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Transport Pollution in India

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Abstract

Road dusts contribute a large fraction of air pollution in urban environment of India. In the present work, contamination assessment of ions and elements *i.e.* F^-, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, As, Cr, Mn, Fe, Ni, Cu, Zn, Pb and Hg in the road dusts of the most industrialized area of central India: Raipur (capital, Chhattisgarh state) is described during year: 2008-2013. In year 2008, the mean content of the element *i.e.* F^-, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, As, Cr, Mn, Fe, Ni, Cu, Zn, Pb and Hgin the dust (n = 5) was found to be 292 ± 112, 5068 ± 2445, 927 ± 280, 3336 ± 1315, 155 ± 65, 4273 ± 1761, 1477 ± 626, 974 ± 243, 9809 ± 2370, 21.2 ± 2.4, 150 ± 30, 12,816 ± 12,522, 157,736 ± 61,542, 60 ± 7, 566 ± 608, 348 ± 154, 296 ± 163 and 0.10 ± 0.09 mg/kg, respectively. The enrichment, concentration variations and sources of the elements are discussed.

Keywords

Road Dust, Heavy Metals, Ions, Contamination, India

1. Introduction

Population growth and economic development in India are contributing many serious environmental calamities *i.e.* environmental pollution, global warming, climate change, etc. [1]. Motored vehicles for land transportation are the foremost transportation method and contribute a major fraction of air pollution [2]. Road transport air pollutants are fugitive in nature, including vehicle, non-vehicle exhaust and road related emissions [3]. The most

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common contaminants in road dusts are metals, inorganic salts, aromatic hydrocarbons, etc. [4] [5]. Sever road dust contamination with toxic metals *i.e.* Cr, Mn, Fe, Ni, Cu, Zn and Pb, was reported due to vehicular emissions in various locations of the world [6]-[16]. In addition, the increased prevalence rate of the air borne diseases in the residents residing nearby the highway was reported [17] [18]. The vast urbanization and industrialization of Raipur city (capital of Chhattisgarh state, India) has been marked since last 10 years due to being one of the biggest market for materials *i.e.* steel, cement, coal and forest products in the country. Hence, in this work the road dust contamination of the highway of Raipur city by 18 elements *i.e.* F^-, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, As, Cr, Mn, Fe, Ni, Cu, Zn, Pb and Hg, is described.

2. Methods and Materials

2.1. Study Area

The road dusts of Raipur city (capital of Chhattisgarh state), India (21˚13'48" N, 81˚37'48" E) was selected for this study. The five locations *i.e.* Tatibandh, Pandari, Birgaon, Sakra and Sarora lie in the highway and freeway were selected for the sample collection, **Figure 1**. The road characteristics of sampling locations are summarized in **Table 1**. In addition, three locations *i.e.* Birgaon, Sakra and Sarora lie in the industrial environment. The traffic intensity (number of vehicles passing per day) in the highway was varied from 70,000 - 120,000, depending upon geography of the location. The samples were collected by using plastic spoon in month of May during years from 2008 to 2013. Four samples from different points of each location were collected, and a composite sample was prepared by mixing the min equal mass ratio. In year 2008, five composite samples were collected, one from each location. In other years, 2009-2013, two composite samples from locations: Birgaon and Sarora were collected in each year. They were kept in a glass bottle (250 ml) and dried at 60˚C in an oven for overnight. The samples were crushed into fine particles by mortar and sieved out the particles of mesh size < 100 µm.

