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## Fractionation of Airborne Fine Particulate-Bound Metals and Associated Health Risks in A Site in Indo-Gangetic Plain

Dinesh Sah, Puneet Kumar Verma, K. Maharaj Kumari and Anita Lakhani

Department of Chemistry

Faculty of Science

Dayalbagh Educational Institute, Dayalbagh, Agra (UP)

### ABSTRACT

Samples of  $PM_{2.5}$  were collected at Bhagwan Talkies near the crossing National Highway 2 in Agra during the Summer and Monsoon seasons, 2016.  $PM_{2.5}$  samples were collected by APM-550 particulate sampler. A sequential extraction procedure was applied to fractionate these fine particle bound metals into four different fractions. Metals were analyzed by ICP-OES. The mean concentration of  $PM_{2.5}$  was  $118.67 \pm 85.38 \mu\text{g}/\text{m}^3$ . The mean total concentration of metals followed the order  $\text{Fe} > \text{Zn} > \text{Cu} > \text{Cr} > \text{Mn} > \text{Pb} > \text{Ni} > \text{As} > \text{Cd}$ . The mobility of the metals were in the following order:  $\text{Cd} (91.9\%) > \text{As} (80.6\%) > \text{Zn} (57.9\%) > \text{Mn} (55.9\%) > \text{Pb} (49\%) > \text{Fe} (45.5\%) \approx \text{Cu} (45.3\%) > \text{Cr} (34.5\%) > \text{Ni} (27.2\%)$  therefore Cd and As could be considered to be the more mobile and bioavailable than other elements. Cd was identified as the most bioavailable metals ( $\text{BI} = 84.8\%$ ) among all metals. The carcinogenic risks for Cr and As were higher than  $1 \times 10^{-6}$  for children and adults indicating potential risk. While the HQ value for Ni was higher than the safe level ( $=1$ ) indicating non-carcinogenic risk to both children and adults.

**Keywords:** Fine particle, Metals, Sequential extraction procedure, Bioavailability, Health risk assessment

### 1. Introduction

Atmospheric heavy metals in urban area may originate from various sources including industrial pollution, traffic emissions, atmospheric deposition, and natural geochemical processes (Mohanraj et al., 2004). These metals can remain in urban environments for a long time or be re-suspended into the atmosphere and thus pose a potential threat to local ecosystems and public health (Li et al., 2015).

Many studies determining and assessing the distribution and environmental risk of metals have used comparisons of total metal concentrations (Shi et al., 2008). However, it is generally recognized that the toxicity, environmental and health effects of metals are basically dependent on their mobility and bioavailability (Sun et al., 2014). Sequential extraction provides quantitative information about the relative bonding strength of metals on various solid phases and their potential reactivity under different physicochemical environmental conditions (Yuan et al., 2011). The BCR sequential extraction procedure, proposed by the European Community's Bureau of Reference (Ure et al., 1993), is one of the most representative procedures and has been widely applied to determine the phases or fractions of metals associated with environmental solids (Feng et al., 2009). Considering the variation of contamination sources for metals in fine particulate matter from urban area, further research of their chemical speciation and environmental risk is of great significance. However, such information is limited in India.

It has been established that elevated concentration of metals in the environment may cause adverse health effects to inhabitants, by affecting the central nervous system, blood-forming, cardiovascular, renal and reproductive systems (Han et al., 2014). Toxic metals may enter the human body mainly via three routes, direct inhalation, ingestion and dermal contact absorption (Kong et al., 2011). In particular, more concern needs to be shown for children than adults because of their frequent hand-to-mouth activities, higher absorption rate from the digestion system, and hemoglobin sensitivity to toxic metals (Zheng et al., 2010).

The main purposes of this study were to study the chemical speciation and mobility potential of heavy metals (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in urban area of Agra, India using the modified BCR sequential extraction method, and to evaluate the human health risk of these metals to both children and adults via inhalation.

