10^{-12}$ | $1.71\times10^{-04}$ | $5.62\times10^{-04}$ | — | — | — | — | $1.54\times10^{-06}$ | $5.05\times10^{-06}$ |
| Cr (IV) | $2.70\times10^{-06}$ | $1.69\times10^{-06}$ | $4.86\times10^{-09}$ | $5.13\times10^{-09}$ | $1.03\times10^{-01}$ | $3.37\times10^{-01}$ | $1.35\times10^{-06}$ | $8.43\times10^{-07}$ | $9.71\times10^{-08}$ | $1.03\times10^{-07}$ | $8.61\times10^{-03}$ | $2.83\times10^{-02}$ |
| Ni | $1.76\times10^{-06}$ | $1.10\times10^{-06}$ | $3.17\times10^{-09}$ | $3.35\times10^{-09}$ | $6.69\times10^{-02}$ | $2.20\times10^{-01}$ | — | — | — | — | $1.74\times10^{-05}$ | $5.72\times10^{-05}$ |
| Pb (Acetate) | $3.94\times10^{-07}$ | $2.46\times10^{-07}$ | $7.10\times10^{-10}$ | $7.50\times10^{-10}$ | $1.50\times10^{-02}$ | $4.93\times10^{-02}$ | — | — | — | — | $1.20\times10^{-06}$ | $3.94\times10^{-06}$ |
| Sum | $5.20\times10^{-06}$ | $3.25\times10^{-06}$ | $9.35\times10^{-09}$ | $9.89\times10^{-09}$ | $1.97\times10^{-01}$ | $6.50\times10^{-01}$ | $1.35\times10^{-06}$ | $8.44\times10^{-07}$ | $9.71\times10^{-08}$ | $1.03\times10^{-07}$ | $8.66\times10^{-03}$ | $2.85\times10^{-02}$ |

*Table S4. Average daily dose of each element from different exposure pathways: $D_{ing}$, ingestion; $D_{inh}$, inhalation; $D_{dermal}$, dermal contact; HQ, hazard quotient; HI, hazard in urban site.*

| Species | $CDI_{ing}$ (mg (kg day)$^{-1}$)$^{-1}$ | | $DAD_{dermal}$ (mg (kg day)$^{-1}$)$^{-1}$ | | $EC_{inh}$ (µg m$^{-3}$)$^{-1}$ | | $HQ_{ing}$ | | $HQ_{dermal}$ | | $HQ_{inh}$ | | $HI$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult |
| Al | $1.23\times10^{-05}$ | $1.53\times10^{-06}$ | $2.21\times10^{-08}$ | $4.67\times10^{-09}$ | $4.66\times10^{-01}$ | $1.53\times10^{+00}$ | $1.23\times10^{-05}$ | $1.53\times10^{-06}$ | $2.21\times10^{-08}$ | $4.67\times10^{-09}$ | $9.33\times10^{-02}$ | $3.07\times10^{-01}$ | $9.33\times10^{-02}$ | $3.07\times10^{-01}$ |
| As (Inorganic) | $7.25\times10^{-08}$ | $9.06\times10^{-09}$ | $3.91\times10^{-10}$ | $8.28\times10^{-10}$ | $2.75\times10^{-03}$ | $9.06\times10^{-03}$ | $2.42\times10^{-04}$ | $3.02\times10^{-05}$ | $1.30\times10^{-05}$ | $2.76\times10^{-06}$ | $1.84\times10^{-01}$ | $6.04\times10^{-01}$ | $1.84\times10^{-01}$ | $6.04\times10^{-01}$ |
| Cd (Diet) | $3.47\times10^{-06}$ | $4.34\times10^{-07}$ | $6.25\times10^{-09}$ | $1.32\times10^{-09}$ | $1.32\times10^{-01}$ | $4.34\times10^{-01}$ | $3.47\times10^{-03}$ | $4.34\times10^{-04}$ | $2.50\times10^{-04}$ | $5.29\times10^{-04}$ | $1.32\times10^{+01}$ | $4.34\times10^{+01}$ | $1.32\times10^{+01}$ | $4.34\times10^{+01}$ |
| Co | $5.50\times10^{-09}$ | $6.87\times10^{-10}$ | $9.90\times10^{-12}$ | $2.09\times10^{-12}$ | $2.09\times10^{-04}$ | $6.87\times10^{-04}$ | $1.83\times10^{-05}$ | $2.29\times10^{-06}$ | $3.30\times10^{-08}$ | $6.98\times10^{-09}$ | $3.48\times10^{-02}$ | $1.15\times10^{-01}$ | $3.48\times10^{-02}$ | $1.15\times10^{-01}$ |
