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CONTAMINATION AND RISK ASSESSMENT OF CR IN ROAD DUST OF ASANSOL: A MEDIUM-SIZED CITY

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ABSTRACT

Occurrence of heavy metals like Chromium (Cr) in road side dust always pose a serious environmental concern. The total concentration of Cr in the <53 μm fraction road dust samples of Asansol was ranged between 8.99 to 250 mg/kg. The chemical speciation of Cr in the present study provides an important input into the labile nature as well as their possible impacts on health and environment. Cr was found to be in following sequence: Residual (89%) > Fe-Mn oxide (7%) > Organic matter (4%) > Carbonates (0%) > Exchangeable (0%) fraction. The Contamination Factor (CF) and Enrichment Factor (EF) have shown minimum to moderate contamination for Cr in road dust collected from Asansol. The present study concluded that health risk was high with regard to total metal (Cr) concentration and negligible when calculated for bioavailable fraction of the metals. The pathway for direct ingestion was dominating for children exposed to Cr while it was dermal contact for adults.

Keywords: Chromium, Road dust, Chemical speciation, Contamination, Health risk

INTRODUCTION

In present days urbanization and non-sustainable industrial processes are destroying the environmental quality. Due to urbanization and industrialization large amount of potentially toxic elements (PTEs like Pb, Ni, Cr, Cd, Zn etc) are released into the environment. Road dust is an environmental media, which indicate the degree of contamination by various pollutants like PTEs, polycyclic aromatic hydrocarbons (PAHs) and other organic pollutants as it act as an important sink for pollutants emitted by vehicle exhaust, brake wear, industrial sources such as power plants, coal combustion, metallurgical industry, auto repair shop, etc. and monitoring of road dust plays a great role in assessing environmental quality (Grigoratos and Martini, 2014; Gunawardana et al., 2012; Loganathan et al., 2013). In recent years, the scientific community has concluded that toxicity, bioavailability, bioactivity, bio-geological distribution/transportation of trace element depends not only on their total concentrations but also on their chemical forms. Sequential extraction procedures for PTEs are widely performed for identification and quantification of different species, forms and association (Kumar et al., 2013; Li et al., 2013; Bhattacharyya et al., 2014**).**

The potential health effects due to oral exposure, inhalation, and dermal contact of road dust depends upon size of dust particles, rate of deposition, rate of transfer to the human organism, chemical composition of dust etc (Singh, 2011; Zhao et al., 2014). Recently health risk assessment a useful tool to determine the toxicity of pollutants by various exposure route i.e., ingestion, inhalation and dermal contact has been used for various environmental media like playground soil, road dust, indoor dust etc. (Ferreira-Baptista and De Miguel, 2005). So the present study aimed to assess the Cr concentration in Asansol with the following objectives: a) determining total concentration of Cr in road dust b) assess the solid phase fractionation of Cr in road dust, c) to assess the degree of contamination of Cr by various geo statistical techniques like Igeo, EF, CF, MF in road dust from different anthropogenic activities by comparing the results with that of other cities, d) determining health hazard for children and adults via ingestion, inhalation and dermal contact to road dust and to compare the total and bioavailable fraction in the road dust of Asansol area of West Bengal, India, e) estimation of health risk posed by Cr exposure through road dust.