## 2. Materials and methods

Sampling was performed on the roof top of a building situated at Bhagwan Talkies near the crossing National Highway 2 in Agra. Samples of PM<sub>2.5</sub> were collected on pre-weighed and desiccated 47 mm quartz fiber filters (Pallflex) by Fine Particulate Sampler (Envirotech APM 550). The sampling was done for 24 hours at a flow rate 16.6 L/min. Samples were collected during the Summer and Monsoon seasons, 2016. Samples of PM<sub>2.5</sub> were sequentially extracted in order to establish the distribution of metals among water soluble, environmentally mobile, bound to carbonate and oxides and environmentally immobile (bound to organic matter and silicates) fractions to determine metal bioavailability, mobility and toxicity. The sequential extraction procedure developed by Fernandez Espinosa et al. (2002) was followed. The reagents and operational conditions followed in each step are given below:

### Step one: (Soluble and exchangeable metals, F1)

15 mL de-ionized water was added to aerosol samples in polyethylene centrifuge tubes, and mechanically shaken for 3h at room temperature. The extracts were then separated from the residues by centrifuging for 20 min at 4000 rpm. Subsequently, the supernatant was decanted and the residues rinsed with de-ionized water by shaking for 15 min and then centrifuged. The decanted supernatant was stored in polyethylene bottle.

### Step two: (Carbonate, oxides and reducible metals, F2).

10 mL NH<sub>2</sub>OH.HCl (0.25M at pH = 2.0) was added to residues from Step 1, and re-suspended by mechanical shaking for 5 h at room temperature. The separation of the extract, collection of the supernatant, and rinsing of residues were the same as described in Step 1.

### Fraction 3(F3): (Bound to organic matter, oxidizable and sulphidic metals).

7.5 mL H<sub>2</sub>O<sub>2</sub> was added drop by drop to the residues from Step 2. The tubes were covered and the contents digested for 1 h at room temperature. The contents were then heated on a hot plate at 95 °C for 1 h and evaporated to near dryness. Step 3 was performed twice. Finally, 15 mL NH<sub>4</sub>OAc (5M at pH= 3) was added to the cool residues, and the extraction procedure was performed as described in Step 1.

### Step four: (Residual metals, F4)

The residue from Step 3 was treated by the procedure used for determination of the elements contents by HNO<sub>3</sub>:HCl:HClO<sub>4</sub> (6:2:5). The contents were heated on a hot plate at 95 °C for 5h and evaporated to near dryness. After cooling, the residues were dissolved in 2% HNO<sub>3</sub>. Concentrations of metals in each fraction were determined by ICP-OES.

## Results and discussion

The mean concentration of PM<sub>2.5</sub> during the study period was 118.67±85.38 µg/m<sup>3</sup>. As shown in Fig. 1, the average concentrations of metallic elements in F1 were in the order of Fe > Zn > Cu = Pb > Ni > Cr > Mn > As > Cd; for F2: Fe > Zn > Cu > Cr > Mn > Ni > As > Pb > Cd; for F3: Fe > Mn > Zn > Cr > Pb > As > Cu > Ni > Cd; and for F4: Fe > Cr > Cu > Zn > Ni > Pb > Mn > As > Cd for PM<sub>2.5</sub> samples. The mean total metal concentrations in the PM<sub>2.5</sub> samples, expressed as volume related concentrations in air (ng/m<sup>3</sup>), decreased in the following order: Fe > Zn > Cu > Cr > Mn > Pb > Ni > As > Cd shown in Fig. 2.

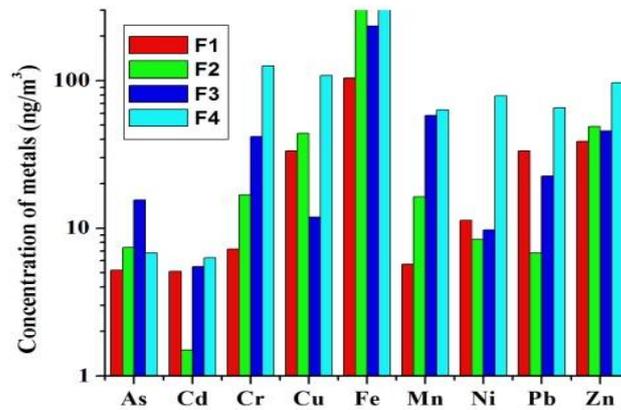


Fig. 1. Concentration of heavy metals in the four fractions (F1, F2, F3 and F4)