| Cr (IV) | $7.44\times10^{-06}$ | $9.30\times10^{-06}$ | $1.34\times10^{-07}$ | $2.83\times10^{-08}$ | $2.83\times10^{+00}$ | $9.30\times10^{+00}$ | $2.48\times10^{-02}$ | $3.10\times10^{-03}$ | $1.79\times10^{-03}$ | $3.78\times10^{-04}$ | $2.83\times10^{+01}$ | $9.30\times10^{+01}$ | $2.83\times10^{+01}$ | $9.30\times10^{+01}$ |
| Cu | $3.15\times10^{-05}$ | $3.93\times10^{-06}$ | $5.67\times10^{-08}$ | $1.20\times10^{-08}$ | $1.20\times10^{+00}$ | $3.93\times10^{+00}$ | $7.87\times10^{-04}$ | $9.84\times10^{-05}$ | $1.42\times10^{-06}$ | $2.99\times10^{-07}$ | | | $7.88\times10^{-04}$ | $9.87\times10^{-05}$ |
| Fe | $3.75\times10^{-05}$ | $4.68\times10^{-06}$ | $6.74\times10^{-08}$ | $1.43\times10^{-08}$ | $1.42\times10^{+00}$ | $4.68\times10^{+00}$ | $5.35\times10^{-05}$ | $6.69\times10^{-06}$ | | | | | $5.35\times10^{-05}$ | $6.69\times10^{-06}$ |
| Hg (Elemental) | $3.92\times10^{-07}$ | $4.90\times10^{-08}$ | $7.06\times10^{-10}$ | $1.49\times10^{-10}$ | $1.49\times10^{-02}$ | $4.90\times10^{-02}$ | | | | | $4.97\times10^{-02}$ | $1.63\times10^{-01}$ | $4.97\times10^{-02}$ | $1.63\times10^{-01}$ |
| Mn (Diet) | $1.43\times10^{-05}$ | $1.78\times10^{-06}$ | $2.57\times10^{-08}$ | $5.43\times10^{-09}$ | $5.42\times10^{-01}$ | $1.78\times10^{+00}$ | $1.02\times10^{-04}$ | $1.27\times10^{-05}$ | $4.58\times10^{-06}$ | $9.69\times10^{-07}$ | $1.08\times10^{+01}$ | $3.56\times10^{+01}$ | $1.08\times10^{+01}$ | $3.56\times10^{+01}$ |
| Ni | $1.96\times10^{-06}$ | $2.44\times10^{-06}$ | $3.52\times10^{-08}$ | $7.44\times10^{-09}$ | $7.43\times10^{-01}$ | $2.44\times10^{+00}$ | $1.78\times10^{-03}$ | $2.22\times10^{-04}$ | $8.00\times10^{-05}$ | $1.69\times10^{-05}$ | $3.71\times10^{+01}$ | $1.22\times10^{+02}$ | $3.71\times10^{+01}$ | $1.22\times10^{+02}$ |
| Pb (Acetate) | $3.09\times10^{-05}$ | $3.87\times10^{-07}$ | $5.57\times10^{-09}$ | $1.18\times10^{-09}$ | $1.18\times10^{-01}$ | $3.87\times10^{-01}$ | $8.84\times10^{-04}$ | $1.10\times10^{-04}$ | $1.59\times10^{-06}$ | $3.36\times10^{-07}$ | | | $8.85\times10^{-04}$ | $1.11\times10^{-04}$ |
| Se | $2.24\times10^{-07}$ | $2.80\times10^{-07}$ | $4.03\times10^{-10}$ | $8.53\times10^{-11}$ | $8.52\times10^{-03}$ | $2.80\times10^{-02}$ | $4.48\times10^{-05}$ | $5.60\times10^{-06}$ | $8.07\times10^{-08}$ | $1.71\times10^{-08}$ | $4.26\times10^{-04}$ | $1.40\times10^{-03}$ | $4.71\times10^{-04}$ | $1.41\times10^{-03}$ |
| V | $9.01\times10^{-08}$ | $1.13\times10^{-07}$ | $1.62\times10^{-10}$ | $3.43\times10^{-11}$ | $3.43\times10^{-03}$ | $1.13\times10^{-02}$ | $1.80\times10^{-05}$ | $2.25\times10^{-06}$ | $1.25\times10^{-06}$ | $2.64\times10^{-07}$ | $3.43\times10^{-02}$ | $1.13\times10^{-01}$ | $3.43\times10^{-02}$ | $1.13\times10^{-01}$ |
| Zn | $2.50\times10^{-06}$ | $3.12\times10^{-06}$ | $4.49\times10^{-09}$ | $9.50\times10^{-10}$ | $9.49\times10^{-02}$ | $3.12\times10^{-01}$ | $8.32\times10^{-06}$ | $1.04\times10^{-06}$ | $1.50\times10^{-08}$ | $3.17\times10^{-09}$ | | | $8.34\times10^{-06}$ | $1.04\times10^{-06}$ |