MATERIALS AND METHODS

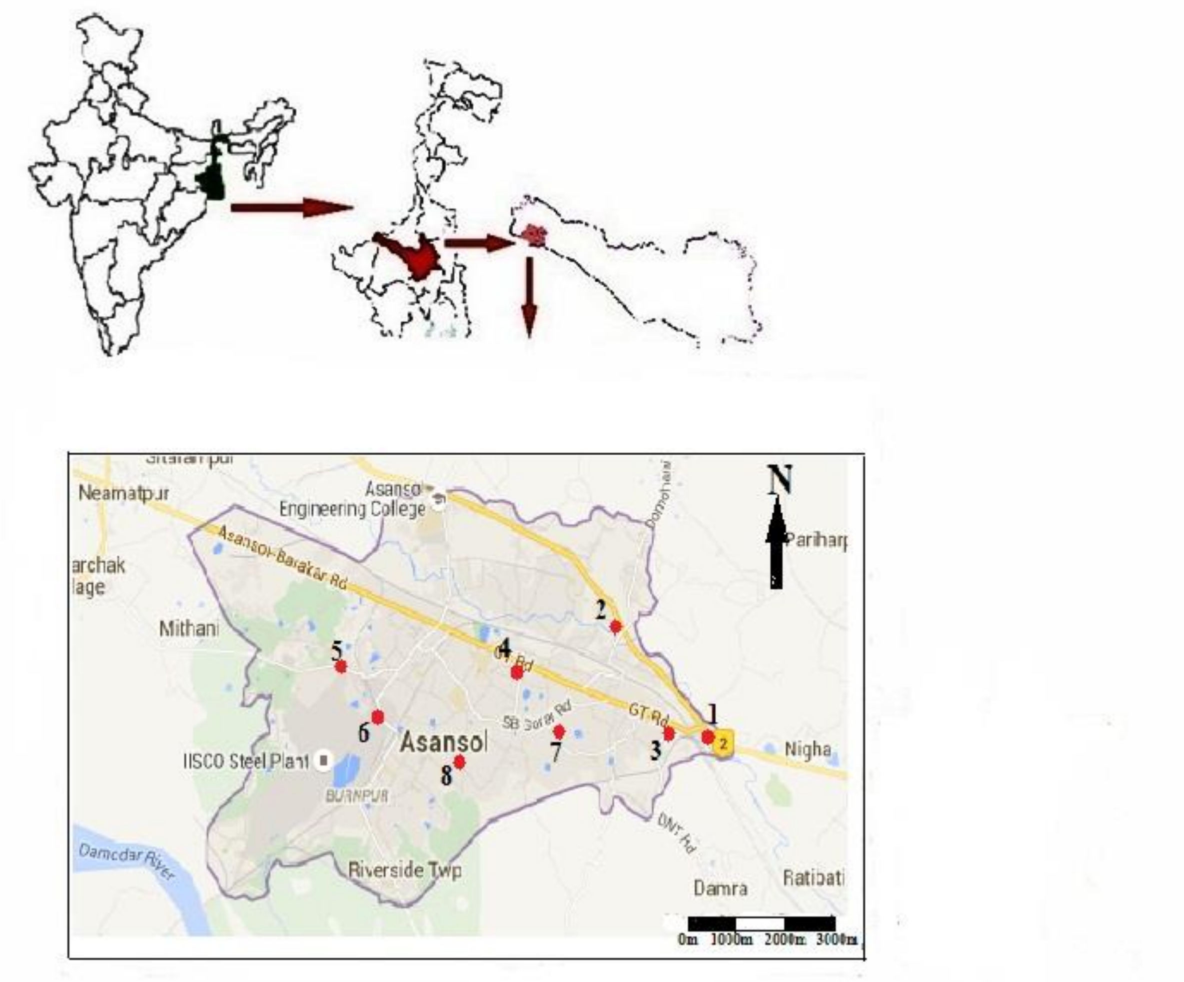

Fig. 1.Map of Asansol

Study area

Asansol is a densely populated city of West Bengal in Eastern India (Fig 1), which is currently facing unprecedented environmental change due to rapid urbanization and non-sustainable industrialization. Asansol is surrounded by coal-mines and various industries like steel, sponge iron, cement, ceramic industries, etc. Moreover Asansol is situated in Grand Trunk Road (G.T. Road) which having high traffic density throughout day and night and connected with Kolkata by National highway from one side and on other side with Dhanbad.

Collection of Samples

A total eight roadside dust samples were collected from different areas with different activities (Table 1) in July, 2012. At each sampling point, roadside dust samples were collected along major roads near national highway, the busy traffic, industrial area and residential areas using a plastic brush and tray. From each site, 3 sampling points, minimum 1 m apart were selected for sample collections (Acosta et al., 2011).Samples were sieved into <53 micron particle size and stored in plastic bags under room temperature until the analysis.