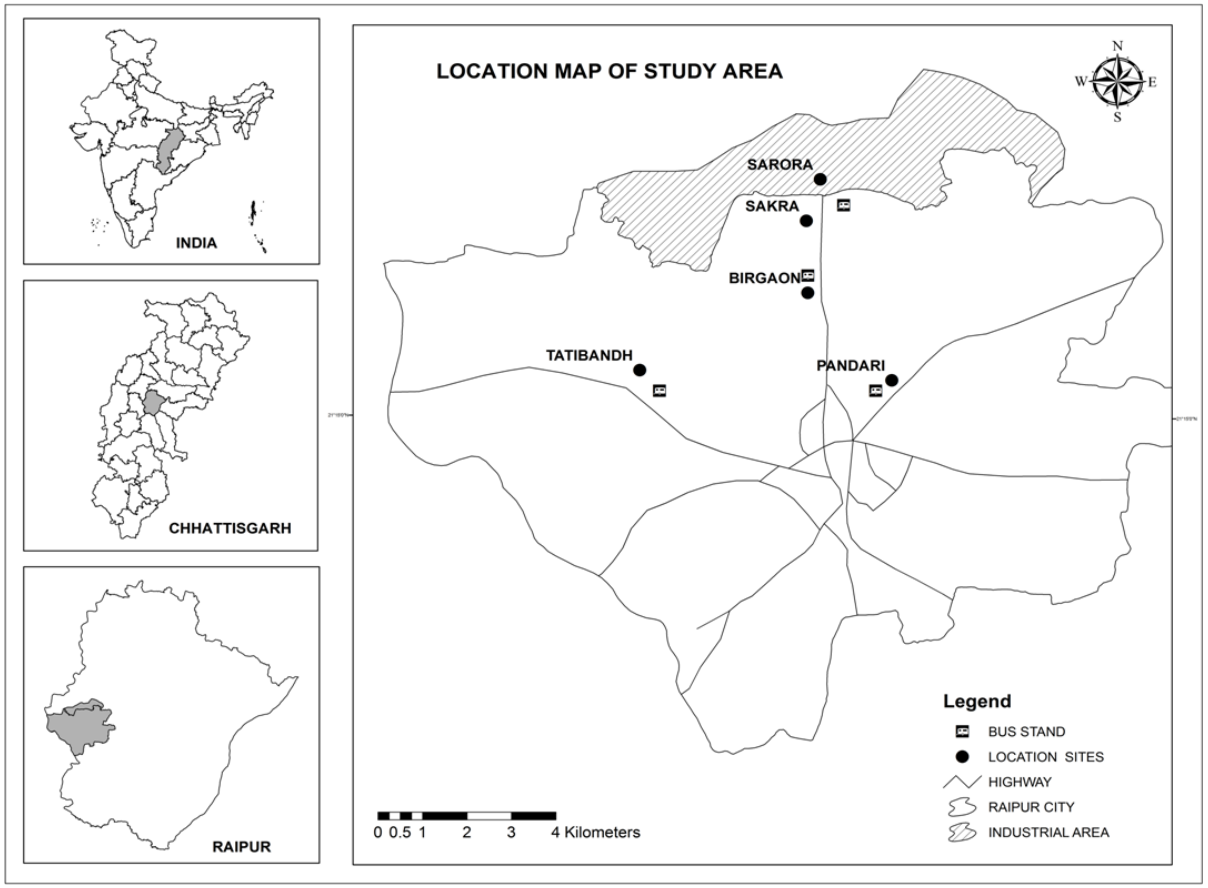


Figure 1. Representation of sampling locations in Raipur city.

Table 1. Road characteristics.

Site	Environmental characteristics	Road type	Traffic intensity per day
Tatibandh	Outer area	Highway	100,000
Pandari	Urban area	Freeway	120,000
Birgaon	Urban area	Highway	80,000
Sakra	Industrial area	Highway	70,000
Sarora	Industrial area	Highway	70,000

2.2. Analysis

A 10.0 g dust sample was extracted with deionized hot water (20 ml) for 6 hrs in the utrasonic bath. The extract was filtered with microfilter of pore size, 2 µm for measurment of pH value. Metrohm ion meter-781 equipped with fluoride ion selective electrode and calomel electrode was employed for monitoring of the fluoride content. The ion strength adjustment buffer (TISAB) was used in a 1:1 volume ratio, by dissolving 58 g NaCl, 5.0 g trans-1, 2, NNNN, cyclodiamine tetra acetic acid and 57 ml glacial acetic with pure water in 1 lit by subsequent adjustment of pH to 5.5 with NaOH solution. The Dionex DX120 ion chromatograph equipped with anion and cation separation columns and conductivity detector was employed for analysis of the ions.