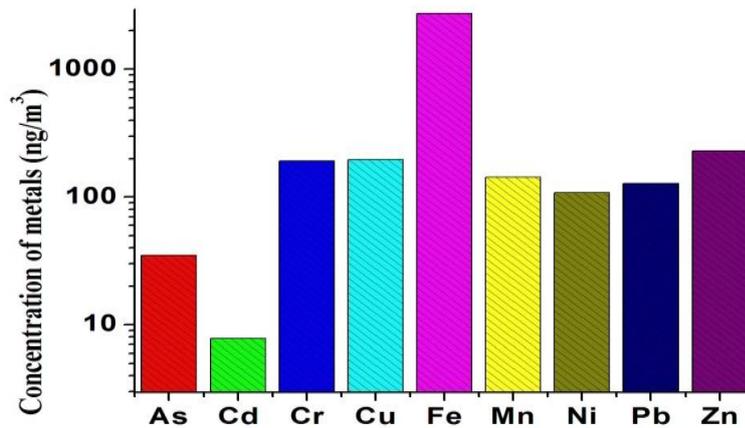


Fig. 2. Total mean metal concentration (ng/m<sup>3</sup>) in PM<sub>2.5</sub>

### Percentage distribution of heavy metals

#### Soluble and exchangeable metals (F1)

Heavy metals in this fraction are mostly mobile and readily available to human beings and other living organisms (Chaudhary and Banerjee, 2007). Hence it has a high potential to contaminate the ecosystem. The relative distribution of metals in this fraction followed the order (Fig. 3): Cd > Pb > Cu ≈ Zn > As > Ni > Mn ≈ Fe ≈ Cr.

#### Carbonate, oxides and reducible metals (F2)

About 19-33% of Cd, As, Cu, Zn and Fe was associated with carbonates, whereas 5-12% of Cr, Mn, Ni and Pb (Fig. 3). The metals in carbonate bound fraction may become more mobile and can be released into the environment causing serious threat when the pH of the environmental media changes. (Bhattacharyya et al., 2014). Thorpe and Harrison (2008) considered the major compounds of Pb in F2 fraction were PbCO<sub>3</sub>, PbSO<sub>4</sub>,

PbO Carbonate bound Cu and Cd is sensitive to environmental changes such as redox potential, pH, and can be mobilized easily.

**Bound to organic matter, oxidizable and sulphidic metals (F3)**

Trace metals bound to various forms of organic matter were extracted in this fraction. As (44.5%) and Mn (40.6%) had higher association followed by Cr (21.6%), Zn (19.8%) and Pb (17.6%), Ni (8.9%), Fe (8.5%), Cd (7.1%) and Cu (6%). If favorable conditions like anoxic, acidic environment occur then it can be leached out as bio-available form which might contaminate the environment.

**Residual metals (F4)**

The residual fraction is the ultimate sink as they are attached to the crystal lattices which cannot be removed or mobilized in normal environmental conditions. A significant amount of Zn, Cd, Pb and Cu were found in this fraction and the order was Ni (72.8%)>Cr (65.5%) >Cu (54.7%)>Fe (54.5%)>Pb(50.9%), Mn(44%)>Zn(42%)> As(19.4%)> Cd(8%)(Fig. 3). Ni, Cr, Cu and Fe were attached at maximum concentration in residual fraction.

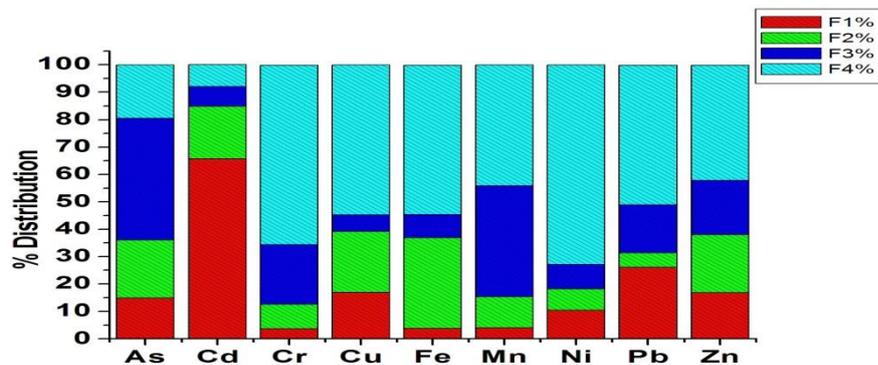


Fig. 3. Chemical partitioning of metal elements in PM<sub>2.5</sub> (F1: soluble and exchangeable metals, F2: carbonates, oxides and reducible metals, F3: metals bound to organic matter and oxidizable and sulfidic metals and F4: residual metals).