Table 1. Sampling sites and locations in Asansol with latitude and longitude

Sites	Location	Latitude	Longitude
Site 1	Kali Pahari (National highway)	23.67408	87.01451
Site 2	Dhadka (National highway)	23.70222	86.98507
Site 3	Ushagram (Busy Traffic)	23.67707	87.00198
Site 4	Hutton Road (bus stand)	23.68697	86.96996
Site 5	New town (Industrial area)	23.68615	86.93381
Site 6	Scop gate (Industrial area)	23.68084	86.93724
Site 7	Mohishila Colony (Residential area)	23.67141	86.98696
Site 8	Vivekananda pally (Residential area)	23.67515	86.96076

Table 2.Protocol for sequential extraction of Cr from road dust

Fractions	Extracting chemicals for 1gm of soil	Temperature and Mixing Time
F1 Exchangeable	8 ml 1M $MgCl_2$ at pH 7	1 hr at 25-30°C
F2 Bound to Carbonate	8 ml 1 M NaOAc, pH 5.0 using HOAc.	5 hrs at 25-30°C
F3 Bound to Fe-Mn Oxides	20 ml 0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc	5 hrs at 96 ± 3°C
F4 Bound to organic Matter	3 ml 0.02M HNO_3 + 5ml 30% H_2O_2 3 ml 30% H_2O_2 5 ml 3.2 M NH_4OAc in 20% (v/v) HNO_3	2 hrs at 85 ±2 °C 2 hrs at 85± 2 °C 30 mins at 25-30°C
F5 Residual	2ml $HClO_4$ and 10 ml HF. 2ml $HClO_4$ and 10 ml HF	8 hrs at 100°C 6 hrs at 190°C

Source: Tessieret al. (1979)

Sequential Extraction Procedure

The sequential extraction (Tessier et al., 1979) was carried out to partition Cr in the road dust into five fractions: exchangeable (F1), bound to carbonate phase (F2), bound to iron and manganese oxides (F3), bound to organic matter and sulfides (F4), and residual or lattice metals (F5). One gram of air dried homogenized road dust sample of $\leq$ 53µm diameter particle size was taken to various leaching treatments (Table 2) to separate the Cr into the five operationally defined fractions (Bhattacharyya et al., 2014). After each step the mixture was centrifuged (Remi instruments, India) at 10000 rpm for 1 hr (Gope et al., 2015). The supernatant was collected into plastic bottles (Tarson) and stored for further analysis.

Analysis

The extracted solutions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) for the determination of Cr concentration in road dust samples.

Contamination Factor (CF)

The level of contamination of road dust by metal is expressed in terms of a contamination factor (CF)calculated as:

$$CF = \frac{Cm\ Sample}{Cm\ Background} \ldots\ldots\ldots\ldots\ldots\ldots \quad (Eqn.\ 1)$$

Where the contamination factor CF < 1 refers to low contamination; 1 ≤ CF < 3 means moderate contamination; 3 ≤ CF ≤ 6 indicates considerable contamination and CF > 6 indicates very high contamination (Tomilson et al., 1980; Chakravarty and Patgiri, 2009; Seshan et al., 2010).

Enrichment Factor (EF)

EF can be used to evaluate the magnitude of contamination of metals in the road dust. EF was computed following the equation proposed by (Zoller et al., 1974; Lehame et al., 1992)

$$EF = (C_M/C_{Fe})_{sample}/(C_M/C_{Fe})_{earth's\ crust} \ldots\ldots\ldots\ldots \quad (Eqn.\ 2)$$

Here$(C_M/C_{Fe})_{sample}$is the ratio of concentration of trace metal(C_M) to that of Fe (C_{Fe}) in road dust sample and $(C_M/C_{Fe})_{earth's\ crust}$is the same reference ratio in the earth crust. The average abundance of Cr and Fe in the reference earth's crust were taken from Taylor (1964). Fe was taken as a reference element because of its immobility and crustal abundance.

Where, EF<2: Deficiently to minimal enrichment; 2 ≤ EF < 5: Moderate enrichment; 5 ≤ EF < 20: Significant enrichment; 20 ≤ EF < 40: Very high enrichment; EF ≥ 40: Extremely high enrichment.

Index of geo-accumulation (I_{geo})

The technique of I_{geo} was adapted for classification of soil contamination by comparing the levels of heavy metal obtained in samples to the background levels using the modified formula (Eqn.1) suggested by Faizet al.(2009). It can be applied to assess the contamination of road dust (Atiemoet al., 2012; Singh, 2011).

$$I_{geo} = log_2\ (C_m/1.5B_m) \ldots\ldots\ldots\ldots\ldots \quad (Eqn.\ 3)$$

Where, C_m = concentration of the metal in road dust, B_m= the geochemical background concentration of the heavy metal or crustal average (Taylor, 1964; Atiemoet al., 2012). The constant 1.5 is to minimize the effect of possible variations in the background values which may be attributed to lithologic variations in the samples (Lu et al., 2009).