The dust samples were digested with HNO_3:H_2O_2 in closed vessel microwave digestion system (MARS 5). The Varian Liberty AX Sequential ICP-AES and Varian AA280FS atomic absorption spectrophotometer equipped VGA-77 (plasma flow: 15 l/min, auxiliary flow: 1.5 l/min, power: 1KW, PMT voltage: 650 V) were used for analysis of the metals in the dust. The VARIAN "SpectrAA" 55B equipped with hydride/cold vapor regenerator accessories was employed for determination of As and Hg. The urban dust reference material, QUA NAS from EU was used for the quality control.

The principal component analysis (PCA) method was used for analyzing relationships among the observed variables [19]. The statistical window software STATISTICA 7.1 was employed for the statistical analysis.

3. Results and Discussion

3.1. Concentration of Ions

The dusts were black in color with mean pH value (n = 5) of 7.6 ± 0.4. The content of water soluble ions *i.e.* F^-, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+} in the road dusts was ranged from 195 - 486, 1615 - 8559, 416 - 1230, 1112 - 4762, 48 - 252, 1902 - 6747, 785 - 2596, 699 - 1264 and 7219 - 13,708 mg/kg with mean value of 292 ± 112, 5068 ± 2445, 927 ± 280, 3336 ± 1315, 155 ± 65, 4273 ± 1761, 1477 ± 626, 974 ± 243 and 9809 ± 2370 mg/kg, respectively, **Table 2**. Among them, Ca^{2+} had the highest content with the lowest value for NH_4^+. The sum of the total content of 9 ions in the five locations of the road was ranged from 1.5% - 3.6% with mean value of 2.4% ± 0.7%. The sum of total concentration of the ions was found to be well correlated (r = 0.94) with the traffic intensity. The highest fraction of the water soluble ions was observed in the vehicle stand sites (*i.e.* Tatibandh and Pandari), mainly due to input of the vehicle exhaust effluents, **Figure 2**.

3.2. Concentration of Metals

The metal content of the road dust is presented in **Table 3**. The content of the heavy metals (HMs) *i.e.* As, Cr, Mn, Fe, Ni, Cu, Zn, Pb and Hg in the dust samples (n = 5) was ranged from, 18.0 - 24.5, 101 - 178, 1871 - 37,809, 48,540 - 227,394, 52 - 74, 119 - 1720, 166 - 603, 165 - 617 and 0.05 - 0.20 mg/kg with mean value of 21.2 ± 2.4, 150 ± 30, 12,816 ± 12,522, 157,736 ± 61,542, 60 ± 7, 566 ± 608, 348 ± 154, 296 ± 163 and 0.10 ± 0.09 mg/kg, respectively. The sum of the total content of 9 metals in the five locations of the road was ranged from 5.2% - 26.6% with mean value of 17.2% ± 7.0%. Among them, Fe and Mn exhibited higher content at the industrial sites, due to running of several iron industries in this region, **Figure 2**. However, three metals *i.e.* Cu, Zn and Pb showed higher content at the vehicular sites, **Figure 2**. Their concentrations were found to be fairly correlated (r = 0.63 - 0.95) with the traffic intensity. The heavy metal contents of the studied area was found to be much higher than other locations of the World, probably due to input of effluents by both vehicular and

Table 2. Content of water soluble ions in road dust, mg/kg.

Site	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
Tatibandh	210	7102	1230	4762	252	5803	1656	1250	13,708
Pandari	360	8559	1058	4656	178	6747	2596	1264	11,497
Birgaon	486	4634	835	3338	136	4059	958	950	8324
Sakra	195	1615	416	1112	48	1902	785	699	8297
Sarora	210	3428	1096	2810	163	2852	1391	707	7219

Table 3. Metal content of road dust, mg/kg.