Table 1: Chemical partitioning of heavy metals in the four different fractions for PM<sub>2.5</sub> samples

	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Mobile phase (%)	80.6	91.9	34.5	45.3	45.5	55.9	27.2	49	57.9
Cf	4.2	11.5	0.52	0.83	0.83	1.27	0.37	0.96	1.4
RAC (%)	14.8	65.7	3.7	16.9	3.8	4	10.5	26	16.8
Risk	Moderate	Very high	Low	Moderate	Low	Low	Low	Moderate	Moderate
Bioavailability Index %	36	84.8	12.6	39.2	36.9	15.3	18.2	31.4	38.1

**Mobility, Bioavailability and Environmental Risk of Metals**

The mobility of the metals based on the sum of the proportions of the F1, F2 and F3 fractions for PM<sub>2.5</sub> samples were in the following order : Cd (91.9%) > As (80.6%) > Zn (57.9%) > Mn (55.9%) > Pb (49%) > Fe

(45.5%)  $\approx$  Cu (45.3%) > Cr (34.5%) > Ni (27.2%)(Table 1). Cd and As had higher proportions in the mobile fractions, and therefore could be considered to be the more mobile and bioavailable than other elements. By contrast, Zn, Mn, Pb, Fe, Cu, Cr and Ni had relative low proportions present in the mobile fractions (<80%). The relative retention time of metals in the environment is evaluated through estimation of contamination factors (Cf). A higher contamination factor for an element implies that it has a lower retention time and higher environmental mobility and higher risk to the local environment. Individual contamination factors (Cf) were determined by dividing the sum of the metal concentration in the mobile fractions by the concentration in the residual fraction (Jamali, 2007). The CF is classified into four groups where the contamination factor  $CF < 1$  means low contamination;  $1 \leq CF < 3$  means moderate contamination;  $3 \leq CF \leq 6$  indicates considerable contamination and  $CF > 6$  indicates very high contamination. The calculated results show that Cr, Cu, Fe, Ni and Pb had the low contamination. Zn and Mn had moderate contamination. As had considerable contamination. Cd had very high contamination showing their lower retention time and high mobility potential (Table 1).

Elements in F1 and F2 fractions can interact with human body fluid through inhalation and/or oral exposure and are considered as bio-accessible fractions. Therefore, the percentage of the first two fractions (F1 and F2) to the total metal concentration (F1, F2, F3 and F4) is used as a bioavailability index which can be used to evaluate the mobile or labile or bioavailable potential of a metal (Feng et al., 2009; Richter et al., 2007). Cr, Mn and Ni had the low bioavailability ( $BI < 30\%$ ) among all the metals. Cu, As, Fe, Pb and Zn had medium bioavailability ( $30\% < BI < 50\%$ ) while Cd was identified as the most bioavailable elements ( $BI > 50\%$ ) as it had the highest percentage bound to exchangeable and carbonates and oxides among all metals (Table 1). The environmental risk of heavy metal pollution can be estimated by the Risk Assessment Code (RAC) defined as the fraction of exchangeable and carbonate fraction (F1) obtained through sequential extraction. If this fraction is <1% the environmental risk posed by the metal is negligible, values between 1-10% imply low risk, moderate between 11-30%; high if the F1 fraction is between 31-50% and very high if greater than 50%. At the present site F1 fraction was between 1-10% for Cr, Fe, Mn and Ni while it is less than 30% for As, Cu, Pb and Zn metals and more than 50% for Cd (Table 1).

#### Health risk assessment of trace metal exposure from $PM_{2.5}$

Human can easily be exposed to metals directly through inhalation and indirectly through ingestion and dermal contact. Metals bound in  $PM_{2.5}$  can easily get deep into human lung tissues through breathing. Accumulation of heavy metals through inhalation over long time period may cause serious health risks. Health risk assessment models of US Environmental Protection Agency (US EPA) were applied to calculate the carcinogenic and non-carcinogenic risks posed to children and adults by metals present in  $PM_{2.5}$ . The exposure concentration (EC) of non-carcinogenic and carcinogenic metals was calculated as:

$$EC = C \times (ET \times EF \times ED) / AT_n$$

Where, C is the metal concentration in  $PM_{2.5}$  ( $\mu\text{g}/\text{m}^3$ ) at the time of exposure; ET = exposure time (hours/day), (taken as 8 h/day in this study); EF = exposure frequency, (250 day/year); ED = exposure duration, 6 years for children and 24 years for adults;  $AT_n$  = average time of exposure; for non-carcinogens,  $AT_n = ED \times 365 \text{ days} \times 24 \text{ h/day}$  and for carcinogens,  $AT_n = 70 \text{ year} \times 365 \text{ days/year} \times 24 \text{ h}$ . All parameters used in the calculation of EC were taken from reports published by the US EPA (US EPA, 2011a). The Hazard Quotient (HQ) for non-carcinogenic elements and Excess Lifetime Cancer Risk (ELCR) for carcinogenic metals was calculated as:

$$HQ = EC / (RfC \times 1000 \mu\text{g}/\text{mg})$$

$$ELCR = IUR \times EC$$

RfC denotes the Reference concentration (RfC) and IUR is the Inhalation Unit Risk. Cr(VI) was calculated as one seventh of total Cr concentration (EPA, 1998) based on the fact that the concentration ratio of Cr(VI) to Cr(III) in the air is, about 1 to 6 (Taner et al., 2013).