Where Igeo – <0, unpolluted; 0-1, unpolluted to moderately polluted; 1-2, moderately polluted; 2-3,moderately to strongly polluted; 3-4, strongly polluted; 4-5 = strongly to extremely polluted; and >5, extremely polluted (Muller, 1969).

Mobility factor (MF)

The mobility factor (MF), an index of potential mobility of metal ions in dust (Narwal and Singh, 1998; Lua et al., 2003) was determined by using the following equation:

$$MF = [(F1+F2+F3) / (F1+F2+F3+F4+F5)] \times 100 \ldots\ldots\ldots (Eqn.\ 4)$$

Here F1, F2, F3, F4 and F5 are the concentration of elements in exchangeable, carbonates, Fe-Mn oxides, organic matter and residual fractions respectively. A high MF indicates that the metal is in a state of high mobility and consequently, its availability to the biological systems will be high (Mahanta and Bhattacharyya, 2011; Huang et al., 2007; Olajire et al., 2003).

Health risk assessment

There are three major pathways of exposure to heavy metals associated with dust. Chronic daily intake (CDI) was calculated for (i) direct ingestion of dust particles (CDI_{ing}); (ii) inhalation of re-suspended particles (CDI_{inh}); and (iii) absorption of heavy metals from skin adhered dust particles (CDI_{dermal}) (Ferreira-Baptista and De Miguel, 2005). The equation for calculation of CDI is given below (US EPA, 1989, 1996; Ferreira-Baptista and De Miguel, 2005;Zheng et al., 2010a).

$$CDI_{ing} = C \times \frac{R_{ing} \times F_{exp} \times T_{exp}}{ABW \times T_{avrg}} \times 10^{-6} \quad \text{(Eqn. 5)}$$

$$CDI_{inh} = C \times \frac{R_{inh} \times F_{exp} \times T_{exp}}{PEF \times ABW \times T_{avrg}} \quad \text{(Eqn. 6)}$$

$$CDI_{dermal} = C \times \frac{SAF \times A_{skin} \times DAF \times F_{exp} \times T_{exp}}{ABW \times T_{avrg}} \times 10^{-6} \quad \text{(Eqn. 7)}$$

where, CDI is the chronic daily intake (mg kg^{-1} day^{-1}); C is concentration of the metal; R_{ing} is the ingestion rate [60 mg dust day^{-1} for children (1–6 years), 30 mg day^{-1} for adults (US EPA, 2011)], R_{inh} is the inhalation rate [20 m^3 day^{-1} for adults, 7.6 m^3 day^{-1} for children (Van-den Berg, 1995)], F_{exp} is exposure frequency[180 day $year^{-1}$ (Ferreira-Baptista and De Miguel, 2005; Hu et al., 2011; Zhenget al., 2010a)], T_{exp} is the exposure duration [6 years for children and 24 years for adults (US EPA, 2001)], A_{skin} is the skin area [2800 cm^2 for child and 5700 cm^2 for adults (US EPA, 2001)], SAF is the skin adherence factor [0.07 mg cm^{-2} h^{-1} (US EPA, 2002; Zheng et al., 2010b) for child and 0.7 mg cm^{-2} h^{-1} (US EPA, 2001; Zheng et al., 2010a)], DAF is the dermal absorption factor (unit less), [0.001 for both child and adults], PEF is the particle emission factor [1.36×10^9 m^3 kg^{-1} for both cases (US EPA, 2001)], ABW is the average body weight [15 kg for child and 70 kg for adults (Hu et al., 2011; US EPA, 1989; Zheng et al., 2010a)], T_{avrg} is the averaging time; for non-carcinogens, Tavrg= T_{exp} *365.