Site	As	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Hg
Tatibandh	24.5	174	9011	162,284	58	1720	447	210	0.090
Pandari	20.2	101	1871	48,540	52	719	603	617	0.197
Birgaon	18.0	169	9274	141,250	60	151	233	165	0.079
Sakra	23.4	178	6113	209,212	74	121	166	192	0.061
Sarora	19.8	130	37,809	227,394	57	119	290	295	0.050

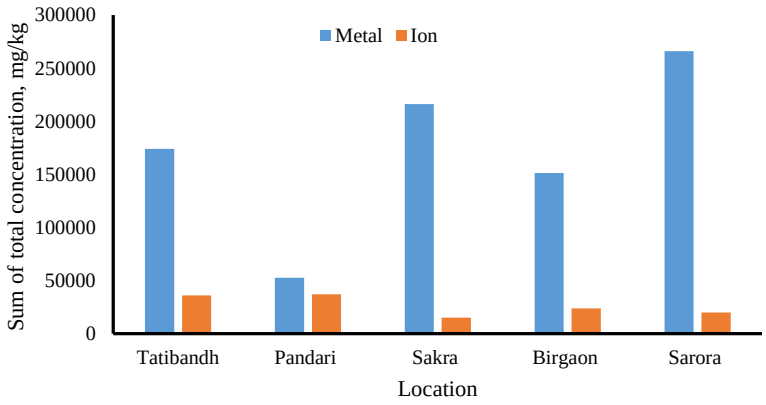


Figure 2. Total concentration of ions and metals in the road dust at five locations of Raipur city.

industrial emissions [6]-[16].

3.3. Correlation, Enrichment and Sources

The PCA analysis was executed on 17 variables (*i.e.* Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, As, Cr, Mn, Fe, Ni, Cu, Zn, Pb and Hg) for the 5 sample sites, **Table 4**. Four factors were extracted and accounted for 94.76% of the total variance. Factor-1 accounted for 50.22% of the total variance. The variables Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Mg^{2+} and Ca^{2+} was correlated with each one by a strong positive loading value. Sodium and Cu showed some moderate loading values on Factor-1, and characterized by the presence of salts and organic matter for which Cu had a great affinity. Factor-2 accounted for 22.50% of the total variance. Chromium and Ni had a strong positive loading value, and Fe presented a moderate loading value. Mercury had a negative loading value on Factor-2, by denoting different sources between Cr, Ni and Hg. Factor-3 represented a 14.23% of the total variance. Manganese showed absolute strong loading values on Factor-3. Manganese was in opposite relation with metals such as Pb, Zn, Cr, Cu, Ni and Fe. This could be explained by the different sources of Mn in relation to the trace metals cited above. Factor-4 accounted for 7.81% of the total variance. Metals *i.e.* Pb, Zn and K^+ had each one a strong positive loading value on factor-4. Arsenic presented a negative loading value, this denoted

Table 4. Varimax factor matrix of chemical constituents.

Parameter	Factor-1	Factor-2	Factor-3	Factor-4
Cl^-	**0.80**	−0.07	0.11	0.57
NO_3^-	**0.80**	−0.07	−0.43	0.40
SO_4^{2-}	**0.92**	−0.20	0.02	0.26
NH_4^+	**0.83**	−0.13	−0.28	0.31
Na^+	**0.77**	−0.25	0.23	0.54
K^+	0.47	−0.20	0.03	**0.85**
Mg^{2+}	**0.96**	0.03	0.19	0.17
Ca^{2+}	**0.96**	0.13	0.21	0.03
Hg	0.33	**−0.74**	0.47	0.20
Fe	−0.17	**0.73**	−0.59	−0.27
Mn	−0.05	0.22	**−0.97**	0.05
Cu	**0.77**	0.27	0.14	0.28
Cr	0.05	**0.98**	0.00	0.04
Ni	0.12	**0.87**	−0.01	0.05
Pb	0.22	−0.01	−0.08	**0.96**
Zn	0.47	0.17	0.02	**0.86**
As	−0.18	0.08	0.52	**−0.79**
Eigenvalue	9.04	4.05	2.56	1.41
% Variance	50.22	22.50	14.23	7.81
Cumulative %	50.22	72.72	86.95	94.76