Table 2

Carcinogenic and non-carcinogenic risks via inhalation exposure to PM<sub>2.5</sub>

Metal	Carcinogenic risk (ELCR)		Non-carcinogenic risk (HQ)	
	Children	Adults	Children	Adults
Cd	$2.71 \times 10^{-7}$	<b><math>1.08 \times 10^{-6}</math></b>	$1.76 \times 10^{-1}$	$1.76 \times 10^{-1}$
Cr(VI)	<b><math>4.48 \times 10^{-5}</math></b>	<b><math>1.79 \times 10^{-4}</math></b>	$6.23 \times 10^{-2}$	$6.23 \times 10^{-2}$
Pb	$3.00 \times 10^{-8}$	$1.20 \times 10^{-7}$		
Ni	$5.07 \times 10^{-7}$	<b><math>2.02 \times 10^{-6}</math></b>	1.76	1.76
Mn			$6.58 \times 10^{-1}$	$6.58 \times 10^{-1}$
As	<b><math>2.94 \times 10^{-6}</math></b>	<b><math>1.17 \times 10^{-5}</math></b>	$5.31 \times 10^{-1}$	$5.31 \times 10^{-1}$
Sum	$4.86 \times 10^{-5}$	$1.94 \times 10^{-4}$	3.19	3.19

Inhalation exposure is typically the primary route of direct exposure to airborne metals. The carcinogenic risks from Cd, Pb and Ni in PM<sub>2.5</sub> samples were less than  $1 \times 10^{-6}$  for children, (Table 2), indicating that the carcinogenic risk posed by those toxic elements to children via inhalation is acceptable while carcinogenic risks for Cr and As were higher than  $1 \times 10^{-6}$  for children and adults indicating potential risk. The carcinogenic risk posed by Cd to adults was higher than  $1 \times 10^{-6}$  indicating potential risk. The integrated risks of these metals were above the acceptable level ( $1 \times 10^{-6}$ ), indicating that the carcinogenic risk posed by these toxic metals to both children and adults via inhalation was not acceptable.

The non-carcinogenic risks from these toxic elements in PM<sub>2.5</sub> via inhalation exposure were also calculated (Table 2). The HQ values for As, Cd, Cr and Mn via inhalation exposure for both children and adults were all lower than the safe level (=1), indicating no non-carcinogenic risks from the inhalation exposure for each single metal. While the HQ value for Ni was higher than the safe level indicating non-carcinogenic risk to both children and adults. HI values for As, Cd, Cr, Ni, Pb and Mn were higher than the safe level (=1), indicating the accumulative non-carcinogenic risks to both children and adults via inhalation. Therefore, adults are subject to more potential carcinogenic and non-carcinogenic risks than children via inhalation.

#### 4. Conclusions

Samples of PM<sub>2.5</sub> were collected during the summer and monsoon seasons, 2016 in Agra, India. The mean mass concentration exceeded the 24 h standard set by the new NAAQS in India. The mean metal concentrations in PM<sub>2.5</sub> decreased in the following order: Fe > Zn > Cu > Cr > Mn > Pb > Ni > As > Cd. The four-step sequential extraction procedure was used to analyze the chemical fractionation of metals. The mobility of the metals was in the following order: Cd > As > Zn > Mn > Pb > Fe ≈ Cu > Cr > Ni. Thus Cd and As could be considered to be the more mobile and bioavailable while Zn, Mn, Pb, Fe, Cu, Cr and Ni had relative low proportions present in the mobile. Cd had very high contamination showing high mobility potential. Cd was identified as the most bioavailable elements. The integrated risks of these metals were above the acceptable level ( $1 \times 10^{-6}$ ), indicating that the carcinogenic risk posed by these toxic metals to both children and adults via inhalation was not acceptable. HI values for As, Cd, Cr, Ni, Pb and Mn were higher than the safe level (=1), indicating the accumulative non-carcinogenic risks to both children and adults via inhalation. Therefore, adults are subject to more potential carcinogenic and non-carcinogenic risks than children via inhalation.

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