The potential non-carcinogenic risks for individual metals were calculated by the following equation (Hu et al., 2011; US EPA, 2007)

$$\textit{Hazard quotient (HQ)} = CDI / R_f D \quad \text{(Eqn. 8)}$$

$$\textit{Hazard index (HI)} = \sum HQ_{(ingestion/inhalation/dermal)} \quad \text{(Eqn. 9)}$$

R_fD is Reference Dose and$CDI_{ing/inh/dermal}$ is chronic daily intake rate through ingestion, inhalation or dermal pathway respectively. Bioavailable Fraction or BAF was the constant ratio of elements content that is bioavailable to their total contents. Hazard index (HI) was calculated as the summation of HQs. HI value greater than 1 indicates of occurrence of non-carcinogenic effects whereas HI lower than 1 shows no significant risk (US EPA, 2001).

RESULT AND DISCUSSION

Total Cr concentration

Cr concentrations in street dust of Asansol varied significantly with sampling sites (Table 3). Total Metal concentration for Cr in different sampling sites of Asansol is presented as contour map in Fig 2. The contour map based on distribution and concentrations of Cr was constructed using a Surfer 11.0 software to characterize the spatial patterns of Cr. The maximum concentration of Cr was found in site 5 which is an industrial area and it might be due to the use of Cr in steel industries as Cr is used for stainless steel and chromate plating (Kabata-Pendias and Mukherjee, 2007). Site 6 which is also an industrial area has got considerable amount of Cr concentration next to site 5. Cr concentrations were low in residential areas and the lowest concentration is associated with Site 7. Wear and tear of tire, break shoe, vehicle body parts and meteorological conditions like prevailing winds from industrial areas towards national highways and busy traffic areas could have been another factor which led to maximum Cr concentration in those areas.

Table 3.Total Cr concentration in road dust of Asansol

Sampling sites	Cr (mg/kg)
Site 1	44.1
Site 2	75.1
Site 3	63.6
Site 4	44.0
Site 7	250
Site 8	129
Site 5	8.99
Site 6	22.8

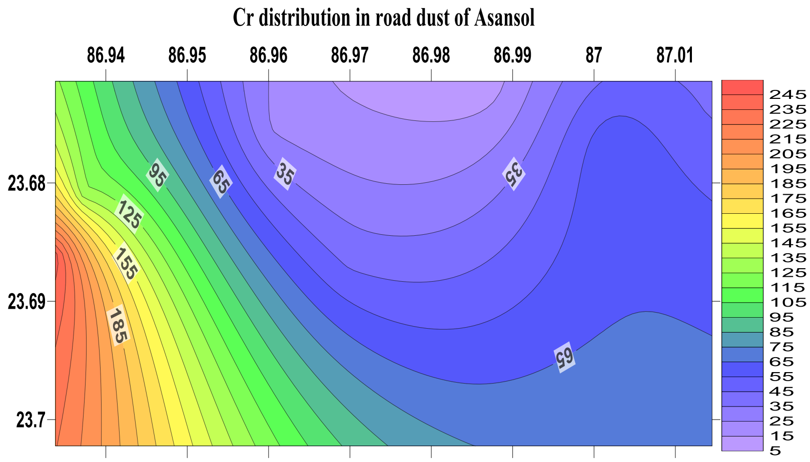

Fig.2.Cr (mg/kg) distribution by contour map in road dust of Asansol

CF, EF and I_{geo} results are depicted in Fig 3. Contamination Factor showed that industrial sites have got moderate contamination level and site 5 has got maximum contamination among all the sites. The present study showed that industrial sites have got significant enrichment with maximum EF value in site 5. Residential sites have minimum enrichment and minimum contamination according to EF and CF respectively. I_{geo} indicated that all the sites are unpolluted except site 5. Site 5 was in unpolluted to moderate pollution level.