Absolute loading values > 0.70, significant at $p < 0.05$.

also different source between Pb and Zn. Vehicular emissions, industrial discharges and urban development are as much sources of heavy metals loadings [20]-[24]. Therefore, the metal deposition over time led to enrichment and caused metal contamination of the dust [4]. Among these metals, As and Hg showed others sources in relation to Pb, Zn, Cr, Cu, Ni and Zn. A 1:1 mass concentration ratio of Zn and Pb in the road dust was found, and their prominent sources expected in the dust are ZnO and Pb used in tire thread and in the motor vehicle wheel balance weights, respectively [25]. Among these sources, vehicular emission was a significant and increasing source of road and soil pollution in urban area. Heavy metals in such environment can come from trimming brake, mechanical abrasion as essential components of many alloy, pipe, wire and tire in motor vehicles. One of the atmospheric pollutants released from vehicular traffic was heavy metals, which can accumulate in surface road and soil from elevated emissions.

The correlation matrix of the ions and metals in the road dusts are presented in **Table 5**, **Table 6**. All ions (except F^-) among themselves had fair to excellent correlation, indicating their common sources, **Table 5**. The content of metals *i.e.* Cr, Mn and Ni among themselves had fair correlation, showing their common origins, **Table 6**. Iron content had fair correlation with metals *i.e.* Cr, Mn and Ni, indicating origin from steel industry and coal burning effluents.

In this study, the average composition of upper crust is used as crustal reference materials [26]. The mean value of Al content in the road dust of the study area was found to be 0.86%. The E_f value for species *i.e.* Ni, Cr, Hg, Fe, As, Mn, Pb, Cu, Zn, Cl^- and SO_4^{2-} was evaluated, and presented in **Figure 3**. The enrichment value (E_f) was grouped into moderately, significantly and highly enriched classes. The first elemental group (Cl^-, SO_4^{2-},

Table 5. Correlation matrix of metal (r).

	F^-	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
F^-	1.00								
Cl^-	0.32	1.00							
NO_3^-	0.00	0.73	1.00						
SO_4^{2-}	0.30	0.96	0.86	1.00					
NH_4^+	0.00	0.78	0.96	0.91	1.00				
Na^+	0.32	1.00	0.69	0.95	0.73	1.00			
K^+	0.30	0.88	0.65	0.77	0.60	0.85	1.00		
Mg^{2+}	0.28	0.96	0.62	0.92	0.75	0.97	0.75	1.00	
Ca^{2+}	0.30	0.79	0.54	0.77	0.73	0.45	0.6	0.91	1.00

Table 6. Correlation matrix of metal (r).

	As	Cr	Mn	Fe	Ni	Cu	Zn	Pb	Hg
As	1.00								
Cr	0.24	1.00							
Mn	−0.50	0.10	1.00						
Fe	0.00	0.66	0.69	1.00					
Ni	0.40	0.79	0.00	0.68	1.00				
Cu	0.36	0.26	−0.22	−0.14	−0.14	1.00			
Zn	−0.79	0.00	0.10	−0.36	−0.36	0.66	1.00		
Pb	−0.82	0.24	0.00	−0.40	−0.30	0.66	0.90	1.00	
Hg	0.00	−0.79	−0.20	−0.94	−0.71	0.26	0.26	0.35	1.00