| F (Soluble fluoride) | $1.29\times10^{-06}$ | $1.61\times10^{-06}$ | $2.32\times10^{-08}$ | $4.91\times10^{-09}$ | $4.90\times10^{-01}$ | $1.61\times10^{+00}$ | $2.15\times10^{-04}$ | $2.69\times10^{-05}$ | $3.87\times10^{-07}$ | $8.18\times10^{-08}$ | $3.77\times10^{-02}$ | $1.24\times10^{-01}$ | $3.79\times10^{-02}$ | $1.24\times10^{-01}$ |
| NO$_3^-$ | $5.88\times10^{-05}$ | $7.35\times10^{-06}$ | $1.06\times10^{-07}$ | $2.24\times10^{-08}$ | $2.24\times10^{+00}$ | $7.35\times10^{+00}$ | $3.68\times10^{-05}$ | $4.60\times10^{-06}$ | $6.62\times10^{-08}$ | $1.40\times10^{-08}$ | | | $3.68\times10^{-05}$ | $4.61\times10^{-06}$ |
| Sum | $2.71\times10^{-04}$ | $3.39\times10^{-05}$ | $4.92\times10^{-07}$ | $1.04\times10^{-07}$ | $1.03\times10^{+01}$ | $3.39\times10^{+01}$ | $3.25\times10^{-02}$ | $4.06\times10^{-03}$ | $2.14\times10^{-03}$ | $4.52\times10^{-04}$ | $8.99\times10^{+01}$ | $2.96\times10^{+02}$ | $8.99\times10^{+01}$ | $2.96\times10^{+02}$ |

**Carcinogenic risks**

| Species | $CDI_{ing}$ (mg (kg day)$^{-1}$)$^{-1}$ | | $DAD_{dermal}$ (mg (kg day)$^{-1}$)$^{-1}$ | | $EC_{inh}$ (µg m$^{-3}$)$^{-1}$ | | $CR_{ing}$ | | $CR_{dermal}$ | | $CR_{inh}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult | Children | Adult |
| As (Inorganic) | $6.21\times10^{-09}$ | $3.88\times10^{-09}$ | $1.12\times10^{-11}$ | $1.18\times10^{-11}$ | $2.36\times10^{-04}$ | $7.77\times10^{-04}$ | $9.32\times10^{-09}$ | $5.83\times10^{-09}$ | $1.68\times10^{-11}$ | $1.77\times10^{-11}$ | $1.02\times10^{-06}$ | $3.34\times10^{-06}$ |
| Cd (Diet) | $2.98\times10^{-07}$ | $1.86\times10^{-07}$ | $5.36\times10^{-10}$ | $5.66\times10^{-10}$ | $1.13\times10^{-02}$ | $3.72\times10^{-02}$ | | | | | $2.04\times10^{-05}$ | $6.70\times10^{-05}$ |
| Co | $4.71\times10^{-10}$ | $2.95\times10^{-10}$ | $8.48\times10^{-13}$ | $8.97\times10^{-13}$ | $1.79\times10^{-05}$ | $5.89\times10^{-05}$ | | | | | $1.61\times10^{-07}$ | $5.30\times10^{-07}$ |
| Cr (IV) | $6.38\times10^{-06}$ | $3.99\times10^{-06}$ | $1.15\times10^{-08}$ | $1.21\times10^{-08}$ | $2.42\times10^{-01}$ | $7.97\times10^{-01}$ | $3.19\times10^{-06}$ | $1.99\times10^{-06}$ | $2.30\times10^{-07}$ | $2.43\times10^{-07}$ | $2.04\times10^{-02}$ | $6.70\times10^{-02}$ |
| Ni | $1.68\times10^{-06}$ | $1.05\times10^{-06}$ | $3.02\times10^{-09}$ | $3.19\times10^{-09}$ | $6.37\times10^{-02}$ | $2.09\times10^{-01}$ | | | | | $1.66\times10^{-05}$ | $5.45\times10^{-05}$ |
| Pb (Acetate) | $2.65\times10^{-07}$ | $1.66\times10^{-07}$ | $4.77\times10^{-10}$ | $5.05\times10^{-10}$ | $1.01\times10^{-02}$ | $3.31\times10^{-02}$ | | | | | $8.06\times10^{-07}$ | $2.65\times10^{-06}$ |
| Sum | $8.62\times10^{-06}$ | $5.39\times10^{-06}$ | $1.55\times10^{-08}$ | $1.64\times10^{-08}$ | $3.28\times10^{-01}$ | $1.08\times10^{+00}$ | $3.20\times10^{-06}$ | $2.00\times10^{-06}$ | $2.30\times10^{-07}$ | $2.43\times10^{-07}$ | $2.04\times10^{-02}$ | $6.71\times10^{-02}$ |