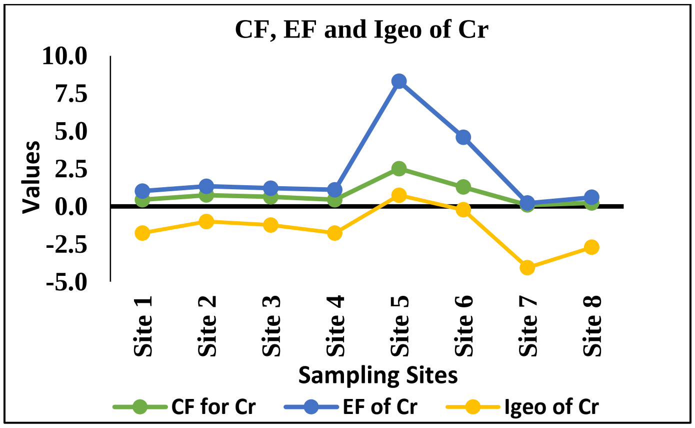

Fig. 3. CF, EF and I_{geo} of Cr in road dust of Asansol

Chemical Speciation

The sequential extraction procedure values which are depicted in Fig 4 showed that Cr is strongly associated with the residual fraction (F5) phase to the extent of more than 85% followed by Fe-Mn oxide phase (F3) by 7%. Banerjee (2003) also reported the maximum attachment of Cr in residual phase in street dust of Delhi, India. Residual phase (F5) is the least mobile phase among all the phases. So mobility of Cr towards environment is very less for Cr. So, most of the Cr concentration was found in immobile phase which was more than 90% (F4+F5). The immobile fractions i.e. residual and organic matter holds maximum concentration of Cr. If favorable conditions like anoxic, acidic environment occur then Cr can be leached out as bio-available form which might affect environment. In present study the sequence was F5>F3>F4>F2>F1 for Cr in road dust of Asansol.
Speciation study revealed that though site 5 has got the maximum total Cr concentration, the maximum bio-available Cr was found in Site 7 which is a residential area. So, the chances of deterioration in the quality of environment as well as human health were more in residential site.

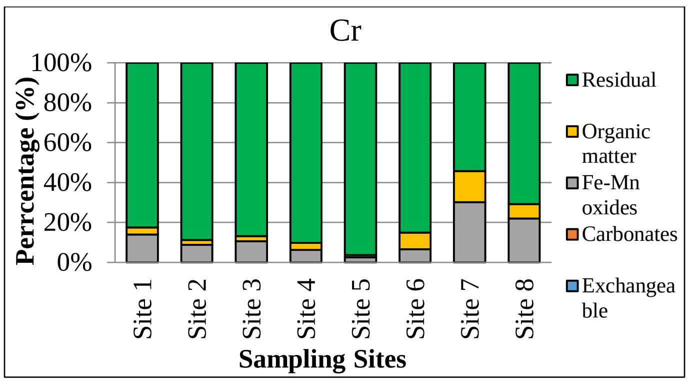

Fig. 4.Chemical fractionation of Cr in road dust of Asansol

MF indicated (Fig 5) maximum mobility in residential sites i.e., site 7 (30.2%) and site 8 (21.9%) whereas minimum mobility was found in industrial site i.e., site 5 (2.59%).

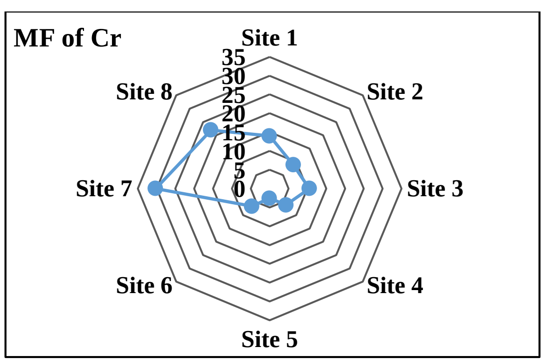

Fig. 5. Mobility Factor of Cr in road dust of all the sites in Asansol

Human spend their maximum time at residence so they are under risk as the mobility of Cr is high in those areas. In order to assess the human health risk due to Cr from total concentration as well as bio-available concentration (F1+F2+F3), risk assessment is carried out.

Health risk assessment

Risk from Total Cr concentration

The results of the health risk assessment of total Cr concentration present in road dust from Asansol are presented in Table 4. Hazard Quotients (HQ) for children were found to be in higher risk from ingestion of road dust (Ferreira-Baptista and De Miguel, 2005) when compared with adults in present study. In case of dermal contact HQs values were high for adults.

So, for Children more precaution should be taken from ingestion and for adults the dermal contact precaution should be taken. HI values were less than 1 in the present study for children and adults both, indicating there was no risk of non-carcinogenic effect as reported by Ferreira-Baptista and De Miguel (2005) in Luanda, Angola. Chabukdhara and Nema, 2013 reported HI>1 for Cr in Ghaziabad, India.