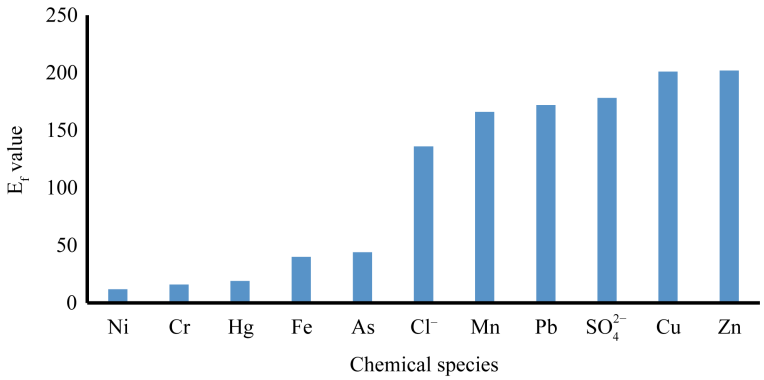
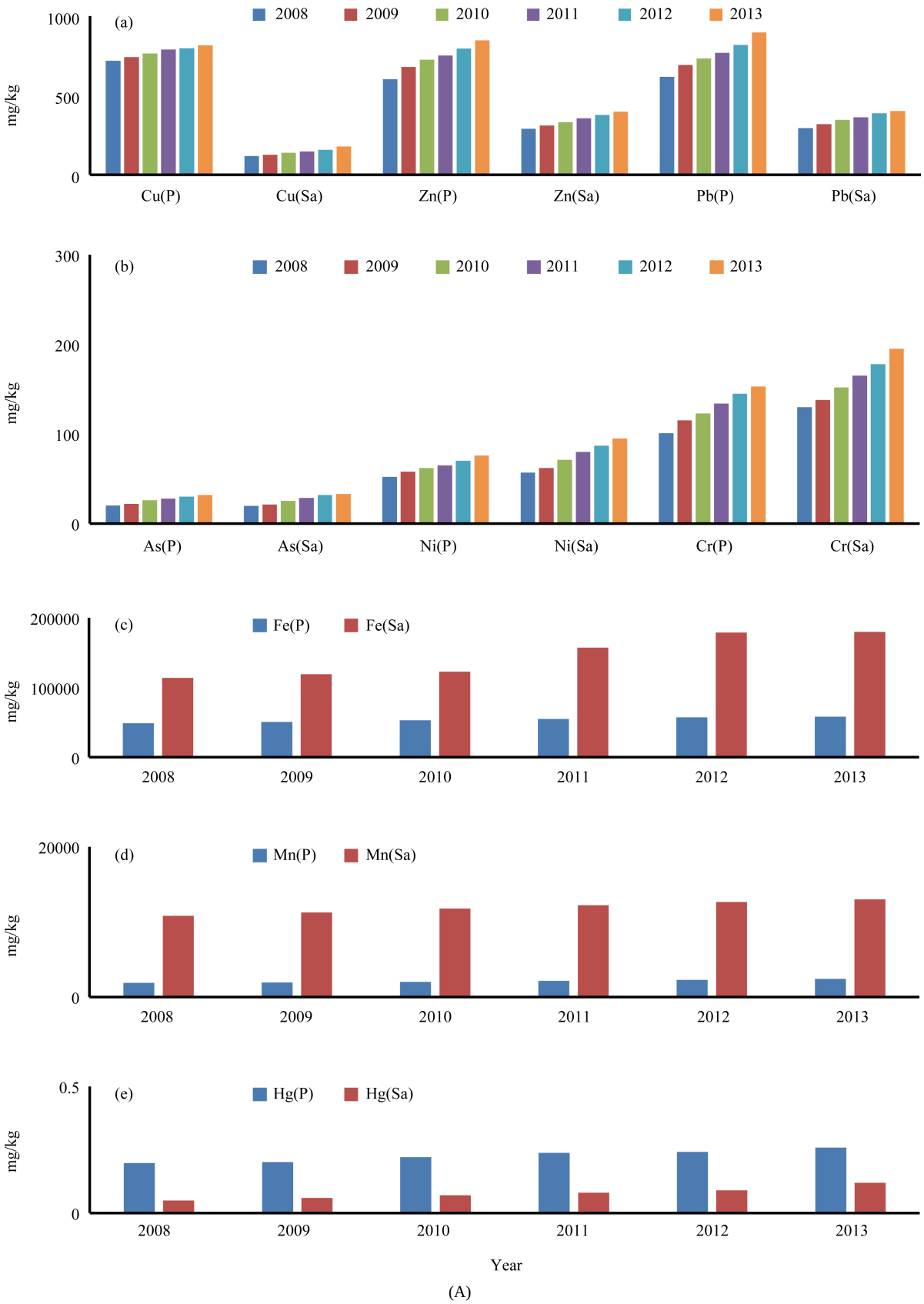
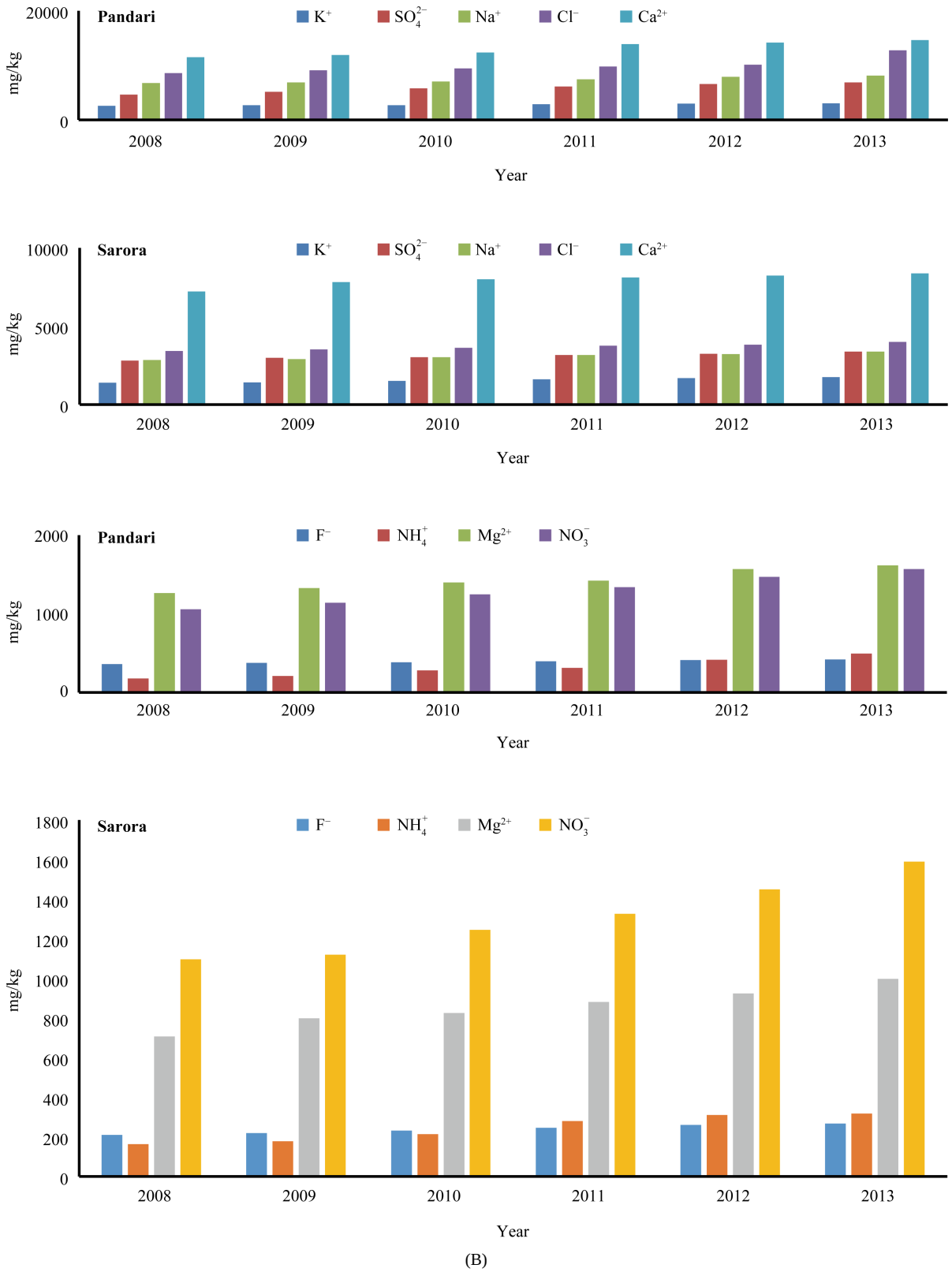