Risk from Bio-available fraction

In case of bioavailable fraction of Cr, HI values (Table 5) indicated that it was very low than 1 for all the sites as there was no chance of occurrence of non-carcinogenic effect like the HI values from the total Cr concentration. But the level of HI values were higher when calculated with total metal concentration though it was < 1. So the present study conclude that the risk from total Cr concentration and risk from bio-available Cr has no non-carcinogenic risk and it was safe for human.

Table 4.Health risk assessment with total metal concentration of Cr in road dust of Asansol

Sites	***Hazard Index (HI) of Total fraction***				
	Target	**Ingestion**	**inhalation**	**Dermal**	**HI= ∑HQ**
Site 1	*Child*	2.90E-02	2.89E-04	1.08E-02	0.04
	Adult	3.11E-03	1.63E-04	1.65E-02	0.02
Site 2	*Child*	4.94E-02	4.93E-04	1.84E-02	0.07
	Adult	5.29E-03	2.78E-04	2.81E-02	0.03
Site 3	*Child*	4.18E-02	4.17E-04	1.56E-02	0.06
	Adult	4.48E-03	2.35E-04	2.38E-02	0.03
Site 4	*Child*	2.89E-02	2.88E-04	1.08E-02	0.04
	Adult	3.10E-03	1.63E-04	1.65E-02	0.02
Site 5	*Child*	1.64E-01	1.64E-03	6.14E-02	**0.23**
	Adult	1.76E-02	9.26E-04	9.37E-02	**0.11**
Site 6	*Child*	8.46E-02	8.44E-04	3.16E-02	**0.12**
	Adult	9.07E-03	4.76E-04	4.82E-02	0.06
Site 7	*Child*	5.91E-03	5.90E-05	2.21E-03	0.01
	Adult	6.34E-04	3.33E-05	3.37E-03	0.00
Site 8	*Child*	1.50E-02	1.50E-04	5.60E-03	0.02
	Adult	1.61E-03	8.45E-05	8.56E-03	0.01

Table 5.Health risk assessment with bio-available concentration of Cr in road dust of Asansol

Sites		***Hazard Index (HI) of Mobile fraction***			
	Target	**Ingestion**	**inhalation**	**Dermal**	**HI= ∑HQ**
Site 1	*Child*	4.05E-03	4.04E-05	1.51E-03	0.01
	Adult	4.34E-04	2.28E-05	2.31E-03	0.00
Site 2	*Child*	4.39E-03	4.38E-05	1.64E-03	0.01
	Adult	4.71E-04	2.47E-05	2.50E-03	0.00
Site 3	*Child*	4.42E-03	4.41E-05	1.65E-03	0.01
	Adult	4.73E-04	2.49E-05	2.52E-03	0.00
Site 4	*Child*	1.79E-03	1.78E-05	6.68E-04	0.00
	Adult	1.92E-04	1.01E-05	1.02E-03	0.00
Site 5	*Child*	4.26E-03	4.25E-05	1.59E-03	0.01
	Adult	4.57E-04	2.40E-05	2.43E-03	0.00
Site 6	*Child*	5.60E-03	5.59E-05	2.09E-03	0.01
	Adult	6.00E-04	3.15E-05	3.19E-03	0.00
Site 7	*Child*	1.79E-03	1.78E-05	6.68E-04	0.00
	Adult	1.92E-04	1.01E-05	1.02E-03	0.00
Site 8	*Child*	3.30E-03	3.29E-05	1.23E-03	0.00
	Adult	3.54E-04	1.86E-05	1.88E-03	0.00

CONCLUSION

The present study concluded that Asansol was unpolluted to moderately polluted and minimal enrichment to significantly enrich with Cr. The variation in result at all sites reflects the role of anthropogenic activity. The fractional concentrations of Cr in urban road dust were mainly associated with residual fraction and the lowest concentration were observed in exchangeable fraction though maximum mobility of Cr was associated with residential sites which is a matter of concern. Actual health risk due to Cr in bio-available fractions and risk in total Cr concentration showed no health risk for humans whereas risk from total metal concentration showed higher values, which could be overestimated. So risk assessment should be done with Bio-available fraction. In Asansol a continuous monitoring is required to assess the levels of bioavailable fraction in street dust.

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