Figure 3. Mean E_f value of metals in the road dust of Raipur city.

Mn, Cu, Pb and Zn) showed a strong E_f value (>100), could be considered as anthropogenic elements. The second group elements (*i.e.* Fe and As) showed a significant E_f values (>20 - <50), could be considered of anthropogenic and crustal origin. The third group elements (*i.e.* Cr, Ni and Hg) having E_f value of <20, could be considered as elements of crustal origin.


(a)
2008
2009
2010
2011
2012
2013
1000
500
0
mg/kg
Cu(P)
Cu(Sa)
Zn(P)
Zn(Sa)
Pb(P)
Pb(Sa)
(b)
300
200
100
0
As(P)
As(Sa)
Ni(P)
Ni(Sa)
Cr(P)
Cr(Sa)
(c)
Fe(P)
Fe(Sa)
200000
100000
(d)
Mn(P)
Mn(Sa)
20000
(e)
Hg(P)
Hg(Sa)
0.5
Year

(A)



(B)

Figure 4. (A) Temporal variation of metal concentration in road dust of Raipur city at two lacations: P = Pandari, Sa = Sarora; (B) Temporal variation of ion concentration in road dust of Raipur city at two locations.

3.4. Chemical Composition of Dust

The sum of total content of the heavy metals and water soluble ions were varied from 8.9% - 28.6% with mean value of 18.2% ± 6.9% in the dust. The mean value of Fe, Mn and Ca in the dust was 15.0 ± 6.1, 1.3 ± 1.2 and 1.0% ± 0.3%, respectively. The contribution of other species *i.e.* As, Ni, Cu, Zn, Pb and Zn was accounted to ≈ 0.14% ± 0.09%. The sum of mean value for the water soluble ions *i.e.* F^-, Cl^-, NO_3^-, SO_4^{2-}, NH_4^+, Na^+, K^+, Mg^{2+} and Ca^{2+} in the dust was 2.6% ± 0.9%. The uncertainty in the dust was ≈ 80.2%, which may include carbons, silica, alumina, organics, etc.

3.5. Temporal Variation of Dust Constituents

The temporal variation studies in the dust contamination were carried out from years 2008 to 2013, **Figure 4(A)**, **Figure 4(B)**. The elements *i.e.* Cl^-, SO_4^{2-}, NO_3^-, Cu, Pb and Zn were largely emitted by the transport vehicles. Other elements *i.e.* Na, K, Mg, Ca, As, Cr, Fe, Ni and Hg were emitted by the multiple sources *i.e.* industrial, vehicular and tire exhausts and crustal materials. The concentration of contaminants related to vehicular effluents was extremely increased in the traffic area of the highway road due to tremendous enhancement in the vehicle frequency, **Figure 4(A)**, **Figure 4(B)**.

4. Conclusion

An enormous enrichment of species *i.e.* Cl^-, SO_4^{2-}, Mn, Cu, Pb and Zn is seen in the heavily rushed vehicle stand sites of the city due to transport effluents. Both correlation analysis and principal component analysis (PCA) were used to determine the sources of the heavy metals and ions. The result gave four components which were natural crust, industrial effluent, vehicular emission, and wear of vehicle parts. A higher temporal variation of species emitted by vehicles was observed.

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